

Texas  
A  
M &  
University  
N - M - R  
Newsletter

CT  
No. 262

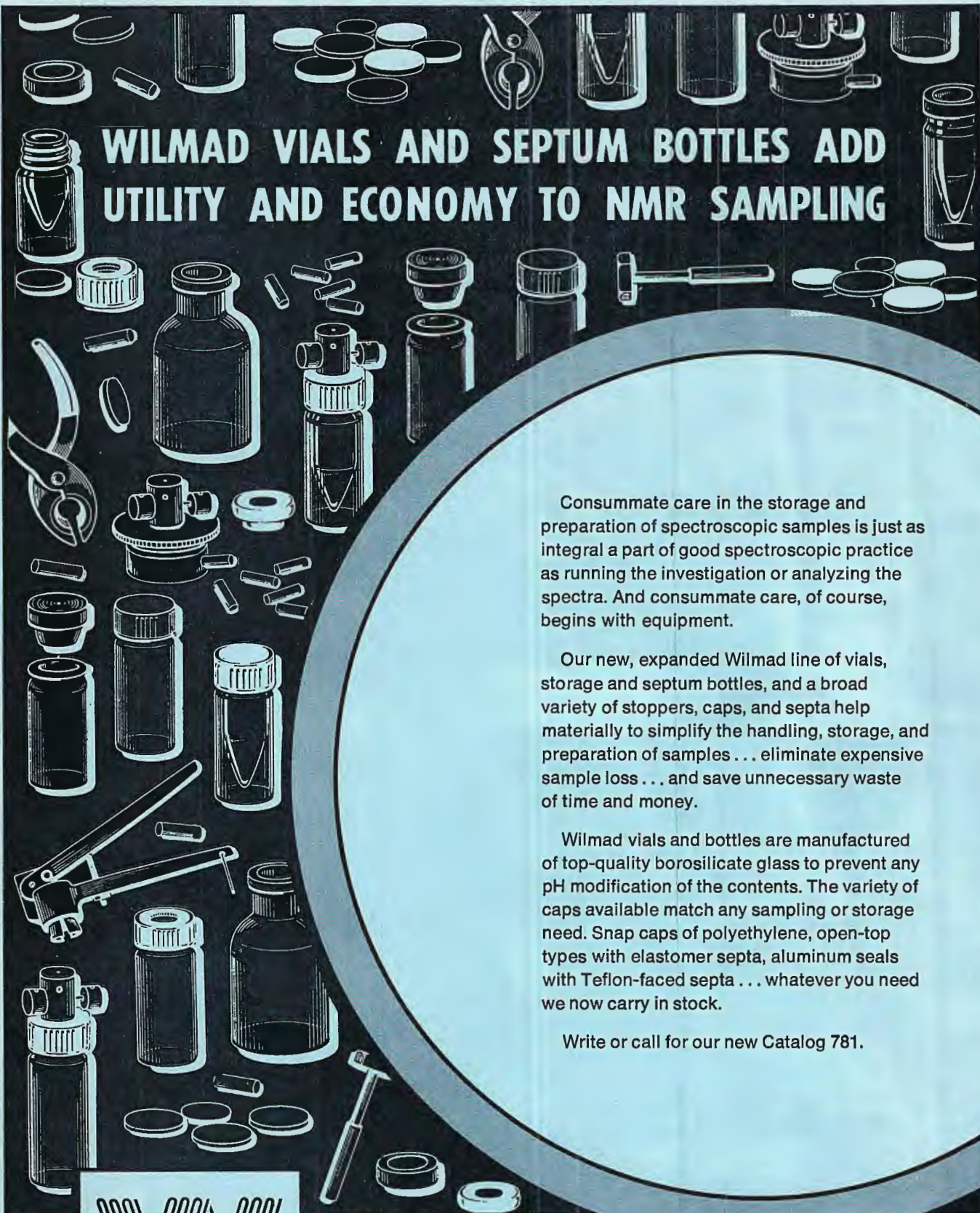
July, 1980

- |   |  |
|---|--|
| <p>M. Hájek and P. Trska<br/>Correlation between the SCS and the EHT<br/>Charge Densities of Azaadamantanes . . . . 1</p> <p>M. Thorpe<br/>Carbon-Fluorine Coupling Constants in<br/>Nitrogen Heterocycles . . . . . 3</p> <p>D. P. Kelly<br/><sup>1</sup>J<sub>CH</sub> Values for Bicyclo[2.1.1]hexanone<br/>from 2D-FT Spectra at 90 MHz . . . . . 5</p> <p>K. V. Vasavada, J. I. Kaplan and<br/>B. D. Nageswara Rao<br/><sup>31</sup>P NMR Lineshapes for Kinase Reactions . . 10</p> <p>D. J. Sardella<br/>On C-F Couplings in Polycyclic Aromatic<br/>Hydrocarbons . . . . . 13</p> <p>H. Booth and J. R. Everett<br/>Stereochemical Effects on <sup>13</sup>C-<sup>13</sup>C<br/>Coupling Constants . . . . . 15</p> <p>D. R. Holecek<br/>Conformational Effects in Solid State NMR. . 17</p> <p>H. Hogeveen and E.M.G.A. van Kruchten<br/>Carbon-13 Studies of Emotionally Insecure<br/>Carbonium Ions [<i>an Editor's Punitive Title</i>] . 19</p> <p>J. Yesinowski<br/><sup>13</sup>C and <sup>31</sup>P Magic-Angle Spinning at<br/>7.05 Tesla . . . . . 24</p> <p>M. R. Willcott<br/>The HP-41C, NMR, and Other Fun . . . . . 26</p> <p>G. Cancellieri, L. Lanzini and L. Cavalli<br/>Chemical Shifts of Protons Attached to<br/>Nitrogen. . . . . 27</p> <p>U. Henriksson and I. Grenthe<br/><sup>13</sup>C Studies of Uranyl-Carbonate Complex . . 29</p> | <p>J. T. Gerig<br/>An Intermediate in the Reaction of 2-halo-<br/>5-nitropyridines with Hydroxide . . . . . 31</p> <p>M. W. Baum, M. Jones, Jr. and N. D. Conrad<br/><sup>13</sup>C NMR of Tetrasubstituted Cyclopropenes. . 33</p> <p>C. S. Springer, Jr.<br/>Simulated NMR Spectra of Metal Cation<br/>Transporting Vesicle Systems; Postdoctoral<br/>Positions Available . . . . . 35</p> <p>P. Bladon and J. Ritchie<br/>Simple Method of Gated Decoupling . . . . . 37</p> <p>R. A. Wind, J. Trommel and J. Smidt<br/><sup>13</sup>C Spectroscopy in Coal Using Carbon-<br/>Proton Cross Polarization and Proton<br/>Dynamic Polarization. . . . . 39</p> <p>R. E. Santini<br/>New Position . . . . . 43</p> <p>K. C. Ramey<br/>Position Available . . . . . 43</p> |
|---|--|

A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.





## WILMAD VIALS AND SEPTUM BOTTLES ADD UTILITY AND ECONOMY TO NMR SAMPLING

Consummate care in the storage and preparation of spectroscopic samples is just as integral a part of good spectroscopic practice as running the investigation or analyzing the spectra. And consummate care, of course, begins with equipment.

Our new, expanded Wilmad line of vials, storage and septum bottles, and a broad variety of stoppers, caps, and septa help materially to simplify the handling, storage, and preparation of samples . . . eliminate expensive sample loss . . . and save unnecessary waste of time and money.

Wilmad vials and bottles are manufactured of top-quality borosilicate glass to prevent any pH modification of the contents. The variety of caps available match any sampling or storage need. Snap caps of polyethylene, open-top types with elastomer septa, aluminum seals with Teflon-faced septa . . . whatever you need we now carry in stock.

Write or call for our new Catalog 781.



### WILMAD GLASS COMPANY, INC.

*World Standard in Ultra Precision Glassware*

Route 40 & Oak Road • Buena, N.J. 08310 U.S.A.

Phone: (609) 697-3000 • TWX 510-687-8911



TAMU NMR NEWSLETTER - ADVERTISERS

Bruker Instruments, Inc. - see p. 22  
 JEOL Analytical Instruments, Inc. - see p. (i) and outside back cover  
 Nicolet Instrument Corporation - see inside back cover  
 Varian Instrument Division - see p. 8  
 Wilmad Glass Company, Inc. - see inside front cover

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. 263 4 August 1980  
 No. 264 1 September 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. 262

Baum, M. W.....	33	van Kruchten, E.M.G.A....	19
Bladon, P.....	37	Lanzini, L.....	27
Booth, H.....	15	Nageswara Rao, B. D.....	10
Cancellieri, G.....	27	Ramey, K. C.....	43
Cavalli, L.....	27	Ritchie, J.....	37
Conrad, N. D.....	33	Santini, R. E.....	43
Everett, J. R.....	15	Sardella, D. J.....	13
Gerig, J. T.....	31	Smidt, J.....	39
Grenthe, I.....	29	Springer, Jr., C. S.....	35
Hájek, M.....	1	Thorpe, M.....	3
Henriksson, U.....	29	Trommel, J.....	39
Hogeveen, H.....	19	Trska, P.....	1
Holeček, D. R.....	17	Vasavada, K. V.....	10
Jones, Jr., M.....	33	Willcott, M. R.....	26
Kaplan, J. I.....	10	Wind, R. A.....	39
Kelly, D. P.....	5	Yesinowski, J.....	24

(i)  
**FT NMR was  
 never "hard,"  
 only certain  
 samples were.**

**... Now with the low cost  
 JEOL FX60QS System  
 High Resolution Solid State  
 NMR becomes routine**



**JEOL**

*Write for a copy of:*  
**"Your High Resolution Solid State  
 NMR Problems and their Solutions..."**  
 \* 235 Birchwood Avenue, Cranford, NJ 07016  
 201-272-8820



VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ

Laboratoř syntetických paliv

166 28 PRAHA 6-DEJVICE, SUCHBÁTAROVA 5

Telefon 332/4168, 32 15 04

Dálnopis 122 744 - VSCH/C

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

Prague, 26. 5. 1980

TITLE: Correlation between the SCS and the EHT charge densities of azaadamantanes

Dear Prof. Shapiro,

Since recently we have studied the dependence of the  $^{13}\text{C}$  chemical shifts in some N- substituted 1-azaadamantanes on the nature of the substituent X. We were looking for a correlation between the SCS (substituent chemical shift) of nine substituents and the EHT charge densities of relevant compounds. As expected, there is no simple correlation between the two sets of variable, but we found that the use of factor analysis can lead to interesting results. With three charge densities for each compound we were able to fully reproduce the SCS of all nine azaadamantanes. In addition it is possible to predict the chemical shift of skeleton carbons for any of the azaadamantanes shown from data on the remaining eight compounds; with one exception the calculated shifts are fairly close to the experimental values.



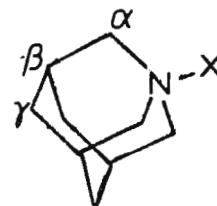
Table I

In brackets - calculated shift obtained by factor analysis using data for the other eight

compounds shown in the table

$$\text{SCS} = \delta_x^1 - \delta_{\text{azaadamantane}}^1$$

$$\delta_{\text{azaadamantane}}^1 = 57.62 (\alpha); 27.31 (\beta); \\ = 35.96 (\gamma)$$



X	SCS <sup>+</sup> <sub>C-α</sub>	SCS <sup>+</sup> <sub>C-β</sub>	SCS <sup>+</sup> <sub>C-γ</sub>
H	-0.8 (10.1)	-1.18 (1.29)	-2.60 (-1.88)
CH <sub>3</sub>	9.2 (11.1)	0.32 (0.22)	-2.83 (-3.62)
ethyl	6.3 (6.8)	0.27 (0.31)	-3.33 (-3.44)
propyl	7.0 (7.7)	0.37 (0.41)	-3.28 (-3.56)
allyl	6.8 (5.0)	0.37 (0.06)	-3.42 (-3.28)
benzyl	6.7 (7.2)	0.37 (0.40)	-3.50 (-3.50)
CH <sub>2</sub> CH <sub>2</sub> OH	7.9 (6.6)	0.32 (0.20)	-3.60 (-3.49)
CH <sub>2</sub> CH <sub>2</sub> Br	7.3 (8.3)	0.32 (0.71)	-3.60 (-3.43)
azaadamantane	0.	0.	0.

<sup>+</sup>in D<sub>2</sub>O, dioxan as internal standard, all shifts with respect to TMS

We achieved best agreement using the following charge densities as factors:

- i) on first atom of substituent X
- ii) on nitrogen atom
- iii) on skeleton carbon

The reason why it is just this choice of factors which gives a good correlation with SCS we hope to find in the electric field effect of the N-X bond.

Yours sincerely

*Milán Hájek*  
Milan Hájek

*Petr Trška*  
Petr Trška

Laboratory of Syntetic Fuels

Department of Organic Chemistry

Prague Institute of Chemical Technology



## Southern Research Institute

KETTERING-MEYER LABORATORY


 2000 NINTH AVENUE SOUTH  
 BIRMINGHAM, ALABAMA 35255  
 TELEPHONE 205-323-6592

June 3, 1980

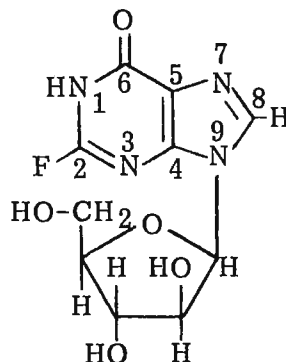
Professor Bernard L. Shapiro  
 Department of Chemistry  
 Texas A & M University  
 College Station, Texas 77843

Dear Barry:

We have been out of the  $^{13}\text{C}$  business for several months now, except for what we have been able to do during time purchased on the WH400 at the University of Alabama in Birmingham. This is because we're waiting for a new data system for the XL-100 to replace the old one. (It died a rather painful death.)

One of the spectra we have acquired during this period is of a metabolite of 2-fluoro-9- $\beta$ -D-arabinosyladenine, which we have proved to be 2-fluoro-9- $\beta$ -D-arabinosylhypoxanthine, I.

I



The  $^{13}\text{C}$  spectrum of I provided fluorine-carbon coupling constants which may be of use to some readers, since there are still not many for nitrogen heterocycles in the literature. I have tabulated these values with those for two other related purines which we have previously reported [1], 2-fluoropurine, II, and 6-amino-2-fluoropurine, III.

Compound	Coupling Constants (Hz) [2]				
	$^1\text{J}_{\text{C}2\text{F}2}$	$^3\text{J}_{\text{C}4\text{F}2}$	$^3\text{J}_{\text{C}6\text{F}2}$	$^4\text{J}_{\text{C}5\text{F}2}$	$^5\text{J}_{\text{C}8\text{F}2}$
I	-215 $\pm$ 3	23 $\pm$ 3	12 $\pm$ 3	8 $\pm$ 3	not resolved
II	-207.5 $\pm$ 0.6	17.1 $\pm$ 0.6	15.9 $\pm$ 0.6	3.7 $\pm$ 0.6	1.8 $\pm$ 0.6
III	-202.0 $\pm$ 0.6	9.2 $\pm$ 0.6	21.4 $\pm$ 0.6	not resolved	not resolved



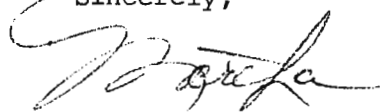
Professor Bernard L. Shapiro

Southern Research Institute

June 3, 1980

Please amend my mailing address to accommodate the Institute's new zip code, 35255, which we are told will help speed up our mail delivery.

Sincerely,



Martha Thorpe  
Senior Chemist

- [1] M. C. Thorpe, W. C. Coburn, Jr., and J. A. Montgomery, J. Magn. Reson., 15, 98-112 (1974).
- [2] Since signs of coupling constants were not determined, the long-range coupling constants are absolute values. It has been established that  $^1J_{\text{CF}}$  values are negative.



ALL COMMUNICATIONS  
TO BE ADDRESSED TO  
THE REGISTRAR

TELEPHONE  
345-1844

TELEGRAMS  
UNI MELB PARKVILLE



# University of Melbourne

DEPARTMENT OF ORGANIC CHEMISTRY

Parkville, Victoria 3052

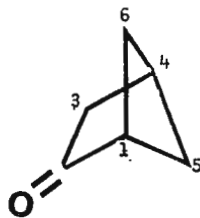
June 3rd, 1980

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

## $^1J_{CH}$ Values for Bicyclo [2.1.1] hexanone from 2D-FT Spectra at 90MHz

Dear Professor Shapiro,

For our continuing study of C-H coupling constants in carbocations<sup>1</sup> we required the values of  $^1J_{CH}$  for the neutral model ketone bicyclo [2.1.1] hexanone (I).



I

	$\delta^{13}C$ ( $\pm 0.05$ ppm)	$J_{CH}$ ( $\pm 0.5$ Hz)
1	56.0 <sub>7</sub>	160.5
2	213.7 <sub>1</sub>	-
3	40.7 <sub>6</sub>	133.5*
4	35.9 <sub>9</sub>	158.1, 12.6, 2.6
5,6	40.9 <sub>3</sub>	143.5,* 7.0

\*  $\pm 0.8$  Hz

$^1J_{C_1H}$  and  $^1J_{C_4H}$  were obtained by the normal gated decoupling technique at field strengths  $\leq 2.3T$ . However, the resonances of  $C_3$  and  $C_{5,6}$  are only separated by  $\sim 4$ Hz at 20 MHz and although the multiplet observed in the gated spectrum indicated that  $J_{C_3H} \neq J_{C_{5,6}H}$ , separate values could not be measured.

Whilst on study leave in Professor H. C. Brown's laboratory last year, I was able to use his Varian FT-80A with the latest software package including SELEX and 2DFT. Selective excitation (SELEX, 20 pulses of 1  $\mu$ sec, 3rd side band)



of  $C_3$  in the absence of  $C_{5,6}$  could not be achieved at 20 MHz.<sup>2</sup> However, a 2D-FT experiment on the FT-80A using 128 data points in each of the  $t_1$  and  $t_2$  time domains ( $f_1$   $250 \pm 3.9$  Hz,  $f_2$   $125 \pm 1.9$  Hz) showed the two couplings as approximately 133 ( $J_{C_3H}$ ) and 144 ( $J_{C_{5,6}H}$ ) Hz.

These values were in fact surprisingly accurate as was shown when we obtained a 2D spectrum on the Nicolet NT-360 at 90 MHz (Purdue Biochemical M.R. Laboratory<sup>3</sup>). By using 512 data points in the two time domains ( $t_1$  256 sample + 256 zero fill;  $f_1$   $200 \pm 0.8$  Hz,  $f_2$   $200 \pm 0.8$  Hz) we obtained well resolved peaks in both frequency domains, giving  $^1J_{C_3H} = 133.5$  and  $^1J_{C_{5,6}H} = 143.5$  Hz. (Figure and Table.)

We are anxiously waiting for the 2D software for the FG/BG disc system of our JEOL FX-100.

Yours sincerely,

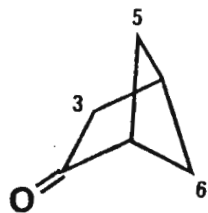


D. P. Kelly,  
Senior Lecturer in Organic Chemistry

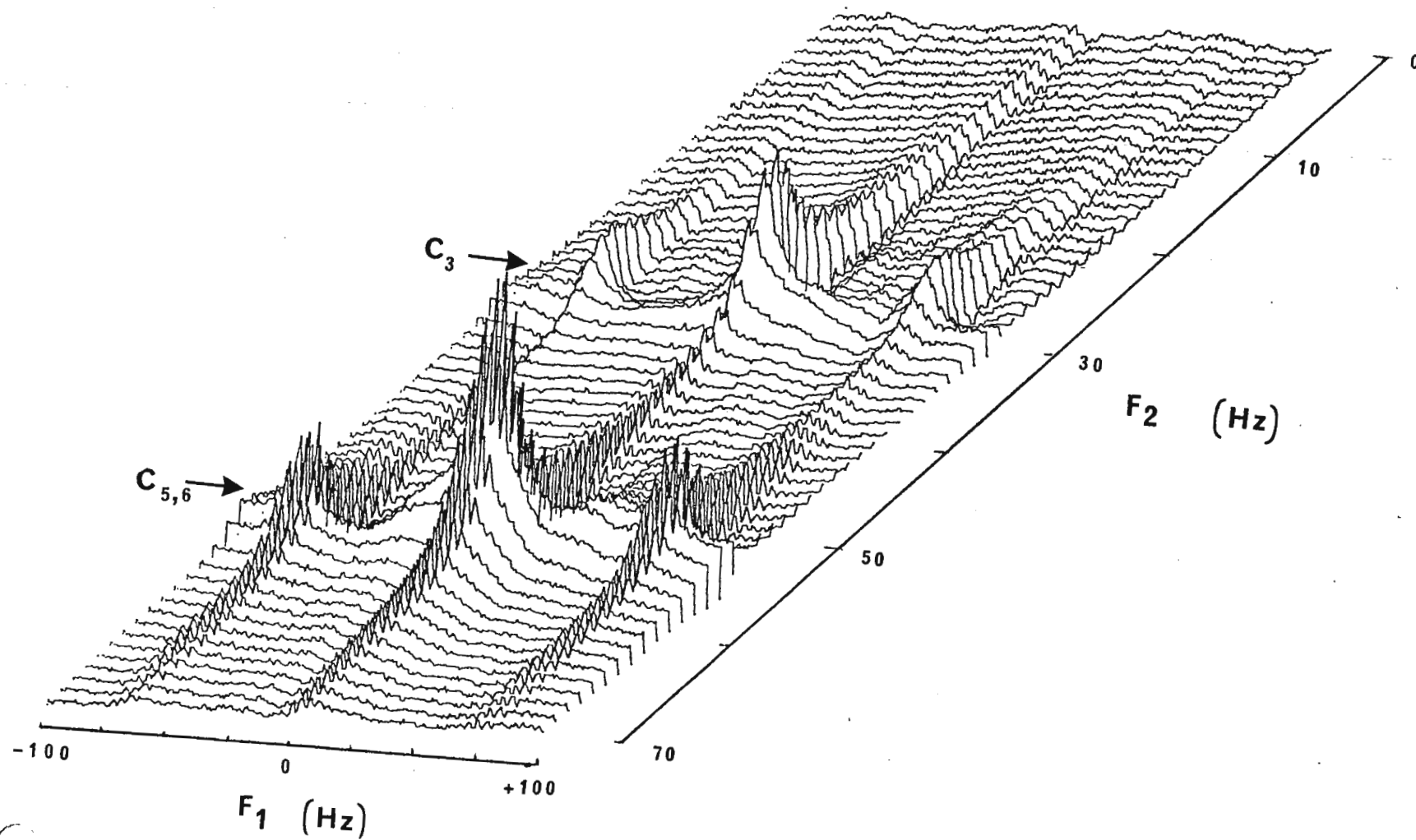
DPK:EC

1. Kelly, D.P., Underwood, G.R., and Barron, P.F., J.Am.Chem.Soc., 1976, 98, 3106.
2. For details of the use of SELEX on the FT-80A, see Varian INTERFACE, 1980, 7, 2.
3. The assistance of Mr M. Westler is gratefully acknowledged.



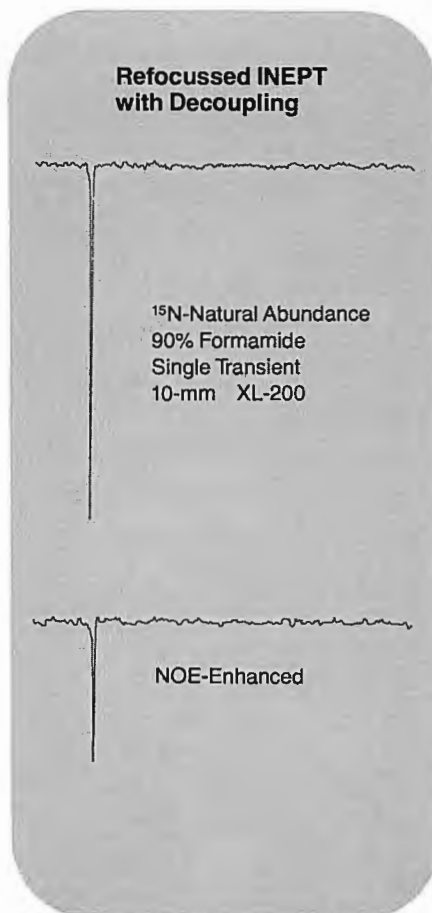
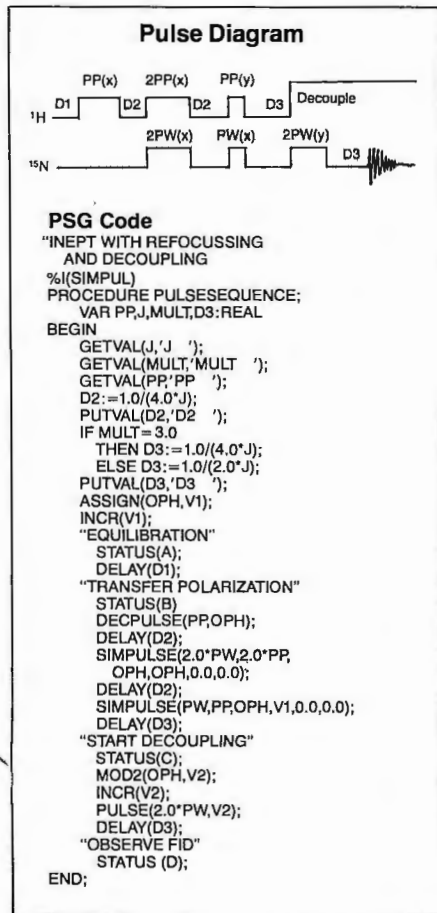


$^{13}\text{C}$  at 90 MHz





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



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

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

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

Illustrated here is a simple implementation of these ideas.

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

## Pulse Sequence Generation

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

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

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

## Acquisition Processor

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

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



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

**Standard Features**

- Computer controlled VT
- $^{19}\text{F}/^1\text{H}$  5-mm VT probe
- $^{15}\text{N}-^{31}\text{P}$  10-mm VT broadband probe
- $^1\text{H}$  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- $\mu\text{sec}$   $^1\text{H}$  90° pulse/15- $\mu\text{sec}$   $^{13}\text{C}$  90° pulse
- Internal  $^2\text{H}$  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**

- $^{19}\text{F}$  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





INDIANA  
UNIVERSITY  
PURDUE  
UNIVERSITY



at INDIANAPOLIS

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

June 16, 1980

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

TITLE:  $^{31}\text{P}$  NMR Lineshapes for Kinase Reactions

Dear Barry:

Kinases are enzymes that catalyze reactions of the type

$\text{ATP} + \text{X} \xrightleftharpoons{\text{Mg}^{2+}} \text{ADP} + \text{XP}$ , in which the terminal phosphoryl group of adenosine triphosphate (ATP) is used to phosphorylate a second substrate (X), e.g., for arginine kinase X is arginine and XP is phosphoarginine. All kinases require a divalent cation, usually  $\text{Mg}^{2+}$ , for activity. By choosing enzyme concentrations in sufficient excess of the substrate concentrations it was demonstrated some time ago that the equilibrium of interconverting enzyme-bound reactants and products could be monitored.<sup>1</sup> Figure 1A is the  $^{31}\text{P}$  NMR spectrum of such an equilibrium mixture for the arginine kinase reaction. The lineshapes in Fig. 1A are primarily governed by chemical exchange effects arising from the exchanges involving the three  $^{31}\text{P}$  nuclei on either side of the reaction when the inter-conversion  $\text{E} \cdot \text{MgATP} \cdot \text{arginine} \rightleftharpoons \text{E} \cdot \text{MgADP} \cdot \text{phosphoarginine}$  (E = enzyme) is in progress on the surface of the enzyme.<sup>1</sup>

The  $^{31}\text{P}$  exchanges in the kinase reactions in which X has no phosphorous are of the general category  $\text{ABC} \rightleftharpoons \text{A'B'} + \text{C'}$  where ABC represent  $^{31}\text{P}$  nuclei in  $\alpha\text{-P}$ ,  $\beta\text{-P}$  and  $\gamma\text{-P}$  of MgATP, A'B' represent  $\alpha\text{-P}$  and  $\beta\text{-P}$  of MgADP and C' the P of the phosphorylated substrate XP respectively. In the absence of exchange the  $^{31}\text{P}$  resonances of MgATP and MgADP show spin-spin multiplets with coupling constants  $J_{\alpha\beta} = J_{\beta\gamma} = 15.0$  Hz for MgATP and  $J_{\alpha\beta} = 18.0$  Hz for MgADP. A reliable determination of the exchange rates from the spectrum - which is of some biochemical significance since the rate of interconversion is exclusively determined in an overall kinetic scheme that has many other steps - thus requires a detailed theory although approximate estimates of the exchange rates can be made by a simple-minded approach.<sup>1</sup>

We now have a computer program to calculate the spectrum for the  $\text{ABC} \rightleftharpoons \text{A'B'} + \text{C'}$  exchange process that places no restrictions on the strength of spin-spin couplings or on the values of exchange rates. The program is based on density matrix theory discussed in the recently published book by Kaplan and Fraenkel.<sup>2</sup> The spectra calculated for a number of rates of phosphoryl transfer ( $\tau^{-1}$ ) between 0 and  $600 \text{ s}^{-1}$  are shown in juxtaposition in Fig. 2. The equilibrium constant  $[\text{E} \cdot \text{MgADP} \cdot \text{phosphoarginine}] / [\text{E} \cdot \text{MgATP} \cdot \text{arginine}] \approx 1.2$ . The calculated spectrum for  $\tau^{-1} = 120 \text{ s}^{-1}$  agrees best with the observed spectrum (see Fig. 1B). This value of  $\tau^{-1}$  is significantly smaller than the estimate of  $190 \text{ s}^{-1}$  made earlier<sup>1</sup>



by ignoring spin coupling effects. The computer simulation also offers the possibility of determining the chemical shifts of some of the nuclei in the reaction complex that are not discernible due to the complicated lineshapes in the spectrum (see the region 4-7 ppm in the spectrum). Finally, note that the exchange considered here does not randomize the relative spin orientation of A and B nuclei and therefore the  $\alpha$ -P resonance of ATP and ADP averaged together, remains a doublet regardless of how rapid the exchange is. This appears to lead to some interesting features that we are presently calculating and shall report to you before long. Best regards.

Sincerely yours,

Kashyap V Vasavada

Kashyap V. Vasavada

Jerome I. Kaplan

Jerome I. Kaplan

B. D. Nageswara Rao

B. D. Nageswara Rao

#### References

1. B. D. Nageswara Rao, D. H. Buttlaire and M. Cohn, J. Biol. Chem. 251, 6981 (1976).
2. J. I. Kaplan and G. Fraenkel, NMR of chemically exchanging systems, Academic press, New York (1980).



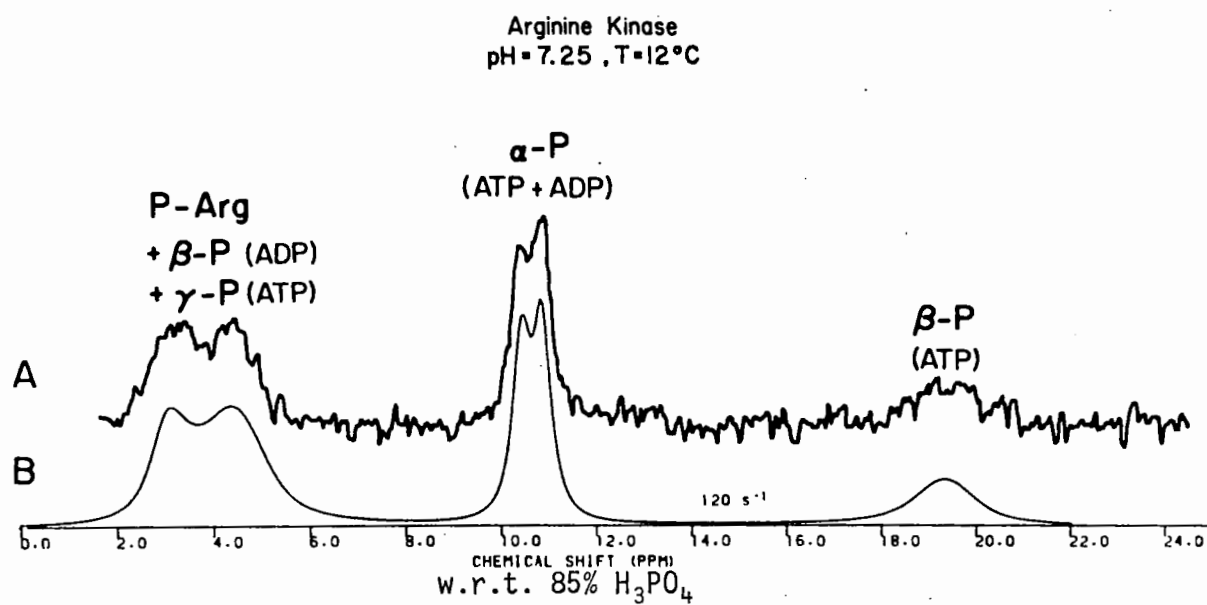


Fig. 1

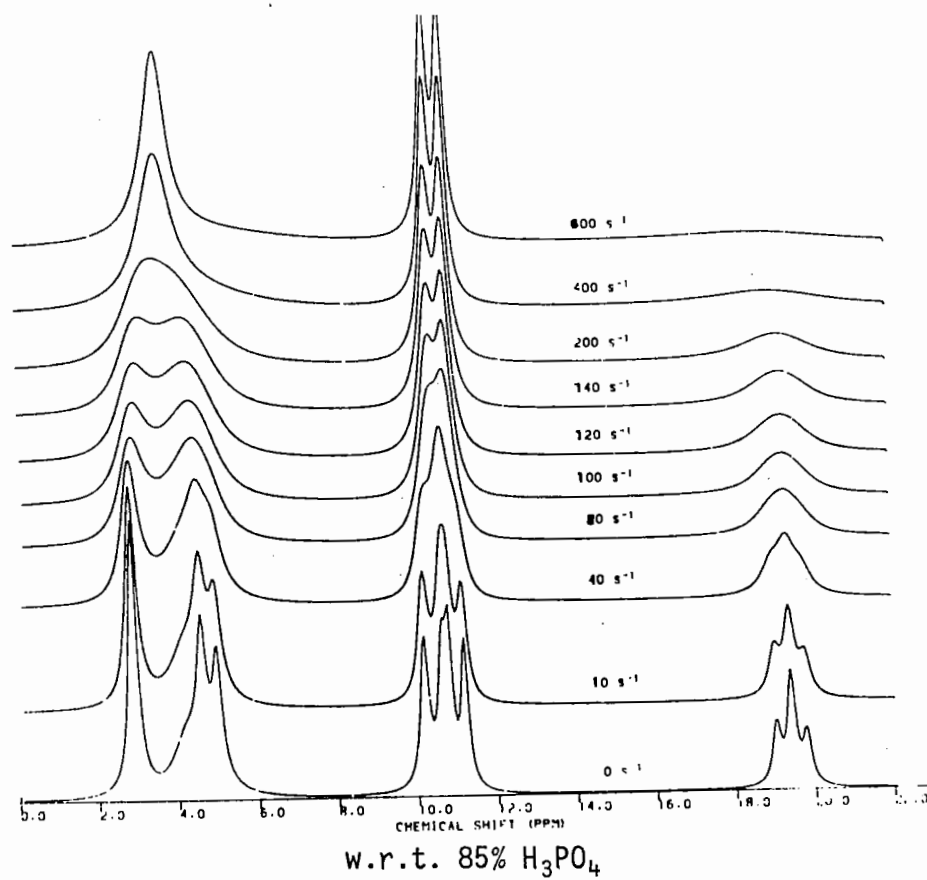


Fig. 2





Boston College, Chestnut Hill, Massachusetts 02167 Telephone (617) 969-0100

Department of Chemistry

June 9, 1980

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

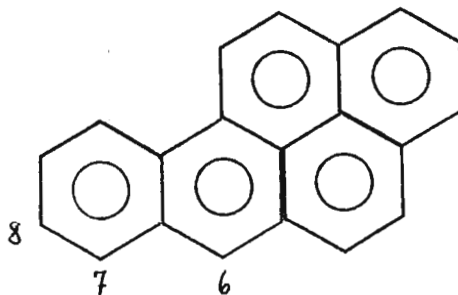
Dear Barry:

I am in receipt of your FINAL ULTIMATUM letter and, suitably chastened, offer the following observations:

"On C-F Couplings in Polycyclic Aromatic Hydrocarbons"

In connection with our studies on the ability of fluorine to attenuate, or even abolish, the carcinogenic activities of polycyclic aromatic hydrocarbons (J. Org. Chem., 1980, 45, 2064), we have been looking at their  $^{13}\text{C}$  NMR spectra as potential indicators of electron redistribution.

Carbon-fluorine coupling allows immediate identification of all carbons in the fluorinated ring. Combination of our data for 7-fluoro- and 8-fluorobenzo[a]pyrene with literature data





for fluorobenzene and 1-fluoro- and 2-fluoronaphthalene led to the following observations:

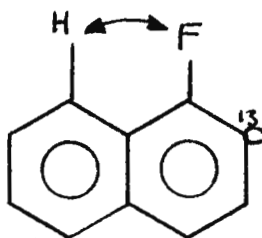
- 1) One-bond CF couplings correlate linearly with the change in  $^{13}\text{C}$  shift upon fluorine substitution:

$$\Delta\delta = 0.629 \text{ } ^1J_{\text{CF}} - 190 \quad (\text{correlation coefficient } 0.90);$$

- 2) Two-bond CF couplings correlate linearly with carbon-carbon  $\pi$ -bond orders (Huckel MO) of the parent hydrocarbons, provided couplings involving " $\alpha$ " - fluorines and " $\beta$ " -hydrogens are not included. Such couplings are overestimated by about 5.1 Hz. The origin of the deviation is unclear. At any rate, the equation

$$^2J_{\text{Cf}} = 46.87 P_{ij} - 8.94 - 5.1 N_{\text{hf}},$$

where  $P_{ij}$  is the CC-bond order and  $N_{\text{hf}}$  (=0 or 1) is the number of peri (1,8) interactions



experienced by an  $\alpha$ -fluorine coupled to a  $\beta$ -carbon, satisfactorily reproduces the observed couplings, the correlation coefficient being 0.97.

Best wishes for an enjoyable summer!

Sincerely yours,

D. J. Sardella  
Associate Professor





# University of Nottingham

Department of Chemistry

UNIVERSITY PARK NOTTINGHAM NG7 2RD  
TEL NOTTINGHAM 56101

HB/JL

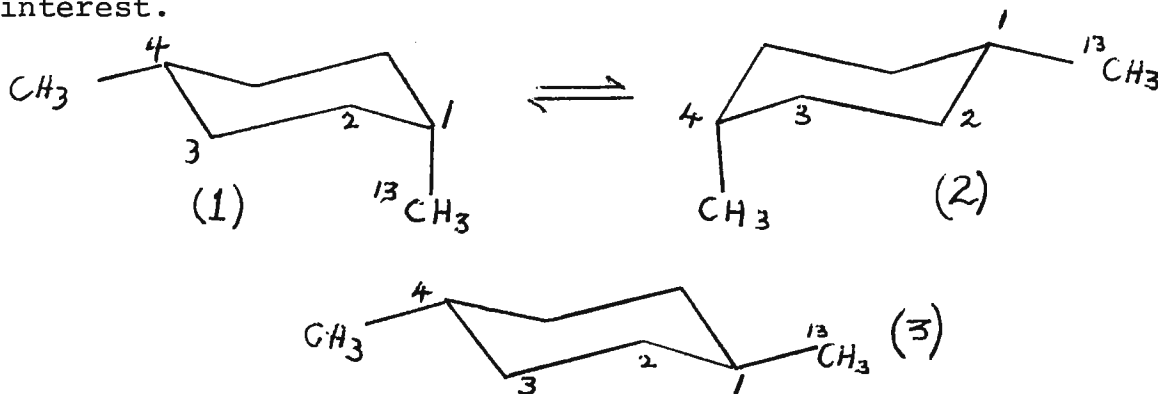
11th June 1980

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

Dear Professor Shapiro,

## Stereochemical Effects on $^{13}\text{C}$ - $^{13}\text{C}$ Coupling Constants

Recent work<sup>1</sup> on isotope effects in cis- and trans-  
[ $^{13}\text{C}$ -1-methyl]-1,4-dimethylcyclohexane has produced incidentally, some  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants which may be of some interest.



The  $^{13}\text{C}$  spectrum of (1  $\rightleftharpoons$  2) at 180 K gave  $^1J(^{13}\text{C}-^{13}\text{C})$  values of 34.6 Hz for (1) and 35.4 Hz for (2). The  $^{13}\text{C}$  spectrum of the trans- isomer (3) gave  $^1J(^{13}\text{C}-^{13}\text{C})$  as 35.6 Hz at 173 K and 35.9 Hz at 301 K. Evidently values for  $^1J(^{13}\text{C}-^{13}\text{CH}_3)$  in methylcyclohexanes depends on the orientation of the methyl group.

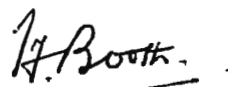
A Karplus-like correlation of  $^3J(^{13}\text{C}-^{13}\text{C})$  with dihedral angle is well established. In agreement, the  $^{13}\text{C}$  signal for C-3,5 gave  $^3J(^{13}\text{C}-^{13}\text{C})$  as 3.4 Hz for (2) and  $\leq 1$  Hz for (1).

Continued...



Of greater interest was the appreciable difference between  $^3J(^{13}C - ^{13}C)$  in (2) (3.4 Hz) and  $^3J(^{13}C - ^{13}C)$  in (3) (4.5 Hz). Since the change from equatorial Me to axial Me causes only slight alteration in dihedral angle<sup>2</sup>, we suggest that the observed difference in  $^3J(^{13}C - ^{13}C)$  for (2) and (3), is largely a substituent effect. The consequences of an alteration in stereochemistry of remote substitution have not been discussed in the recent papers of Barfield<sup>3,4</sup>, but our observations do recall roughly similar effects on  $^3J(^1H - ^1H)$  values, which we noted<sup>5</sup> in 1968.

Yours sincerely,



Dr. H. Booth.

H. Booth  
J.R. Everett\*

1. H. Booth and J.R. Everett, to be published.
2. H. Booth and P.R. Thornburrow, J. Chem. Soc. (B), 1971, 1051.
3. M. Barfield, J. Amer. Chem. Soc., 1980, 102, 1.
4. M. Barfield, J.L. Marshall and E.D. Canada, J. Amer. Chem. Soc., 1980, 102, 7.
5. H. Booth and P.R. Thornburrow, Chem. and Ind., 1968, 685.

\* Present address: Department of Chemistry,  
McGill University,  
Montreal,  
Quebec.



## Shell Development Company

A Division of Shell Oil Company



Westhollow Research Center  
P. O. Box 1380  
Houston, Texas 77001

June 16, 1980

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

Dear Professor Shapiro:

Approximately six months have elapsed since we completed the installation of a Bruker CXP-200 NMR Spectrometer at the Westhollow Research Center. We find that the CXP-200 performs well as a high-resolution multi-nuclear spectrometer regardless of the physical state of the sample.

To demonstrate some of our results from solid samples we have enclosed a  $^{13}\text{C}$  cross-polarization magic-angle spinning (CP-MAS) spectrum (Figure 1A) of p,p' isopropylidenediphenol (commonly called Bisphenol Acetone or BPA). The spectrum in Figure 1A was obtained from approximately 200 mg of BPA placed in a perdeuterated poly(methyl methacrylate) (PMMA) Andrew sample spinner. Although the spinner design allows one to routinely reach spinning rates on the order of 5000 rps with Delrin spinners, the present perdeuterated (PMMA) spinner does not have sufficient material strength to achieve this high rotational rate. As a result we could not move all of the spinning side bands (SSB) outside of the upfield region of interest. In order to place the SSB in a spectral region where they did not interfere with the upfield resonances we set the spinning rate at 3525 rps. Other pertinent parameters were: number of scans = 328, contact time = 4 msec.,  $\text{H}_2$  field strength = 15 gauss, and pulse delay = 2 sec.

The aromatic region (Figure 1B) clearly shows that the four protonated aromatic carbon atoms meta to the OH are separated into two well-resolved resonance groups, which are labeled (3) and (4). We believe this is a consequence of the relative orientation of the two aromatic rings which are fixed in the solid state. In addition, each of the aromatic resonance groups shows "fine structure" which arises from slight conformational variations of the molecule in the solid state. This "fine structure" is a good demonstration of a "distribution" of isotropic chemical shifts which arises from solid state effects since a high-resolution  $^{13}\text{C}$  NMR spectrum of BPA dissolved in  $\text{CDCl}_3$  contains only six resonances in total.

Please credit this contribution to C. A. Reilly's subscription.

Sincerely yours,

D. R. Holecek

DRH/pkm



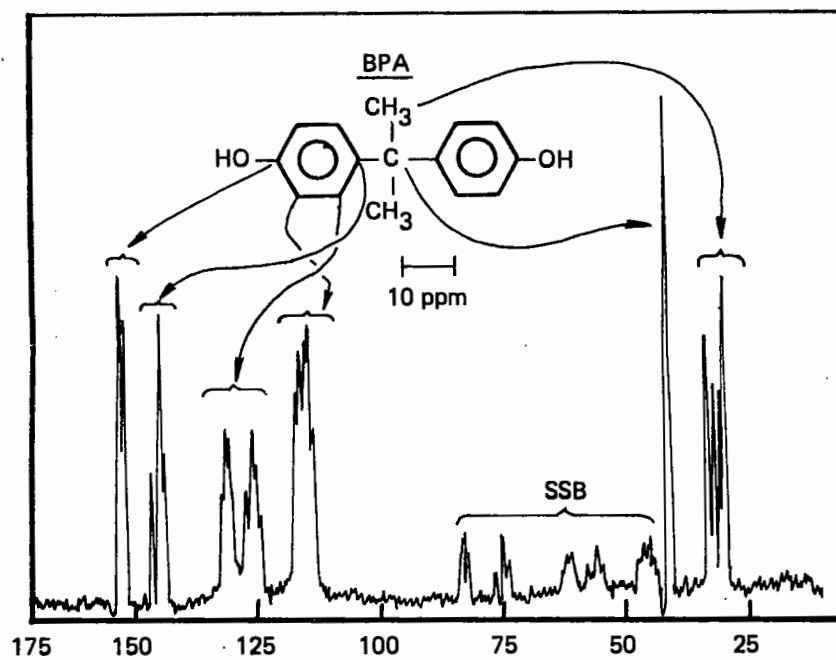


Figure 1A.

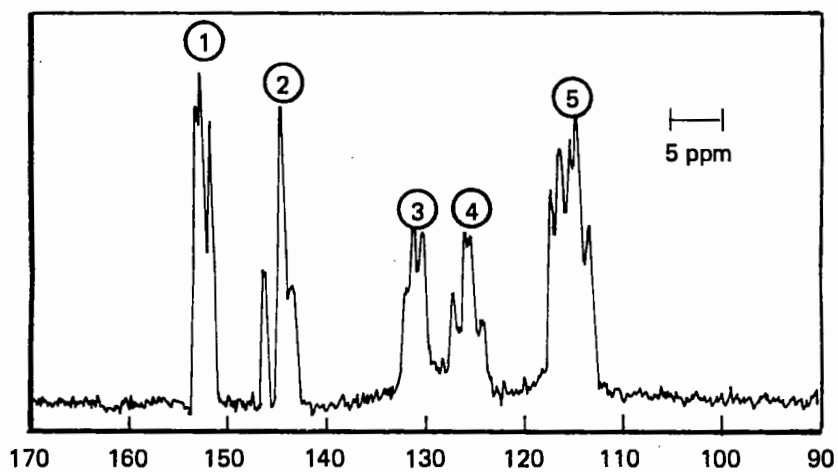


Figure 1B.

04040





DEPARTMENT OF ORGANIC CHEMISTRY  
ZERNIKELAAN, GRONINGEN  
THE NETHERLANDS  
TEL.: 050 - 11

HH/tld

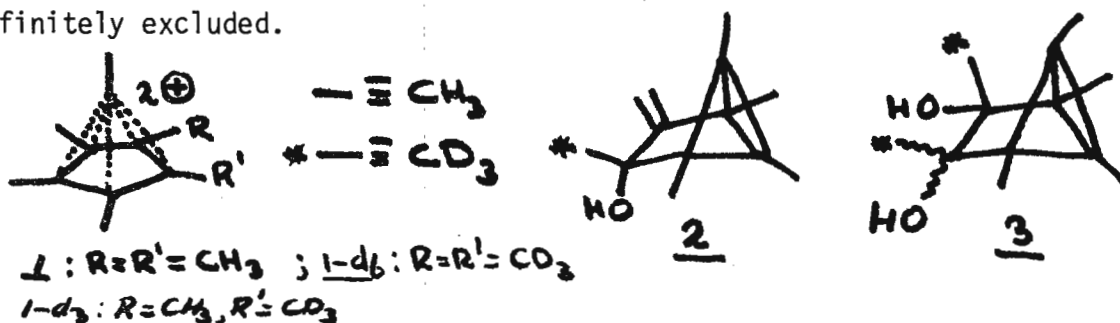
Dr. Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, TX 77843  
USA

Groningen, June 23, 1980

Dear Professor Shapiro,

Recently Saunders reported a new method for distinguishing rapidly equilibrating carbonium ions from static, symmetrical ones (classical vs. non-classical) by deuterium induced perturbation of  $^{13}\text{C}$  NMR chemical shifts.<sup>1</sup> Single peaks due to unlabeled carbonium ions are split into two signals for the deuterium substituted ions: their separation is a strong indication for the nature of the carbonium ion. Relatively large splittings (upto 100 ppm) are found for classical ions, undergoing rapid shifts, while static and non-classical ions give rather small (<2 ppm) splittings.

We applied this method to the pyramidal dication 1.<sup>2</sup> Although several indications exists that 1 has a non-classical structure, a rapid equilibrium cannot be definitely excluded.



Starting from compounds 2 and 3 we obtained deuterium labeled dications 1-d<sub>3</sub> and 1-d<sub>6</sub>, respectively. The C-13 spectra of these ions show a splitting of 0.43 ppm characteristic for non-classical carbonium ions. The spectra have been recorded on a Bruker HX-360 operating at 90.52 MHz.

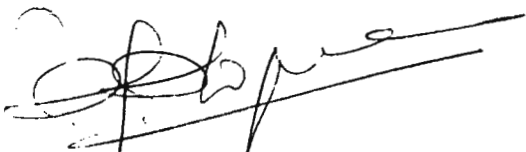


Groningen, June 23, 1980

1. M. Saunders, L. Telkowski and M.R. Kates, J. Am. Chem. Soc., 99, 8070 (1979);  
M. Saunders and M.R. Kates, *ibid.*, 99, 8071 (1979); M. Saunders, M.R. Kates,  
K.B. Wiberg and W. Pratt, *ibid.*, 99, 8072 (1979).
2. H. Hogeveen and P.W. Kwant, Acc. Chem. Res., 8, 413 (1975).

With best regards,

Sincerely Yours,



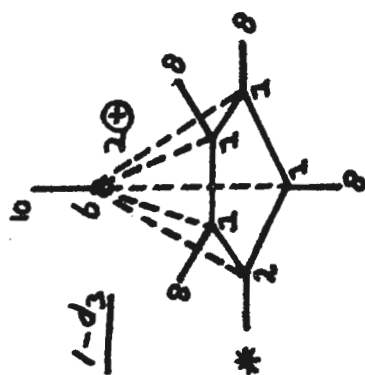
H. Hogeveen



E.M.G.A. van Kruchten

Please credit this contribution to the account of Dr. W.D. Weringa.





0.43 ppm  
 $\leftrightarrow$  (39.3 Hz)

1

2

4

\* sideband

$CD_2Cl_2$

ppm 12  
 10  
 8  
 6  
 4  
 2  
 0

150

125

100

75

50

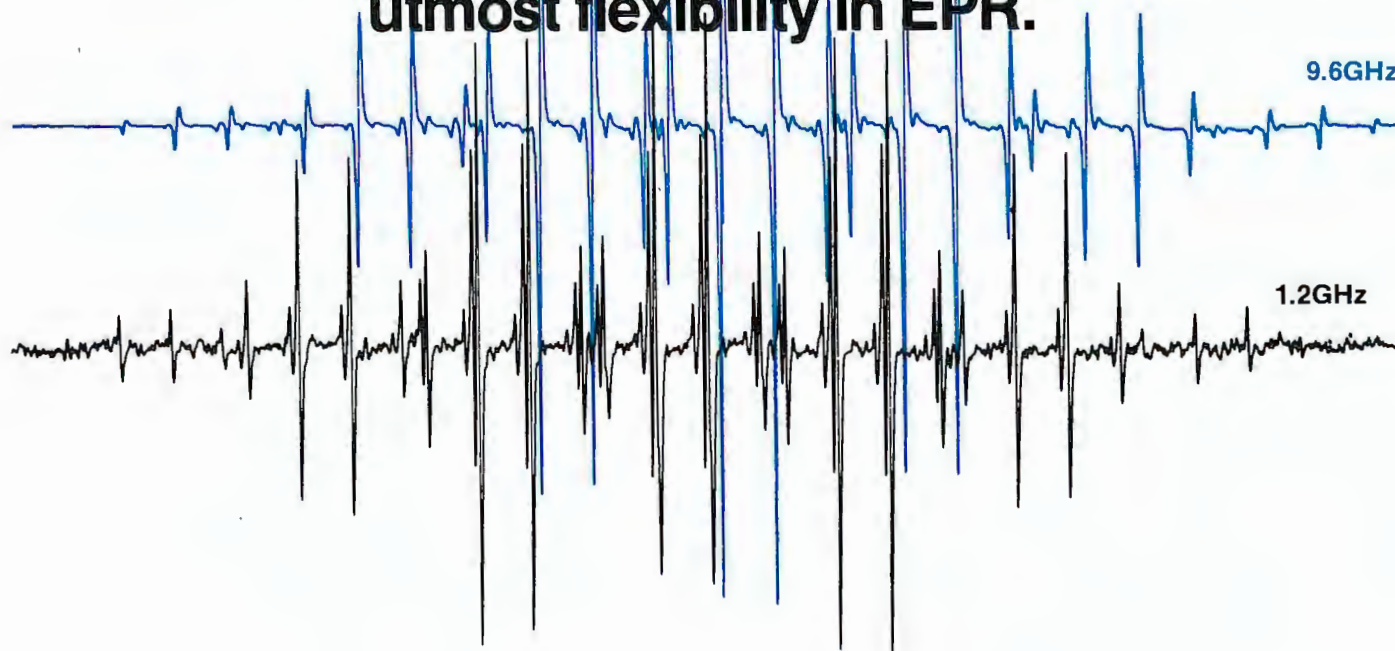
25

0



# Bruker $\equiv$ EPR EPR $\equiv$ Bruker

Now the chemist, physicist and  
biochemist can choose  
5 frequencies between 1 and 35 GHz for  
utmost flexibility in EPR.

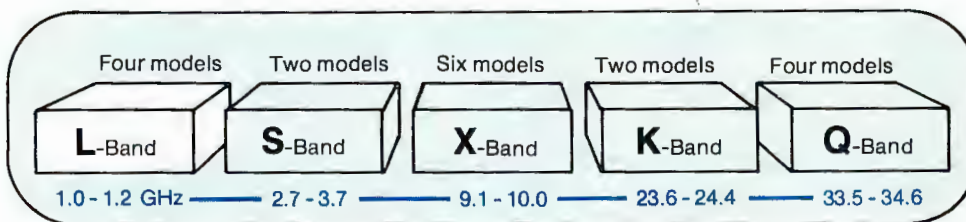


Take, for example, the Bruker ER-200D,  
select the L-Band microwave module, run a  
sample of a highly resolved radical and compare  
the spectrum to the one obtained at 9.6 GHz.  
Note the second-order splittings at L-Band.

*There is simply no alternative.*

Bruker offers a series of EPR spectrometers,  
microwave bridges and magnets which offer truly  
unique versatility. Completely modular in con-  
cept with total digital control, the ER-Series  
leaves nothing to be desired for demanding re-  
search work where flexibility of instrumentation  
and operating modes is mandatory.

All these Bruker  
microwave bridges are  
controlled by the  
same digital control  
unit: ER-048 B/C



For details on the ER-Series or a demo,  
write or call Dr. A. Heiss at  
Bruker Instruments, Manning Park,  
Billerica, MA 01821, (617) 667-9580.





**For information on EPR and NMR  
instrumentation and accessories  
your prime source  
is the nearest Bruker office:**

Bruker Instruments, Inc.  
Manning Park, Billerica, MA 01821  
(617) 667-9580

201 San Antonio Circle, Suite 152  
Mountain View, CA 94040  
(415) 941-3804

539 Beall Ave., Rockville, MD 20850  
(301) 762-4440

1603 Darwin Court, Wheaton, IL 60187  
(312) 668-4441

**Call or mail this coupon to the nearest Bruker office.**

.....  
**Please send me more information on the new ER-Series**

The information is needed for future planning ☐ for purchase after 6 months ☐

for immediate purchase ☐ Please have your EPR specialist contact me ☐

My telephone number is: (     ) \_\_\_\_\_

I am also interested in NMR systems ☐ My field of application is: \_\_\_\_\_

Name: \_\_\_\_\_

Institute/Company: \_\_\_\_\_

Address: \_\_\_\_\_

City/State/Zip: \_\_\_\_\_





## THE PROCTER &amp; GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175  
CINCINNATI, OHIO 45247

May 23, 1980

 $^{13}\text{C}$  and  $^{31}\text{P}$  Magic-Angle Spinning at 7.05 Tesla

Dear Dr. Shapiro:

We received a Bruker CXP-300 wide-bore spectrometer system last autumn, equipped for: 1)  $^{13}\text{C}$  magic-angle spinning (MAS) with 3 rotor sizes (6, 9, and 13mm o.d.) and  $^{31}\text{P}$  magic-angle spinning; 2) proton-enhanced  $^{13}\text{C}$ ; 3) high-power  $^1\text{H}$  and multinuclear; 4) high-resolution  $^1\text{H}$  and multinuclear (20mm tubes).

Although the installation is not yet complete, we can show examples of magic-angle spectra we have obtained. The  $^{13}\text{C}$  MAS-NMR spectrum of hexamethylbenzene in the small Delrin rotor (Figure 1) shows a relatively narrow ( $\Delta\nu_{1/2}=1.3\text{ppm}$ ) aromatic peak since the angle has been accurately adjusted. At the relatively high spinning speed used (5.6kHz), the spinning sidebands arising from the large aromatic carbon chemical shift anisotropy are fairly small; we have been able to obtain spectra at spinning speeds of up to 7.5kHz before the Delrin rotor disintegrated.

Figures 2 and 3 show  $^{13}\text{C}$  MAS-NMR spectra of Whatman #40 filter paper, a fairly-highly-crystalline form of cellulose I polymorph, and mercerized sewing thread (cellulose II). The perdeuterated Plexiglas rotor used yields some background peaks. The resolution is no better than that recently reported<sup>1,2</sup> at lower fields; a dispersion of chemical shifts is likely, since for crystalline sucrose the anomeric carbon resonance is significantly sharper ( $\Delta\nu_{1/2}=0.3\text{ppm}$ ). We do not observe a distinct splitting of the low-field anomeric carbon as reported by Atalla *et al*<sup>1</sup>, but slight differences in either resolution or sample characteristics could be responsible. The sensitivity at higher fields is of course markedly better, giving good spectra in less than an hour.

As part of a collaborative effort with Bill Rothwell and J. S. Waugh at MIT, we have been investigating the  $^{31}\text{P}$  MAS-NMR of calcium phosphates.<sup>3</sup> Figure 4 is the spectrum of octacalcium phosphate recently obtained on our spectrometer and shows an improvement in resolution over spectra obtained at lower fields (4.0T), since three rather than two peaks can be resolved. We have assigned the upfield peak to  $\text{HPO}_4^{2-}$  groups, and the downfield peaks to  $\text{PO}_4^{3-}$  groups.<sup>3</sup> We are continuing to use  $^{31}\text{P}$  NMR to characterize phosphate groups in crystalline, non-stoichiometric, and amorphous phosphate salts.

Please credit this letter to Dr. S. A. Goldman's account; future TAMU correspondence should be addressed to me.

Sincerely,

THE PROCTER & GAMBLE COMPANY  
Research & Development Department

James Yesinowski  
513 977-2551

<sup>1</sup> R. H. Atalla, J. C. Gast, D. W. Sindorf, V. J. Bartuska, and G. E. Maciel, *J. Amer. Chem. Soc.*, 102:9, 3249 (1980).

<sup>2</sup> W. L. Earl and D. L. VanderHart, *J. Amer. Chem. Soc.*, 102:9, 3251 (1980).

<sup>3</sup> W. P. Rothwell, J. S. Waugh, and J. P. Yesinowski, *J. Amer. Chem. Soc.*, 102:11, 2637 (1980)



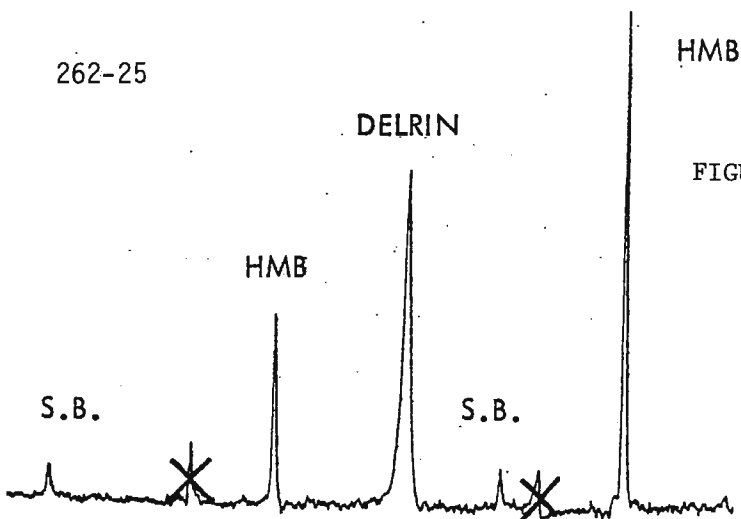


FIGURE 1:  $^{13}\text{C}$  MAS-NMR of hexamethylbenzene in small Delrin rotor,  $4\mu\text{s}$   $^1\text{H}$   $90^\circ$  pulse, 3ms cross-polarization, 4 scans, spin rate = 5.6kHz ("ghost" peaks are crossed out)

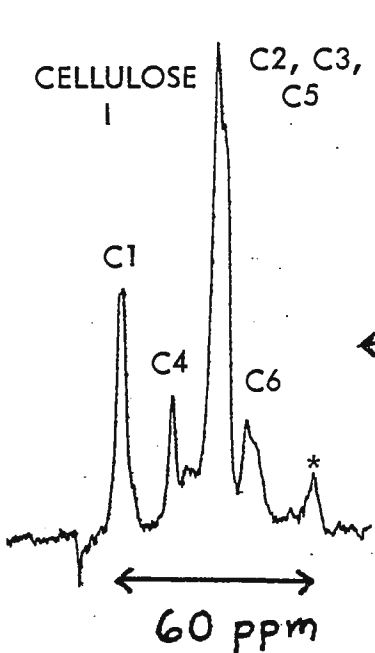
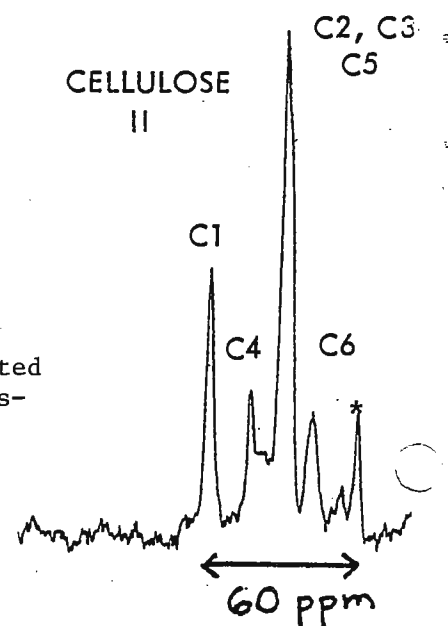


FIGURE 2:  $^{13}\text{C}$  MAS-NMR of cellulose I (Whatman #40 filter paper), medium perdeuterated rotor,  $5.3\mu\text{s}$   $^1\text{H}$   $90^\circ$  pulse, 3 ms cross-polarization, 630 scans (40 minutes) (asterisk on background signal from rotor)

FIGURE 3:  $^{13}\text{C}$  MAS-NMR of cellulose II (mercerized sewing thread), medium perdeuterated rotor,  $5.3\mu\text{s}$   $^1\text{H}$   $90^\circ$  pulse, 3ms cross-polarization, 115 scans (8 minutes) (asterisk on background signal from rotor)



$^{31}\text{P}$  NMR WITH "MAGIC-ANGLE SPINNING"  
OF SOLID  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$

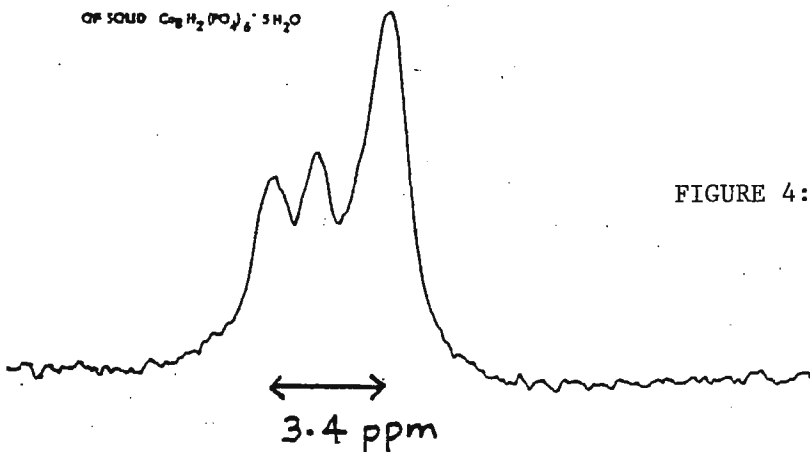


FIGURE 4:  $^{31}\text{P}$  MAS-NMR of  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ ,  $7\mu\text{s}$   $^1\text{H}$   $90^\circ$  pulse, 1ms cross-polarization, 165 scans (11 minutes)





**University of Houston**

**Central Campus**  
Houston, Texas 77004



**Department of Chemistry**  
713/749-2612

30 June 1980

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

The HP - 41C, NMR, and other fun.

Dear Barry,

I have been busy trying the limits of the newest hand held HP calculator, and I have found it is good for a number of NMR calculations. It has been nearly trivial to program a numerical solution of the Bloch equations, solutions for off resonance decoupled  $^{13}\text{C}$  NMR spectra, as in Mac Donald and Mazurek, J. Magn. Resonance, 28, 181 (1977); and the Cooley - Tookey FFT algorithm. The speed is not awesone, but it is also not bad. For instance, a 64 point array can be transformed in four minutes. There is a potential for much more efficient programs and hence better speed. As a teaching device the 41C is hard to beat, though the \$295 list price is deceptive. It takes ca \$900 to get all of the extras, that one would like, including the pointer/plotter.

I suspect an NMR calculation program for 4 or maybe 5 spins could be fit in with a little luck, but that is still in the future. I would be happy to share programs, advice, etc. with any of the other NMR users of the 41C or prospective owners.

Sincerely,

Bsb

M. Robert Willcott  
Professor of Chemistry

/fh



**EUTECO IMPIANTI S.P.A.**

CASELLA POSTALE 3843 - 20100 MILANO  
TELEFONO: 02-64.670 - TELEX: 331111

Prof. B.L. SHAPIRO,

Paderno D., 19/05/1980

Texas A & M University  
College of Science,  
Dpt. of Chemistry  
College Station,  
TEXAS 77843 U. S. A.

Dear Prof. Shapiro,

recently we had the necessity to indicate with a simple and relatively fast method the presence of all three classes of amines (primary, secondary and tertiary) in a mixture and to determine their relative quantities. F. Mozayeni (Appl. Spectr. 33, 520, 1979) suggests the following method : addition of trifluoroacetic acid,  $\text{CF}_3\text{COOH}$ , to the sample to convert the amines to their salts, evaporation of the excess acid, dissolution of the residue in  $\text{CDCl}_3$ . In this way three separate peaks due to protonated amines ( $\text{NH}_3^+$ ,  $\text{NH}_2^+$  and  $\text{NH}^+$ ) appear in the 7 to 11 ppm region of the spectrum.

We have found that this procedure can be simplified. It is enough to dissolve the sample in DMSO and to add an excess of  $\text{CF}_3\text{COOH}$  to the solution. Without any other additional work, three separate peaks for  $\text{NH}_3^+$ ,  $\text{NH}_2^+$  and  $\text{NH}^+$  appear at low field of the NMR spectrum. The advantage of this procedure is obvious for long-chain amines, the salts of which normally have poor solubility in  $\text{CDCl}_3$  but are soluble in DMSO. The Figure hereby attached shows an example of the separation for n-butylamine (I), n-di-butylamine (II) and n-ethyl-piperidine (III). The chemical shifts due to protonated amines groups appear at 8.00  $\delta$  ( $\text{NH}_3^+$ ), 8.67 ( $\text{NH}_2^+$ ) and 9.80 ( $\text{NH}^+$ ),

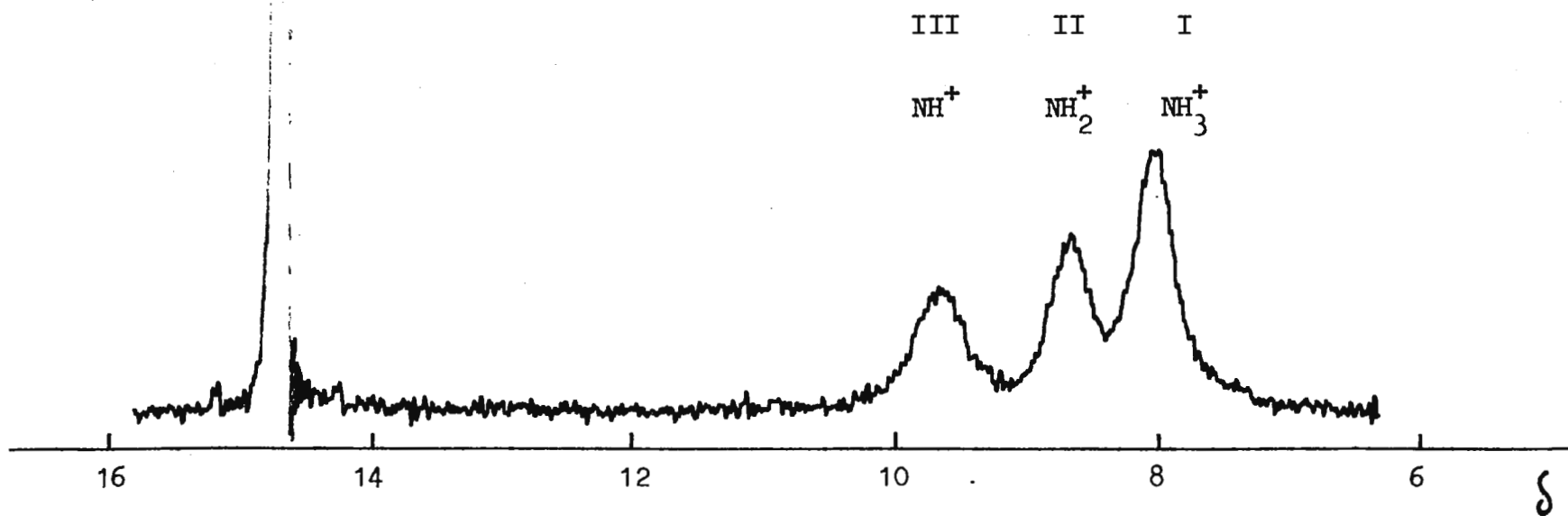
yours sincerely,

G. Cancellieri L. Lanzini L. Cavalli  
*G. Cancellieri L. Lanzini L. Cavalli*

Centro Ricerche  
v. Reali, 4  
20037 Paderno D. (MI) ITALY



excess  $\text{CF}_3\text{COOH}$



from TMS



Department of Physical Chemistry and  
Department of Inorganic Chemistry  
THE ROYAL INSTITUTE OF TECHNOLOGY  
S-100 44 STOCKHOLM 70 Sweden

Stockholm, June 18, 1980

Professor B L Shapiro  
Department of Chemistry  
Texas A&M University  
COLLEGE STATION  
Texas 77843 U S A

Dear Professor Shapiro,

$^{13}\text{C}$  studies of uranyl-carbonate complex

With carbonate as ligand the  $\text{UO}_2^{2+}$  ion forms a mononuclear complex  $\text{UO}_2(\text{CO}_3)_3^{4-}$  and a polynuclear complex  $[(\text{UO}_2)_3(\text{CO}_3)_6]^{6-}$ . Using  $^{13}\text{C}$  enriched carbonate, spectra are easily obtained from 10 mM solutions. Figure 1a shows a room temperature spectrum with separate signals from mononuclear complex and excess of  $\text{HCO}_3^-$ . The complexed carbonates have their resonance at 6.39 ppm downfield from an external 20 mM  $\text{HCO}_3^-$  solution. The signals coalesce upon heating due to the increased ligand exchange rate. Figure 1b shows the spectrum from a solution containing the polynuclear complex. The signal at 6.0 ppm probably originates from non-bridging carbonates since its shift is close to that of the mononuclear complex. The bridging carbonates have their resonance at 7.31 ppm. The kinetics in this system is presently studied in combination with stopped-flow measurements. We are also investigating the structure of the polynuclear complex (linear or triangular ?) in combination with X-ray diffraction from concentrated solutions.

Yours sincerely



Ulf Henriksson



Ingemar Grenthe



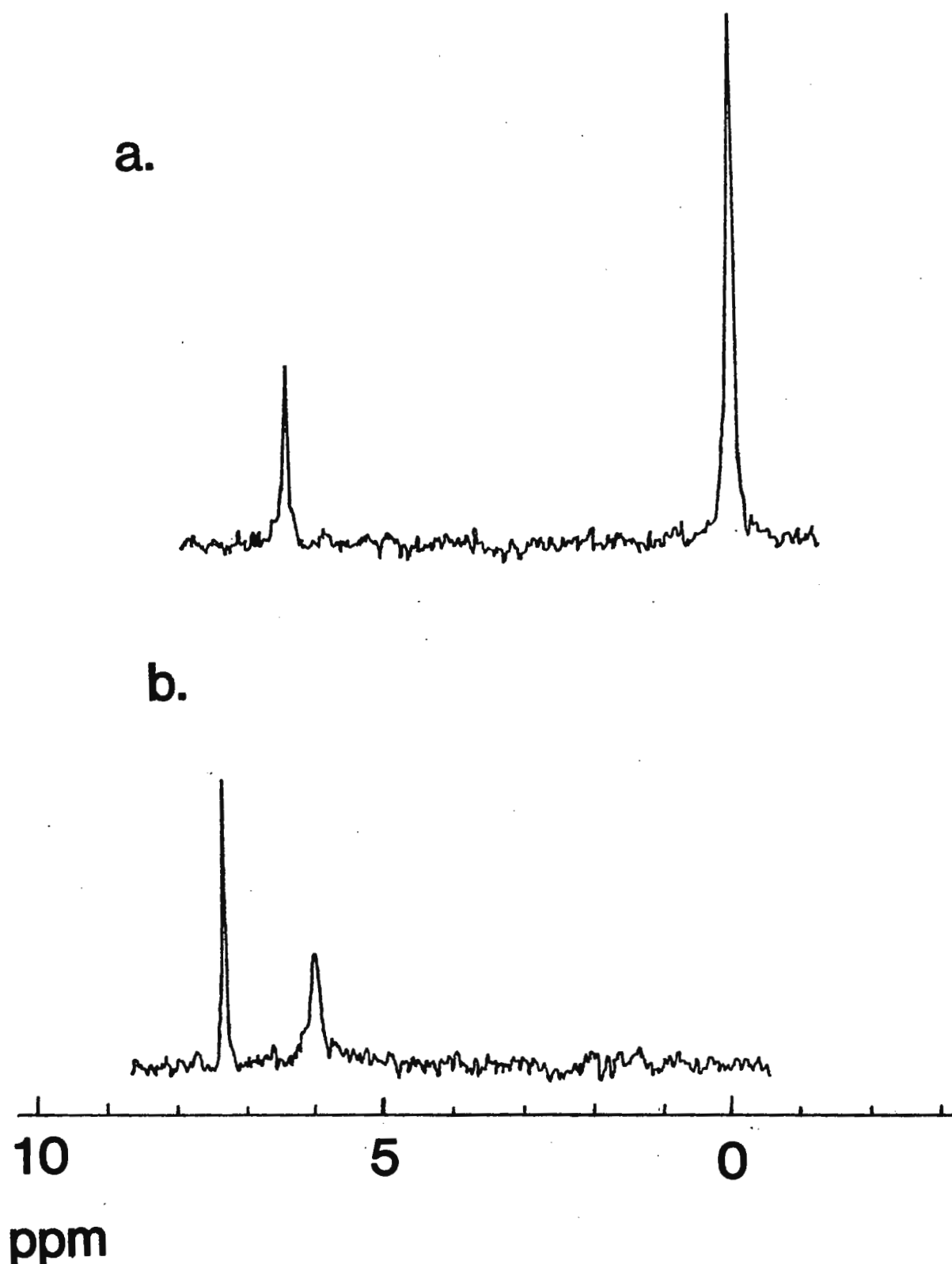


Figure 1. 50 MHz  $^{13}\text{C}$  spectrum from uranyl-carbonate solutions ( $[\text{UO}_2^{2+}] = 10 \text{ mM}$ ). a) Mononuclear complex  $\text{UO}_2(\text{CO}_3)_3^{4-}$  and excess of  $\text{HCO}_3^-$ . b) Polynuclear complex  $[(\text{UO}_2)_3(\text{CO}_3)_6]^{-6}$ . The shifts are downfield from external 20 mM  $\text{NaHCO}_3(\text{aq})$ . All samples contain 3 M  $\text{NaClO}_4$  as ionic medium.



## UNIVERSITY OF CALIFORNIA, SANTA BARBARA

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

June 18, 1980

DEPARTMENT OF CHEMISTRY

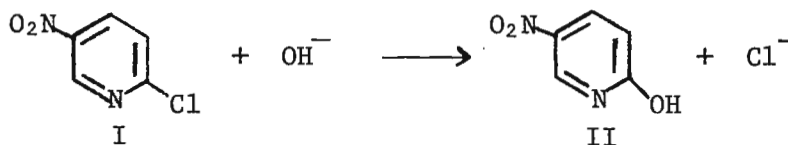
SANTA BARBARA, CALIFORNIA 93106

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

"An Intermediate in the Reaction of 2-halo-5-nitropyridines with Hydroxide"

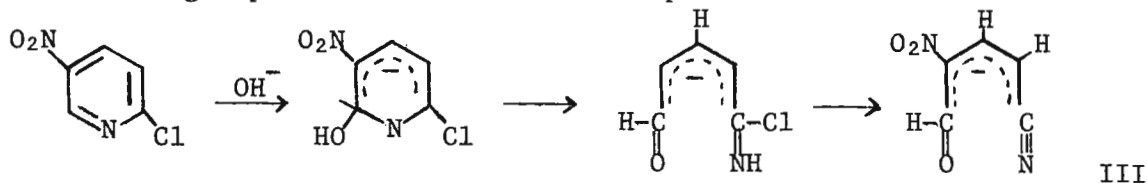
Dear Barry:

Dr. John Reinheimer, who is visiting the department on sabbatical leave, brought with him an interesting problem in organic reaction mechanism. When a 2-halo-5-nitropyridine such as I is treated with less than two molar equivalents of hydroxide in dimethylsulfoxide solution a new, yellow species is formed; it is not the expected product, 2-hydroxy-5-nitropyridine(II), however. Compound II is formed if an excess of hydroxide is present.



Using an nmr tube as the reaction vessel it was possible to obtain carbon and proton spectra of the new material and Figure I shows some carbon spectra which we obtained at 25.4 MHz under conditions where proton decoupling was incomplete, so that proton-bearing carbons would appear as broadened resonances.

By means of these data as well as information from uv and ir spectroscopy, the structure of the intermediate formed in this reaction was deduced to be III. The carbon signal at 182 ppm is assigned to the aldehyde carbonyl while the non-protonated carbon resonance at 120 ppm likely arises from the nitrile. Both of these functional groups are evident in the ir spectra.



The evidence marshalled to support the proposed structure for the intermediate formed in this reaction and the conversion of this structure to the ultimate product II are discussed in a manuscript which has been accepted by J. Org. Chem. Suffice it to say that this work provides yet another example of a structural problem that likely could not have been solved readily without carbon nmr spectroscopy.

Sincerely yours,

*Tom*

J. T. Gerig  
 Professor of Chemistry



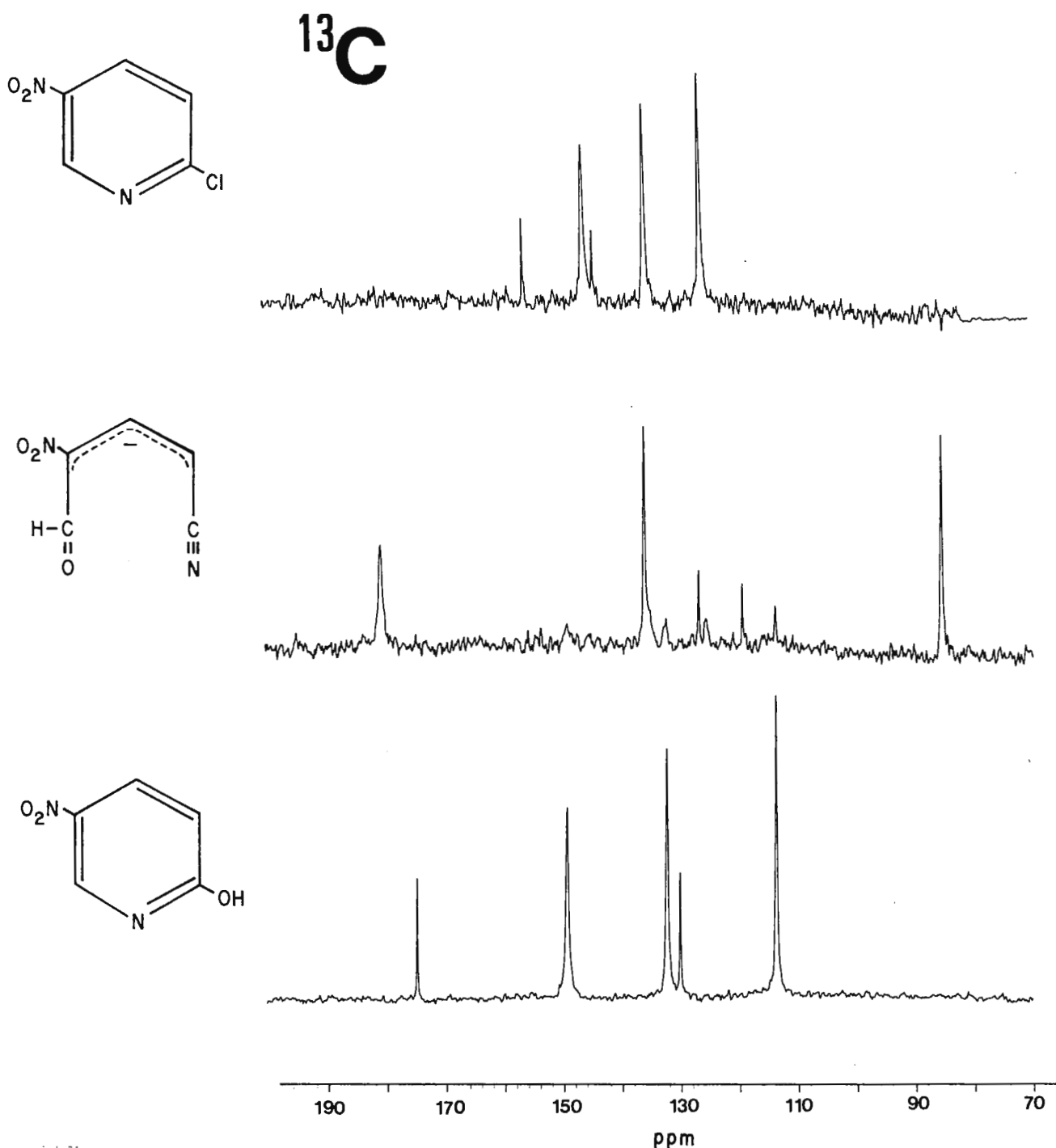


Figure 1. Carbon-13 spectra of reactant, intermediate and product in the conversion of 2-chloro-5-nitropyridine to the 2-hydroxy compound. Sample temperature was  $\sim 34^\circ$ ; the signal from a capillary of neat dioxane was set at 67.4 ppm relative to TMS.



Princeton University

DEPARTMENT OF CHEMISTRY

PRINCETON, NEW JERSEY 08544

June 18, 1980

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

Title:  $^{13}\text{C}$  NMR of Tetrasubstituted Cyclopropenes

Dear Professor Shapiro:

We recently found it necessary to run the  $^{13}\text{C}$  spectra of some interesting tetrasubstituted cyclopropenes, structures I - IV. Their chemical shift data are presented below, with the exception that the " $\text{Sp}^3$ " carbon of cyclopropenes II and IV could not be forced up out of the baseline, even under conditions with a good signal-to-noise ratio. Liz Williams ran the  $^{29}\text{Si}$  spectra for us on compounds I and III,<sup>1</sup> the shifts being 1.18 $\delta$  and 1.84 $\delta$  respectively. All chemical shifts are in ppm downfield of TMS.

Sincerely,

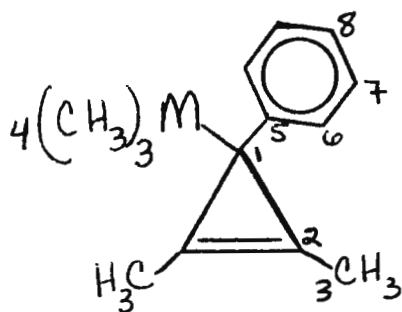
*Mary W. Baum*

Mary W. Baum\*, Maitland Jones, Jr.  
and Neal D. Conrad

MB/bc  
enclosure

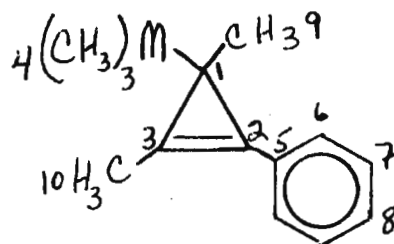
<sup>1</sup>B. Coleman, N. D. Conrad, M. W. Baum and M. Jones, Jr.  
JACS, 101, 7743 (1979).





I, M = Si

II, M = Ge



III, M = Si

IV, M = Ge

	I	II	III	IV
1.	23.29		14.5	
2.	110.6	111.99	119.6	121.53
3.	10.64	10.53	116.4	118.17
4.	-0.54	-1.39	-1.45	-2.42
5.	149.9	150.46	130.6	129.28
6*.	127.9	127.98	128.42	128.46
7*.	127.8	127.38	128.40	128.46
8.	124.3	124.35	126.8	126.95
9.			20.8	22.23
10.			11.2	11.40

\*may be interchanged.



**Stony Brook**

June 23, 1980

Professor Bernard L. Shapiro  
TAMU NMR Newsletter  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843TITLE: SIMULATED NMR SPECTRA OF METAL CATION TRANSPORTING  
VESICLE SYSTEMS / POSTDOCTORAL POSITIONS AVAILABLE

Dear Barry:

The NMR spectrum of a nucleus in the headgroup region of phospholipid molecules on the inside surfaces of single bilayer vesicles changes as paramagnetic metal cations are transported into the interiors. We have recently been working on a line-shape theory for simulating the time dependence of such a spectrum. The theory is based on a stochastic differential equation describing the ion translocation process and has yielded some interesting results. The accompanying Figure shows some sample simulations for vesicles whose inner headgroup resonance (say, a  $^1\text{H}$ ,  $^{31}\text{P}$ , or  $^{13}\text{C}$  peak) is located at +30 Hz (width at half height, 10 Hz) at time zero when there are no paramagnetic ions inside. This hypothetical vesicle population has a distribution of mediating species which averages to 200 per vesicle and these species must act as dimers to translocate ions. The concentration of paramagnetic ions outside at time zero is such that, at equilibrium, the inside resonance will have been shifted upfield to +140 Hz (width, 20 Hz, this corresponds roughly to a 220 MHz  $^1\text{H}$ -N(CH $_3$ ) $_3$  experiment where ca. 150  $\text{Eu}^{+3}$  ions have entered the average vesicle at equilibrium). In each of the simulations, mediating "events" occur at the same average rate of  $10^{-8}$  sec $^{-1}$ . However, the relative "efficiencies" of the events differ in the different simulations. The parameter  $\rho$  is a dimensionless, exponential measure of the efficiency. For very efficient mediating events, say, large pore activation, the spectra show "all or nothing" behavior (a), i.e. the vesicles are of only two types; those which have received all their 150  $\text{Eu}^{+3}$  ions and those which have not. For very inefficient mediating events, say, mobile carrier transbilayer diffusion, the spectra show "slow leakage" behavior (d). For intermediate efficiencies, rich spectra are observed (b and c). Other interesting spectra are predicted for very low mediator levels. Some experimental spectra with similar line-shapes have been observed.

This work was done in collaboration with:

David Z. Ting  
Sunney Chan  
Patrick S. Hagan

} at Cal. Tech.

and

Jimmie D. Doll at Stony Brook

Best regards,

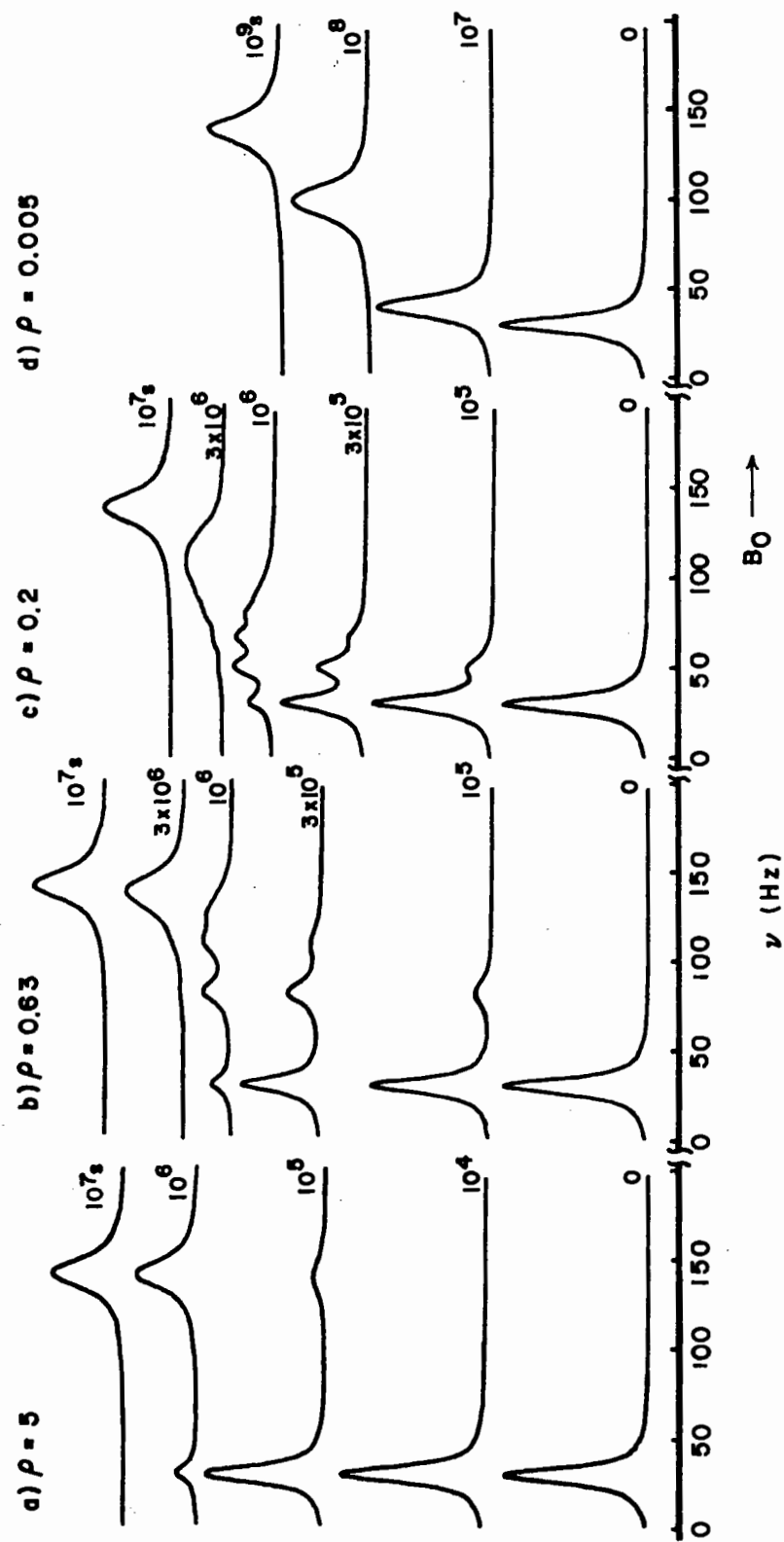
*Charlie Springer*Charles S. Springer, Jr.  
Associate Professor of Chemistry

CSS/job

P. S. There are postdoctoral possibilities on a number of various magnetic resonance projects (both NMR and ESR), generally in biological areas, available with Paul Lauterbur, Larry Dalton, Larry Altman, Arnold Wishnia, or myself at Stony Brook.

P.P.S. Please credit this contribution to the Paul Lauterbur / Stony Brook subscription.









University  
of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building,  
295 Cathedral Street, Glasgow G1 1XL Tel: 041-552 4400

25th June, 1980.

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

Dear Barry,

'Simple method of gated decoupling'

Our Jeol PFT-100 system is now rather long in the tooth and lacks many of the facilities now provided as standard with modern systems. Up till now we have got by without the ability to do gated  $^{13}\text{C}\{^1\text{H}\}$  double resonance, but the need has now arisen, and we spent some time looking into the easiest way of providing this facility.

Fortunately the necessary logic output is provided by the computer interface, and we derive the proton 100 MHz frequency from a Schlumberger FS120 frequency synthesiser which is capable of being controlled remotely. We use the gating waveform to drive a DIL relay which switches the synthesiser frequency between 99.996 MHz (on) and 89.996 Mz (off). The tuned circuits of the power amplifier effectively alternates the output to zero in the latter case. We were agreeably surprised by the adequate switching performance of the relay and synthesiser. The circuit is shown in the figure.

Yours sincerely,

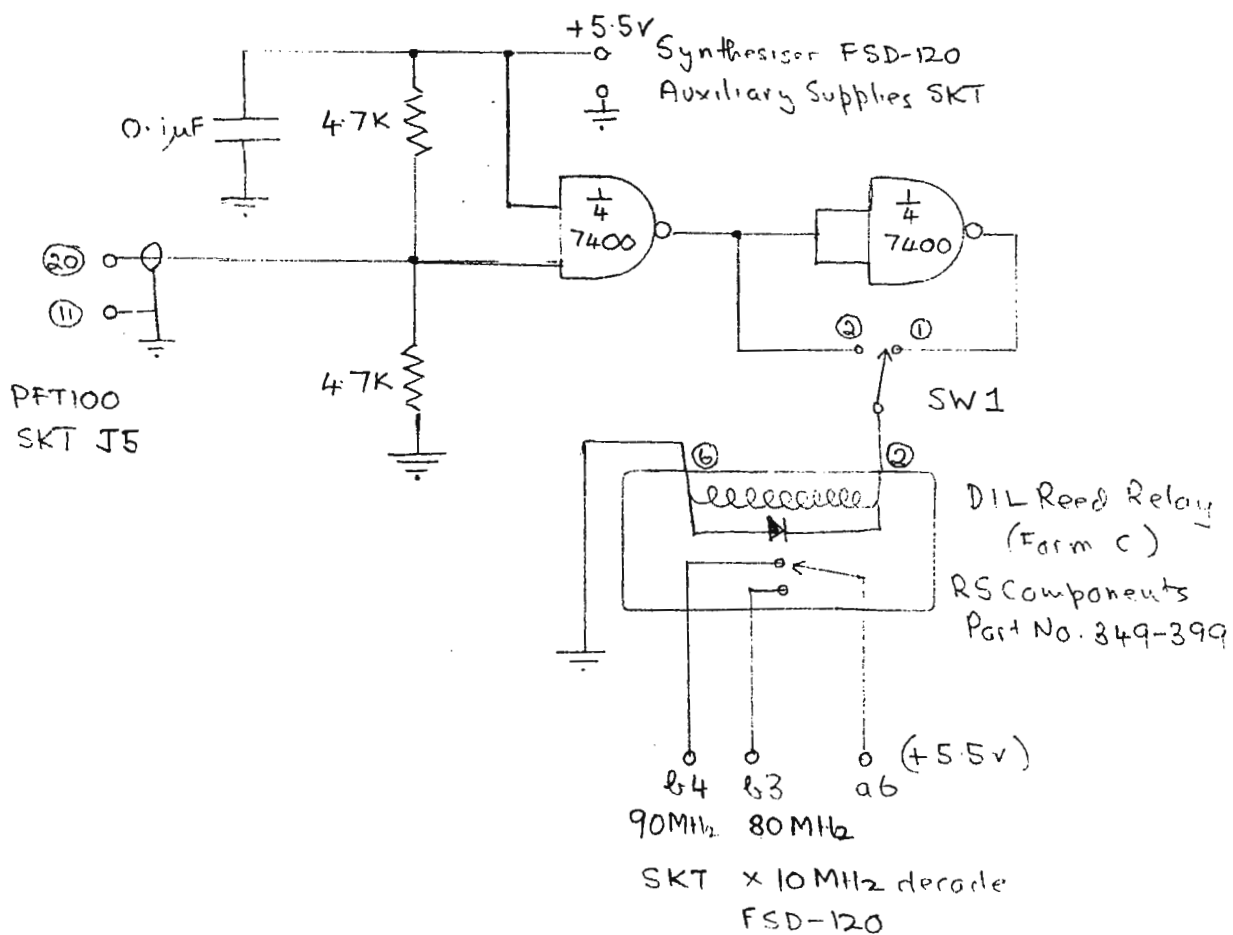
*Peter Bladen*

Dr. Peter Bladen

*John Ritchie*

John Ritchie.





GATED DOUBLE RESONANCE  
 USING REMOTE CONTROLLED  
 FREQUENCY SYNTHESISER





# TECHNISCHE HOGESCHOOL DELFT

## Laboratorium voor Technische Natuurkunde

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

Uw kenmerk	Uw brief van	Ons kenmerk	Datum	Delft, Lorentzweg 1
		RAW/mvs	26th June 1980	Doorkiesnummer (015) 786157

### Onderwerp

$^{13}\text{C}$  spectroscopy in coal using carbon-proton cross polarization and proton dynamic polarization

Dear Professor Shapiro,

It has been shown [1] that the aromatic/aliphatic character of coal can be derived from its  $^{13}\text{C}$  spectrum. To this end the  $^{13}\text{C}$  signal is observed while decoupling the protons, whereas the proton-carbon cross polarization technique is applied to reduce the measuring time [2]. However, in practice usually a few hours is needed to obtain a reasonable signal-to-noise ratio. Now it is well-known that coal contains many radicals, and we asked ourselves the question whether a dynamic polarization experiment [3] could be used to enhance the proton polarization and so, via the cross polarization, the  $^{13}\text{C}$  polarization. This would provide an extra reduction in measuring time of, theoretically, a factor  $(660)^2 = 4.10^5$ ! Indeed we found [4] that irradiating near an esr frequency of 22 GHz gives an enhancement of the proton signal of 14 to 30, depending on the carbon content of the coal. During the last couple of months we extended our Bruker XP 4-100 spectrometer with a second modulator (driven by the Bruker pulse programmer) and transmitter, and we constructed a probe suitable for the combined experiment of dynamic polarization, cross polarization and decoupling. As an esr frequency we chose 39.43 GHz, corresponding to a proton frequency of 60 MHz and a  $^{13}\text{C}$  frequency of 15 MHz. We obtained the following results:

(i) For a 4 mm i.d. degassed sample and a 7 W klystron a proton enhancement was found varying from ca. 4 to 10. This is less than at 22 GHz because of lack of esr power (for a 100 W klystron enhancement factors of 20 to 50 are predicted).

(ii) Figure 1 shows the first preliminary result of the  $^{13}\text{C}$  spectrum of a coal with a carbon content of ca. 91% (with dynamic polarization the proton signal was enhanced with a factor 10). Fig. 1a shows the result after a cross polarization experiment only, fig. 1b is the result of combined dynamic polarization and cross polarization. The difference in sensitivity is conclusive: With



dynamic polarization in half the time a sensitivity is obtained which is at least a factor 10 larger than without DNP.

The fact that we still needed 2100 scans to obtain the spectrum of fig. 1b is due to the fact that the sensitivity of the spectrometer is down, probably because of extra noise induced in the  $^{13}\text{C}$  channel while decoupling the protons. Fig. 2 shows the  $^{13}\text{C}$  spectrum of adamantane after 200 scans, which illustrates the low sensitivity. At the moment we are busy, besides improving the sensitivity of the spectrometer, with the construction of a probe which will enable us to perform magic angle spinning of the sample as well.

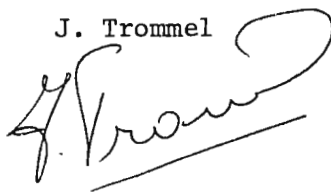
- [1] G.E. Maciel, V.J. Bartuska and F.P. Miknis, Fuel 58, 391 (1979)
- [2] A. Pines, M.G. Gibby and J.S. Waugh, J. Chem. Phys. 59, 569 (1973)
- [3] A. Abragam and M. Goldman, Rep. Prog. Phys. 41, 395 (1978)
- [4] R.A. Wind, J. Trommel and J. Smidt, Fuel 58, 900 (1979)

Yours sincerely,

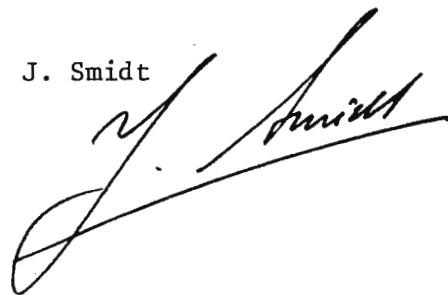
R.A. Wind



J. Trommel



J. Smidt



Please credit this letter to J. Smidt.



$^{13}\text{C}$  spectrum of coal, 91% carbon content

$^1\text{H}$ :  $f_0 = 60.000$  MHz, matching field = lock field = 10 Oe

$^{13}\text{C}$ :  $f_0 = 15.091$  MHz, matching field = 40 Oe

ESR:  $f_0 = 39.43$  GHz, 7 Watt

matching time = 0.9 msec, recycle delay = 1 sec

$T = 296$  K

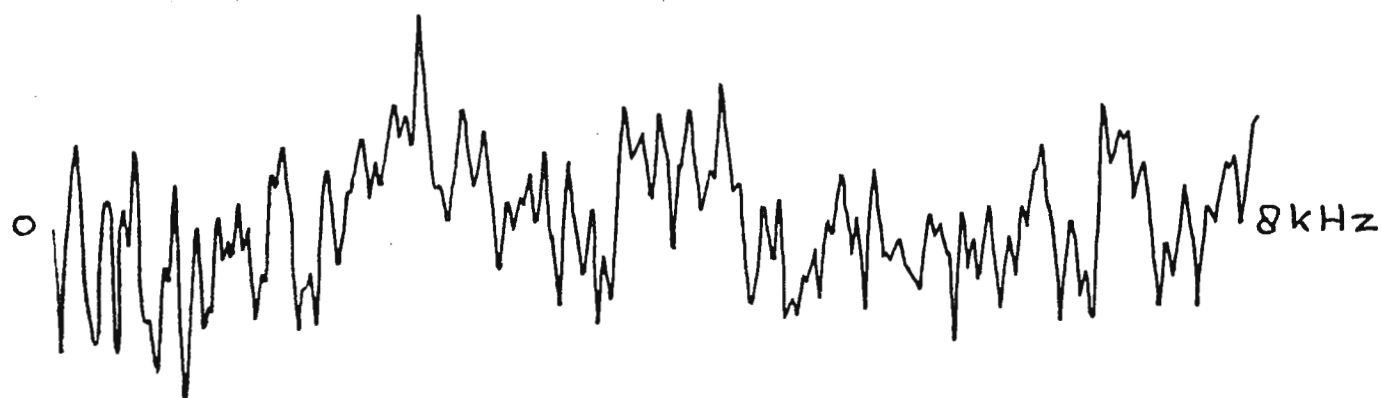


Fig. 1<sup>a</sup>. Cross polarization only, 3500 scans

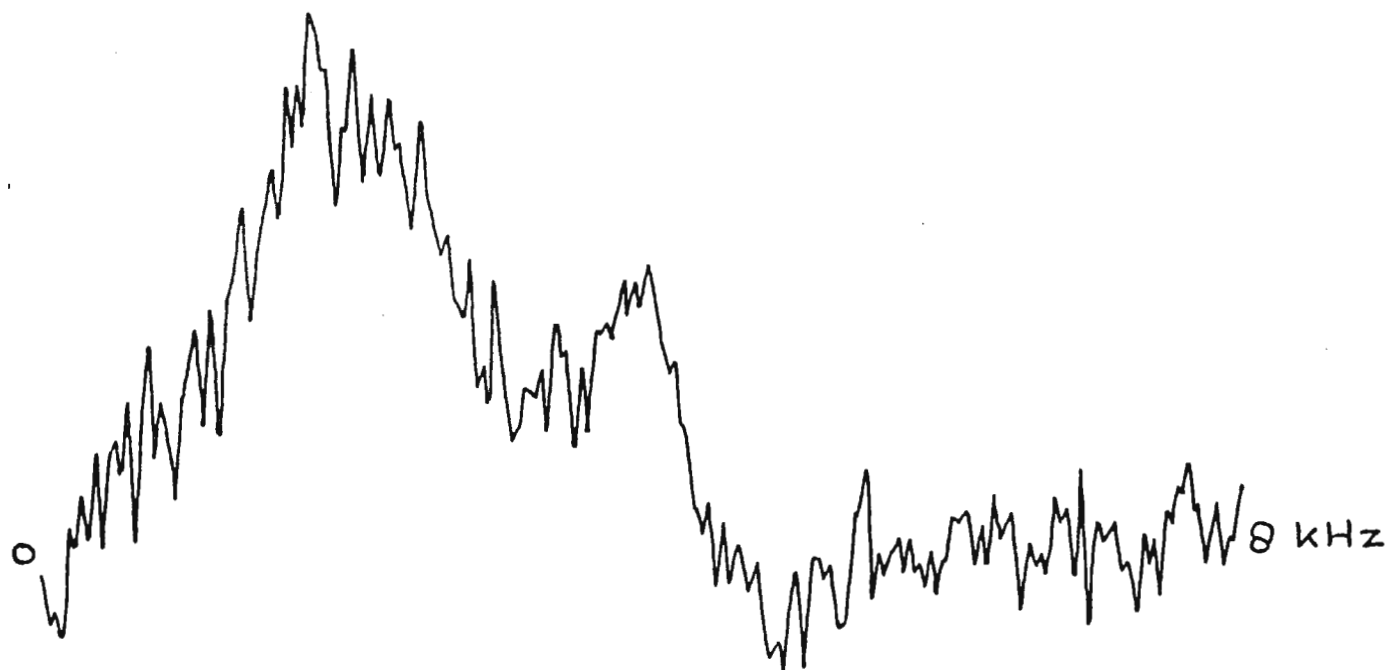
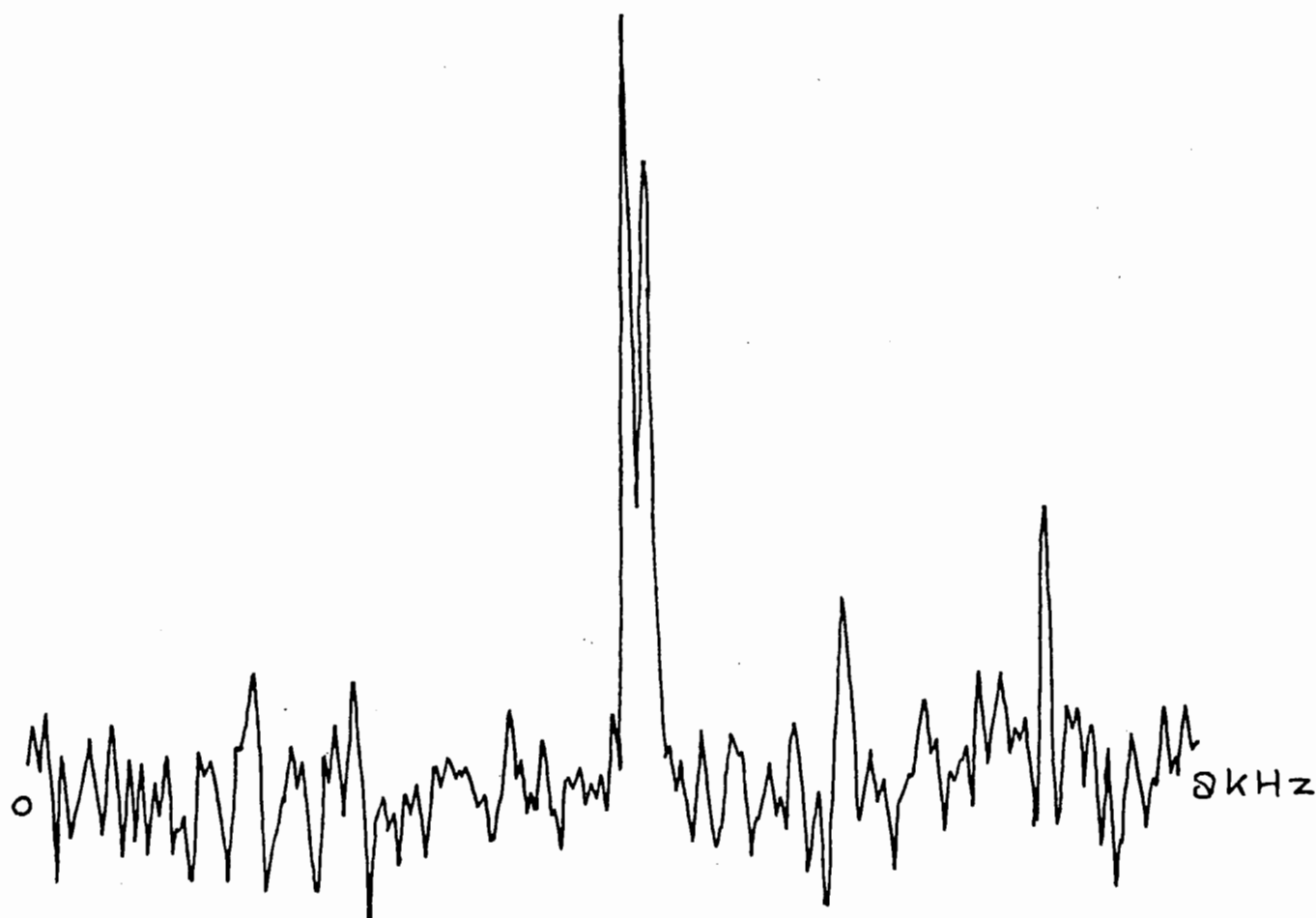


Fig. 1<sup>b</sup>. Cross polarization + dynamic polarization,



Fig. 2.  $^{13}\text{C}$  spectrum of adamantane

same data as Fig. 1. Matching time = 5 msec,  
recycle delay = 2 sec



Cross polarization only, 200 scans



NEW POSITION

INSTRUMENTATION SPECIALIST. Purdue Magnetic Resonance Laboratory has a Professional staff opening. A unique opportunity for an experienced electronics engineer or scientist to work on instrumentation and/or software development of 200 MHz wide bore and 470 MHz multinuclear NMR spectrometers and on applications to biomedical experiments. Experience with either analog, RF, and digital electronics or software is essential. Current areas of interest include NMR probe design, CIDNP, and novel pulse sequences. Primary responsibility is to maintain and enhance the capability of the NMR Facility; routine responsibilities include maintenance, repairs, experimental set-up, and teaching or assisting users. Possibilities for advancement and independent work. Competitive salary. Applicants with experience in other areas of scientific instrumentation will be given full consideration. Dr. R. E. Santini, Department of Chemistry, Purdue University, West Lafayette, IN 47907 [(317) 494-8671/494-8528]. Purdue University is an Equal Opportunity/Affirmative Action Employer.

---

ARCO Chemical Company  
500 South Ridgeway Avenue  
Glenolden, Pennsylvania 19036  
Telephone 215 586 4700



Research & Development

June 24, 1980

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

Dear Barry:

We have an immediate opening for an NMR Spectroscopist. The primary responsibilities of this individual would include operations of CFT-20 and A-60 spectrometers, data interpretation, and the application of NMR techniques to a wide variety of chemical problems. The ideal candidate for this entry level position should have a PhD in Chemistry and experience in the application of NMR methods to structural determination. A strong background in organic chemistry is also desirable.

Interested parties should submit a resumé to me at the above address.

Best regards,

  
K. C. Ramey

KCR:jak

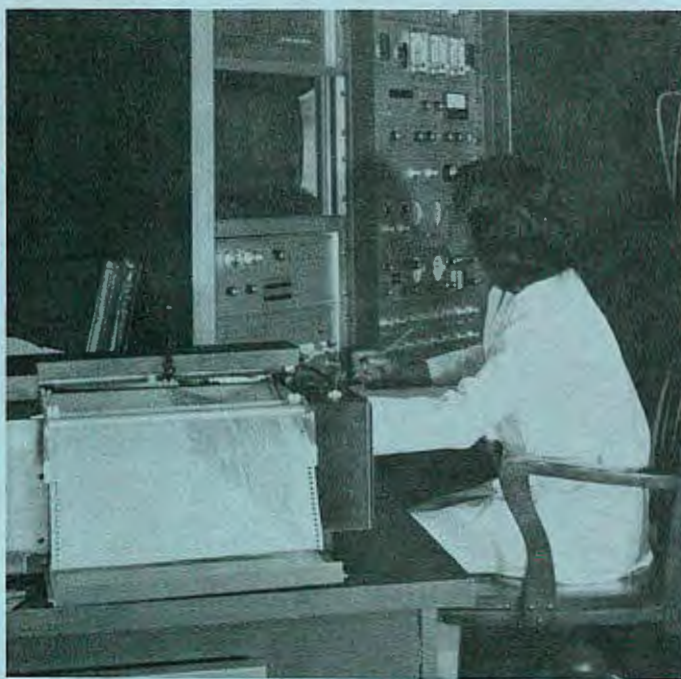


# NT-Series Fourier Transform Superconductive Magnet NMR Spectrometers

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<sub>1</sub>, T<sub>2</sub>, 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 <sup>13</sup>C studies of high molecular weight polymers.
- Automated T<sub>1</sub> and T<sub>2</sub> measurements.
- Chemical dynamics studies.
- Temperature-programmed experiments.
- <sup>31</sup>P experiments on living organs.

**NTC** 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 ( $^{13}\text{C}$ ) with  
Magic Angle Spinning  
High Resolution Probe ( $^{13}\text{C}/^1\text{H}$ )

## FX-200

Dual Probe ( $^{13}\text{C}/^1\text{H}$ )  
Broad Band ( $^{15}\text{N}$  to  $^{31}\text{P}$ )  
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