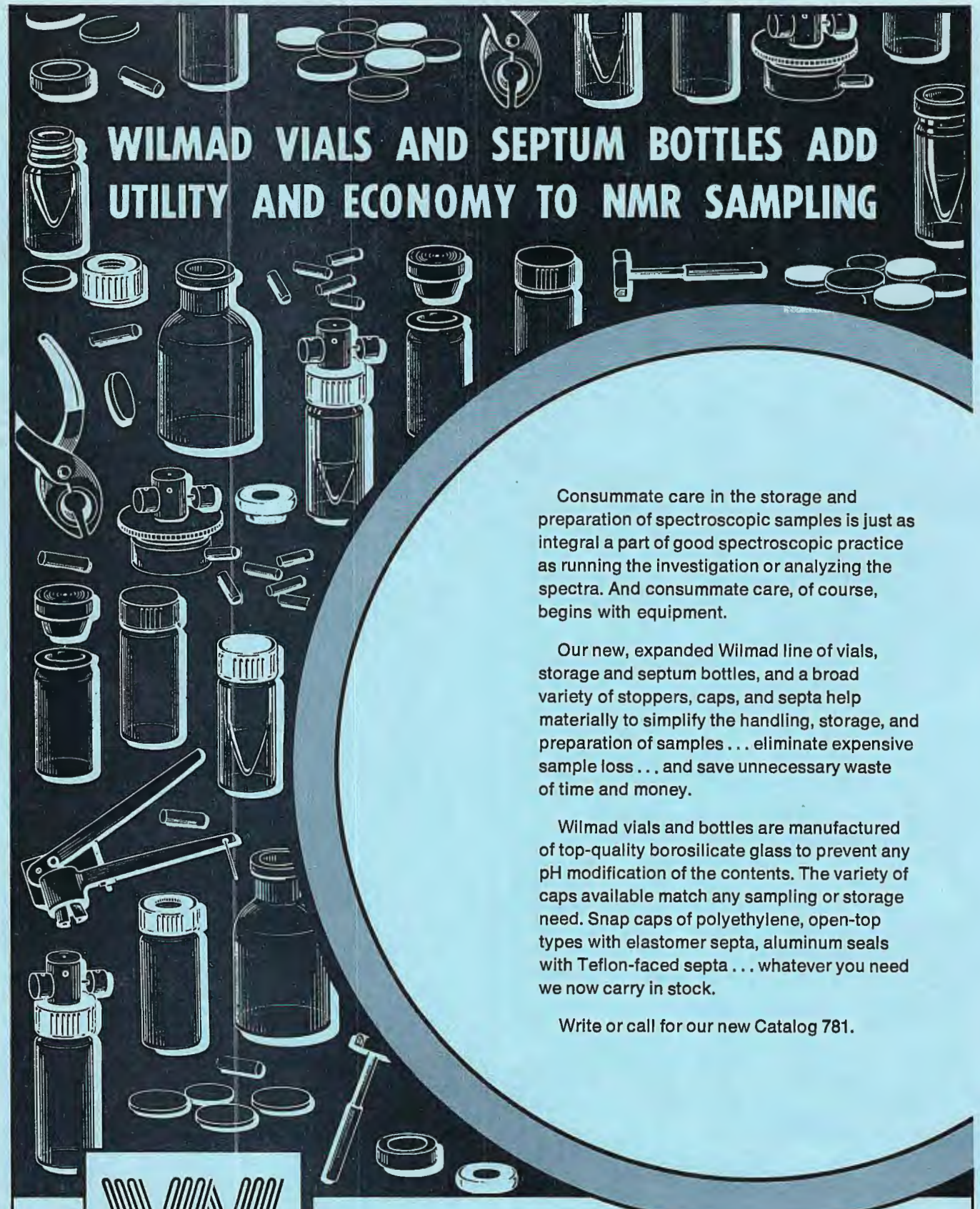
Texas A&M University N-M-R Newsletter

NO. 250

JULY, 1979



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

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

TAMU NMR NEWSLETTER - SPONSORS

Abbott Laboratories
Bruker Instruments, Inc.
Eastman Kodak Company
JEOL Anaoytical Instruments, Inc.
Dr. R. Kosfeld, Abt. Kernres., Inst. f. Phys. Chem.,
TH Aachen (Germany)
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
The Lilly Research Laboratories, Eli Lilly & Co.
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. 251: 6 August 1979
No. 252: 3 Sept. 1979

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. 250

THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175
CINCINNATI, OHIO 45247

May 21, 1979

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

Dear Barry:

Orienting Lyotropic Lamellar Liquid Crystals for ^2H NMR

We have been using macroscopically-oriented samples in our ^2H NMR characterization of the lamellar liquid-crystalline phase of 3,6,9,12-tetraoxadocosanol -- water. A convenient method for orienting lamellar directors for this phase is to: (1) raise the sample temperature above the lamellar/isotropic phase transition (50°C for 67 weight % tetraoxadocosanol); (2) draw the isotropic phase into a narrow i.d. flat cell; (3) cool the sample back through the phase transition. Director orientations in a sufficiently thin flat cell are normal to the glass surface. We have been using a 50 μm x 8 mm x 80 mm i.d. flat cell custom made for us by the J. C. Scanlon Co. This flat cell can be closed off at both ends to maintain a constant sample composition.

The procedure described above should be useful for orienting any lamellar phase which has a thermally-accessible, fluid, single-phase isotropic region. It has obvious advantages over alternate procedures for orienting lyotropic lamellar phases, such as pressing the phase between glass plates, which often yield inhomogeneous samples with poorly-defined compositions. The use of oriented samples instead of non-oriented samples having a random distribution of director orientations has advantages for ^2H NMR spectroscopy of lamellar phases. These include: (1) reduced sample-size, (2) increased resolution, (3) improved quantitation, (4) the ability to scale a spectrum to a convenient spectral width, and (5) the detection of any long-lived distribution of local molecular orientations relative to the director orientation.

Some characteristic ^2H NMR spectra obtained using a flat-cell-oriented lamellar phase are shown in the Figure. These spectra were recorded for 67 weight % 1,1,2,2-d_4-3,6,9,12-tetraoxadocosanol at 13.8 MHz on our multinuclear Bruker HX-90 spectrometer. Field/frequency stabilization was provided by a home-built ^{19}F external lock. A quadrupolar echo pulse sequence was used to minimize the effects of probe ringing at this frequency. A modified Varian E-229 goniometer

Dr. Bernard L. Shapiro
May 21, 1979

was used to adjust the angle between the cell normal and the magnetic field. The spectra shown are for angles of 0°, 50°, and 90°, respectively, at a temperature of 25°C. The quadrupolar splittings show the expected $(3\cos^2\theta-1)/2$ variation.

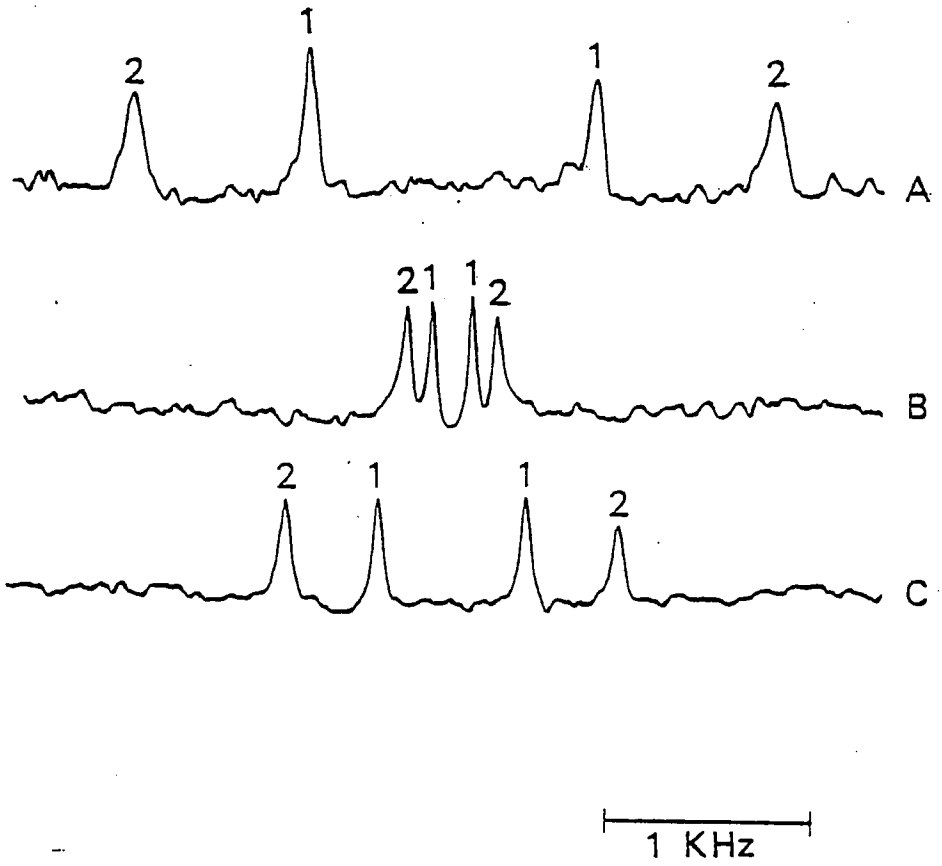
Sincerely yours,

THE PROCTER & GAMBLE COMPANY
Research and Development Department

Steve Goldman

Stephen A. Goldman

dlj



^2H NMR spectra of $CH_3(CH_2)_9(OCH_2CH_2)_3OCD_2CD_2OH$ in the lamellar phase.
(A) Oriented sample, $\Theta = 0°$
(B) Oriented sample, $\Theta = 50°$
(C) Oriented sample, $\Theta = 90°$

Numbers correspond to chain positions.

UNIVERSITY OF DENVER
An Independent University
University Park, Denver, Colorado 80208

Department of Chemistry / 303 · 753-2436

May 24, 1979

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

Dear Barry:

We are struggling to perform the most elementary NMR experiment - the detection of a ^{1}H resonance. What makes it challenging, and interesting, is that we are measuring the ^{1}H NMR signal of the solvent in an EPR sample tube while it is inside the EPR cavity. One of the toughest problems is to design an NMR probe coil that will not interfere with the EPR cavity tuning.

While we were working on this project Varian marketed an NMR gaussmeter with a probe small enough to fit inside the cavity, but the Varian system does not permit you to measure simultaneously the NMR and EPR signals inside the cavity. We have achieved this with some aqueous nitroxyl samples, but consider our results too rudimentary to display yet.

This work is being done in conjunction with Dr. David J. Greenslade at the University of Essex, England.

Sincerely,

Gareth

Gareth R. Eaton
Associate Professor

Sandy

Sandra S. Eaton
Assistant Professor
University of Colorado
at Denver

GRE: SSE:cs

UNIVERSITY OF SOUTH FLORIDA
TAMPA • ST. PETERSBURG • FORT MYERS • SARASOTA

DEPARTMENT OF CHEMISTRY
TAMPA, FLORIDA 33620

813:974-2144
SUNCOM: 574-2144

June 5, 1979

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

Dear Barry:

Having just received your "pink form" (which has now turned yellow), I feel I had better get in a contribution without too much delay. On that basis, the following short *and valuable* contribution is humbly(?) submitted.

When doing stastical fits of one set of physical values to another, two statistical functions are commonly used: the correlation coefficient (R) and the agreement factor (A). While neither one of these is as good an indication of the quality of a fit as is the standard deviation with respect to a particular parameter, they do have their uses.

However, neither function can be of much use if misinterpreted. In particular the following error occasionally crops up: For perfect agreement between, say, X and Y, A = 0 and R = 1. Thus, one occasionally sees,

$$|R| = 1 - A$$

The above equation is grossly incorrect. The agreement factor is seldom wrongly defined; it is R which suffers. So, to correct some workers in the errors of their ways, let it be known that *the* correct form of R (given as R^2 for convenience) is as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^{N} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{N} (y_i - \bar{y}_i)^2}$$

Here, for N data points in a fit of y *vs.* x (y ≡ f(x)), the y_i are *observed* values of y, the $\hat{y}_i$ are the optimum calculated values, and $\bar{y}$ is the arithmetic mean of the observed y's.

Sincerely yours,

Milt

Milton D. Johnston, Jr.
Associate Professor of Chemistry

250-5
UNIVERSITÄT TÜBINGEN
PHYSIKALISCHES INSTITUT
Prof. Dr. O. Lutz

D-7400 TÜBINGEN 1, den 30.05.1979
Morgenstelle
Telefon (0 70 71) 29 67 14

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

^{135}Ba and ^{137}Ba NMR studies

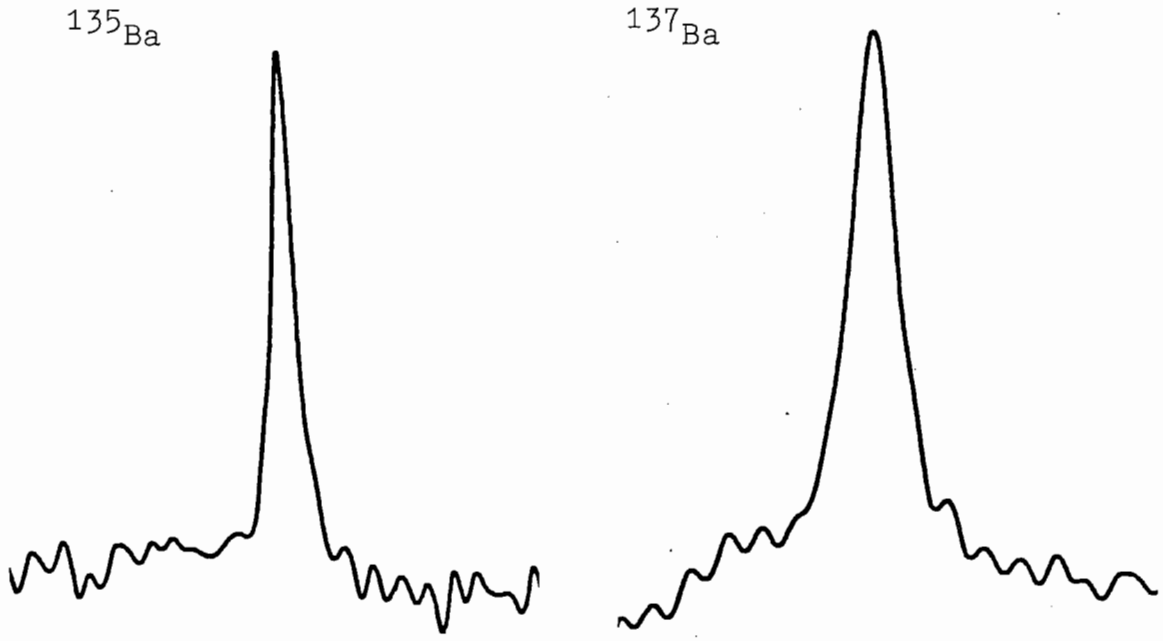
Dear Professor Shapiro,

All alkaline earth elements have a least one stable isotope which is susceptible to NMR studies and in the last years some investigations on ^{9}Be, ^{25}Mg, ^{43}Ca and ^{87}Sr have been reported (1). But for barium systematic NMR investigations of the isotopes ^{125}Ba and ^{137}Ba have not been published. This is certainly due to the quadrupolar broadening of the NMR lines and the low receptivity. In Fig. 1, ^{135}Ba and ^{137}Ba NMR signals of a 0.5 molal aqueous solution of $BaCl_2$ are given together with experimental data. These broad signals have been detected with a modified probe which had a dead time of less than 100 μs at 10 MHz. The measuring time for an acceptable signal-to-noise ratio is such that systematic investigations in aqueous solution could be performed for evaluating magnetic moments, chemical shifts, linewidths and the ratio of the quadrupole moments (2,3).

Sincerely yours
O. Lutz
(O. Lutz)

(1) See for instance references (1) through (15) given in the following reference (3).
(2) H. Krüger, O. Lutz, and H. Oehler, Phys.Letters A62, 131 (1977)
(3) O. Lutz and H. Oehler, Z.Physik, A 288, 11 (1978)

Fig.1: Barium NMR signals of a 0.5 molal solution of $BaCl_2$ in H_2O by Fourier transform quadrature detection accumulating 50 000 free induction decays within 25 min.



	^{135}Ba	^{137}Ba
Larmor frequency at 2.11 T	8.94 MHz	10.00 MHz
Natural abundance	6.6 %	11.3 %
Receptivity in a 0.5 m solution (Proton = 1)	$2.9 \ 10^{-6}$	$7.1 \ 10^{-6}$
Linewidth	(650 ± 70) Hz	(1500 ± 150) Hz

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

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

May 31, 1979

Dr. Barry L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas
U.S.A. 77893

Re: Observing ^{2}H on ^{1}H probe on the WH-400

Dear Barry:

Recently we were studying the percentage incorporation of ^{2}H in ethylidene cyclopropane by ^{1}H NMR. It occurred to us that we could observe ^{2}H directly by using the lock circuitry in the ^{1}H probe, changing a few cables and switching the console and preamp to ^{2}H. The ^{1}H receiver coil could also be used as the ^{1}H decoupler coil.

Shown in the Figure is the normal ^{1}H NMR spectrum (A) of the indicated mixture, B is the ^{1}H coupled ^{2}H spectrum and C is with ^{1}H broad band decoupling (0.5 watts) using the ^{1}H receiver coil. Initially we expected incorporation only at one position, but clearly the ^{2}H results indicate a 4:1 ratio. This technique provides a quick check to those interested in studying ^{2}H incorporation mechanisms. Switching over from ^{1}H to ^{2}H by this method requires about a minute and one is ensured of excellent H_o homogeneity. The only drawbacks is the need for the ^{2}H hardware and a very stable H_o.

Sincerely,

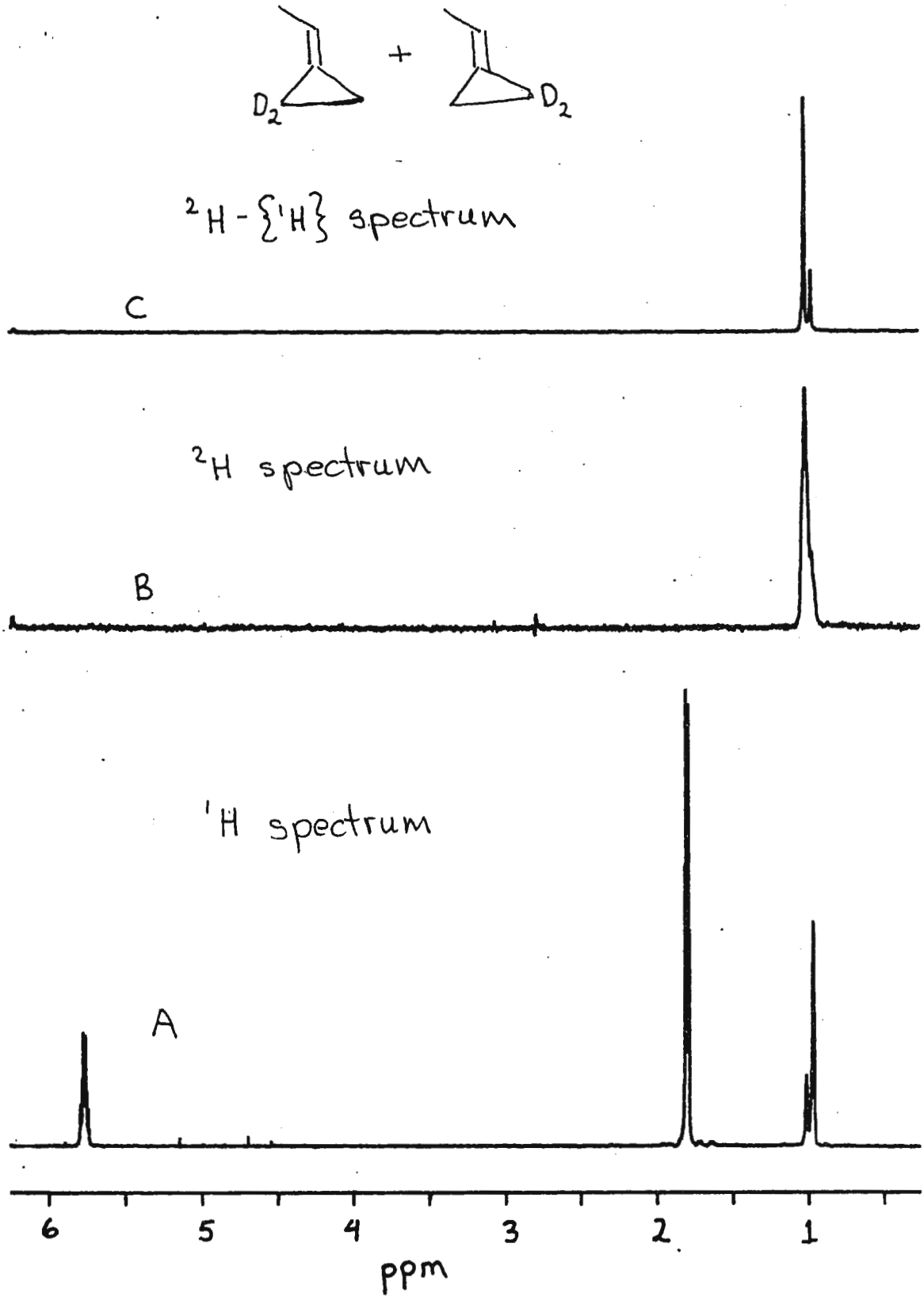
Tom

Tom Nakashima

TN/ss

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

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



THE UNIVERSITY OF NORTH CAROLINA
AT
CHAPEL HILL

Department of Chemistry

The University of North Carolina at Chapel Hill
Venable and Kenan Laboratories 045 A
Chapel Hill, N.C. 27514

31 May 1979

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

Short Title: ^{13}C NMR Substituent Effects in Unsaturated Organosulfur Compounds

Dear Barry:

During the course of our ^{13}C NMR investigations of acyclic and conformationally homogeneous cyclic systems, we have come across some rather interesting and unusual substituent effects in unsaturated acyclic organosulfur compounds. For example, the terminal olefinic carbons (Cδ) in diallyl sulfoxide, sulfone, as well as the methyl fluoroborate salt are deshielded by 6.69, 8.51, and 6.77 ppm, respectively, relative to the parent sulfide (Table 1). Such large deshielding effects at Cδ (1) are highly unusual particularly in open chain compounds (2). The shifts of the Cβ carbons are within the expected range of 20-24 ppm (2) in response to the deshielding caused by the increased electronegativity of the oxidized sulfur atom (3,4). The γ substituent shifts are shielding and 2-3 ppm larger than those noted in analogous saturated systems (2). Although we do not have sufficient data at the present time to discuss the merits of concepts like hyperconjugation, homoconjugation, and field effects as related to carbon-13 shifts, it seems clear that the sulfur moiety plays a unique role in perturbing or polarizing the olefinic bond.

Similar ^{13}C NMR studies of the divinyl series (Table 2) show anomalous deshielding γSO and γSO_2 effects (5) of 8.3 and 4.85 ppm for the sulfoxide and sulfone, respectively. Here, the βSO and βSO_2 effects are only 6-8 ppm deshielding in contrast to the ca. 20-25 ppm characteristic of the saturated analogues (2). These effects appear to be consistent with an inductive rather than a resonance effect.

A more complete analysis of these unusual shifts may provide a better insight into both the nature of sulfinyl and sulfonyl interactions with π systems and the resulting effects on the proximal carbons.

Please credit this contribution to our colleague, Dr. David L. Harris.

Sincerely,

John C. Dyer

Slayton A. Evans, JR.
Associate Professor

SAE:llw

Table 1. ^{13}C NMR Chemical Shifts of Diallyl Organosulfur Compounds

$(CH_2=CH-CH_2)_2X$, X = S, SO, SO_2, $\overset{+}{S}$-Me

$\delta \quad \gamma \quad \beta$

Compound	Cβ	Cγ	Cδ
X = S	33.28	134.43	116.85
X = SO	54.26	125.82	123.54
X = SO_2	56.47	125.02	125.36
X = $\overset{+}{S}Me$, BF_4^-	42.27	128.03	123.62

Table 2. ^{13}C NMR Chemical Shifts of Divinyl Organosulfur Compounds

$(CH_2=CH)_2X$, X=S, SO, SO_2

$\gamma \quad \beta$

Compound	Cβ	Cγ
X = S	129.95	114.80
X = SO	134.1	123.0
X = SO_2	137.19	129.65

References and Footnotes

(1) The carbons adjacent to sulfur are β to the substituent(s) on sulfur (e.g., lone pair electrons, oxygen atom, methyl).
(2) G. Barbarella, P. Dembeck, A. Garbesi, and A. Fava, Org. Magn. Resonan., 8, 108 (1976).
(3) J. B. Lambert, D. A. Netzel, Hsiang-ning Sun, and K. K. Lilianstrom, J. Am. Chem. Soc., 98, 3778 (1976).
(4) S. S. McCrachren and S. A. Evans, Jr., Submitted to J. Org. Chem.
(5) βSO, βSO_2, γSO, and γSO_2 effects are determined as $\Delta\delta = \delta_{oxide(s)} - \delta_{sulfide}$

TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129
817-921-7195

Department of Chemistry

June 6, 1979

Dr. Barry L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Tx.

Dear Barry:

Dispersion vs. absorption plots (DISPA) provide a novel and convenient method for examining line broadening processes in NMR (Alan Marshall, 20th ENC, Analytical Chem., 50,756 and 764 (1978)). Unfortuneately, the light pen system with the FX-60 doesn't offer the flexibility to do the whole job in the machine. Consequently, I have been looking at a system of interest using semi-handgenerated plots.

One first acquires, transforms and phase adjusts the FID as usual with the light pen system. For reasons not known to me, examination of the real and imaginary displays at this point gives curves which are not properly phase adjusted. Stick with the original display, scale expand and plot the absorption mode of the line of interest. To get the proper dispersion mode first set the base line marker (BA) on the correct base line. Then set the spot frequency (SP) on the maximum of the absorption curve. Phase adjust to bring the spot down to the base line and plot the dispersion curve. The rest is a matter of hand plotting values of absorption vs. dispersion. This is facilitated by drawing a set of parallel vertical lines as shown in the example below.

The curve shown here is for the α-carbon of pyridine perbromide in the presence of a great excess of bromine. When one adds bromine to pyridine ($CDCl_3$) the α- and γ-lines move upfield while the β-line moves downfield. The behavior is the same as for protonation. The formation of the perbromide is effectively quantitative. Upon adding excess bromine the γ-line first broadens and then the α-line. The β-line remains sharp throughout. The DISPA plot of normal pyridine lines are semicircles indicating Lorentzian line shapes. The DISPA plots for the α-/or γ- carbons in excess bromine are raised off the semicircle at the left end. This is indicative that line broadening is caused by an exchange process.

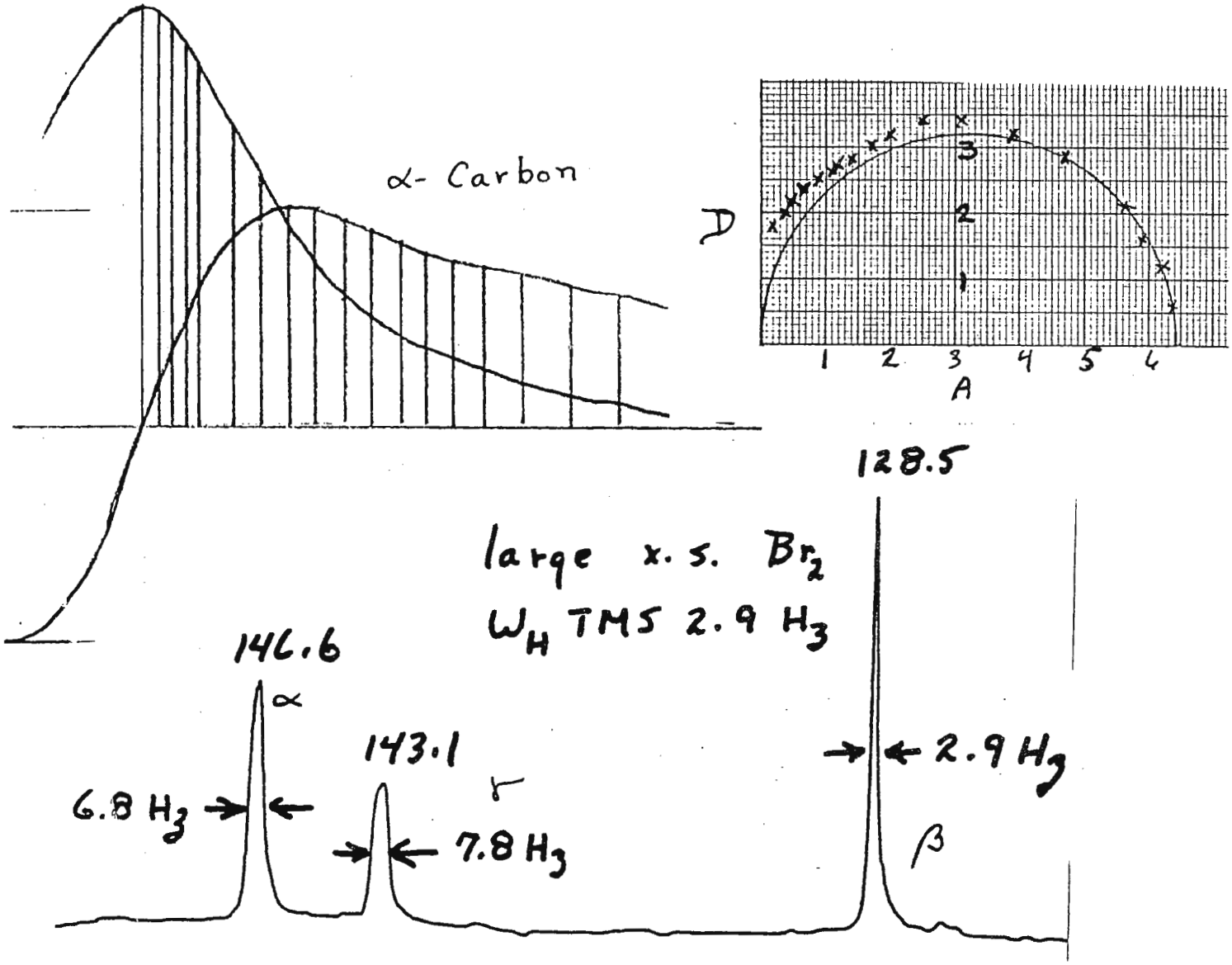
One possibility is that the excess bromine oxidizes the perbromide to a cation radical which exchanges with the neutral perbromide. However, an ESR study failed to reveal any radicals in the system.

Quinoline is known to undergo bromination more readily than pyridine by an addition-elimination mechanism which involves covalently bound bromine at the α-/or γ-carbon. Quinoline also shows line broadening in the C-13 NMR at much lower bromine concentrations than those required for pyridine. Thus, it may be that an analogous pyridine species is responcible for the exchange broadening observed here.

Best regards,

Bill

W.B. Smith



varian/611 hansen way/palo alto/california 94303/u.s.a./415/493-4000

June 22, 1979

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

Dear Barry:

Solid State Spectra of Optically Active Isomers

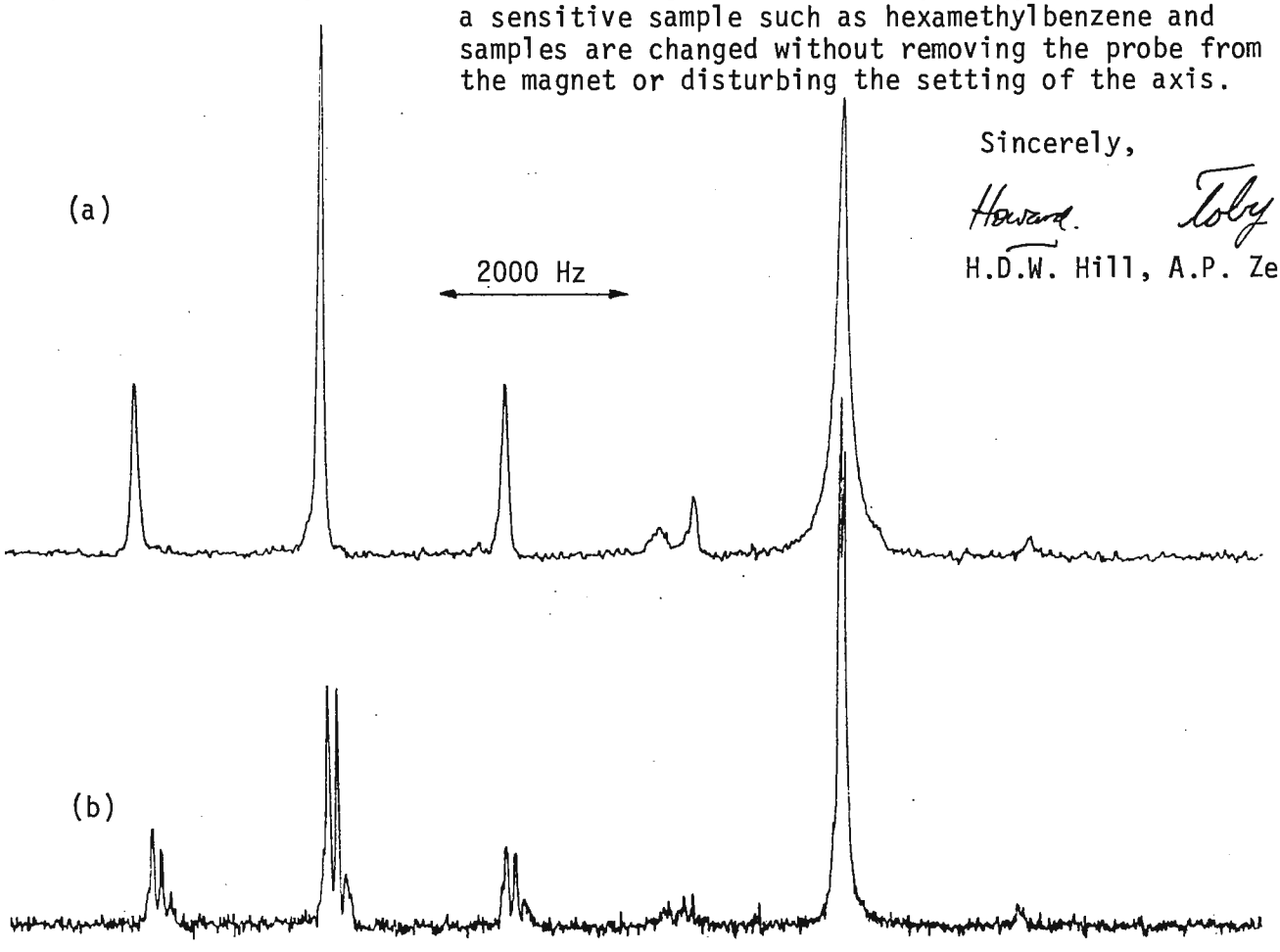
We have recently been examining a number of solid samples using the new Magic Angle Spinning Accessory for the XL-200. The accompanying spectra show an interesting example of different forms of an optically active material. Spectrum (a) is from the meso- and spectrum (b) from the L-isomer of sodium ammonium tartrate. The samples were prepared by Dr. Jacobus of Tulane University. Structural differences between the different isomers clearly influence the spectra. In addition to the splitting for the L-isomer, there is a difference in the chemical shift between the methylene and carboxylic carbons in the two spectra. Other forms of the compound are being prepared in an attempt to further understand the details of the spectral variations.

The samples were packed into Kel-F rotors and the spectra were recorded using cross polarization and a decoupling field strength of about 40 KHz. The spinning rate was approximately 1950 Hz (slightly different for each of the two spectra). The adjustment of the spinning axis to the magic angle is made with a sensitive sample such as hexamethylbenzene and samples are changed without removing the probe from the magnet or disturbing the setting of the axis.

Sincerely,

Howard Toby

H.D.W. Hill, A.P. Zens



If your superconducting FT NMR can't achieve a dynamic range of 6,000,000:1 or better...

...you just don't have an XL-200!

Without the 32-bit word size of its acquisition processor and the floating-point arithmetic used in the weighting and Fourier transformation of the accumulated data, you haven't got a chance. You simply can't match the extraordinary dynamic range attainable with the XL-200 —evidenced in the 200-MHz ^1H NMR spectrum you see here.

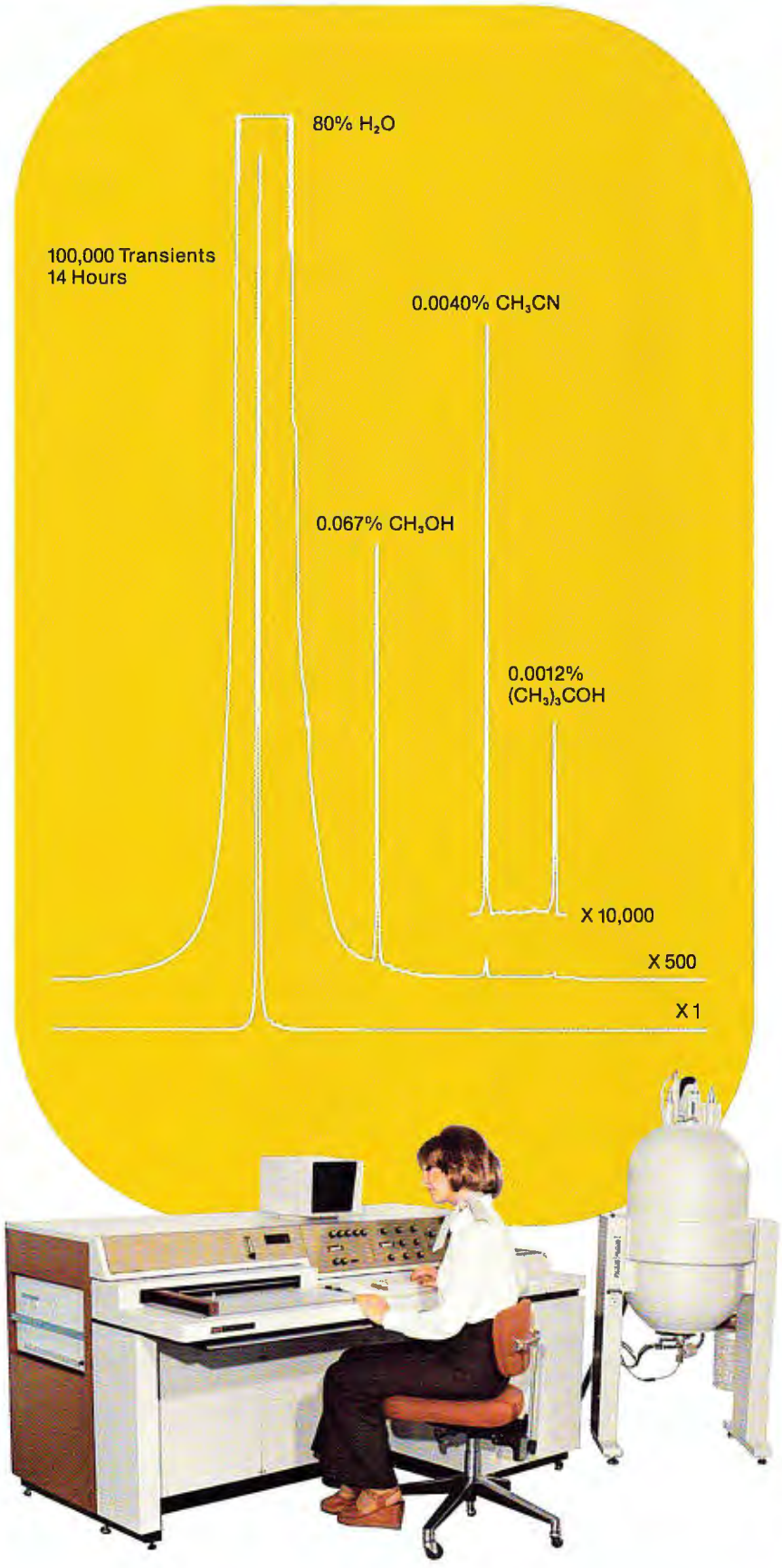
There are other unique aspects of the XL-200's data handling and spectrometer control system: a 13-bit ADC, which accommodates stronger signals on each transient; a standard 32K CPU, independent of the acquisition processor and programmed in a high level language; a built-in, interactive 5M-word disk with dual platters; a large, flicker-free raster scan display.

The software is exceptionally sophisticated. It permits multitasking (simultaneous acquisition, processing, printing, etc.) and queuing (automatic sequential execution of requested tasks) on the same or on different NMR experiments. You can also array parameters (up to three variables, including temperature) within a given experiment; create your own convenient macrocommands; generate your own special or general-purpose pulse sequences in a simple, English-like code.

Then, there's the matter of the XL-200's broadband accessory which, with only a single probe, enables you to observe a host of nuclei (including ^{13}C) between 20 and 81 MHz. And there's the remarkable low-loss dewar system, which operates over three months on only 25 liters of liquid helium.

The XL-200 is in a class by itself—with a price tag and an operating economy that belie its advanced design.

For more information on the features you may be missing, write Varian Associates, Inc., Box D-070, 611 Hansen Way, Palo Alto, CA 94303.



Regional Offices:
Florham Park, NJ (201) 822-3700
Park Ridge, IL (312) 825-7772
Houston, TX (713) 783-1800
Los Altos, CA (415) 968-8141

varian

Sales Offices

CALIFORNIA
9901 Paramount Boulevard
Downey, CA 90240
Phone: (213) 927-3415

375 Distel Court
Los Altos, CA 94022
Phone: (415) 968-8141

COLORADO
4665 Kipling, Suite 1
Wheatridge, CO 80033
Phone: (303) 425-0413

GEORGIA
6650 Powers Ferry Road
Suite 100
Atlanta, GA 30339
Phone: (404) 955-1392

ILLINOIS
205 W. Touhy Avenue
Park Ridge, IL 60068
Phone: (312) 825-7772

KENTUCKY
Executive Park, Suite 110
Louisville, KY 40207
Phone: (502) 897-0171

MARYLAND
4701 Lydell Drive
Cheverly, MD 20781
Phone: (301) 772-3683

MASSACHUSETTS
83 2nd Avenue
Burlington, MA 01803
Phone: (617) 272-4152

NEW JERSEY
25 Hanover Road
Florham Park, NJ 07932
Phone: (201) 822-3700

NEW YORK
6489 Ridings Road
Syracuse, NY 13206
Phone: (315) 437-6464

OHIO
25000 Euclid Avenue
Euclid, OH 44117
Phone: (216) 261-2115

TEXAS
Plaza Southwest
5750 Bintliff Drive, Suite 202
Houston, TX 77036
Phone: (713) 783-1800

WASHINGTON
300 120th Avenue
Bldg. 2, Suite 230
Bellevue, WA 98005
Phone: (206) 454-2910

MEXICO
Fco. Petrarca 326
Mexico 5, D.F.
Phone: (905) 545-4077

SOUTH AMERICA
Varian Industria e Commercio Ltda.
Av. Dr. Cardoso de Melo, 1644
CEP 04548, Sao Paulo, Brazil
Phone: 240-1622

CANADA
Varian Associates of Canada Ltd.
45 River Drive
Georgetown, Ontario
Canada L7G 2J4
Phone: (416) 457-4130

PARTS AND SUPPLIES CENTER
670 East Arques Street
Sunnyvale, CA 94086
Phone: (408) 245-5420

Service Centers

VID Service Headquarters
670 East Arques Street
Sunnyvale, CA 94086
Phone: (408) 245-5420

Eastern Service Center
25 Hanover Street
Florham Park, NJ 07932
Phone: (201) 822-3700

Midwestern Service Center
205 West Touhy Avenue
Park Ridge, IL 60068
Phone: (312) 825-7772

Southern Service Center
Plaza Southwest
5750 Bintliff Drive
Houston, TX 77036
Phone: (713) 783-1800

Western Service Center
375 Distel Circle
Los Altos, CA 94022
Phone: (415) 968-8141

Canadian Service Center
45 River Drive
Georgetown, Ontario
Canada L7G 2J4
Phone: (416) 457-4130

Other Instrument Division sales offices and representatives are located in: Argentina, Australia, Bahamas, Belgium, Brazil, Canada, Chile, Colombia, Costa Rica, Denmark, Dominican Republic, Ecuador, England, Finland, France, Germany, Guatemala, Hong Kong, Indonesia, Israel, Italy, Japan, Korea, Malaysia, Netherlands, New Zealand, Panama, Peru, Philippines, Puerto Rico, Republic of China, Singapore, Sweden, Switzerland, Thailand, United States, Venezuela, West Indies.

varian

Department of Chemistry

The Florida State University
Tallahassee, Florida 32306

June 22, 1979

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

Permanent Staff Position:
B.S. or M.S. Spectroscopist or Chemist

Dear Barry:

We have a permanent staff position open in the FSU NMR laboratory. Duties include operation of our two superconducting spectrometers as well as several smaller systems, instruction of students in operation, maintenance of laboratory sample throughput, and routine instrument maintenance (under the guidance of Dick Rosanske, our senior instrument man). This position offers an interesting opportunity with both service and research activities of the nmr laboratory involved. State-of-the-art multi-nuclei Fourier Transform NMR and laboratory data processing techniques are utilized; direct nmr experience is desirable but is not required.

This State Career Service position has a salary range of approximately $13,500 - $18,000, plus hospitalization and retirement benefits. The position is available immediately. Interested persons should write or call (collect, 904-644-5503) and, separately, have two letters of recommendation forwarded.

Best regards,

George C. Levy
Professor

GCL:dht

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

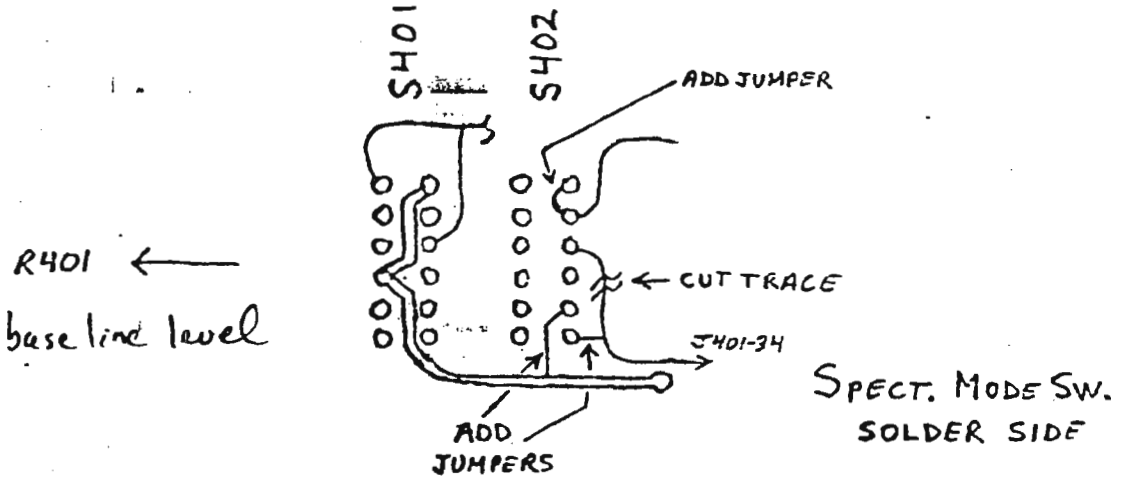
June 12, 1979

EM 390/360L Spin Decouple Modification

Dear Barry:

Since last fall Varian's EM-390/360L spectrometers have been delivered with the ability to use the homonuclear lock oscillator for either locking on, or to perform homonuclear decoupling experiments. With Varian's assistance we have modified our older EM-390 for dual use of the lock oscillator. This modification is simple to carry out and should take about one hour to complete and test. To carry out the modification:

1. Turn the system power off and remove the console cover.
2. Locate J 1007 (Auto Shim) at the upper left corner of the component side of the main front panel circuit board (see schematic No. 87-145-702, Electronic Console).
3. Cut the vertical run of the circuit board trace at the right of J 1007 just above the T junction at J 1007-14.
4. Solder one end of a jumper wire to the trace above the cut.
5. The other end of the jumper wire is soldered to pin 19 of J 1008 which is located on the other side of the front panel circuit board near the bottom of the board. The connection is now J 1008-19 to TB1001-34 to P 401-34.
6. As indicated in Figure 1, modify the solder side of the spectrometer control switch board. Switch 402 is the lock level switch.
7. Replace the console cover and turn the system power on.



The lock level pushbutton is now used to switch the lock oscillator over to be used as a spin decoupler. The decoupler position is set with the lock frequency course and fine controls. The decoupler power is adjusted with the lock power control. The approximate decoupler power is obtained by multiplying the lock power setting by 100. With the lock level switch depressed the lock gain and lock phase controls are non-functional. When using the lock oscillator to decouple the lock mode switch should be in the stand-by position.

Since we had purchased the EM-3930 spin decoupler accessory we were able to perform triple resonance experiments as can be seen in Figure 2. The lock oscillator is not as clean a frequency source as the EM-3930 decoupler since it was not originally designed as a decoupler. The spectrometer can not be operated with a field/frequency lock when the lock oscillator is used as a decoupler source. Good temperature control is essential to minimize drift. Despite these caveats this simple modification allows decoupling experiments to be carried out with no addition capital expenditures.

We would like to thank Dick Kelly, Art Becker and Barbara Erwine of Varian for their assistance. Please credit this contribution to Bruce Martin's account.

Best wishes,

Bill

W. C. Hutton
Research Associate

WC:ttn

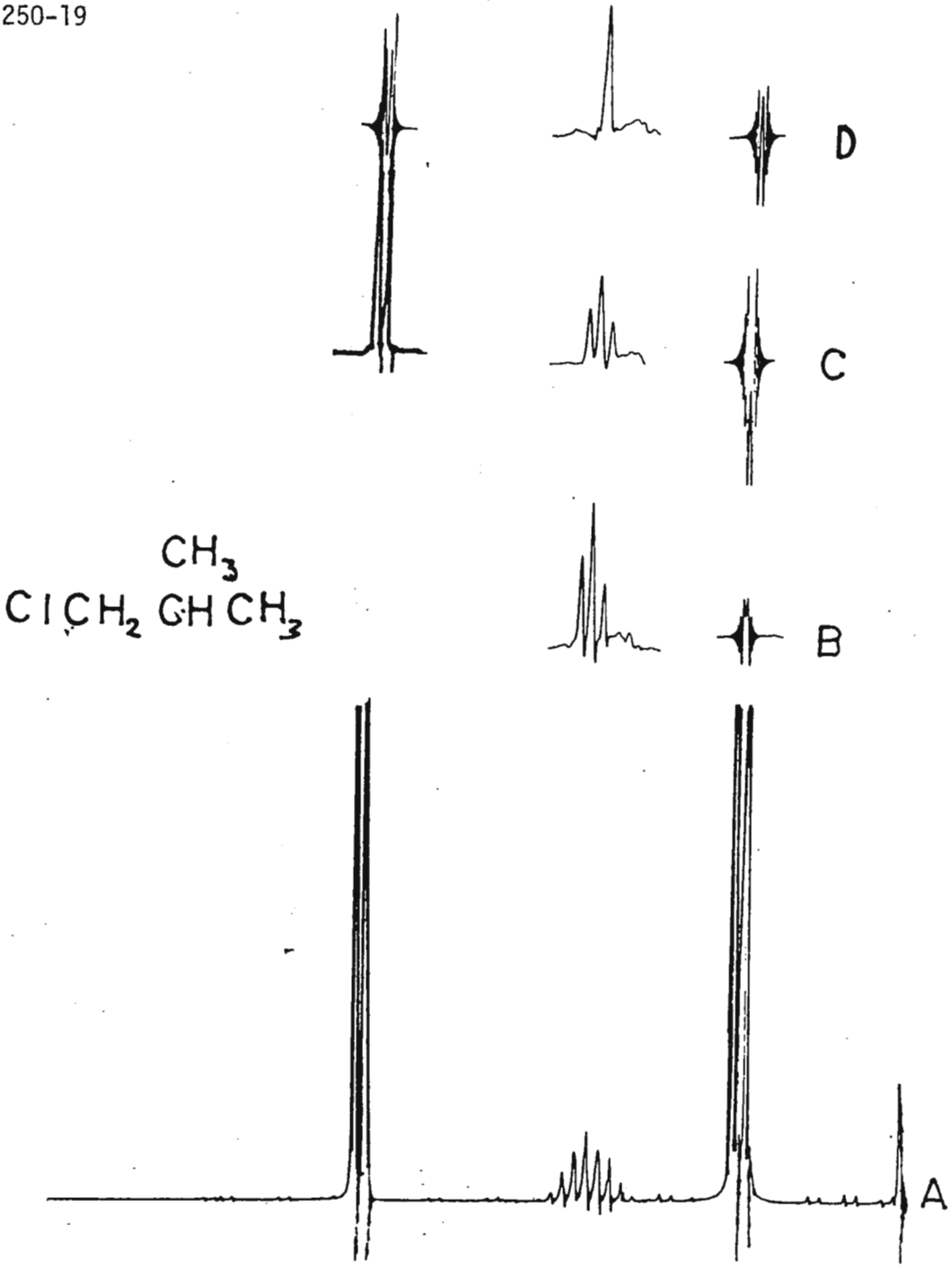


Figure 2. EM-390 Triple Resonance; A. normal spectrum of 1-chloro-2-methyl propane; B. with the methyls decoupled using the lock oscillator; C. with the methyls decoupled using the optional Varian EM-3930 decoupler; D. triple resonance using both sources for simultaneously decoupling the methyl and methylene resonances.

Research Resources Center

UNIVERSITY OF ILLINOIS AT THE MEDICAL CENTER, CHICAGO

FACILITIES:
Bioinstrumentation
Biostatistics
Electron Microscope
Environmental Stress
Instrument Shop
Nuclear Magnetic Resonance
Scientific Computer

Mailing Address:
P. O. 6998 (933 Bldg.)
Chicago, IL 60680

Location:
1940 West Taylor Street
Chicago, IL 60612

June 6, 1979

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

Dear Dr. Shapiro:

The Nuclear Magnetic Resonance Facility (NMRF) of the Research Resources Center (RRC) is seeking a young scientist whose primary duties would be the operation and teaching the use of nuclear magnetic resonance spectrometers (e.g., Bruker CXP 180; Bruker HFX-5, Varian DP-100-15") to investigators on this campus. The position is at the Senior Scientist-Assistant Professor level (salary commensurate with experience) beginning September 1, 1979. Although the RRC is a "service oriented center" and thus much of the individual's time would be spent assisting campus investigators, time will be available for independent/collaborative research. If you know of someone who would be interested in this position, kindly have him/her submit a curriculum vitae. The University of Illinois is an affirmative action/equal opportunity employer.

Your assistance in helping us find an individual to fill this position will be greatly appreciated.

Sincerely,

S. F. Marotta

S. F. Marotta
Associate Director

SFM:kam

NMR Advisory Committee

M. Barany
N. Farnsworth
D. Fiat
T. Henderson
M. Johnson
R. Walter

250-21

University of Edinburgh

Department of Chemistry

West Mains Road, Edinburgh, EH9 3JJ Scotland.

Yr. ref.:
Our ref.: ASFB/JG

Tel. 031 - 667 1081
Extn. 3416

8th June, 1979.

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

Dear Professor Shapiro,

Modification to VCT - the cassette driver programme for the XL-100

One of this programme's more useful features is its capability to rewrite any file on the tape. However, we have found that multiple re-use of this 'update' command can give rise to problems. Due to some obscure inaccuracies in the recording process, updating a file in the middle of a series often seems to overwrite the adjoining ends of the two files bracketing it. This causes read errors (error 45) when attempting to read either of these two files, rendering them inaccessible. This effect seems worse the further up the tape you go.

Normally, after writing a new file, VCT reads the next tape address and then writes it in the library at the beginning of the tape, for use as the starting point for writing the next new file. I have modified the VCT programme so that a gap of five tape addresses is left between files.

To make changes to VCT the 'alternate' cassette system programmes @VCT and K@AID must be used. After making the changes in core with K@AID, the modified VCT programme, which I have called VCT! ('VCT-shriek'), has to be copied onto tape. This is not quite as straightforward as it seems and I got into quite a fankle when I first tried it. The difficulty lies in the need for VCT! to be read by the cassette bootstrap. On detecting a word of zeros followed by a high byte of zeros the bootstrap stops reading and jumps to the VCT starting address. As originally assembled VCT has this bootstrap stopper sequence only at the end, but as soon as the programme runs, it turns up in a number of other places too. Thus, VCT must be modified and rewritten on the tape without being run.

Here is the sequence of operations, with my entries underlined:

```
                                1 Insert master cassette and enter VCT by running at
>                                 076000 or typing ED in the spectrometer programme
V*N4.                           2 Load and run @VCT
V@M1.                           3 Load but do not run VCT
A=0040.
V@N3.                           4 Load and run K@AID
K@C77502.                       5 Make changes in VCT
077502 (064213) 5121,              INCR BS,AD
077503 (014176) 124067,            ADD  DE4
077504 (001002) 5012,              TAB
077505 (077517) 54210,             STA  BADRS
077506 (002000) 14173,             LDA  WRTF
077507 (076023) 1002,              JAP  NAD1
077510 (006010) 77517,
077511 (136701) 14057,             LDA  DE3
077512 (002000) .
K@C77571.
077571 (000003) 136701. DE3 DATA '=A' This data word is not otherwise used.
K@K                             6 Load and run @VCT
V@U                             7 Insert standard formatted cassette and update VCT...
[VCT.
01.VCT      .076000.077775.0001.076454.
[VCT!.....                        ...to VCT!
A=0039.
V@                              8 Repeat step 7 for subsequent cassettes.
```

The effect of the modification can be seen by comparing the tape addresses in these two libraries, generated from the spectrometer programme before and after alteration of VCT:

```
>VP                                                >VP
01.VCT      .076000.077775.0001.076454.    01.VCT!     .076000.077775.0001.076454.
02.TAPE 14  .000000.000000.0100.076000.    02.TAPE 14  .000000.000000.0100.076000.
03. ONE     .000300.020504.0101.000010.    03. ONE     .000300.020504.0101.000010.
04. TWO     .000300.020504.0377.000010.    04. TWO     .000300.020504.0382.000010.
05. THREE   .000300.020504.0634.000010.    05. THREE   .000300.020504.0644.000010.
06. FOUR    .000300.020504.0875.000010.    06. FOUR    .000300.020504.0890.000010.
07. FIVE    .000300.020504.1103.000010..   07. FIVE    .000300.020504.1122.000010..
```

The capacity of a cassette remains unchanged by the insertion of the gaps, at 20 8K data files.

Best wishes,

Alan S. Boyd

Alan Boyd

ETH EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE
ZÜRICH

Institut für Molekularbiologie und Biophysik
Prof. Dr. K. Wüthrich

HPM-Gebäude
Telefon 01 57 57 70

Postadresse:
Institut für Molekularbiologie
und Biophysik
ETH - Hönggerberg
CH - 8093 Zürich

Prof. B.L. Shapiro
Department of Chemistry
Texas A and M University

College Station, Texas 77843

USA

Zurich, 13th June 1979

Use of Deuterated Micellar Detergents for High Resolution ^{1}H NMR Studies of Membrane Proteins

Dear Barry:

Although high resolution NMR, particularly in conjunction with X-ray crystallography, has yielded much useful information on conformation and dynamics of globular, water-soluble proteins, there remain protein classes for which much less information is available. In the case of membrane-bound proteins, the problem of associated lipids has precluded detailed conformational studies by either high resolution NMR or X-ray diffraction.

Recently we have been examining by high resolution ^{1}H NMR complexes formed between membrane polypeptides or proteins and fully deuterated detergent micelles. [1,2] Fig. 1 shows a one dimensional 360 MHz ^{1}H NMR spectrum of melittin, a polypeptide of 26 amino acids from bee venom, bound to fully deuterated micelles of dodecylphosphocholine. The dots in Fig. 1 denote resonances from residual protons in the detergent. The critical points in this figure are that by use of micelles a well resolved high resolution ^{1}H NMR spectrum of the polypeptide is obtained and that by deuteration the resonances of the detergent, which is in fifty fold molar excess, can effectively be removed from the spectrum. The high resolution obtained for the micelle bound polypeptide chain is emphasized by the inserts in Fig. 1, which show two-dimensional J-resolved ^{1}H NMR spectra of the methyl and αCH regions of micelle-bound melittin. The conformation of the micelle-bound melittin is being investigated at present, and the method is also in use for

studies of larger size globular proteins. The comparable resolution obtained for polypeptides in solution and in micelles suggests that for small globular proteins high resolution NMR of protein-micelle complexes provides a means for studying protein conformational features which may be important to functional properties of membranes.

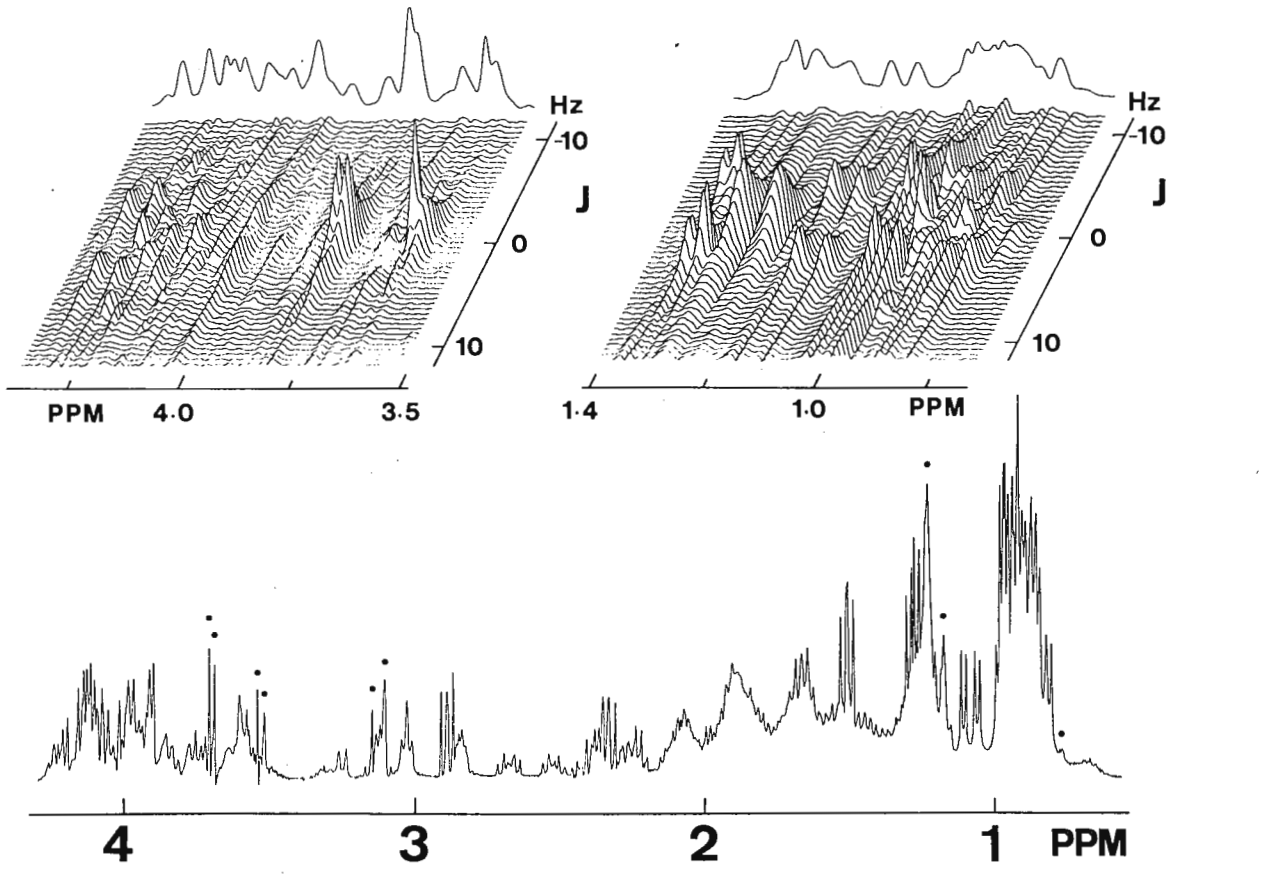
Yours sincerely,

L. R. Brown Kurt

Larry R. Brown Kurt Wüthrich

References:

1) J. Lauterwein, C. Boesch, L.R. Brown & K. Wüthrich, Biochim. Biophys. Acta, in press.
2) L.R. Brown, Biochim. Biophys. Acta, in press.



250-25

Department of Chemistry
University of Canterbury Christchurch 1 New Zealand

14 June 1979

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

Dear Professor Shapiro,

More on Resolution Enhancement

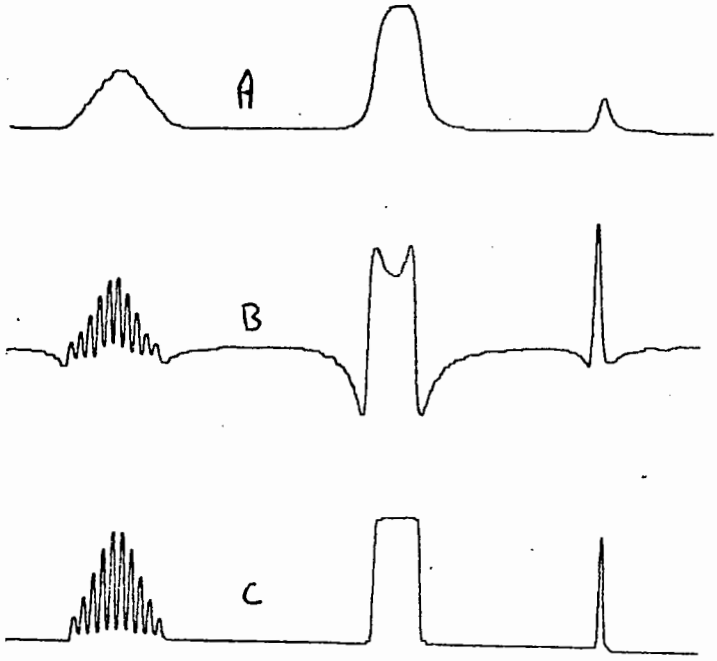
The recent spate of articles on techniques for resolution enhancement in FT spectra leaves one in a quandary as to which method is the best for any particular situation. As each new technique has been described, very little in the way of comparison with previous methods has been attempted. I have now surveyed the application of the various methods, Lorentzian narrowing[1], convolution-difference[2], sine bell[3], phase-shifted sine bell[4], combination exponential sine bell[5], trapezoidal[6] and Lorentzian-Gaussian conversion (double exponential)[1,7] to a number of spectral examples. The results of the comparisons will be published shortly, but there appears to be a clear preference for the double exponential function (Gaussian conversion), since this technique provides for the best S/N ratio and minimum baseline distortion when all of the methods are used to produce the same degree of resolution enhancement on the same spectral example. Furthermore, the Gaussian function is simple to operate, using two parameters which are readily related to the appearance of the FID which is being manipulated. As an illustration of the absence of base-line distortion in the application of this method, three examples are shown below. Spectrum A is a repeat of the example used by Gassner et al[6], and consists of, from right to left, a single Lorentzian line, $\nu_{\frac{1}{2}}$=5Hz, a superposition of ten, equal intensity lines of $\nu_{\frac{1}{2}}$=5Hz at 2Hz intervals, and a collection of ten lines of $\nu_{\frac{1}{2}}$=5Hz with a Gaussian distribution of intensities at 4Hz intervals. Spectrum B, also as given by Gassner et al[6], results from the application of the sine bell function to the FID corresponding to A, while Spectrum C followed from a similar application of the Gaussian function. Notice the absence of baseline distortion, the absence of the artifactual appearance of the centre band when compared to B, and the greater degree of resolution enhancement.

1. Ernst, in "Adv. in Magn. Reson." Vol. 2, Academic Press, 1966.
2. Campbell et al, J. Mag. Res., 11, 172 (1973).
3. DeMarco and Wüthrich, J. Mag. Res., 24, 201 (1976).

4. Wagner and Wüthrich, TAMU NMR 226-9.
5. Guéron, J. Mag. Res., 30, 515 (1978).
6. Gassner et al., J. Mag. Res., 30, 141 (1978).
7. Ferrige and Lindon, J. Mag. Res., 31, 337 (1978).

Sincerely yours,

J.W. Blunt.



250-27

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

Department of Chemistry

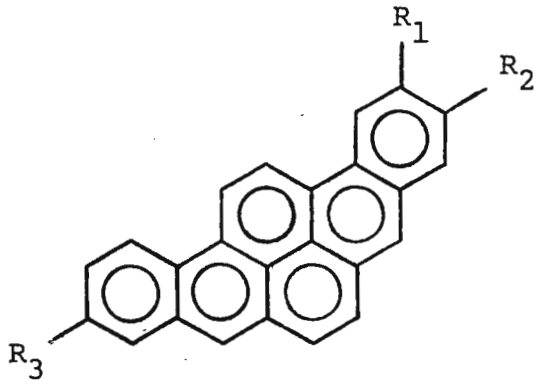
June 14, 1979

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

Dear Barry;

Transmission of Electronic Effects Over Large Distances

In connection with our studies on the effect of fluorine substitution on the carcinogenic activity of dibenzo[a,i]pyrene we became interested in the rates of deuteriodeprotonation of



Isomer	R_1	R_2	R_3
I	H	H	H
II	F	H	H
III	H	F	H
IV	F	H	F

positions 5 and 8 in compounds I-IV, monitored by 270 MHz NMR. We assigned H-5 and H-8 by synthesis of 90% enriched II-5-^{13}C and III-8-^{13}C. The relative rates of deuteriodeprotonation

(conc. D_2SO_4 at 0°) are given below. Interestingly, attachment

	Isomer			
position	I	II	III	IV
5	1.00	0.70	1.00	0.58
8	1.00	1.00	0.90	0.27

of fluorine to a carbon bearing a partial positive charge in the appropriate carbonium ion leads to no change in rate, while fluorine at a nonconjugated carbon reduces' the rate of deuterium incorporation.

These results indicate (a) cancellation of resonance and "polarization" (π_F or π_{orb}) effects at conjugated carbons, and (b) transmission of "polarization" effects over quite large distances. In addition, the fact that position 5 in II is also deactivated seems to suggest that a polarization effect akin to π_{orb} is operative, rather than π_F (wherein the half of the molecule adjacent to fluorine acquires a π-excess, leading one to expect activation). Finally the data are in accord with some of our CNDO calculations of electron distributions in phenylheptatrienyl cations, which indicate the relative importance of "resonance" and "field" effects to approach a value of about -1.8 at large distances from the site of substitution. Since the ratio of Swain and Lupton's R and F parameters is 0.48, the net effect will be close to zero, indicating cancellation at large distances.

The observation that resonance effects can be neglected at large distances while "inductive" or "polarization" effects exert the dominant influence (at least for fluorine) is intriguing and not what I would have predicted a priori from organic intuition.

Best wishes to all.

Sincerely,

D.J. Sardella
Associate Professor

DJS/bl

250-29

UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

May 31, 1979

Dear Barry:

On September 19 of this year there will be a one-day symposium on High Resolution ^{13}C NMR Spectroscopy of Solids, which I am chairing. This symposium will be part of the Sixth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies. The meeting will be held throughout the week of September 16-21 at the Philadelphia Sheraton Hotel in Philadelphia, PA. The speakers for the ^{13}C NMR session and the titles of their talks are as follows:

MODERN NMR METHODS ON COHERENT AVERAGING. J. S. Waugh, Department of Chemistry, MIT, Cambridge, MA 02139

^{13}C NMR IN CURED EPOXIES: RESOLUTION AND RELAXATION CONSIDERATIONS. A. N. Garroway, W. B. Moniz and H. A. Resing, Chemistry Division, Naval Research Laboratory, Washington, D. C. 20375

^{13}C NMR STUDIES OF SEMICRYSTALLINE POLYMERS: POLYETHYLENE AND CELLULOSE. William L. Earl, Center for Fire Research, and D. L. VanderHart, Center for Materials Research, National Bureau of Standards, Washington, D. C. 20234

VARIABLE-TEMPERATURE MAGIC-ANGLE SPINNING ^{13}C NMR STUDIES OF ORGANIC SOLIDS AND BULK POLYMERS. J. R. Lyerla and C. S. Yannoni, IBM Research Laboratory, San Jose, CA 95193, and C. A. Fyfe, Dept. of Chemistry, Univ. of Guelph, Guelph, Ontario, Canada

^{13}C NMR STUDIES OF FOSSIL FUELS AND OTHER NATURALLY OCCURRING SOLIDS. G. E. Maciel and V. J. Bartuska, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

MOLECULAR MOBILITY AND STRUCTURE OF HEMOGLOBIN-S AND FIBROUS COLLAGEN. Dennis A. Torchia, National Institute of Dental Research, National Institutes of Health, Bethesda, MD 20014

SOLID STATE NMR OF PROTEIN-NUCLEIC ACID COMPLEXES. S. J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, PA

The ^{13}C NMR symposium has been designed to provide a broad background of both theory and application.

The full meeting program, as well as information about registration, may be found in the July issue of Analytical Chemistry or the July-August issue of Applied Spectroscopy.

Sincerely,

Dave

David L. VanderHart
Structure and Properties
Polymer Science and Standards Division

The modular construction of the CXP allows the following combinations:

Type	Frequency Range / MHz x-Nuclei	$F^{19}+H^1$	Magnet Systems Iron / Cryo	Air Gap mm	Field Strength T
CXP 100	4 – 100		B-E 38 (15")	30	2.114
CXP 200	8.5 – 85	188 – 200	B-C 47/90	89.5 ⌀	4.698
CXP 300	12.5 – 125	282 – 300	B-C 70/90	89.5 ⌀	7.047

Computer controlled high power NMR pulse spectrometers, fully frequency variable. — Widest application range:

- **Multinuclear HR-Spectroscopy**
- **Wideline studies on paramagnetic solutions, polymers and solids**
- **HR in solids, e. g. PE-NMR with or without MAS and multiple pulse NMR**
- **Kinetics using lineshape analysis**
- **Frequency dependent studies**
- **Pure NQR**
- **NMR of magnetic materials**

W.-GERMANY BRUKER-PHYSIK AG
Silberstreifen, 7512 Karlsruhe-Rheinstetten
Tel. (0721) 5 11 85–89, Tx. (07) 826836

SWITZERLAND SPECTROSPIN AG
Industriestr. 26, 8117 Zürich-Fällanden
Tel. (01) 8 25 48 55–59, Tx. 54 850

NETHERLANDS BRUKER SPECTROSPIN NV
Jan van Gentstraat 148, Badhoevedorp
Tel. (02968) 56 97, Tx. 11 511

SCANDINAVIA BRUKER SPECTROSPIN AB
Vasavägen 11, S-184 00 Åkersberga
Telephone 08-732 90 40

FRANCE BRUKER SPECTROSPIN SA
Rue de l'industrie, (67160) Wissembourg
Tel. (88) 00 3388-94 05 10, 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 Miglioretti, 2, 20161 Milano
Tel. (02) 64 64 261, Tx. 37 263

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

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

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

For further information please contact any of the Bruker offices listed here.

BRUKER

National Research Council Canada
Conseil national de recherches Canada

Division of Biological Sciences
Division des sciences biologiques

File Référence

13 June 1979

Professor B.L. Shapiro
Texas A and M NMR Newsletter
College Station, Texas 77843
U. S. A.

Dear Barry,

HIGH/LOW/POWER/RESOLUTION/FIELD NMR

In answer to your gentle yellow threat, we would like to describe our recent excursions into contemporary NMR technology; in March this year we began serious research on our Bruker CXP-300 spectrometer.

This instrument is of interest to your readers as it represents the compromise with which many of them will be faced. Most of our chemical colleagues wanted a spectrometer with the highest possible field, sensitivity, and dispersion. On the other hand, we wanted one to do large spectral widths, broad lines, and solid state experiments such as cross-polarization (^{13}C, ^{1}H; ^{31}P, ^{1}H) with magic angle spinning (CP MAS). For the CP MAS experiments one runs into increasing difficulty at higher magnetic fields.

Our instrument has a wide bore (9 cm) 7.0 Tesla magnet and broad band receiver and transmitter. Samples may be run in the transverse solenoid coil (for solids) or Helmholtz coil (for high resolution) configuration. Although tubes of diameter as large as 30 mm could in principle be accommodated, we compromised at 15 mm for the broad band multinuclear high resolution experiments, 10 mm for our fixed-frequency ^{13}C and ^{31}P probes, 5 mm for ^{1}H high resolution, and 10 or 7.5 mm for solids. Using the decoupler coil as a receiver, ^{1}H can be run in the 10 or 15 mm tubes as well. Similarly, ^{2}H can be run on the lock channel in all tube sizes (high resolution).

In the high resolution mode the spectrometer has exceeded all our expectations (and Bruker's specs!). For example, with natural abundance ^{13}C of 10% ethyl benzene, 15 mm broad band probe, single shot, we obtain a S/N ratio of 160:1, corresponding to 1440:1 for the more usual 90% sample. With natural abundance ^{15}N of N-methyl formamide, 90% in DMSO, 15 mm broad band probe, single shot, we obtain S/N of 55:1 with NOE, and 19:1 without NOE (gated decoupling). A problem we did not anticipate, which does restrict our throughput, is the shimming of the wide-bore magnet for samples of narrow diameter; this is a very time-consuming process.

Ottawa, Canada
K1A 0R6

Professor B.L. Shapiro 13 June 1979

The broad line spectra are where the CXP really shines. In the Figure we show the "before" (23 KG system) and "after" (CXP-300) ^2H NMR spectra of a liquid crystalline phospholipid sample containing α,α-d_2-stearic acid. The CXP not only gives greater sensitivity due to higher field and shorter dead time, but provides a more faithful representation of the powder line shape from which the very useful moments can be calculated. Our rough estimates of the gains in sensitivity and operating time are shown on the Figure. In collaboration with Dr. H. Saitô, here on leave from the National Cancer Central Research Institute of Japan, we have seen corresponding improvements in the ^{13}C spectra of carbohydrate gels.

We have performed CP MAS experiments on the standard samples. For adamantane (which does most of the line narrowing by itself) we obtain S/N = 250:1 and a linewidth of 15 Hz under standard conditions of 2 scans with 1 contact (10 msec) each. Thus far we have not had much success with other samples, in part due to the slow learning process, and also to difficulties with precession of the bullet rotor. Low density samples such as aqueous liquid crystals or carbohydrate gels will not spin at all with our present rotors. Bruker is presently investigating solutions to these problems.

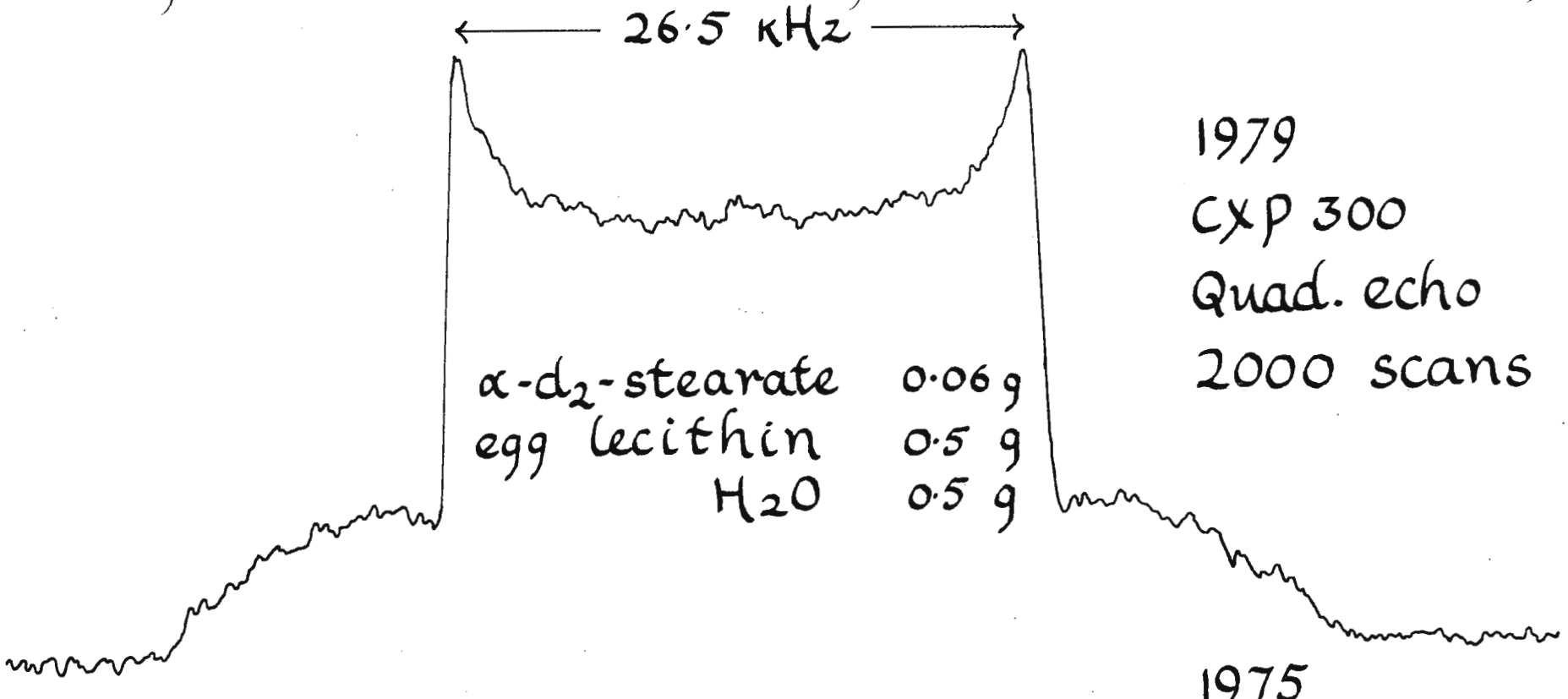
Overall it is a great feeling to have taken a large quantum jump instrumentally. Hopefully the science will follow the same process.

One of us (R.A.B.) is happy to announce that he has recently joined the continuing staff of the National Research Council of Canada.

With best personal regards,

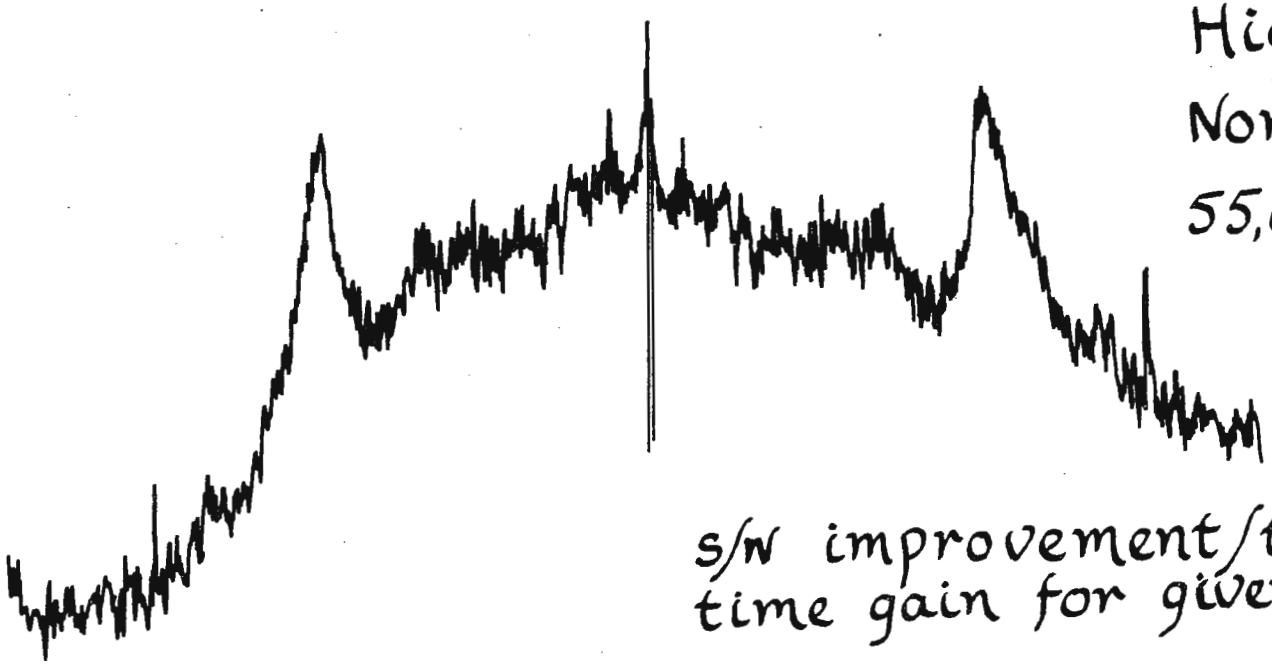
Andy Ian Leo

R. Andrew Byrd Ian C.P. Smith Leo A. Turner



1979
CXP 300
Quad. echo
2000 scans

α-d_2-stearate 0·06 g
egg lecithin 0·5 g
H_2O 0·5 g



1975
High res. 23 kGauss
Normal FT mode
55,000 scans

s/N improvement/time = 50
time gain for given s/N = 2500

250-34

STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

STANFORD MAGNETIC RESONANCE LABORATORY

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

June 14, 1979

Biological ^{13}C Relaxation Standard and
High Field Pulse Defects

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

Dear Dr. Shapiro,

In search of a water-soluble compound to monitor the performance of the modified HXS-360 spectrometer for ^{13}C relaxation studies of biological macromolecules in aqueous solutions, we have hit upon the use of the nonionic surfactant, Triton X-100. This surfactant is an isooctylphenyl-polyoxyethylene ether and shows well-resolved protonated and non-protonated ^{13}C resonances from aromatic, oxyethylene and aliphatic carbons. The spread in chemical shifts and T_1 relaxation times (Table I) is adequate to encompass most ^{13}C shifts and relaxation times that we would typically encounter for biological studies. The surfactant is highly stable, available in large quantities and very soluble in aqueous environments, where it forms micelles. A 0.4M solution is typically observable in 16 scans.

The Triton sample has been most useful in revealing inadequacies in the pulse excitation power for 90 MHz ^{13}C measurements over the 200 ppm range of most interest. The 200 ppm range translates to a spectral window of ±10 kHz at 84.6 kGs. At large spectral offsets from the QPD frequency, the ^{13}C resonances in a 180-τ-90 inversion recovery experiment in fact are <u>not</u> inverted (Fig. 1 and 2). As discussed by Levy and Peat (2), the lack of inversion will distort T_1 values calculated using peak intensities. For small molecules, this is not a major problem, since the <u>integrated area</u> of the peak appears to still follow exponential behavior. In fact, the T_1 values for the 30-40 ppm lines in Fig. 1 and 2 were found to be within 10% of each other when using integral fits to the 3-parameter fitting routine of Nicolet software. For biological samples with overlapping lines, however, peak areas are not easily measured, and the inadequate pulse power at large offsets remains a serious problem.

For the present time, we are carrying out our biological ^{13}C measurements with the spectral offsets adjusted so that the regions of interest

To: Dr. Barry Shapiro
From: Dr. Anthony Ribeiro
June 14, 1979

fall near the QPD frequency. However, this process is clearly time-consuming for work with dilute biochemicals.

We shall be grateful to hear comments from any party.

Sincerely,

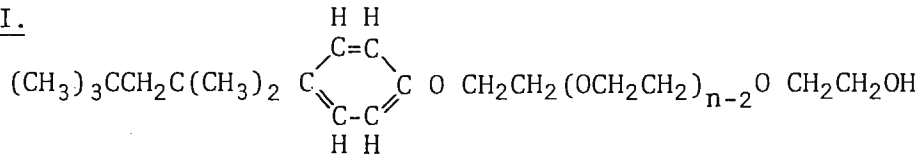
Anthony Ribeiro

Anthony Ribeiro

(1) A. A. Ribeiro and E. A. Dennis, J. Chem. Phys. 80, 1746-1753 (1976).

(2) G. D. Levy and I. R. Peat, J. Magn. Res. 18, 500-521 (1975).

Table I.



(b) [c]e [d] (a) o n m p g h i,j,k f l

Peak	δ(ppm)	T_1(sec)
a	31.6	0.20
b	31.7	0.26
c	32.0	1.80
d	37.7	0.13
e	56.8	2.50
f	60.4	1.40
g	67.1	0.21
j	69.7	0.53
l	71.8	1.30
m	113.8	1.50
n	126.6	0.22
o	141.5	0.24
p	156.3	2.80

Assignments are from reference (1).
Chemical shifts are downfield from external TMS.

Figure 1.

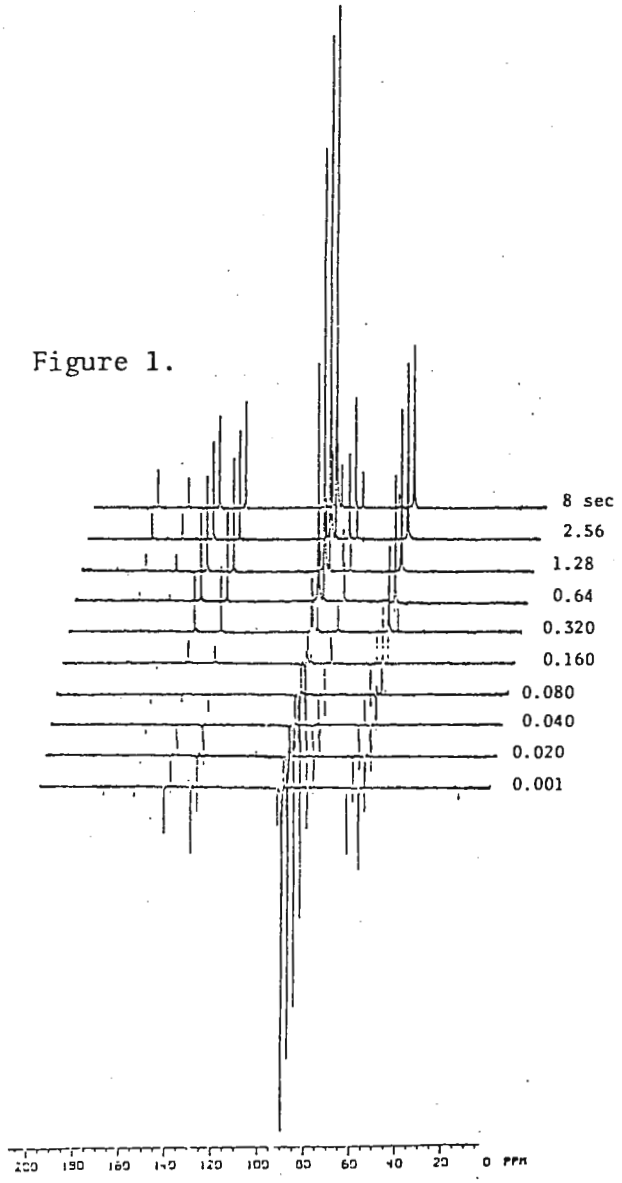
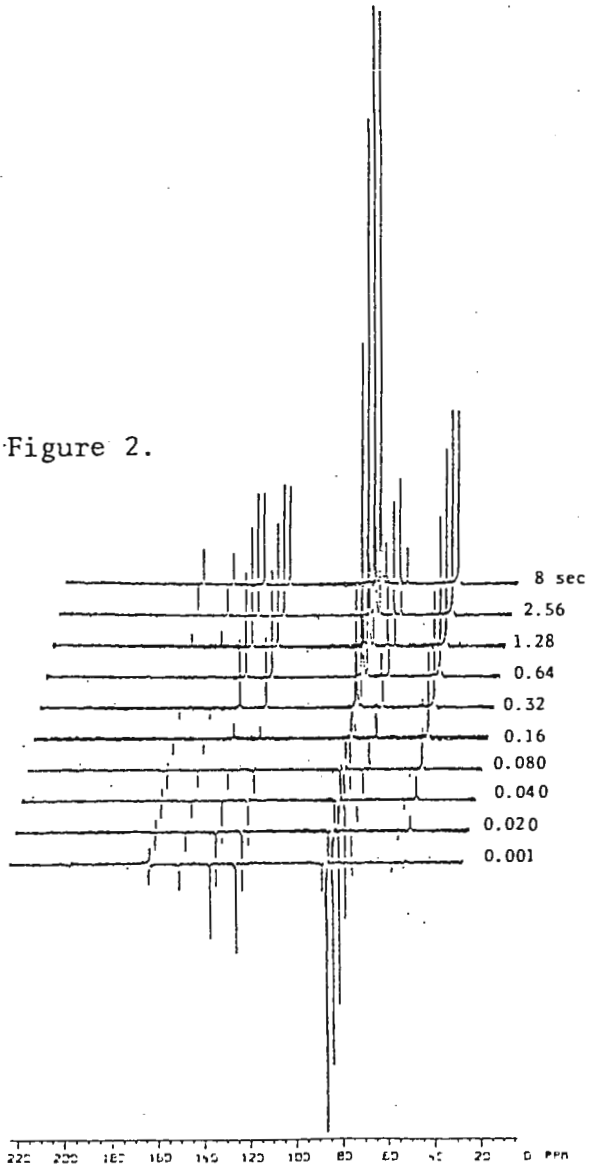


Figure 2.



La Trobe University
BUNDOORA / VICTORIA / AUSTRALIA 3083
TELEGRAMS AND CABLES: LATROBE MELBOURNE

DEPARTMENT OF
ORGANIC CHEMISTRY

TELEPHONE: 478 3122

19th June, 1979.

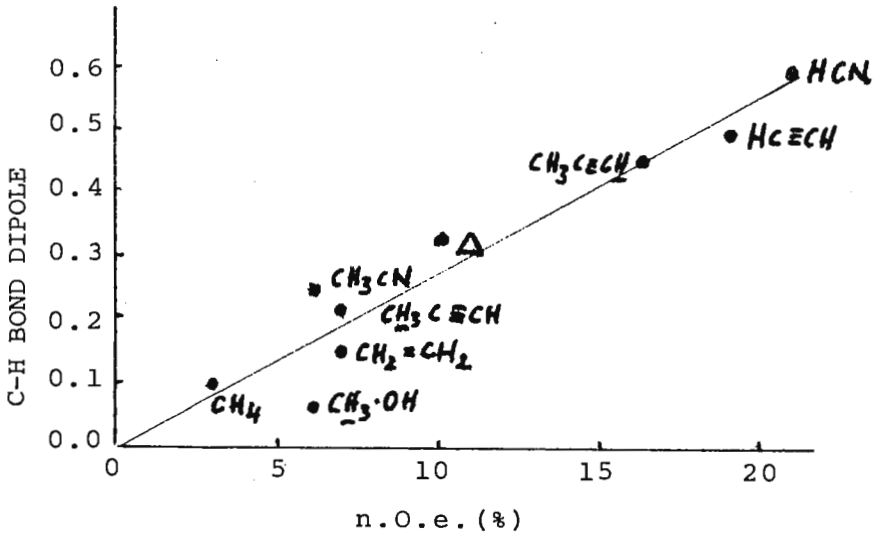
Professor B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, Texas 77843.

INTERMOLECULAR n.O.e's.

Dear Professor Shapiro:

We have been studying solute-solvent interactions for some time now using the intermolecular nuclear Overhauser effect. In these experiments the solvent resonance of a carefully degassed solution is irradiated and intensity changes in the solute resonances are observed, using external lock and intensity reference capillaries.

As an example of some of this work here we reproduce our results on benzene solutions. The observed n.O.e. is plotted against the bond dipole. This has been calculated by the CNDO method (which appears to be as good as any and reproduces the total dipole moment quite well). In spite of the shortcomings of the calculation and the fact that four different spectrometers were used, the correlation is good. With small molecules containing large dipoles in the immediate vicinity of the proton observed, e.g. CH_3-CHO, CH_3-NO_2, there are obvious difficulties and these fall off the line. However, when these "neighbouring effects" are taken into consideration, the correlation is restored. Currently we are calculating these "dipolar fields" around larger molecules.



Sincerely,

B. Ternai.

B. TERNAI.

G.R. SMITH.

250-39

THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS
DEPARTMENT OF CHEMISTRY

June 15, 1979

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

TWO DIMENSIONAL FT NMR SPECTROSCOPY WITH A WH-90/NIC-80

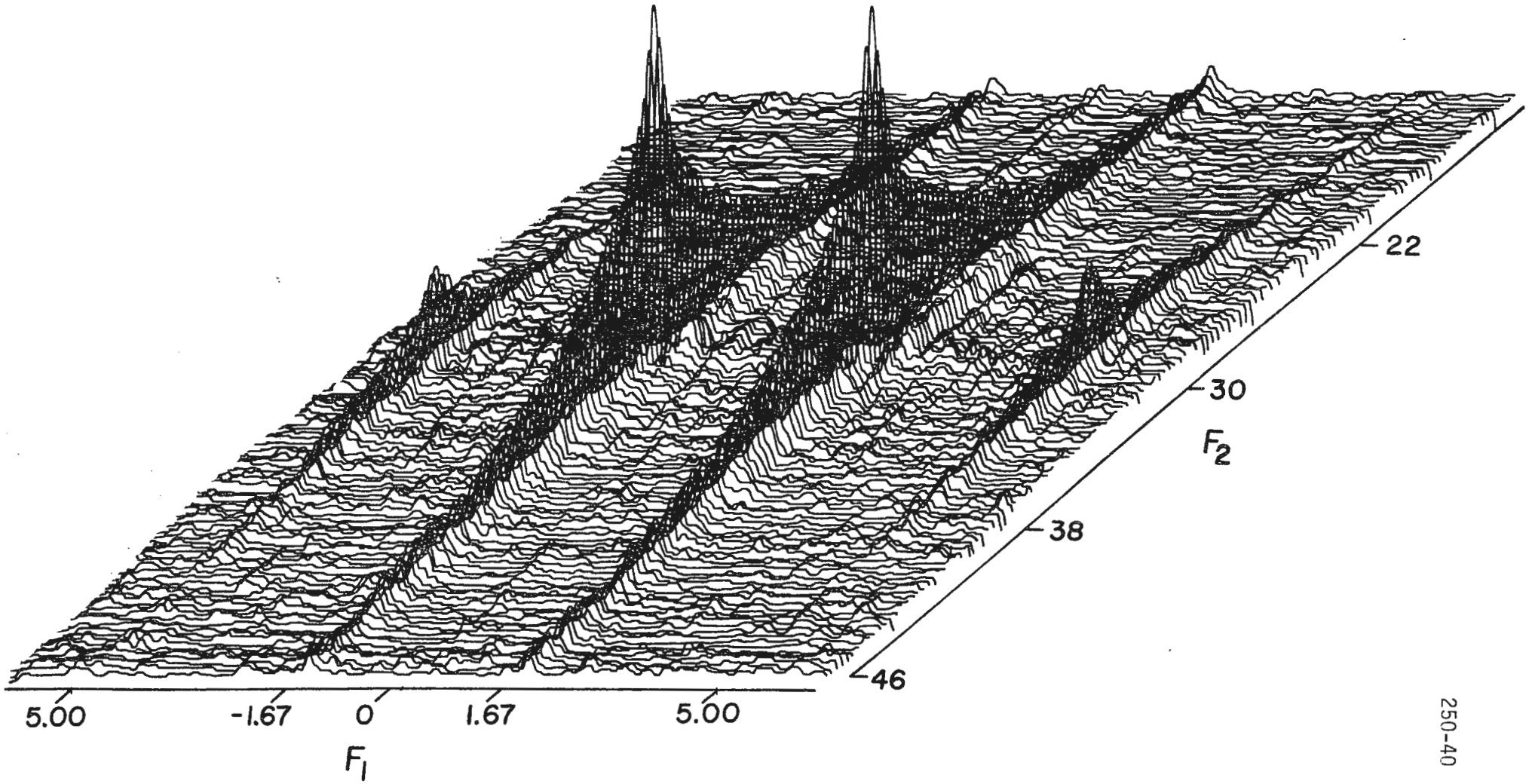
Dear Barry:

The enclosed two-dimensional ^{13}C FT spectrum of acetic acid represents our first result by this technique; it is a J-spectrum of the natural abundance carboxyl carbon of acetic acid obtained by the amplitude modulation technique of Bodenhausen et al (1) and displayed in the absolute value mode. Frequencies in the F_1 dimension are $\pm$ 3J/4 and $\pm$ J/4. The 128 sets of ^{13}C echoes, which were collected with 52 scans per set, were Fourier transformed in the quadrature mode using Nicolet NTCFT software with a NIC-80 computer and a 600K disk. Unfortunately, we could not make use of several 2D software modules, which were written by Geoffrey Bodenhausen, and kindly sent to us by Bob and Regitze Vold. It was necessary to write a computer program to perform the transposition of the spectra. After some minor modifications, the remaining operations were performed with the NTCFT software. Under the conditions of the experiment, the field inhomogeneity limited line width of the spectrometer was 1.0 Hz, whereas the line widths in the multiplet are only 0.09 Hz. Clearly, future applications will include measurements of coupling constants which at least one of our colleagues feels are "too small to be of interest." The brutal finality of your golden letter prevented us from obtaining a more polished spectrum.

Sincerely yours,

Steve Walter Mike Barfield

(1) G. Bodenhausen, R. Freeman, R. Niedermeyer, and D. Turner, J. Magn. Resonance, 26, 133 (1977).



250-40

MONTEDISON

Professor Bernard Shapiro
Dpt. of Chemistry
Texas A & M University
College Station - TX 77843 - USA

DIPE/PM/CER
Stab. Petrolchimico
via della Chimica
30175 Porto Marghera
(Venezia) ITALY

Dear Professor Shapiro,

Title: ^{13}C quali- and quantitative analysis of a linear elastomeric polyurethane

We have just analyzed in our laboratory a commercial copolymer of polyurethanes by ^{13}C pulsed NMR spectroscopy with a Bruker WH 90. A 13% (w/v) solution was used in 10 mm o.d. tubes at 130°C with the following experimental conditions: pulse angle = 45°, cycle time: 7 sec, sweep width: 6000 Hz, memory: 8 K. About 2000 sweeps were needed to obtain a satisfactory signal to noise ratio in the decoupled spectrum. From the comparison of the chemical shifts obtained with those of model compounds it is easy to assign the lines of the spectrum and to determine qualitatively the components of the copolymer: butanediol (BUT), adipic acid (ADA) and methane-bis(p-phenyl isocyanate) (MDI). The lines arising from α- and β-methylenes of butanediol are doublets owing to the fact that the diol is bonded to either the adipic acid or the isocyanate.

For a quantitative analysis of the copolymer it is also important to know the T_1 values of the single lines, at least for those which are necessary for the determination. We have therefore decided to exclude the carbonyl and the aromatic junction carbons and have obtained the data reported in the Table at the following experimental conditions using the inversion recovery method: cycle time: 12 sec, number of spectra: 6, delay between 180° and 90° pulses: 6 sec, $6/\sqrt{3}$ sec, 6/3 sec, etc. Owing to the overlapping of the lines of the doublets, the T_1 values for the carbons are of course less reliable, but the conditions of the first spectrum are sufficient for the quantitative analysis.

From the integrals (Table 1) we calculate that the molar ratios of the components are

ADA : BUT : MDI = 25.5 : 44.5 : 30

Observing that the butanediol is less than 50%, i.e. the minimum acceptable value in this copolymer, we take another spectrum without the NOE effect, decoupling only during the acquisition time and then waiting 12 seconds.

From the integral reported in Table 1, the molar ratios are

ADA : BUT : MDI = 27 : 46 : 27

but a remarkable difference is observed in the integrals of the lines δ_7 and δ_8 of MDI: we think that δ_8 is too large (likely in the industrial synthesis a crude MDI containing trimers and other compounds was used). Then taking into account only the δ_8 line of MDI we obtain the following result

ADA : BUT : MDI = 28 : 47.5 : 24.5

which is better and more reliable than the previous one.

TABLE 1

Chemical shifts (EMDS = 0)	Assignements	T_1(sec)	Relative integrals with NOE	without NOE
δ_1 = 22.23	$\beta\underline{C}H_2$ of ADA	2.3	19	14
δ_2 = 23.27	$\beta\underline{C}H_2$ of BUT	2.7	35	23
δ_3 = 23.72	$\beta\underline{C}H_2$ of BUT	1.3		
δ_4 = 31.58	$\alpha\underline{C}H_2$ of ADA	2.3	20	13
δ_5 = 61.55	$\alpha\underline{C}H_2$ of BUT	2.2	35	23
δ_6 = 62.13	$\alpha\underline{C}H_2$ of BUT	0.9		
δ_7 = 117.37	$\underline{C}$H m, o of MDI	1.8	45.5	24
δ_8 = 126.92	$\underline{C}$H o, m of MDI	2.0	52	30
δ_9 = 133.88	j, j of MDI	undet.	14	14
δ_{10} = 135.44	j, j of MDI	undet.	17.5	15
δ_{11} = 152.01	O$\underline{C}$ONH	undet.	14	13
δ_{12} = 170.66	$\underline{C}$OO	undet.	8	12

Yours sincerely

Giorgio Gurato

GIORGIO GURATO

Giorgio Rigatti

GIORGIO RIGATTI*

(*) Physical Chemistry Institute of the University
via Loredan 2 - Padova

250-43

(303)491-6455

Colorado State University
Fort Collins, Colorado
80523

Department of Chemistry

June 20, 1979

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

Dear Barry:

Our Regional NMR Center here at Colorado State University has begun operation. Persons interested in having samples run or using the facilities should contact me for additional information.

We anticipate adding another staff member shortly and we hope the following announcement is of interest to your readers:

NMR instrument specialist for the Regional NMR Center at Colorado State University, to be based on three Nicolet superconducting nmr spectrometers (including one with magic-angle spinning) and a JEOL FX-100. Starting annual salary of $13,000 to $15,000. Candidate must have a degree in science or engineering or equivalent experience, with a background or interest in nmr. Duties include providing nmr service, instrument maintenance, instrumentation development, and technique development. Applications should include curriculum vitae and bibliography and three letters of recommendation, and should be sent to Professor G.E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Application deadline is July 31, 1979. Starting date is Aug. 1 - Oct. 1, 1979. Colorado State University is EEO/Title IX Employer. Equal Opportunity Office: 314 Student Services Building.

Sincerely,

Bruce

Bruce L. Hawkins
Manager, Regional NMR Center

lb

Carnegie-Mellon University

Department of Chemistry
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213

(412) 578-3149

July 11, 1979

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

Dear Barry:

In memory of Robert Rowan III, who died at an early age last year, a number of friends are organizing the Robert Rowan III Memorial Symposium, to be held at Mellon Institute after the ACS meeting in Washington. We will have registration and an informal gathering on the evening of the 14th September and an all day program of papers on the 15th.

We anticipate having an excellent meeting with the theme "Determination of Biochemical Structures by NMR". Among those who have already agreed to speak are:

Ian Armitage	R. J. Highet
Robert G. Bryant	Chien Ho
David Cowburn	Koji Nakanishi
J. A. Ferretti	James Prestegard
Frank R. N. Gurd	Philip Yeagle

This is an invitation to all readers of TAMUNMR to attend. Brian Sykes, Jerry Glickson and I are acting as an organizing committee. A postcard to any of us will bring information about accommodations, program, etc.

The proceeds of the meeting will go to establish a trust fund for Bob's children; attend if you can.

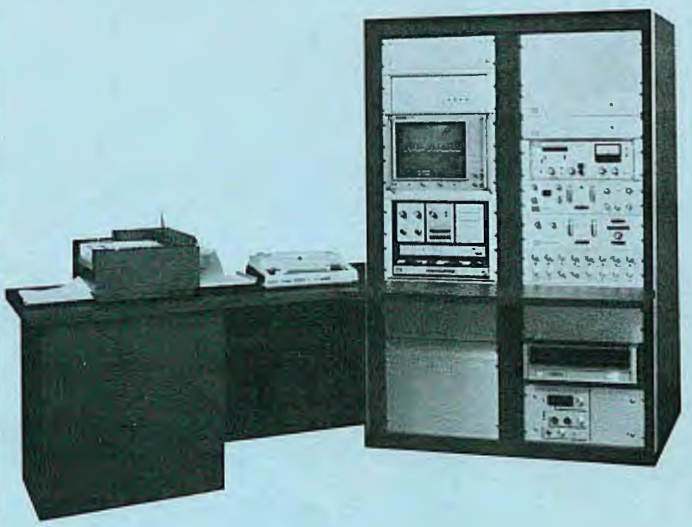
With best wishes,

Sincerely,

Aksel A. Bothner-By

AAB/mmg

NT-150 A WIDE-BORE, FT-NMR SYSTEM FROM NICOLET



For routine NMR and state-of-the-art techniques such as:

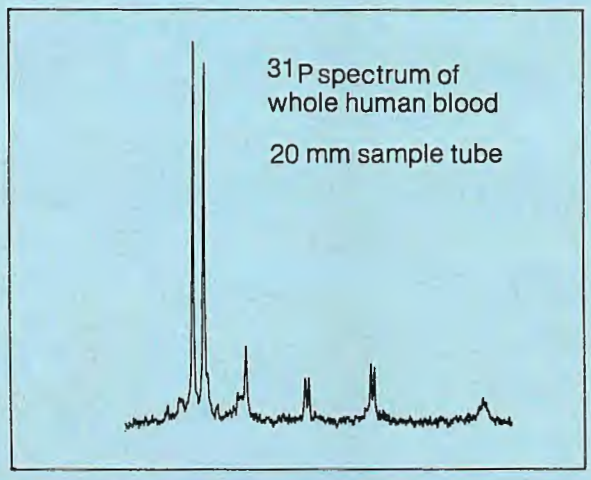
- ^{31}P experiments on living organs.
- Cross-polarization studies on solids.
- ^{13}C studies of high molecular weight polymers.
- Two-dimensional FT-NMR.

FEATURES INCLUDE:

- 3.5T superconducting magnet with 10 cm room-temperature bore.
- Straight-through access to sample area.
- Quick-disconnect probes for rapid changeover.
- 5, 12 and 20 mm sample tubes as standard, 30 mm optional.
- Quadrature phase detection as standard.
- Computer-controlled audio filter from 100 Hz to 51,100 Hz in 100 Hz steps.
- Nicolet 1180 data system with simultaneous acquisition, processing and plotting.
- Digital plotter with plot lengths selectable from 1 cm to 900 cm.

OPTIONS INCLUDE:

- NT-150 MF: broad-band multi-nuclei observe for 4 to 60 MHz.
- NT-150 CP: optimized system for Waugh-Pines cross-polarization studies.



For more information or to discuss your applications, please telephone or write.

NICOLET TECHNOLOGY CORPORATION
145 East Dana Street
Mountain View, California 94041
Phone: 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