

---

Connecting an AM Spectrometer and an IBM RS/6000 Computer to an HP 7550 Plotter . . . . .	Cottrell, C. E.	2
High Voltage Variable Capacitor Design . . . . .	Soher, B. J., Weinberg, I., and Barker, P. B.	5
A Relatively Cheap and Reliable Method of Storing NMR Data . . . . .	Helm, L.	6
Structure Analysis with 2D NMR Techniques . . . . .	Huang, Q.	9
Field-Sweep CW NMR Using a Balanced Bridge/Network Analyzer. . . . .	Wu, X., and Butler, L. G.	13
Discrimination of Diastereomeric Dioxolane Compounds Using Gd(III)-Induced $^{13}\text{C}$ Relaxation Rate Enhancements . . . . .	Huskens, J., Peters, J. A., and van Bekkum, H.	17
$^2\text{H}$ Study of Phase Behavior of a Surfactant in Deuterium Oxide . . . . .	Blum, F. D.	18
First Observation of Rh-Rh Two-Bond Spin-Spin Coupling . . . . .	Read, M., Glaser, J., and Sandstroem, M.	21
Proton Shifts in Three-Center, Two-Electron C-H-C Bonds in Carbocations . . . . .	Roberts, J. D.	25
Cutting Ham in the k Space . . . . .	Cremillieux, Y., Diop, A., Graveron-Demilly, D., and Briguet, A.	26
Resource-Limited Oxygen Shifts? . . . . .	Howarth, O. W.	29
Lineshape Deconvolution - Who Needs Software? . . . . .	Meder, R.	30
Suppression of $t_1$ Noise and Solvent Artifacts in 2D NMR Spectra of Proteins . . . . .	Norton, R. S.	35
Sensitivity-Enhanced 3D NOESY-TOCSY: Applications to Transferred NOEs . . . . .	Ni, F.	39
Mapping of Spectral Densities of NH Motions in Proteins . . . . .	Peng, J. W., and Wagner, G.	41

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 open 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.



TABLE 1. DEUTERATED SOLVENTS.

Cat. No.	Description	Formula	Min. bp. (°C)	Density (g/ml)	MP (°C)	BP (°C)	-X <sub>v</sub> X 10 <sup>6</sup> @ (°C)
D-11	Acetone-d <sub>6</sub>	CD <sub>3</sub> COCD <sub>3</sub>	99.6%	1.17	-17	56.8	0.551 (32)
D-120	Acetone-d <sub>6</sub> + 1% TMS		99.6%				
D-13	Acetone-d <sub>6</sub>	CD <sub>3</sub> COCD <sub>3</sub>	99.8%	0.87	-34	57	0.460 (20)
D-121	Acetone-d <sub>6</sub> + 1% TMS		99.8%				
D-129	<p>Cost-conscious quality NMR solvents offered by Wilmad, such as CDCl<sub>3</sub>, are frequently priced lower than more traditional sources. Included in this offering are the most common solvents, like Acetone-d<sub>6</sub>, Benzene-d<sub>6</sub>, D<sub>2</sub>O, and DMSO-d<sub>6</sub>, as well as some of the most unusual solvents for specialty applications, like 1,1,2,2-Tetrachloroethane-d<sub>2</sub>, Octane-d<sub>8</sub>, and Trifluoroacetic Acid-d.</p>						
D-14	Chloroform-d	CDCl <sub>3</sub>	99.8%	1.50	-64	62	0.543 (20)
D-21	Chloroform-d + 1% TMS		99.8%				0.611
D-122							
D-130							
D-28	Chloroform-d	CDCl <sub>3</sub>	99.8%	1.50	-64	62	0.740 (20)
D-31	Chloroform-d + 1% TMS		99.8%				

VARIAN  
BOX/500 SHEETS

Cat. No.	Size	Instrument Model	Type
WCV-100 (S-100A)	11" X 26"	HA-100, HA-150, HA-100D	Gridded-Two Color
WCV-60 (S-60C)	11" X 26"	A-60, S-60, A-60D	Gridded-Two Color
WCV-XL (S-XL)	11" X 26"	XL-100, XL-150, XL-200, XL-300, XL-400	Gridded-Two Color
WCV-XLFT-100	11" X 26"	XL-100, XL-150 and FT	Gridded-Two Color
WCV-XL-200	11" X 26"	XL-200, XL-300, XL-400	Gridded-Two Color

**WILMAD HAS YOUR CHART!**

We provide the largest variety of paper and pens for NMR recorders or plotters available anywhere. Included in these listing are the newest spectrometers from Varian, Bruker, (and IBM), General Electric and JEOL, as well as the latest models, such as the Hewlett Packard 7475A, 7550A, and Thinkjet 2225A, Zeta 8 or 8A, and Western Graphtec 4730 plotters and printers.

WCV-20 (CFT-20)	11" X 16 3/4"	CFT-20, FT-80, FT-80A	Gridded-Two Color
WCV-11 (CFT-11)	11" X 17"	All Models up to 16 1/2" or 16	Blank

## Searching for the Unusual Requirement? WILMAD HAS YOUR ANSWER!

The most comprehensive offering of “widgets, gadgets and specials“ for NMR spectroscopy, including:

**Spatula for 5mm NMR Tubes**  
**Three types of Valve NMR Tubes**  
*(including the new J. Young Valve Tube)*  
**Solvent Jet NMR Tube Cleaners**  
**pH Electrode for 5mm NMR Tubes**

**Taperlok® NMR Tubes**  
**A multitude of Coaxial Inserts**  
**Alumina NMR Tube for Si-29 Studies**  
**Ultra-thin wall NMR Tubes**  
**Throwaway "THRIFT" and "ECONOMY" NMR Tubes**

## Serving the Spectroscopic Aftermarket



## WILMAD GLASS COMPANY

**Route 40 and Oak Road • Buena, NJ 08310 U.S.A.**  
**609-697-3000 • TWX 510-687-8911**  
**FAX 609-697-0536**

## TEXAS A&amp;M NMR NEWSLETTER

NO. 404, MAY 1992

## AUTHOR INDEX

Barker, P. B. . . . . 5	Diop, A. . . . . 26	Meder, R. . . . . 30	Roberts, J. D. . . . 25
van Bekkum, H. . . . 17	Glaser, J. . . . . 21	Ni, F. . . . . 39	Sandstroem, M. . . . 21
Blum, F. D. . . . . 18	Graveron-Demilly, D. . 26	Norton, R. S. . . . 35	Soher, B. J. . . . . 5
Briguet, A. . . . . 26	Helm, L. . . . . 6	Peng, J. W. . . . . 41	Wagner, G. . . . . 41
Butler, L. G. . . . . 13	Howarth, O. W. . . . 29	Peters, J. A. . . . 17	Weinberg, I. . . . . 5
Cottrell, C. E. . . . . 2	Huang, Q. . . . . 9	Read, M. . . . . 21	Wu, X. . . . . 13
Cremillieux, Y. . . . 26	Huskens, J. . . . . 17		

## TEXAS A&amp;M NMR NEWSLETTER

NO. 404, MAY 1992

## ADVERTISER INDEX

American Microwave Technology, Inc. . . . . 27	GE NMR Instruments . . . . . 19, inside back cover
Bio-Rad, Sadtler Division . . . . . 3	Hitachi Instruments, Inc. . . . . 31
Bruker Instruments, Inc. . . . . 7	JEOL . . . . . outside back cover
Cambridge Isotope Laboratories, Inc. . . . 37	Varian . . . . . 23
Chemagnetics, Inc. . . . . 15	Wilmad Glass Company, Inc. . . . . inside front cover
Doty Scientific, Inc. . . . . 11	

## SPONSORS OF THE TAMU NMR NEWSLETTER

Abbott Laboratories	The Monsanto Company
ATI Instruments	Nalorac Cryogenics Corporation
Bruker Instruments, Inc.	New Methods Research, Inc.
Burroughs Wellcome Co.	Norell, Inc.
*Cambridge Isotope Laboratories, Inc.*	Otsuka Electronics/Chemagnetics
Cryomagnet Systems, Inc.	Oxford Instruments
The Dow Chemical Company	Petroleum Recovery Institute
The Du Pont Merck Pharmaceutical Company	The Procter & Gamble Company, Miami Valley Labs
Eastman Kodak Company	Programmed Test Sources, Inc.
E. I. du Pont de Nemours & Company	Shell Development Company
GE NMR Instruments	Tecmag
JEOL (U.S.A.) Inc., Analytical Instruments Division	Unilever Research
The Lilly Research Laboratories, Eli Lilly & Company	Union Carbide Corporation
Millipore Corporation, Waters Chromatography Division	Varian, Analytical Instrument Division

*\*Welcome to this new Sponsor!*

## FORTHCOMING NMR MEETINGS

Gordon Research Conference: Magnetic Resonance in Biology and Medicine, Tilton, NH, **July 13 - 17, 1992**; Contact: Dr. A. M. Cruickshank, Gordon Research Center, University of Rhode Island, Kingston, RI, 02881-0801; (401) 783-4011/3372; FAX: (401) 783-7644.

ISMAR 92 (The XIth Meeting of the International Society for Magnetic Resonance), Vancouver, B.C., Canada, **July 19 - 24, 1992**; Chairman: C. Fyfe. Contact: ISMAR 92, Dept. of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1. Tel: (604) 822-2293; FAX: (604) 822-2847; EMAIL: ismar@unixg.ubc.ca; BITNET: ismar@ubcmtsg.bitnet.

Science Innovation '92, New Techniques and Instruments in Biomedical Research (sponsored by the AAAS), San Francisco, **July 21-25, 1992**; Workshops on biomedical imaging, chemical and structural NMR; Plenary session on NMR on Fri., July 24. Contact: Science Innovation '92, P.O. Box 630285, Baltimore, MD 21263; fax (202) 289-4021.

34th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado, **August 8-14, 1992**; Contact: M. C. Goldberg, P.O. Box 25046 MS 424, Lakewood, CO 80225; (303)236-4728.

Eleventh Annual Scientific Meeting and Exhibition, Society of Magnetic Resonance in Medicine, Berlin, Germany, **August 8-14, 1992**; Contact: S.M.R.M., 1918 University Ave., Suite 3C, Berkeley, CA 94704; (415) 841-1899, FAX: (415) 841-2340.

XV International Conference on Magnetic Resonance in Biological Systems, Jerusalem, Israel, **August 16 - 21, 1992**; Contact: Prof. Gil Navon, XV ICMRBS, P. O. Box 50006, Tel Aviv 61500, Israel; Tel. (972-3) 5174571, Fax: (972-3) 655674/660325.

MRI in the Applied Sciences, Duke University, Durham, North Carolina, **October 25-28, 1992**; Contact: Society of Magnetic Resonance in Medicine, 1918 University Ave., Suite 3C, Berkeley, CA 94704; (510) 841-1899; FAX: (510) 841-2340.

High Resolution NMR Spectroscopy (a residential school), University of Sheffield, England, **April 1993[sic]**; Organizer: Dr. B. E. Mann (Sheffield); For information, contact Ms. L. Hart, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, England; Tel.: 071-437-8656.

Additional listings of meetings, etc., are invited.

*Please see notices on page 42.*



Campus Chemical Instrument  
Center

176 West 19th Avenue  
Columbus, OH 43210-1173  
Phone 614-292-3446

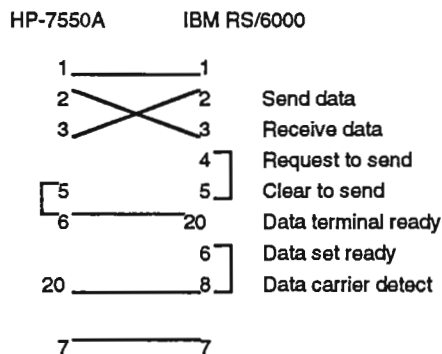
Professor Barry L. Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

April 10, 1992  
(received 4/13/92)

**RE: Connecting an AM spectrometer and an IBM RS/6000 computer to a HP 7550 plotter.**

Dear Barry,

We plot our Bruker AM-500 data on an HP-7550A plotter, and we can also plot data from an IBM RS/6000 computer that we use for off-line data processing. At the moment we are experimenting with Hare's Felix program Version 2.0. In order to eliminate any need to change either the configuration of the plotter or to change the RS-232 cables, the RS-232 cables from both the spectrometer and the IBM computer are attached to a serial auto switch. The switch we are using requires hardwire handshaking so the RS/6000 had to be configured for the DTR protocol. This auto switch can be set to 1 of 4 ports manually or it can rapidly scan its input ports and if the DTR line (20) of a port becomes active it locks on that port. In order for the automatic switch to work with the Risc system 6000 an RS-232 cable had to be wired as shown below:



The pref31 file has to be changed to ESC . P3: ESC . Y: IN; for hardwire handshaking. Felix adds a command to the start of the plot file that is PS3 or 4, where PS stands for page size. I am not certain if this is an old HPGL command or one that has been revived. Regardless it is not recognized by the HP 7550 plotter. Fortunately, the plotter ignores the instruction leaving only a complaint on the lcd display.

To facilitate transfer of data from the ASPECT computer for remote processing, I have written a program that transfers ASCII and data files between a PC and the ASPECT 3000. This program uses the same hardware as described by Markley et al<sup>1</sup>. The data can then be transferred via ethernet to the RS/6000. There it is converted into the old format for Felix. If anyone has a listing of the locations of the parameters that can go into the new format, I would appreciate seeing it. The manual for 2.0 only lists a few parameters and there is an error in my copy of the manual. I can be reached by e-mail at ccottrel@magnus.acs.ohio-state.edu or the shorter address of cottrell.2@osu.edu. Please credit this to Alan Marshall's account.

Sincerely,

*Charles Cottrell*

Charles E. Cottrell  
Senior Research Associate

1. Zs. Zolnai, W.M. Westler, E.L. Ulrich, and J.L. Markley, *J. Magn. Reson.* 88,511(1990).



# Structure Elucidation

## CSEARCH

Offers identical presentation on Sun, Silicon Graphics, or VMS

Reads  $^{15}\text{C}$  NMR peak tables directly

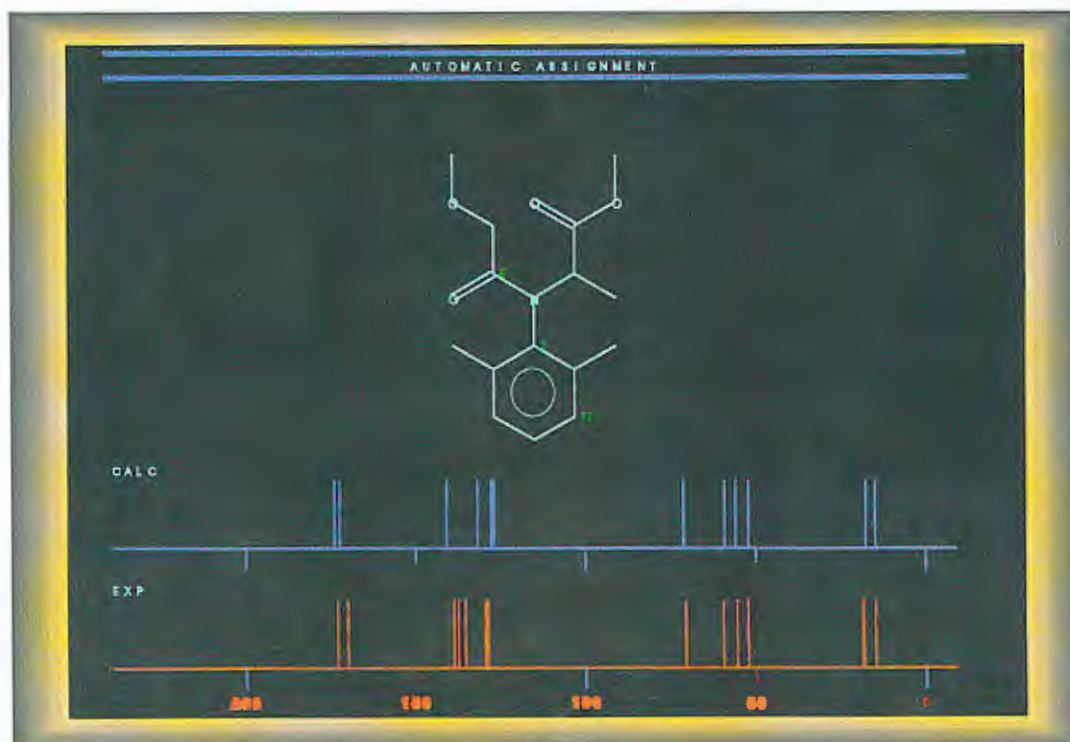
Confirms calculated with measured spectrum

Finds structurally related compounds by spectral matching

Calculates spectra for compounds not in the database

Sun is a trademark of Sun Microsystems, Inc. VMS is a trademark of Digital Equipment Corporation. Silicon Graphics is a trademark of Silicon Graphics, Inc.

Comparison of the calculated spectrum of a proposed structure with its measured spectrum. The intelligence of CSEARCH is demonstrated by favorable comparison for a structure not contained within the database of 52,000 spectra.



**BIO-RAD**

**Sadtler  
Division**

Main Office, 3316 Spring Garden Street, Philadelphia, Pennsylvania 19104.  
Telephone: (215) 382-7800. Telefax: (215) 662-0585. TWX: 710 670-1186.

# Those with the BEST INFORMATION WIN

**Sadtler User Library Manager - C:\ULIB\TST12-27**

File	Edit	View	Add	Security	Help				
Rec ID	Locked	Chemical Name/ID	IR Spec	NMR Peaks	Coup Const	Chem Struc	Phys Prop	MS Peaks	
1	X	A-1290	X		X	X	X	X	
2	X	A-4578	X	X		X	X	X	

**Define Physical Properties**

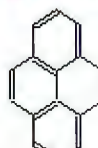
Technique	CDCL3
Melting Point	126C
Boiling Point	
Molecular Weight	
Molecular Formula	
Sadtler Reference Number	ST141
Wiswesser Line Notation	
CAS Registry Number	
RTECS Number	
Comments	Starting point for our oxidation s

Current Template: U\_Lib

Buttons: OK, Cancel, Restore, Clear All, Add Prop

**Structure**



Buttons: Edit, Delete

Software and  
Databases  
for Personal  
Computers



**Sadtler  
Division**

Main Office, 3316 Spring Garden Street, Philadelphia, Pennsylvania 19104.  
Telephone: (215) 382-7800. Telefax: (215) 662-0585. TWX: 710 670-1186.

**THE JOHNS HOPKINS UNIVERSITY**  
**SCHOOL OF MEDICINE**  
*and*  
**THE JOHNS HOPKINS HOSPITAL**

DEPARTMENT OF RADIOLOGY  
 AND  
 RADIOLOGICAL SCIENCE

Mailing Address:  
 THE JOHNS HOPKINS HOSPITAL  
 Baltimore, Md. 21205

March 28th 1992 (received 4/11/92)

Professor B.L. Shapiro,  
 TAMU NMR Newsletter,  
 966 Elsinore Court,  
 Palo Alto, CA 94303

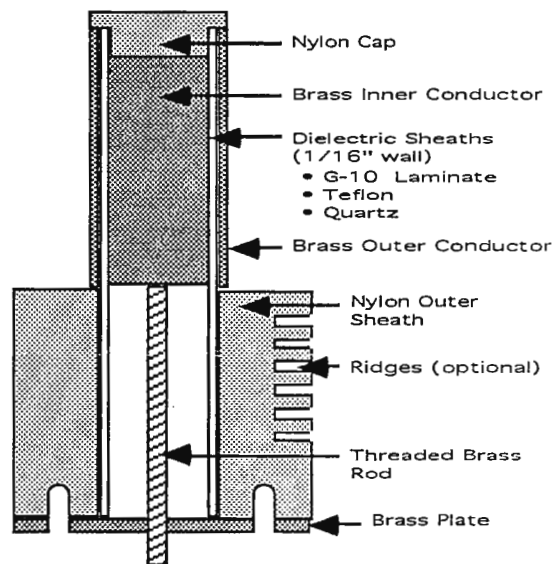
High Voltage Variable Capacitor Design

Dear Professor Shapiro,

Thank you for your ultimatum. We have recently been designing and building radiofrequency coils for proton and phosphorus spectroscopy of the human brain in a 1.5 Tesla magnet. Some of the designs require high voltage variable capacitors in the range of 1-50pF which can withstand transmitter powers of up to 2 kW. Since commercially available capacitors in the desired capacitance/breakdown voltage/Q factor range are often (a) prohibitively expensive, (b) unavailable, (c) non-MR compatible (i.e. paramagnetic), (d) geometrically incompatible with the probe design, and (e) any combination of (a)-(d), we have been investigating the possibility of constructing our own capacitors.

The maximum voltage across the capacitor depends on the power of the RF transmitter P and the Q of the system of which the capacitor is a part. Given that  $V_{Rp-p} = V_{avg} \sqrt{2} = \sqrt{2 \cdot P \cdot R}$ , and that the maximum reactive voltage across the capacitor  $V_{max} = V_{50p-p} \cdot Q$ , then an amplifier output of 2 kW, with  $R = 50 \Omega$  and  $Q = 100$ , will generate an expected  $V_{max}$  of around 45kV across the capacitor.

Tubing constructed of fiberglass epoxy laminate (G-10), Teflon (PTFE), and fused silica (quartz) were chosen as the dielectric materials because of their high dielectric strengths and low dissipation factors. Dielectric strengths and loss tangents were 28.5 kV/mm and  $2 \times 10^{-2}$ , 25 kV/mm and  $2 \times 10^{-4}$ , and 35kV/mm and  $5 \times 10^{-4}$  respectively. A cylindrical geometry was selected based on available materials and ease of construction. For a cylindrical capacitor with dielectric at a radius of  $r_0$ , dielectric thickness d, length L, and relative dielectric constant  $\epsilon_r$ , capacitance is  $C = 2\pi r_0 L \epsilon_r \epsilon_0 / d$ . Of the materials tested, quartz gave the highest Q factor but was prone to flashover due to lack of a tight seal between the quartz and the insulator separating the inner and outer conductors. The G-10 was very lossy giving unacceptably low Q values. Teflon was the easiest to machine to avoid flashover, and when loaded with a sample, coil Q values were not significantly different between Teflon and quartz. Higher breakdown voltages should be obtainable by increasing the dielectric wall thickness.



The capacitor design illustrated here is relatively simple and can be built at low cost. Teflon appears to be the most suitable dielectric material for this application.

Sincerely yours,

*Brian J. Soher*

Brian J. Soher

Irving Weinberg

*Peter B. Barker*

Peter B. Barker





Université de Lausanne - Faculté des Sciences  
INSTITUT DE CHIMIE MINÉRALE ET ANALYTIQUE

Place du Château 3, CH - 1005 LAUSANNE (Switzerland)  
tel. (021) 316 38 00 fax. (021) 316 38 01

Prof. Bernard L. Shapiro  
966 Elsinore Court  
Palo Alto, CA 94303  
U S A

15 April, 1992 (received 4/20/92)

### A RELATIVELY CHEAP AND RELIABLE METHOD TO STORE NMR DATA

Dear Prof. Shapiro,

For a long time storage of NMR data was a big problem in our Institute. Studying ligand exchange of metal complexes we use quite often the so called "isotopic substitution technique" to measure very slow rates. We mix for example a deuterated complex with a protonated ligand in a diluent and record  $^1\text{H}$  spectra in fixed time intervals. Between 30 and 100 FIDs are then recorded and stored on disk. If we study temperature dependence and the dependence on ligand concentration, several hundred spectra have to be stored and kept until complete analysis. We are using Bruker spectrometers that are equipped with ASPECT computers. For a long time we transferred data for backup and storage to an ASPECT satellite station with a magnetic tape unit connected. This procedure was very time consuming, especially if you would like to read back an old spectrum sitting at the end of the tape reel.

Since several months we own a REO-650 5.25" erasable optical disk system connected to a SUN workstation. At the beginning of this year we started to transfer data to the workstation via Bruknet (Brukers Ethernet protocol) and store it on optical disks. Care has to be taken to use the "P" option on the Bruknet demon running on the workstation. This option splits every datafile in two files: one for the parameters and one for the actual data. If the NMR data are transferred back to the ASPECT computer, Bruknet assembles the files in one, which can be read by the DISNMR program. The advantages of this method are:

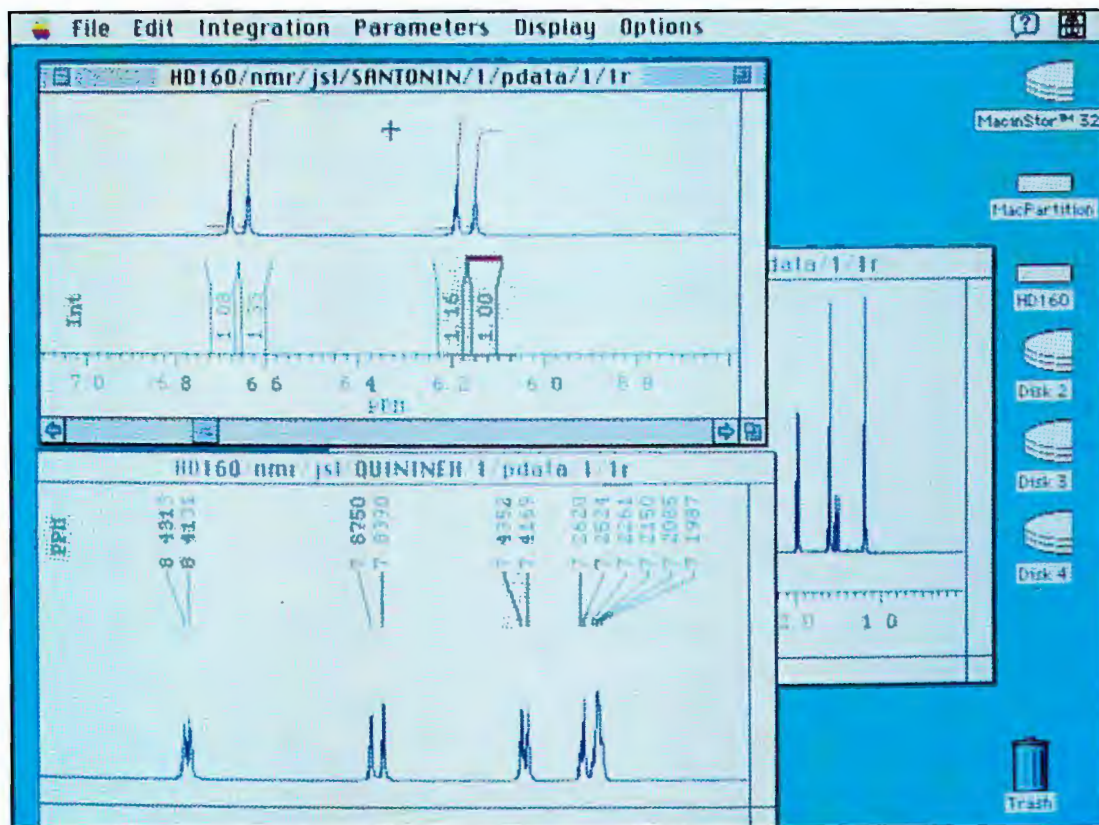
1. fast storage and *recovering* of data because the access to individual files is easy
2. relatively cheap and reliable storage medium (one optical disk can hold about 2 times 300 Mbyte and costs about \$350, making this medium less expensive per Mbyte than magnetic tapes)
3. because our PCs are linked to the workstation data can be transferred via Ethernet (ftp) to the PCs and treated there using Brukers WIN NMR

Dr. L. Helm

Please credit this contribution to the subscription of Prof. A.E. Merbach, University of Lausanne



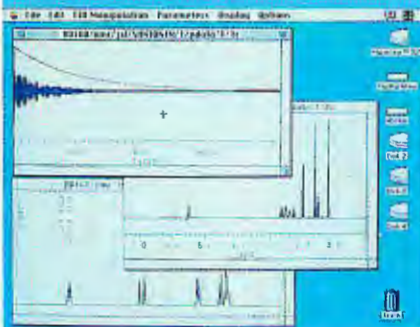
# WIN-NMR™



WIN-NMR,™ Bruker's successful and popular NMR off-line processing package for personal computers has been released for the Apple Macintosh II® family. WIN-NMR allows NMR spectroscopists to turn their Macintosh computers into powerful workstations for Bruker NMR spectrometers. Careful adherence to the Apple User Interface guidelines assures effortless learning of the application and fun NMR data processing. WIN-NMR, in conjunction with your favorite Macintosh word processor, database, or chemical structure drawing package can be a convenient and powerful spectroscopic productivity tool.

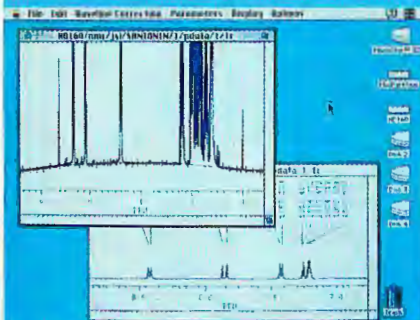






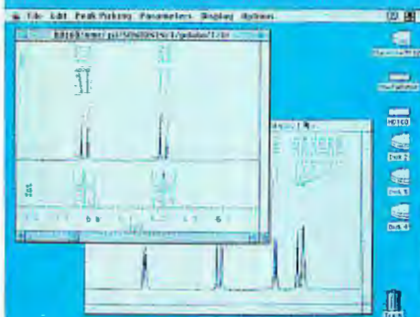
WIN-NMR can process FID and spectral data from all Bruker NMR spectrometers. The WIN-NMR data format used is identical to that of the UXNMR and UXNMR/P software. Data conversion routines are provided for all Aspect 2000/3000 based NMR spectrometers.

Data can be transferred between the X-32 and the Macintosh via Ethernet® using the TCP/IP protocol. Data can be transferred from Aspect 2000/3000 computers using Kermit® or via an intermediate Ethernet server.



Automatic or interactive baseline correction with user control over the type and order of the function used in the correction. The entire spectrum, or only a user selected region can be corrected.

The selected baseline points can be stored in a file and used over a series of spectra or as a standard correction for a specific probehead and experiment.



Automatic or interactive peak integration. In automatic integration the user has control over the integration threshold and grouping of multiplets. The automatically determined integrals can be individually manipulated once the automatic selection process is complete. The integration parameters can be stored for future use.

In interactive integration the user has complete control over each individual integral including integration limits, slope and bias. Integral areas can be calibrated to reference peaks or to determine percent composition for the sample.



Data can be plotted on your favorite plotter or laser printer through the use of the standard Apple printer drivers or through third party plotter drivers such as MacPlot® or Plottergeist®.

The use of the cut and paste facility can be used for transferring graphics between Macintosh applications. Facilities are provided to export peak picking and integration reports, as well as ASCII data to your favorite word processor or mathematics package for further manipulation.

## System Requirements

The WIN-NMR software is compatible with Macintosh System software 6.0.3 or higher, including System 7.0. Hardware requirements are a Macintosh II family CPU with a hard disk, math co-processor, and four megabytes of RAM. All Macintosh compatible printers are supported with output at the full resolution of the printer.

Ethernet is a registered trademark of Xerox, Inc. • MacPlot is a registered trademark of Microspot, Ltd. • Kermit is a registered trademark of Columbia University. PLOTtergeist is a registered trademark of Palomar Software. • WIN-NMR is a registered trademark of Bruker-Franzen Analytik. Apple, Macintosh, System 6.0.3, System 7.0, and Apple Logo are registered trademarks of Apple Computer, Inc.

W.-GERMANY BRUKER  
ANALYTISCHE MESSTECHNIK GMBH  
Silberstreifen, D-7512 Rheinstetten 4  
Tel. (0721) 5161-0, Fax (0721) 5171 01

FRANCE BRUKER SPECTROSPIN SA  
34, rue de l'Industrie, F-67160 Wissembourg  
Tel. (03) 86 20 20 20, Fax (03) 86 20 20 20

SWITZERLAND SPECTROSPIN AG  
Industriest. 26, CH-8117 Fällanden  
Tel. (01) 8 25 91 11, Fax (01) 8 25 96 96

NETHERLANDS BRUKER SPECTROSPIN NV  
Bruynvisweg 18, NL-1530 AB Wormer  
Tel. (75) 28 52 51, Fax (75) 28 97 71

SCANDINAVIA BRUKER SPECTROSPIN AB  
Enghälsingan 6, S-183 39 Täby  
Tel. (0 04 68) 7 58 03 35, Fax (0 04 68) 7 92 51 68

SPAIN BRUKER ESPAÑOLA, S.A.  
Cochabamba, 21-2-A, 28016 Madrid  
Tel. (1) 2 59 20 71 Fax (1) 2 59 33 91

BELGIUM N.V. BRUKER SPECTROSPIN S.A.  
27, Av. des Courses/ Wedrennenlaan, B-1050 Bruxelles  
Tel. (02) 648.53.99, Fax (02) 648.86.34

ITALY BRUKER SPECTROSPIN SRL  
Via Giovanni Pascoli, 70/3, I-20133 Milano  
Tel. (02) 70 63 63 70-73, Fax (02) 23 61 294

U.K. BRUKER SPECTROSPIN LTD.  
Banner Lane, Coventry CV4 9GH  
Tel. (02 03) 85 52 00, Fax (02 03) 46 53 17  
JAPAN BRUKER JAPAN CO. LTD.  
21-5, Ninomiya 3-Chome, Tsukuba-shi Ibaraki  
305 Japan. Tel. 0289-52-1234, Fax 0289-58-0322

USA BRUKER INSTRUMENTS, INC.  
Manning Park, Billerica, Mass. 01821  
Tel. (508) 667-9580, Fax (508) 667-3954

USA BRUKER INSTRUMENTS, INC.  
2880 Zanker Rd., Suite 106, San Jose, CA 95134  
Tel. (408) 434-1190, Fax (408) 434-1019

CANADA BRUKER SPECTROSPIN LTD.  
555 Steeles Ave., Milton Ontario L9T 1Y6  
Tel. (416) 876-4641, Fax (416) 876-4421

AUSTRALIA BRUKER (AUSTRALIA) PTY. LTD.  
Unit 7, 163 McEvoy Stret, Alexandria NSW 2015  
Tel. (02) 550-6422, Fax (02) 550-3687





College of Liberal Arts and Sciences  
 Department of Chemistry  
 Box U-60, Room 151  
 215 Glenbrook Road  
 Storrs, CT 06269-3060  
 FAX — (203) 486-2981

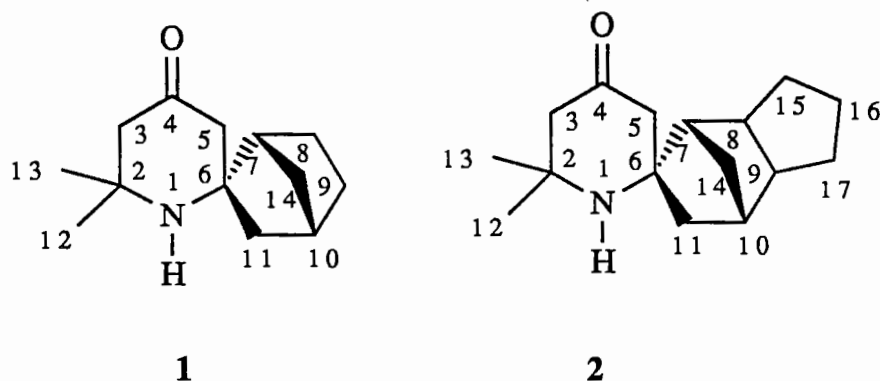
April 18, 1992 (received 4/22/92)

Dr. Bernard L. Shapiro  
 Tamu NMR Newsletter  
 966 Elsinore Court  
 Palo Alto, CA 94303

### Structure Analysis With 2D-NMR Technique

Dear Dr. Shapiro:

we have been interested in the synthesis of chiral nitroxides of the TEMPO type. The structures of two chiral precursors of some nitroxides are shown below. The structural problem is the orientation of the bridgehead  $\text{CH}_2$  with respect to the piperidine ring, that is whether it is "in front" with respect to the nitrogen or "in back".



We have concluded that in both structures, The  $\text{CH}_2$  is back as drawn. The evidence for these structures is based upon INEPT,  $^1\text{H}$ - $^{13}\text{C}$  COSY,  $^1\text{H}$ - $^1\text{H}$  COSY and  $^1\text{H}$ - $^1\text{H}$  NOESY spectra, as measured on a Bruker AC-270 NMR Spectrometer. The proton and carbon shifts are given in the attached Table.

The actual structures are based on NOESY enhancement observed between the bridgehead  $\text{CH}_2$ -protons and those on carbons 5, 7, 10, and 11 for both structures. In addition, there is an enhancement between the protons on carbon 11 and those on the axial methyl group on carbon 2. In structure 1, it is clear that there is no NOESY enhancement between the protons on carbon 8 and 9 and those on carbon 5. This is less clear in structure 2 because one of the protons on carbon 8 or 9 is unpredictably far down field.







College of Liberal Arts and Sciences

Department of Chemistry

Box U-60, Room 151

215 Glenbrook Road

Storrs, CT 06269-3060

FAX — (203) 486-2981

**Proton Chemical Shifts****Carbon Chemical Shifts**

Proton	1	2	Carbon	1	2
H3 <sub>1</sub>	2.30	2.24	2	55.4	55.5
H3 <sub>2</sub>	2.27	2.28	3	54.1	55.0
H5 <sub>1</sub>	2.42	2.36	4	210.7	210.9
H5 <sub>2</sub>	2.29	2.41	5	49.2	54.0
H7	2.15	1.87	6	64.5	64.0
H8 <sub>1</sub>	1.42	2.48	7	47.0	51.2
H8 <sub>2</sub>	1.93		8	23.4	41.0
H9 <sub>1</sub>	1.23	1.88	9	28.8	40.7
H9 <sub>2</sub>	1.56		10	36.4	47.2
H10	2.20	1.84	11	49.2	48.6
H11 <sub>1</sub>	1.14	1.04	12	29.4	29.2
H11 <sub>2</sub>	1.70	1.69	13	32.5	32.6
H12a	1.19	1.18	14	38.0	32.4
H13e	1.27	1.24	15		31.8
H14 <sub>1</sub>	1.28	0.92	16		27.3
H14 <sub>2</sub>	1.58	1.86	17		31.4
H15 <sub>1</sub>		1.27			
H15 <sub>2</sub>		1.37			
H16 <sub>1</sub>		1.21			
H16 <sub>2</sub>		1.65			
H17 <sub>1</sub>		0.97			
H17 <sub>2</sub>		1.82			

Please credit this contribution to Dr. Thomas K. Leipert's account.

Sincerely,

Qingtao Huang



An Equal Opportunity Employer

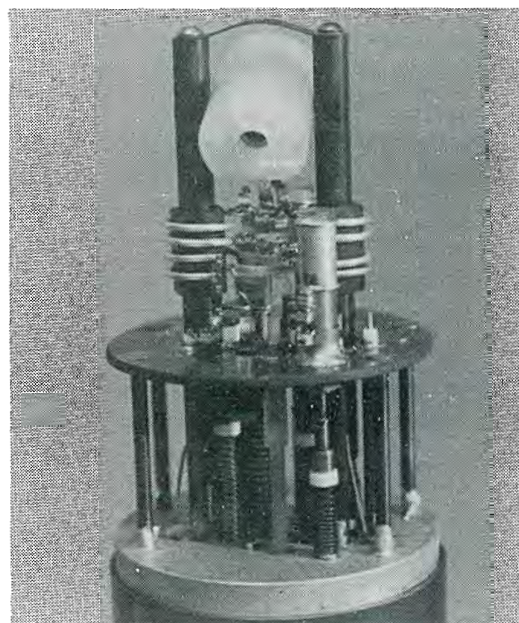
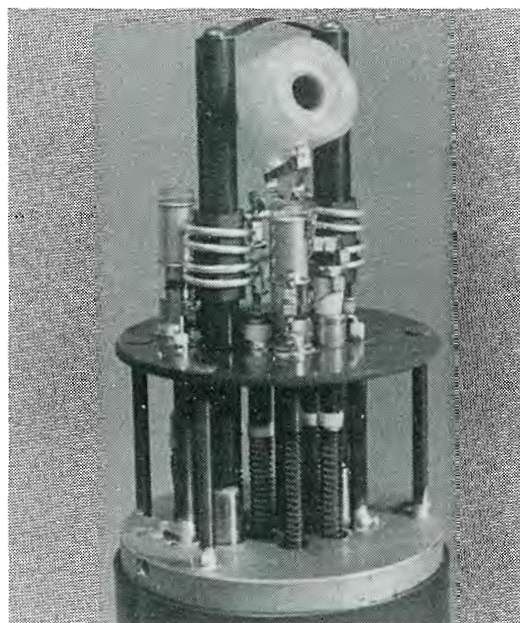


## Doty Scientific, Inc.

On May 7, 1992 Doty Scientific celebrated its 10th birthday!

### *A Decade of Innovation (and 670 NMR Probes)*

- |        |                                   |        |                                   |
|--------|-----------------------------------|--------|-----------------------------------|
| ➤ 1982 | 7 mm MAS at 5 kHz                 | ➤ 1987 | 1000 G/cm Pulsed Field Gradient   |
| ➤ 1982 | Triple-Tuned MAS                  | ➤ 1987 | 7 mm MAS at 9 kHz                 |
| ➤ 1983 | Single-Crystal Probes             | ➤ 1988 | 650°C MAS                         |
| ➤ 1984 | 5 mm MAS at 9 kHz                 | ➤ 1989 | Precision Temperature Controller  |
| ➤ 1984 | Multinuclear Observe for Solids   | ➤ 1990 | Dynamic Angle Spinning            |
| ➤ 1985 | 19 mm MAS                         | ➤ 1991 | 14 mm MAS at 7 kHz                |
| ➤ 1987 | CRAMPS Probes                     | ➤ 1992 | 3.5 mm MAS at 25 kHz              |
| ➤ 1987 | Actively Shielded Gradient Probes | ➤ 1992 | 300°C Pulsed Field Gradient Probe |
| ➤ 1987 | 5 mm MAS at 17 kHz                | ➤ 1992 | 10 mm MAS at 10 kHz               |



An innovative way to "fit it all in" on a triple-tuned probe.

In the last 10 years we have provided our customers with the first commercially available probes for many challenging NMR experiments. During this time, we have also built a reputation for quality. Less recognized may be our competitive pricing. We have always offered the best probes at prices well below the competition's — usually 60% of their price. We enter our second decade as an American company with a continued commitment to provide the best probes, rf accessories, and control systems at the lowest prices with the fastest service.

Our eleventh year will see record levels of innovation, as we deliver user-friendly DOR probes, automatic MAS sample changing, 800°C MAS, and other probes according to your needs. Thank you for your continued support.

Doty Scientific, Inc.  
700 Clemson Road  
Columbia, SC 29223  
USA

Phone (803) 788-6497  
Fax (803) 736-5495

# ***Pricing for Doty Scientific NMR Probes***

## ***Actively Shielded Gradient Probes***

	<b>Grad Coil Set Only</b>	<b>GES, PFG Probes</b>	<b>MRI-M Probes</b>
	<b>X-Y-Z</b>	<b>Z</b>	<b>X-Y-Z</b>
5 to 15 mm	\$ 16,000	\$ 19,000	\$ 28,000
16 to 30 mm	19,000	21,000	32,000

Prices for Standard, Double-Tuned, Fixed-Frequency Probes below 8.4 T

For multinuclear option, add \$ 2000

For single-tuned probes, subtract \$ 2000

**High temperature PFG probes with VT range of -160 to + 300°C . . . . . \$ 28,000**

## ***High Resolution Probes***

**High-Resolution Probe . . . . . \$ 11,000**

-100°C to 140°C, 5 mm to 10 mm, <sup>1</sup>H decouple, <sup>2</sup>H lock, fixed observe frequency

\* For multinuclear option, add \$ 2000

\* For single-tuned probes with lock, subtract \$ 2000

\* For narrow bore with samples greater than 12 mm, add \$ 1000

\* For wide bore with samples greater than 20 mm, add \$ 1000

**High-Temperature High-Resolution Probe . . . . . \$ 18,000**

-170°C to 380°C, 5 mm to 10 mm, <sup>1</sup>H decouple, <sup>2</sup>H lock, fixed observe frequency

## ***Solids Probes***

**Wideline VT Single-Tuned High-Power Probe . . . . . \$ 7,400**

5-mm or 8-mm, includes ten sample containers

**Wideline VT Multinuclear Double-Tuned High-Power Probe . . . . . \$ 11,400**

5-mm or 8-mm, includes ten sample containers

**Standard CP/MAS Multinuclear 5-mm or 7-mm Probe . . . . . \$ 16,500**

*Probe and Accessories kit . . . . . \$ 20,500*

**High-Speed CP/MAS Multinuclear 5-mm or 7-mm Probe . . . . . \$ 19,000**

*Probe and Accessories kit . . . . . \$ 25,300*

**Single-Tuned VT Probe for <sup>1</sup>H or <sup>19</sup>F CRAMPS . . . . . \$ 11,500**

*Probe and Accessories kit . . . . . \$ 15,400*

## ***High Temperature Probes -100° to + 650°C***

**-100° to +650°C Wideline Single-Tuned, Multinuclear Probe . . . . . \$ 25,000**

**-100° to +650°C CP/MAS Balanced-RF, Multinuclear Probe . . . . . \$ 36,000**

**-100° to +650°C CP/MAS Multi-X Probe, Accessories & Temp Controller .. \$ 51,000**





LOUISIANA STATE UNIVERSITY  
AND AGRICULTURAL AND MECHANICAL COLLEGE  
Department of Chemistry

Dr. B. L. Shapiro, Editor  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94393

April 10, 1992  
(received 4/16/92)

### A Field-Sweep CW NMR Using a Balanced Bridge/Network Analyzer

Dear Dr. Shapiro:

We use a Hewlett-Parkard 4195A Network/Spectrum Analyzer for probe tuning, and recently tested the device as a detector for CW NMR. Briefly, in the network analyzer mode, the HP4195A has an RF output (10Hz to 500MHz) and two inputs (one for reference port, one for test port); the amplitude and phase ratio of these two inputs can be measured as a function of frequency. With the addition of two reflection bridges (magic tee), a probe, and a swept magnetic field, an NMR is created. The magnet is normally associated with an MSL 200. The Kepco power supply is used to sweep the field about 22.4 kHz via the  $Z_0$  shim.


Bridge circuits are common in old style NMR <sup>1,2</sup>. A coaxial bridge was used successfully as a nuclear quadrupole resonance detector <sup>3</sup>, and lastly a balanced bridge system can also make low temperature NMR more convenient <sup>4</sup>.

The test sample is adamantane in a 7 mm rotor spinning at the magic angle at a rate of 3 kHz in a field of 4.7 Tesla. Figure 1 shows the actual configuration of the system. Briefly, the first bridge is used as a power splitter, the second is the balanced bridge. Under normal pulsed <sup>1</sup>H NMR condition, a five line pattern is expected with a really great signal-to-noise ratio. In the first attempt (shown in Figure 2), the S/N seems to be about 100-fold less with this setup. Improvements could come with better impedance balancing of the bridge and incorporation of digital lock-in amplification. A modified version of this configuration will serve as one of our future NMR detectors for the new-low temperature, high-magnetic field system.

Commands and suggestions will be appreciated.

Sincerely,

  
Xiao Wu

  
Les Butler

1. P. Kesselring and M. Gautschi, J. of sci. Instrum., 1967, vol 44, p911-916
2. D. R. Torgeson, Rev. of Sci. Instrum., 1967, vol 38, p612-615
3. M. P. Klein and D. E. Phelps, Rev. of Sci. Instrum., 1967, vol 38, p1545-1546
4. T. J. Gramila, "Experimental Techniques and Special Devices", *Experimental Techniques in Condensed Matter Physics at Low Temperatures*, Addison - Wesley Publishing Company, Inc.

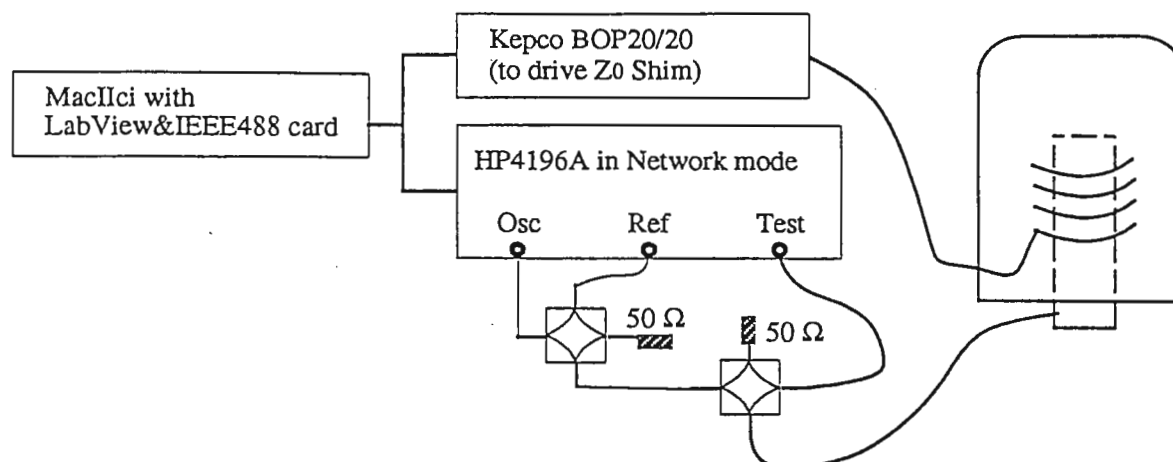


Figure 1. Experimental setup

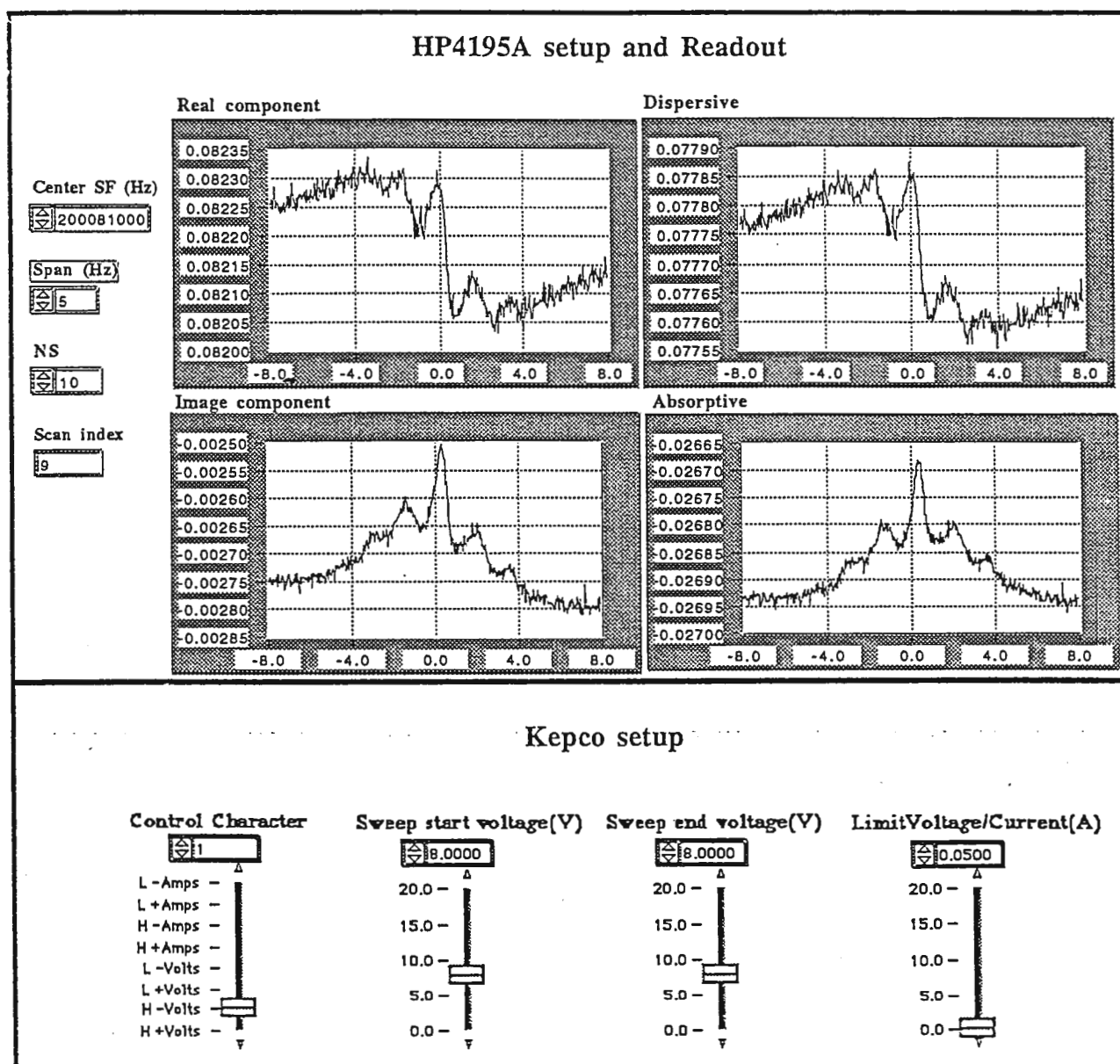


Figure 2. LabView program front panel

# What's the difference between the new CMX spectrometer and the competition?



We took the complicated and made it simple.

## Computer System

- Choice of SUN or Silicon Graphics computer
- X-Windows™ software on the spectrometer
- High-speed communications for "real time" display

## Advanced Console Design

- Full *channel modularity*
- Full channel expandability
- Easy customer access

## RF Design

- High IF design provides clean RF
- Ultra fast amplitude, phase, and frequency control
- Direct digital synthesis

## Digital Design

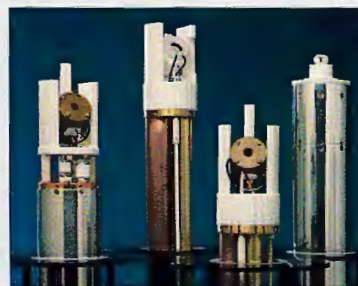
- High-speed 100 MHz pulse programmer on each channel
- Complete pulse program flexibility
- Multiple expansion capability

## Solids Probes System

- PENCIL™ spinning system for high stability MAS
- Constant spinning speed from  $-150^{\circ}\text{C}$  to  $+250^{\circ}\text{C}$
- COAX design affords superior tuning and RF capability for multiple resonance experiments
- High-stability, microprocessor-controlled, speed controller

## Ergonomics

- Superior comfort, functionality and increased work space for optimum productivity



## Chemagnetics

2555 Midpoint Drive  
Fort Collins, Colorado 80525  
(303) 484-0428  
1 (800) 4 OTSUKA

*Dedicated to Design Excellence*

PENCIL is a trademark of Chemagnetics, Inc.  
X-Windows System is a trademark of the Massachusetts Institute of Technology



## Chemagnetics Workshop Set For August 7 & 8

Dear NMR Colleagues:

I'd like to invite you to an NMR workshop that you won't want to miss -- especially if you're attending the Rocky Mountain Conference. Each year, following the conference in Denver, Chemagnetics invites a number of NMR scientists to give seminars on advanced topics and organizes a 2-day opportunity for spectroscopists to visit and get up-to-date on the latest in solid-state NMR. This year's workshop will be held August 7 and 8, 1992 in Fort Collins, Colorado.

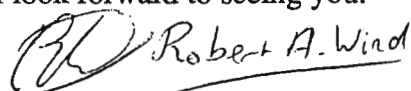
We are privileged to have luminaries from both academia and industry. Below is a list of seminars that will be presented on Friday. Saturday will feature hands-on demonstrations of advanced solids techniques, including DOR, fast MAS, and liquids microimaging.

Speakers and topics for the Friday session:

- |                                                           |                                                                                 |
|-----------------------------------------------------------|---------------------------------------------------------------------------------|
| • <b>Dr. Brad Chmelka</b> , UC - Santa Barbara            | Practical Applications of 2-D exchange NMR in Polymers                          |
| • <b>Dr. Jim Haw</b> , Texas A&M University               | Recent Developments in MAS NMR                                                  |
| • <b>Dr. Dave Duff</b> , Raychem Corporation              | Triple Resonance Experiments on Protonated and Fluorinated Polymers             |
| • <b>Dr. Robert Botto</b> , Argonne National Laboratories | NMR Imaging: A Chemical Microscope for the Analysis of Heterogeneous Materials  |
| • <b>Dr. Lucio Frydman</b> , UC - Berkeley                | NMR Imaging of Flow                                                             |
| • <b>Dr. Robert Tycko</b> , AT&T Bell Labs                | New Approaches to Structure Determination in the Solid State                    |
| • <b>Dr. Ann McDermott</b> , Columbia University          | Applications of Rotational Resonance in Enzyme-active Sites                     |
| • <b>Dr. Hellmut Eckert</b> , UC - Santa Barbara          | Heteronuclear X-Y Double Resonance NMR Experiments in Solid Inorganic Materials |
| • <b>Dr. Gerald S. Harbison</b> , SUNY                    | Solid-State NMR of Highly-Oriented DNA Fibers and Drugs Bound to DNA            |

If you would like to attend, I urge you to register today. Registrations are limited to 60 people on the first day and 15 for day two. There is no fee to attend the seminar, but registrants are responsible for their own transportation from the Denver airport to Fort Collins (approx. \$13), for the hotel, and meals. To help defray your costs, rooms at Chemagnetics' discount rate of \$34 have been booked at the nearby Ramada Inn. Please call to register today at 1-800-4-OTSUKA and ask for Jan Anderson.

I look forward to seeing you.



Robert Wind  
Director of Research and Development

### Postdoctoral Position

The Research and Development Department at Chemagnetics has a postdoctoral opening for a Ph.D. NMR spectroscopist. Experience with solids and NMR and/or MRI techniques and hardware is required. The work involves the development and evaluation of novel solid-state techniques in biosystems. The successful candidate must be interested in working in a problem-solving environment and be able to work as a member of a team.

Interested candidates should send their resume to: D. Hasler, Chemagnetics, Inc., 2555 Midpoint Drive, Fort Collins, CO 80525. For further information, contact Robert Wind (303) 484-0428. EOE

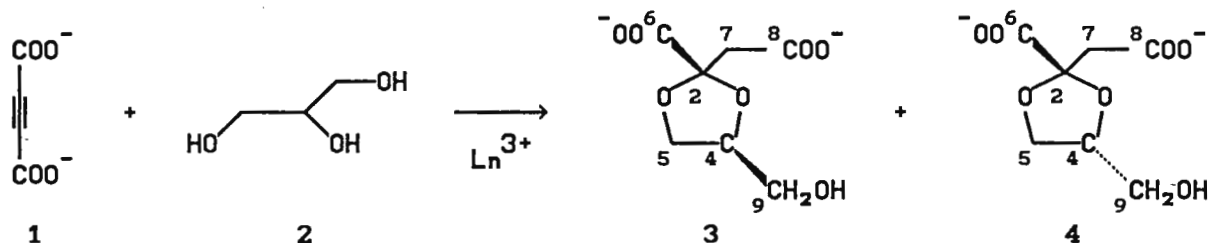
## Discrimination of Diastereomeric

### Dioxolane Compounds Using Gd(III)-Induced Carbon-13 Relaxation Rate Enhancements

(received 4/6/92)

Dear Dr. Shapiro,

A topic of our investigations is the addition of hydroxyl compounds to unsaturated carboxylic acids with the use of lanthanide(III) ions as template. A specific example is the addition of ethylene glycol to acetylene dicarboxylate (1), which yields a 2,2-disubstituted dioxolane. It appeared that this reaction proceeds *via* a diadduct, in which two ethylene glycol units are attached to the acetylene dicarboxylate chain, and which gives an intramolecular ring closure only after decomplexation. Addition of glycerol (2) to acetylene dicarboxylate yields a mixture of the two dioxolanes 3 and 4 (see scheme), of which one, further called A, is three times more abundant than the other (B). With the use of standard  $^{13}\text{C}$  NMR, NOESY, and NOE experiments we could not clarify the configuration of these diastereomers.



Gd(III)-induced  $^{13}\text{C}$  relaxation rate enhancement measurements are normally used to get an idea of the steric conformation of organic ligands in lanthanide complexes. We successfully applied this technique to discriminate between the two dioxolane diastereomers. From the data given in the table it can be concluded that in both diastereomers the Gd(III) ion is preferably coordinated by C6 and probably one of the ether oxygens as shown by a two times higher relaxation rate enhancement for C6 than for C8. The relaxation rate enhancement of C9 of A was only a third of that of C9 of B. This implicates that in the latter compound C9 is at the same side of the dioxolane ring as C6 and therefore structure 3 can be assigned to it.

By this example we have shown that Gd(III)-induced  $^{13}\text{C}$  relaxation rate enhancement measurements can be a powerful tool in discriminating between strongly related compounds. Yours sincerely,

carbon atom	$1/T_1$ [ $10^4 \text{ s}^{-1}$ ]	
	A (4)	B (3)
C2	1.565	1.588
C4	0.627	0.910
C5	0.515	0.804
C6	5.286	5.310
C7	0.885	0.940
C8	2.499	2.450
C9	0.223	0.646

Gd(III)-induced  $^{13}\text{C}$  relaxation rate enhancements (100 MHz,  $30^\circ\text{C}$ ) of 3 and 4 (2 M in  $\text{D}_2\text{O}$ ) extrapolated to  $\rho = [\text{Gd}]/[\text{ligand}] = 1$

Jurriaan Huskens,

Joop A. Peters,

Herman van Bekkum



## Almaden Research Center

International Business Machines Corporation

F. D. BLUM  
 IBM Research Division  
 Polymer Science and Technology  
 650 Harry Road, K93/801  
 San Jose, California 95120-6099  
 TEL: (408) 927-1441; FAX: (408) 927-3310  
 BITNET address: FBLUM at ALMADEN  
 INTERNET address: FBLUM at ALMADEN.IBM.COM

March 28, 1992 (received 3/31/92)

Dr. Barry Shapiro  
 TAMU Newsletter  
 966 Elsinore Ct.  
 Palo Alto, CA 94303

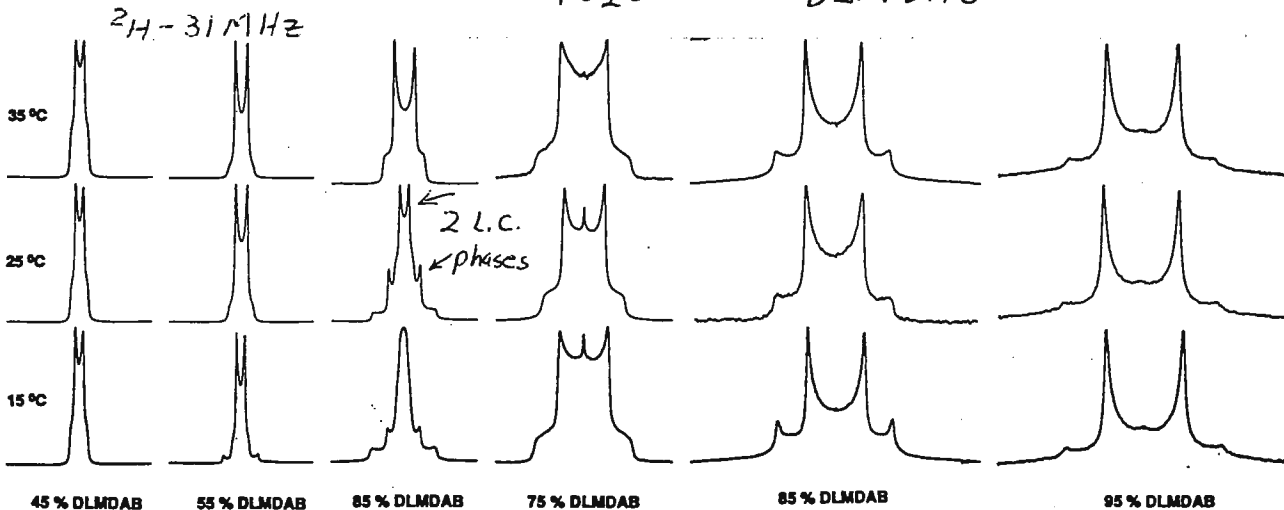
Dear Barry:

As you can see, I am at IBM. I will be on leave here for a half year. I would like to share some work that Jack Uang did with me at Missouri. We have synthesized a new surfactant that has a very long name that I will call DLMDAB. This surfactant forms liquid crystals with water over a wide range of temperatures. The use of deuterium oxide with DLMDAB provides a convenient way of probing the phase behavior of such a system. We find that along with X-ray, a good deal of information can be obtained about the system. Shown below is the partial NMR phase diagram of the system.

At 15 and 25 degrees, two different liquid crystals are formed at high and low surfactant concentrations. At 15 degrees, there is an apparently isotropic phase between them. At 25 degrees there is an isotropic phase plus the presence of two superimposed liquid crystalline powder patterns. This is from two liquid crystalline phases in equilibrium. The only difference between these is the different amounts of water in each. This is the third system that I know of where this type of behavior has been seen. If anyone wants a preprint of the paper, let me know. (Please credit this to my account in Missouri.)

Sincerely,

Frank D. Blum



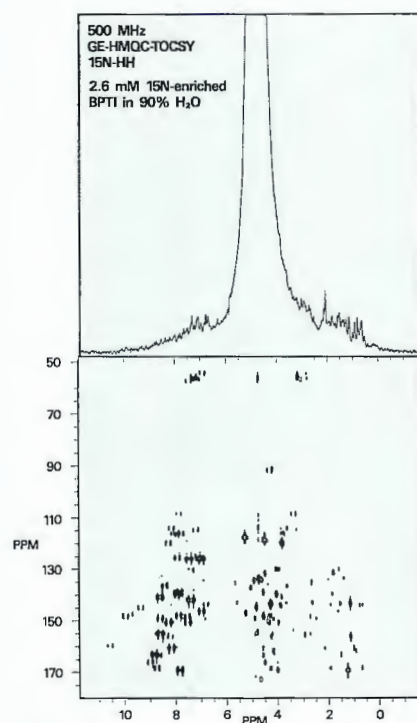


# Gradient Enhanced Spectroscopy: a new, practical answer

By Frank Huang, PhD and  
Paul Calderon, MS

Making Gradient Enhanced Spectroscopy (GES) a viable method for high resolution spectroscopy has long been of interest to researchers. The obvious benefits in speed and information content were too often overshadowed by the drawbacks of signal loss and distortion.

Technology developed at GE NMR Instruments has overcome these



Gradient Enhanced Spectroscopy technique applied to an HMQC-TOCSY experiment demonstrates excellent water suppression without the need for presaturation or selective excitation.

## Research Implications

- ▶ Speed without phase distortion or signal loss.
- ▶ Practical for 1D, 2D, 3D and 4D experiments.
- ▶ Accommodates proton and heteronuclear GES techniques.

challenges. The S-17 Gradient Enhanced Spectroscopy Accessory with integrated inverse probehead makes GES practical for a broad range of applications in 1D, 2D, 3D and 4D experiments.

## A better design

The use of a three-axis, actively-shielded gradient set allows GE to overcome the inherent drawbacks of previous GES technology—most notably, phase distortion and signal loss:

**Active shielding.** Eddy current effects are the major source of phase distortion in GES spectra. Active shielding prevents interaction of strong gradients with magnet and shim components—the source of eddy current effects.

**Fast, strong gradients.** Short gradient pulses of 35 G/cm minimize signal loss during pulse sequences.

## Applications advantages

With its integral inverse probehead, the S-17 Accessory can accommodate proton as well as heteronuclear GES techniques.

Gradient fields of 35 G/cm are able to suppress water in aqueous samples and to improve performance in heteronuclear experiments. Other applications advantages:

- ▶ Eliminates phase cycle requirements and subtraction error.
- ▶ Reduces T1 noise.
- ▶ Reduces collection times for 2D, 3D and 4D data sets.
- ▶ Provides lineshape independent water suppression in multiple quantum coherence selection experiments.
- ▶ Provides lineshape independent water suppression via diffusion differences for large molecular weight samples.
- ▶ Improves water suppression in experiments using selective time reversal RF pulses.
- ▶ Separates cross-correlation and exchange phenomena in NOESY experiments.
- ▶ Distinguishes chemicals inside the cell from those outside in whole cell applications.

For additional information on the S-17 GES Accessory, write to GE NMR Instruments, 255 Fourier Ave., Fremont, CA 94539. Or call toll free:

1-800-543-5934



**GE NMR Instruments**

# Gradient-Enhanced $^{15}\text{N}$ HMQC

The pulse sequence and the coherence pathway diagram for a  $^{15}\text{N}$  GE-HMQC are shown in Fig. 1. The pulse sequence was a standard  $^{13}\text{C}$  GE-HMQC experiment (1) with different gradient amplitudes to account for the difference between the gyromagnetic ratios of  $^{13}\text{C}$  and  $^{15}\text{N}$ . The  $90^\circ$  proton pulse creates transverse magnetization which evolves into an anti-phase state with respect to  $J(\text{NH})$  coupling at the end of the period  $\Delta$  (where  $\Delta = 1/(2J_{\text{NH}})$ ). The antiphase components are converted into heteronuclear zero- and double-quantum coherence by the  $^{15}\text{N}$   $90^\circ$  pulse and the multiple quantum coherences are allowed to evolve during  $t_1$ . The  $180^\circ$   $^1\text{H}$  pulse in the center of the evolution period serves to eliminate the  $^1\text{H}$  chemical shift evolution, yielding pure  $^{15}\text{N}$  chemical shifts along that axis. The zero- and double-quantum signals are then coherence-order labeled by the gradient pulses G1 and G2. After conversion into antiphase proton magnetization by the last  $^{15}\text{N}$   $90^\circ$  pulse, the desired components are refocused by the gradient G3 and detected. The application of a gradient pulse results in a phase factor being applied to the magnetization which is dependent upon gradient strength, duration, the distance from the gradient isocenter, the gyromagnetic ratios of the coupled nuclei, and the desired coherence order. The relative amplitudes of the labeling and refocusing gradient pulses will determine the selection of a specific coherence pathway and are calculated to suppress magnetization components arising from the solvent and other protons not coupled to  $^{15}\text{N}$  spins.

The fundamental principle of coherence selection using gradients is that for a pathway to be detected, the cumulative phase factor during the acquisition must be zero:

$$G_1 p'_1 + G_2 p'_2 + G_3 p'_3 = 0. \quad [1]$$

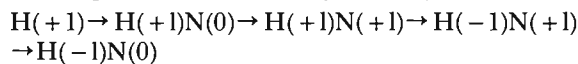
The subscripts denote steps in the pulse sequence where  $p'$  defines a composite coherence order for the heteronuclear case which includes the gyromagnetic ratios of the coupled nuclei:

$$p' = p^1\text{H} + (\gamma^{15}\text{N}/\gamma^1\text{H}) p^{15}\text{N} \quad [2]$$

and  $p^1\text{H}$  and  $p^{15}\text{N}$  are the coherence orders for the  $^1\text{H}$  and  $^{15}\text{N}$  spins respectively.

In the coherence pathway diagram, the relevant values of  $p'$  are given to the left and the relative gradient areas

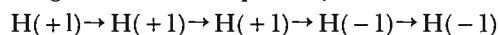
(gradient strength  $\times$  duration) are given next to each gradient pulse. The following pathway (shown in Fig. 1):



is detected using a 5:5:1 ratio of gradient areas, since according to Equation 2:

$$5(1.1) + 5(-0.9) + 1(-1.0) = 0 \quad [3]$$

where the numbers in the parentheses refer to the composite coherence orders. Using these relative gradient areas, protons not coupled with  $^{15}\text{N}$  spins may pass through an alternate pathway:



which results in a net phase factor:

$$5(1.0) - 5(-1.0) + 1(-1.0) = -1 \quad [4]$$

Thus, signals from this pathway remain defocused during the acquisition.

A 2D  $^{15}\text{N}$  GE-HMQC spectrum of  $^{15}\text{N}$  enriched BPTI is shown in Fig. 2. The spectrum was collected using a 5 mm inverse probe on an Omega<sup>TM</sup> PSG 500 spectrometer equipped with an S-17 gradient accessory. Half-sinusoid-shaped gradient pulses were applied simultaneously along the X, Y and Z axes with a maximum gradient strength of  $\approx 20$  Gauss/cm and a duration of 3.5 ms. A matrix size of  $2048 \times 128$  resulted in 3.5 Hz resolution in the  $\omega_2$  dimension and 10 Hz in the  $\omega_1$  dimension. No decoupling was applied.

Gradient-enhanced experiments provide a viable alternative to traditional phase-cycling methods for the selection of coherence pathways. In cases where the sensitivity is adequate, gradient selection can substantially reduce the collection time in multi-dimensional experiments. The  $^{15}\text{N}$  GE-HMQC data presented here has none of the  $t_1$ -noise from cancellation artifacts usually present in phase-cycled versions of the HMQC experiment. In addition, since the suppression of the single-quantum signals is done prior to acquisition, the receiver gain may be increased, which results in a substantial increase in signal-to-noise. For these reasons, gradient pulses should be the method of choice for coherence selection in HMQC experiments.

## Reference

1. R.E. Hurd and B.K. John, *J. Magn. Reson.* **91**, 648 (1991).

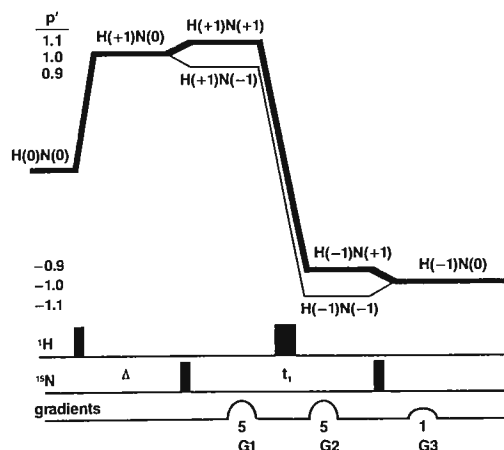


Fig. 1

Pulse Sequence and the coherence pathway diagram for a  $^{15}\text{N}$  GE-HMQC experiment.

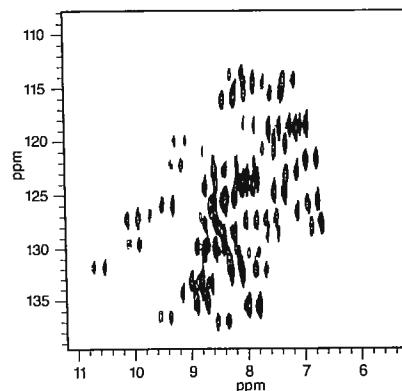


Fig. 2

A 2D GE-HMQC spectrum of  $^{15}\text{N}$  enriched BPTI. The sample was 2.6mM in 90%  $\text{H}_2\text{O}$ . The data collection time was 2.6 hours.



**KTH**  
(The Royal Institute of Technology)

April 2, 1992  
(received 4/7/92)

Dept. of Inorganic Chemistry

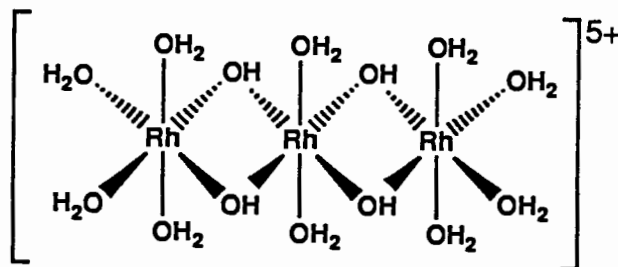
## First Observation of Rhodium–Rhodium Two–Bond Spin–Spin Coupling.

Dear Prof. Shapiro,

During the last decade,  $^{103}\text{Rh}$ –NMR has grown considerably in importance as a tool for rhodium chemists despite the very low relative sensitivity ( $D_p = 3 \cdot 10^{-5}$ ) and long relaxation times.

Our group is presently interested in structural investigations in aqueous solution of the hydroxo bridged polymeric species formed on hydrolysis of rhodium(III). Due to their kinetic stability several species can be isolated one by one from a hydrolysed mixture by ion–exchange chromatography and studied at room temperature.  $^{103}\text{Rh}$ –NMR has been the method of choice; however, we have also measured  $^{17}\text{O}$ –NMR,  $^1\text{H}$ –NMR, EXAFS, LAXS, *far*–IR and Raman spectra.

Beside the monomer,  $[\text{Rh}(\text{OH}_2)_6]^{3+}$ ,  $\delta_{\text{Rh}} = 9915.8$  ppm, and the dimer,  $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{--OH})_2\text{Rh}(\text{OH}_2)_4]^{4+}$ ,  $\delta_{\text{Rh}} = 9997.4$  ppm, a third species was obtained which gave two  $^{103}\text{Rh}$ –NMR signals having relative intensities 2:1,  $\delta_{\text{Rh}} = 9966.4$  and 10003.6 ppm, respectively. This result surprised us since in the otherwise analogous chromium(III) system the trimeric species has been found to have a triangular arrangement of equivalent chromium atoms. A high resolution spectrum was recorded of the suspected trimer and after Gaussian resolution enhancement the signals at 9966.4 and 10003.6 ppm were found to be split into a doublet (1:1) and a triplet (1:2:1) respectively,  $^2J_{\text{Rh,Rh}} = 1.5$  Hz. The observed spin–spin coupling was interpreted in terms of an  $\text{AX}_2$  spin system ( $I_{\text{Rh}} = \frac{1}{2}$ ): the triplet arises from the central nucleus (A) through coupling to the two equivalent terminal rhodium nuclei (X), which in turn give rise to a doublet.



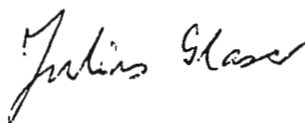


The splitting pattern and the ratio in the observed intensities ( $A:X = 1:2$ ) between the two signals allowed us to confirm both the nuclearity and the structure of the trimer,  $[\text{H}_2\text{O}]_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_2(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4]^{5+}$ , from a single experiment. To our knowledge this is the first observation of rhodium–rhodium two–bond spin–spin coupling.

*Yours sincerely,*



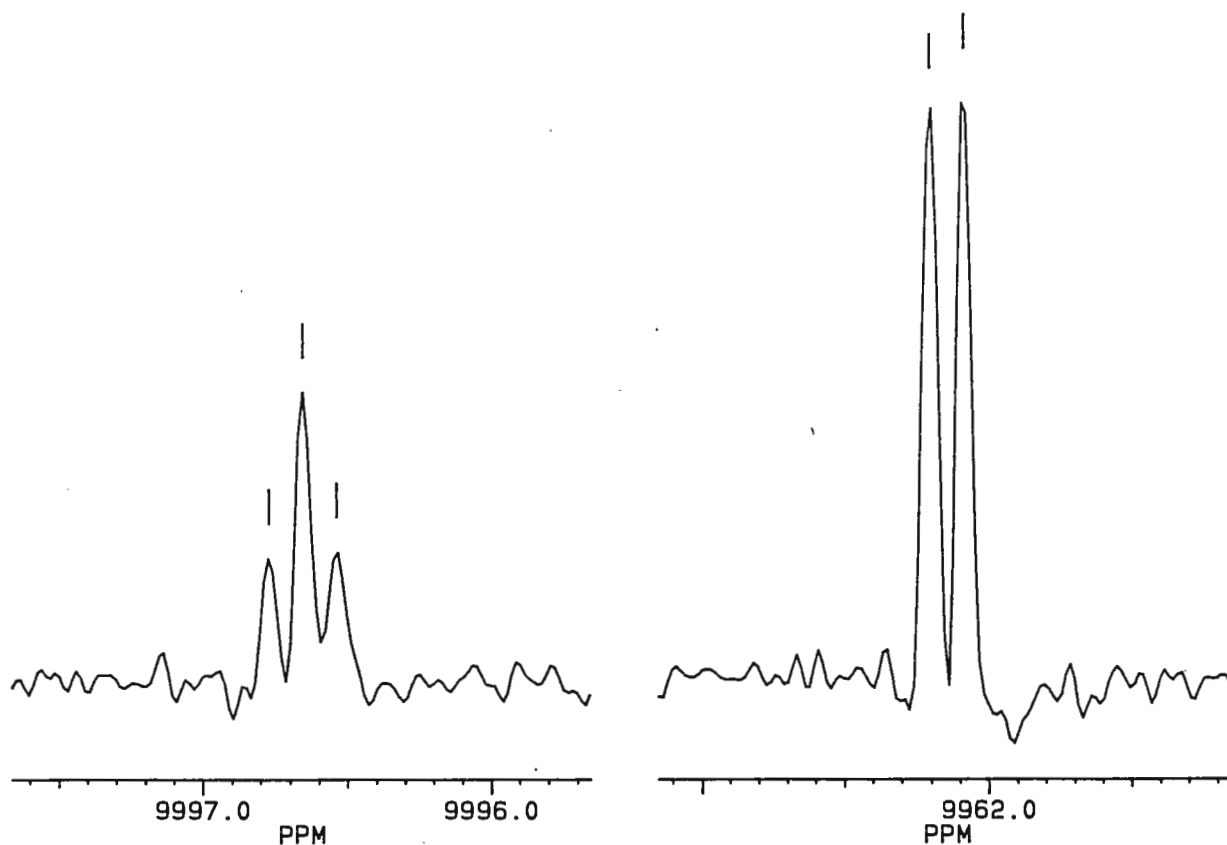
Michael Read



Julius Glaser

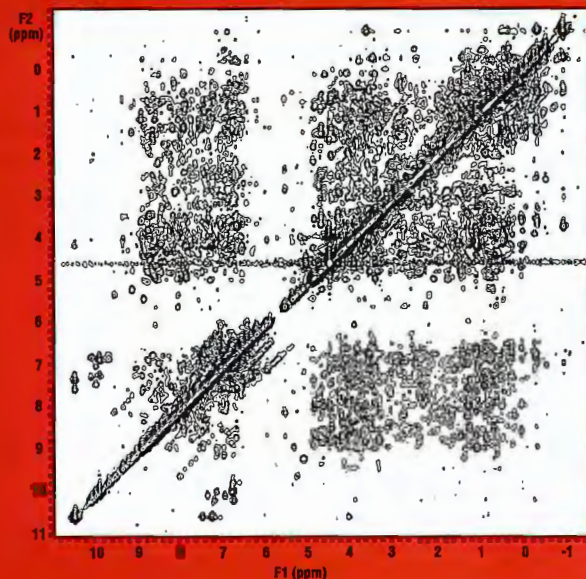


Magnus Sandström

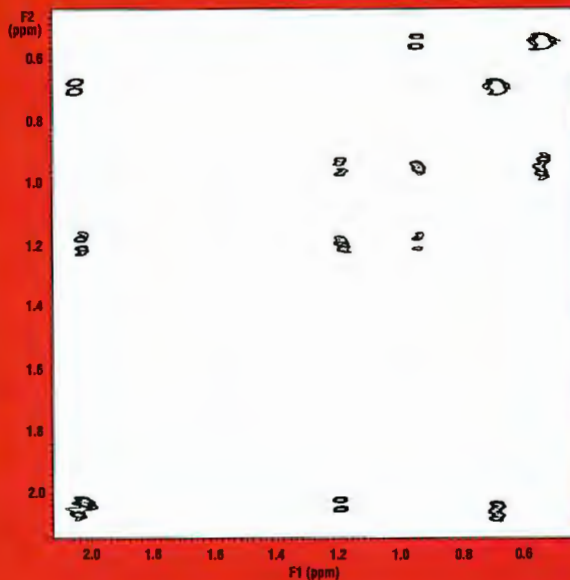


Expansion of the resolution-enhanced  $^{103}\text{Rh}$ -NMR spectrum of an aqueous solution ( $[\text{Rh}] = 0.4 \text{ M}$ ) of the linear trimer,  $[\text{H}_2\text{O}]_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_2(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4]^{5+}$ , recorded at 12.6 MHz, 298 K. The spectrum is referenced to  $\Xi(^{103}\text{Rh}) = 3.16 \text{ MHz}$ .

# Varian provides Pulsed Field Gradients for extraordinary water suppression and throughput.



*This NOESY spectrum of 5mM Lysozyme in 90%  $H_2O/D_2O$  was obtained on a UNITY® 500 MHz spectrometer equipped with Varian's new pulsed field gradient module.*



*This COSY spectrum of 1% 3-Heptanone in  $CDCl_3$  was obtained in only 7 seconds on a UNITY® 500 MHz spectrometer equipped with Varian's new pulsed field gradient module.*

Whether your application is structure determination of biological macromolecules or high throughput in an organic synthesis environment, Varian's Pulsed Field Gradient (PFG) module provides a new problem solving tool. Varian's new PFG module is designed specifically with high resolution liquids applications in mind. Outstanding probe performance, combined with Varian's new ultra-stable low-noise gradient amplifier technology, provides

extraordinary water suppression performance through coherence pathway selection or diffusion. Using Varian's PFG module will increase throughput dramatically by elimination of phase cycling. For more information, contact the Varian office near you.

# Varian's Pulsed Field Gradient module is comprised of a probe and amplifier.

## Probes

- Excellent liquids specifications for uncompromised high resolution liquids performance
- Extremely short delays between gradients and acquisition for highest sensitivity and minimal spectral distortions
- Acoustic ringing minimized with new gradient coil mounting

## Amplifier

- Ultra-stable low-noise circuitry with thermal shunting for uncompromised stability and gradient pulse reproducibility
- Transconductance circuitry to provide the ultimate in reproducible gradients and eliminate matching
- Eddy current compensation for minimal gradient off time
- Optimal choice of gradient strength for high resolution applications



# CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA, CALIFORNIA 91125

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING  
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

JOHN D. ROBERTS  
INSTITUTE PROFESSOR OF CHEMISTRY,  
EMERITUS

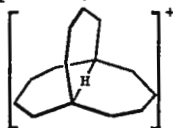
Dr. Bernard L. Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

April 13, 1992

(received 4/15/92)

Dear Barry:    **Proton Shifts in Three-Center, Two-Electron C-H-C Bonds in Carbocations**

Tipping of your orange spot (it was black for RLS) causes me to call the attention of the TAMU fraternity to the unusual proton shifts reported for three-center, two-electron C-H-C bonds in carbocations. The situation is very nicely summarized by Cornell chemists, J.E. McMurry and T. Lectra in *Accounts of Chemical Research*, 1992, 25, 47-53. Because of prior entanglements in the carbocation field, I have been much intrigued by these shifts of the bridging protons, which can be observed for bicyclo[4.4.4]tetradecyl and



The bicyclo[4.4.4]tetradecyl carbocation

related cations in magic acid solutions, often even at room temperature. The facts are that this kind of proton comes at -3.5 ppm in the [4.4.4] cation, where the C-H-C angle is expected to be  $180^\circ$  and moves still farther upfield when the C-H-C angle is less than  $180^\circ$  and reaches -6.5 ppm with the [6.4.2] cation, where the angle is estimated to be  $113^\circ$ . An essentially linear correlation exists between the C-H-C angles and the proton shifts. McMurry states that the reasons for the correlation of proton chemical shift and C-H-C angle are not clear. And it does not seem that the shifts are consistent with simple considerations of the electron densities surrounding the bridging protons.

The large diamagnetic shifts could result from the second-order paramagnetic effect operating at the carbons so as to produce a large upfield shift of the bridging protons in something like the way that the nucleus of a non-hydrogen-bonded hydrogen in an O-H group has a large upfield shift. Thus, the primary shift effect arises not from the electron density at the protons, but from the circulation of electrons around the bridge carbons, when the C---C axis is perpendicular to the applied field. This circulation would produce a paramagnetic effect at the carbons and a consequent diamagnetic effect at the proton. In order to make sense of the changes of shift with the C-H-C angles, I have to postulate that this effect on the shift for the bridging proton in the [4.4.4] cation is larger than observed, perhaps -7 ppm, or even more. The effect might be enhanced because the carbon valence shells of the C-H-C groupings are not fully occupied, and so make the paramagnetic circulations larger than for normal saturated carbons.

Two effects might be expected to operate when the C-H-C angle becomes smaller than  $180^\circ$ . First, when the C---C axis is perpendicular to the magnetic field, the proton is not expected to be in the same favorable position to experience the maximum diamagnetic effect from the circulation around the carbons relative to when the C-H-C angle is  $180^\circ$ . This should cause paramagnetic shifts, contrary to what is observed. However, an opposite effect would result from contributions of a second-order paramagnetic effect directly at the bridging hydrogen as the result of admixture of some p-character to the hydrogen bonding orbitals by the electrostatic influence of the positive carbons flanking it. This sort of effect has been invoked to account for the substantial paramagnetic proton shifts observed for linear O-H--O hydrogen bonds. Any such contribution to the C-H-C proton shifts would surely be expected to diminish when the C-H-C bond angle becomes less than  $180^\circ$ . Thus, if this effect is important, but not important enough to completely overcome the diamagnetic shift, then one can rationalize the shifts. I expect that the intrepid readers of TAMU NMR will have superior explanations based on gauge invariance calculations, but how about something qualitative that we can use to help students understand shifts better?

With best wishes,

Very truly yours,

*Jack*

LABORATOIRE DE RÉSONANCE MAGNÉTIQUE NUCLÉAIRE  
UNIVERSITÉ CLAUDE BERNARD LYON I



Bâtiment 721  
43, boulevard du 11 Novembre 1918  
69622 Villeurbanne Cedex  
Tél. 72.44.82.67 - Secr. 72.44.80.84  
Fax (33) 72.44.81.99

March 30, 1992  
(received 4/6/92)

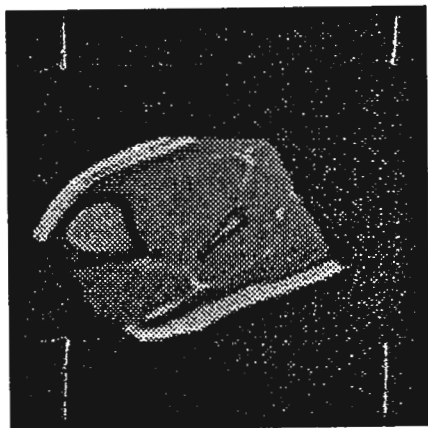
Dr Bernard L. SHAPIRO  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

Cutting ham in the k space

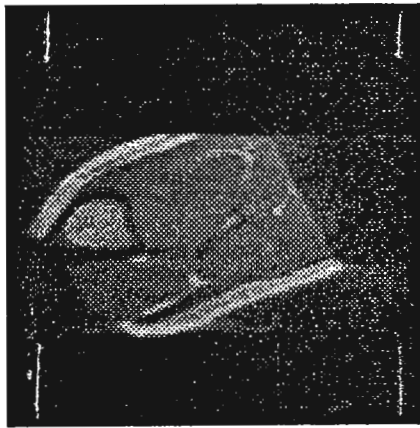
Dear Dr Shapiro,

It is well known that imaging can be performed using the half of the k space. This propriety works well in MRI as in Optics and it may be turned into profit in order to limit the amount of data and to reduce the time necessary for an image acquisition. This feature may considerably accelerate 3D imaging or any kind of imaging performed with low sensitivity signals of porous materials or polymers .

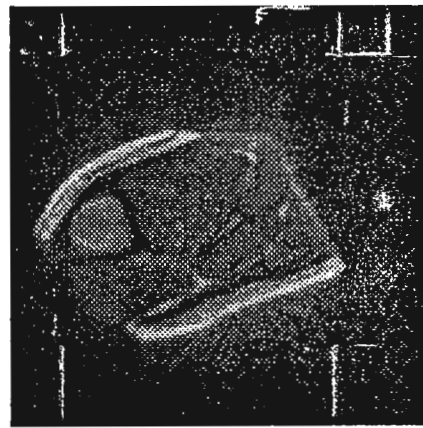
This fact is illustrated using a 2D experiment on ham at .13 Tesla where full echoes are acquired in the time domain as well as in the coding gradient direction. The images are reconstructed in three manners. First, the normal 2DFT is performed (Fig.a). In Fig.b, the k space is cut orthogonally to the time direction at the top of the echoes. A first order phase correction is performed after FT along the time domain. This phase correction may be required because sampling does not necessarily coincide with the top of the echo. It is also possible to cut the k space orthogonally to the coding gradient direction (Fig.c), in this case, the top of the echo is perfectly defined when the phase encoding is zero. For cases b and c, the signal was zero filled in order to keep the same matrix size (128x128).



a



b



c

5 mm slice of Italian Parma ham with bone

We observe that signal to noise ratio is slightly reduced. In case b, the image quality seems to depend on the phase correction. Nevertheless, in all cases the image quality is not fundamentally different, and the use of half k space is efficient.

Sincerely,

Y. CREMILLIEUX

A. DIOP

D. GRAVERON-DEMILLY

A. BRIGUET



## INTRODUCING

*American Microwave Technology is adding a NEW broadband amplifier product to the 3000 series NMR product family.*

*The Model 3426 is specifically designed for low field NMR applications and operates over the 10–90 MHz frequency range with 1000 watts of peak pulse power.*



Model 3425

## KEY FEATURES

- 10–90 MHz frequency range for low field NMR/NMRI applications
- 1000 watt RF output power for solids applications
- Linearity  $\pm 1.0$  dB for shaped pulses
- Noise blanking within 20 dB of KTB in less than 2  $\mu$ s for multipulse applications
- Low Pulse Droop, less than 5% to 20 ms for spin locking applications
- RF based protection, envelope detection for optimum performance envelope, user convenience and safety
- Dual Mode operation for pulse and CW type signals
- Digital forward and reflected RF peak power meter for tuning and monitoring

3080 Enterprise Street ■ Brea, CA 92621 ■ (714) 993-0802 ■ Fax (714) 993-1619

PLACE  
29¢  
POSTAGE  
HERE



3080 Enterprise Street,  
Brea, CA 92621



## AMT 3000 SERIES PRODUCTS

MODEL	FREQUENCY	POWER
3137	200–500 MHz	50 W
3135	200–500 MHz	150 W
3134	200–500 MHz	300 W
3200	6–220 MHz	1000 W
3205A	6–220 MHz	300 W
3206	6–220 MHz	150 W
3425	10–90 MHz	2000 W
3426	10–90 MHz	1000 W
3417	20–200 MHz	2500 W

## ABOUT RF ENVELOPE DETECTION

*AMT NMR/NMRI amplifiers use a dual mode, Pulse/CW, RF envelope detection system for optimum user flexibility and safety. The pulse mode provides user adjustable pulse width and duty cycle limits. The CW mode limits average power allowing CW type signals at reduced power levels. AMT has added user selectable dual-range RF power limiting to provide protection for sensitive probe hardware.*

*The RF envelope detection system samples the actual RF output signal providing protection independent of the noise blanking control signal. This allows the amplifier to be continuously enabled for optimum output power stability and blanked during data acquisition.*



Model 3205A



Model 3200

## NEW FEATURES FOR THE 3000 SERIES PRODUCTS

- Faster noise blanking, less than 1  $\mu$ s
- User selectable Hi/Low RF output power limits
- Enhanced LED status indication

Please send me more information on...

- ☐ AMT NMR amplifiers
- ☐ AMT NMRI amplifiers
- ☐ AMT Laboratory Class A linear amplifiers

Are you considering the purchase of an RF power amplifier in the next 6 months? \_\_\_\_\_

What special NMR/NMRI requirements does your company have? \_\_\_\_\_



3080 Enterprise Street ■ Brea, CA 92621 ■ (714) 993-0802 ■ Fax (714) 993-1619

Name \_\_\_\_\_

Title \_\_\_\_\_

Company \_\_\_\_\_

Address \_\_\_\_\_

City \_\_\_\_\_ State \_\_\_\_\_ Zip code \_\_\_\_\_

Country \_\_\_\_\_

Phone: (       )       FAX: (       )

## CENTRE FOR NUCLEAR MAGNETIC RESONANCE

Department of Chemistry  
Tel: 523187  
DR. OLIVER W. HOWARTH

University of Warwick  
Coventry CV4 7AL

Department of Physics  
Tel: 523523 Ext. 2403  
DR. RAY DUPREE

Dr. Bernard L Shapiro  
966 Elsinore Court  
Palo Alto, CA 94303

## RESOURCE-LIMITED OXYGEN SHIFTS?

Dear Barry,

March 11th, 1992  
(received 3/30/92)

Anyone who measures  $^{17}\text{O}$  NMR shifts of transition-metal oxoanions will know that some peaks have an annoying way of disappearing, usually behind more dominant resonances. It can be hard work to be sure of their presence, e.g. by pH variation or careful integration. One of the problems is that one is often unsure of the likely shift of the missing resonance. I would like to suggest a simple rule which we find helpful in such cases. After compiling a fair amount of data, we have noticed that *the sum of the oxygen shifts divided by the number of metal atoms is roughly constant for a given metal, whatever the geometry of the oxoanion*. The table below gives this shift sum per metal for known isopolyvanadates, molybdates and tungstates. It also gives a few sums for heteropoly species with central, tetrahedral  $\text{XO}_4$  units. These are calculated by ignoring the shifts of the central oxygens; in fact they never differ much from those of the isolated  $\text{XO}_4^{n-}$  unit. The shift sums do vary somewhat from metal to metal, but typically by only 5-10% for any one metal, despite metal geometries that vary from tetrahedral to octahedral, and individual O shift variations with pH of up to 300 ppm. The same principle also works, after due averaging, for related species containing more than one of these metals.

Oxygen shift sums per metal

Anion	Shift sum per V	Anion	Shift sum per Mo	Anion	Shift sum per W
$\text{VO}_4^{3-}$	2260	$\text{MoO}_4^{2-}$	2116	$\text{WO}_4^{2-}$	1680
$\text{HVO}_4^{3-}$	2292	$\text{Mo}_2\text{O}_7^{2-}$	2269	$\text{W}_6\text{O}_{19}^{2-}$	1585
$\text{V}_2\text{O}_7^{4-}$	2288	$\text{Mo}_6\text{O}_{19}^{2-}$	2056	$\text{W}_7\text{O}_{24}^{6-}$	1615
$\text{V}_3\text{O}_{10}^{5-}$	2302	$\text{Mo}_7\text{O}_{24}^{2-}$	2021	$\text{W}_{10}\text{O}_{32}^{4-}$	1604
$\text{V}_{10}\text{O}_{28}^{6-}$	2221	$\alpha\text{-Mo}_8\text{O}_{26}^{4-}$	2161	$\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$	1661
$\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$	2232	$\beta\text{-Mo}_8\text{O}_{26}^{4-}$	2090	$\alpha\text{-HW}_{12}\text{O}_{40}^{7-}$	1578
$\text{H}_3\text{PV}_{14}\text{O}_{42}^{6-}$	2257*	$\text{PMo}_{12}\text{O}_{40}^{3-}$	2069*	$\alpha\text{-H}_2\text{W}_{12}\text{O}_{40}^{6-}$	1583
$\text{H}_6\text{PV}_{14}\text{O}_{42}^{3-}$	2235*	$\text{SiMo}_{12}\text{O}_{40}^{4-}$	2063*	$\text{PW}_{12}\text{O}_{40}^{3-}$	1605*
				$\text{SiW}_{12}\text{O}_{40}^{4-}$	1593*
				$\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}^{6-}$	1588*

\*ignoring  $\text{XO}_4$  unit(s)

The above table provides a theoretical challenge as well as a useful empirical rule. By summing the shifts we are assessing how much they differ from that of water. Very roughly speaking, the shift of any one oxygen is a measure of its covalent bonding to the nearest metal atom. (For this reason it also correlates well, though not linearly, with the reciprocal of the shortest MO bond distance.) The MO bonds have both  $\sigma$  and  $\pi$  components, and show some evidence of delocalisation. Thus there are some analogies with the distribution of (nominally)  $\pi$ -electron spin densities in aromatic systems, where any gain at one carbon is offset by losses at other carbons. One could describe such shifts as resource-limited. Also, the MO bond length sums will remain roughly constant if the metal atoms merely move within an oxygen coordination shell of fixed geometry under the influence of e.g. electrostatic forces. Even so, the shift sum constancies listed above are remarkable, and I would invite readers to offer a deeper explanation of them.

With my best regards

Oliver Howarth



# WOOD TECHNOLOGY DIVISION FOREST RESEARCH INSTITUTE

Postal Address: Private Bag 3020, Rotorua, New Zealand.  
Telegraphic Address: 'Frestra' Rotorua, N.Z.  
Fax: 0-7-347-9380  
Telephone: 0-7-347-5899 Telex: NZ21080

01 April 1992 (received 4/6/92)

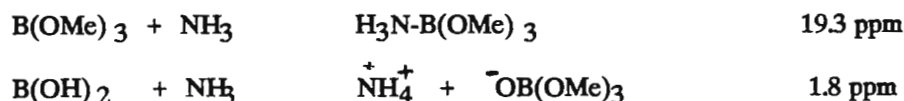
Dr Bernard Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto CA 94303  
UNITED STATES OF AMERICA

Dear Dr Shapiro

RE: Lineshape deconvolution - *who needs software?*

I was in dread of receiving your ultimatum, knowing that I didn't have much material that I was able to talk about. Thankfully I was in the middle of developing a method when your ultimatum arrived.

We are currently producing trimethyl borate (TMB) from boric acid and methanol. The problem has been being able to analyse for TMB and boric acid in the azeotrope by NMR as they have very similar shifts in dimethylacetamide (19.8 and 19.4 ppm respectively). Since we lack deconvolution software we considered exploiting their differences in chemical reactivity. By bubbling ammonia gas through the azeotrope two reactions occur;



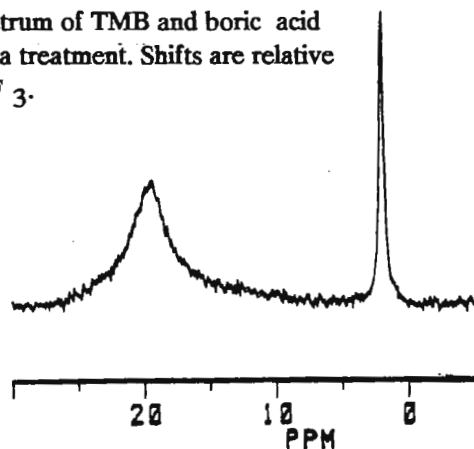
The two species now have resonances well separated (Fig. 1) so that they are readily integrated to obtain ratios of boric acid to TMB in the azeotrope.

Incidentally, if anyone can recommend a good deconvolution package for a 386 or 486 I would be keen to know.

Your sincerely

Roger Meder

Figure 1. Spectrum of TMB and boric acid after ammonia treatment. Shifts are relative to external  $\text{BF}_3$ .





# Model R-1200 Rapid Scan 60 MHz NMR Spectrometer



*The Model R-1200 Rapid Scan, 60 MHz NMR Spectrometer scans 10-20 times faster than conventional cw instruments. Performance is enhanced significantly and features, available only with more expensive, higher field instruments are included as standard.*

- **Scan times are ten to twenty times faster** than conventional cw instruments. Total microprocessor control provides superior performance and a new level of user convenience for 60 MHz NMR.
- **Digital signal processing ensures drift free operation** and eliminates the need for rescanning and tedious tuning of the instrument. Spectra are obtained faster and more conveniently.
- **Our unique Field Cure™ corrects field drift** and allows the accumulation of multiple spectra for improved signal-to-noise ratios faster than the time required for a single scan with a conventional instrument.
- **Correlation analysis eliminates ringing** and its interference with peak discrimination and chemical shift calculations. Effective resolution is significantly enhanced.
- **Chemical shift values are calculated by the microprocessor** and can be printed directly on the NMR spectrum, eliminating time consuming manual measurements.
- **Digital integration eliminates phasing** problems and the need to reintegrate if field drift occurs.
- **Post-run processing of stored spectra** allows the user to select any peak as a reference for correct chemical shift calculations.
- **Maximum resolution is set in less than one minute** by a single keystroke, eliminating the tedious and time consuming procedure required by conventional instruments.
- **A high quality, 4-pen printer/plotter** provides publishable spectra including, chemical shift values, operating parameters, and spectral data.

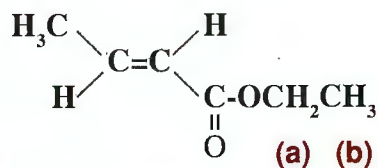


Hitachi Instruments, Inc.



\*\*\* HITACHI NMR R-1200 \*\*\*

# SAMPLE & SOLUTION



Ethyl Crotonate

## \*\* ACQUISITION PARAMETER \*\*

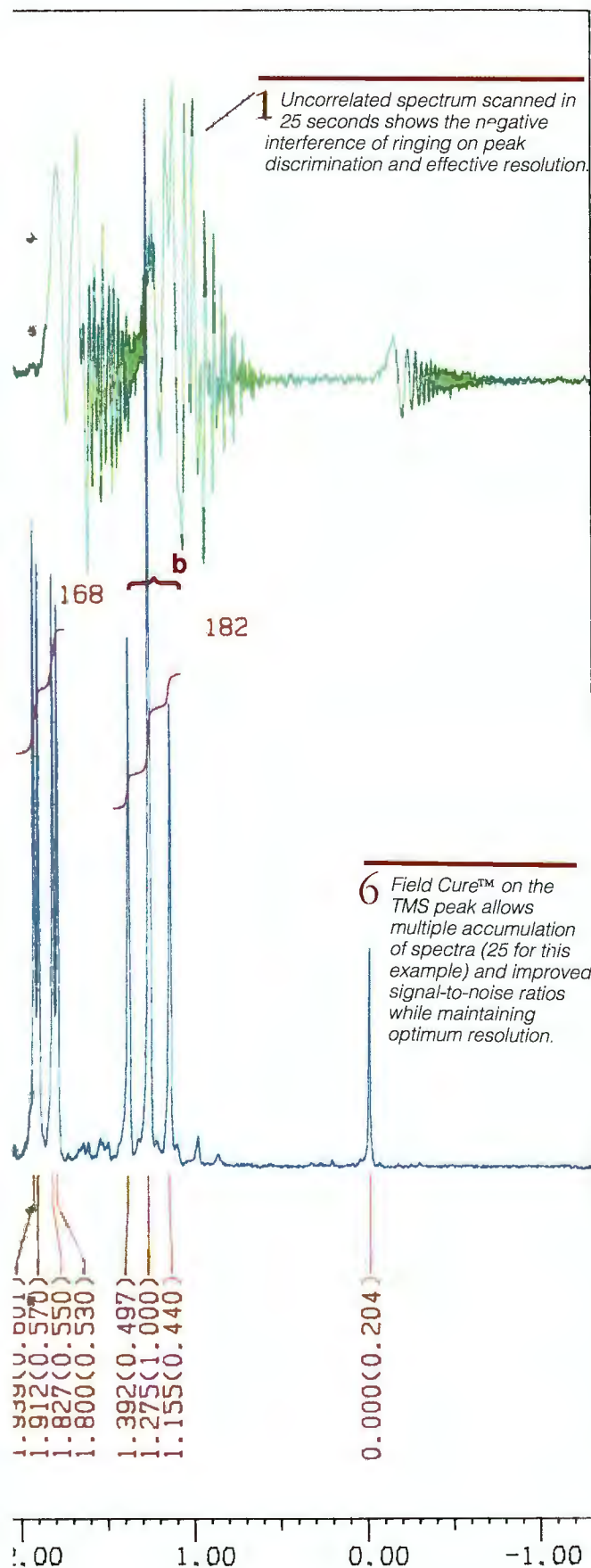
SPECTRUM WIDTH : 10.00 ppm  
FILTER : 100.00 Hz  
AMPLITUDE  
SPECTRUM : 8  
SWEEP RATE : 25 sec  
NO. OF ACCUMU. : 25  
H1 LEVEL : NOR  
H2 LEVEL :  
H3 LEVEL :

## \*\* PROCESSING PARAMETER \*\*

SCALE EXP. : 10.00 ppm  
AMPLITUDE  
SPECTRUM : 8  
INTEGRAL :  
MEMO :

8 Acquisition and processing parameters are stored and can be printed automatically so that data and operating conditions are linked.

OPERATOR :  
DATE : . . .





# Technical Specifications

Nucleus	$^1\text{H}$ or $^{19}\text{F}$ or $^{31}\text{P}$
Resonance Frequency	60 MHz
Field Intensity	1.41 Tesla with Permanent Magnet
Resolution	0.4 Hz or less (full line width at half height of TMS signal).
Sensitivity	30:1 single scan of 1% ethyl benzene 180:1 sixty scans of methylene quartet
Integrator	Digital integration
Filter	100, 10, 5, 2.5, 1, 0.5, 0.25 Hz
Sweep Width	10, 20, 100 PPM 50, 100, 200, 300, 400, 500 Hz
Sweep System	Digital Scan
Sweep Time	1-1000 sec.
Field Lock	Proton internal lock
Double Resonance	Standard
Triple Resonance	Optional
Data Density	4096 points/scan
Interface	RS232C standard
Monitor	Oscilloscope
Recorder	4-pen, multicolor, printer/plotter for A3 chart size. Effective recording width is 270 x 400 mm

## Installation Specifications

Room Temperature	16-30°C with <2°C/hr. fluctuation
Power Supply	115 V $\pm$ 10%, 60 Hz. 4-5 Amp.
Magnet Weight	250 kg (550 lbs.)
Dimensions	1450 mm(4'8") x 840 mm(2'8") x 800 mm(2'6") high

## Order Information

<b>435-2491</b>	R-1200 Rapid Scan 60 MHz NMR Spectrometer
<b>435-2546</b>	Oscilloscope
<b>AN0-0166</b>	Sample tube 0.5 mm OD Pkg/100
<b>AN0-0167</b>	Sample tube caps-red Pkg/100
<b>AN0-0168</b>	Sample tube caps-white Pkg/100
<b>435-2501</b>	Triple Resonance Accessory





381 Royal Parade,  
Parkville, 3052,  
AUSTRALIA

Phone +61 3 389 965  
FAX +61 3 389 9655

March 27, 1992 (received 4/3/92)

Dr. B.L. Shapiro,  
TAMU NMR Newsletter,  
966 Elsinore Court,  
Palo Alto CA 94303,  
USA.

Dear Barry,

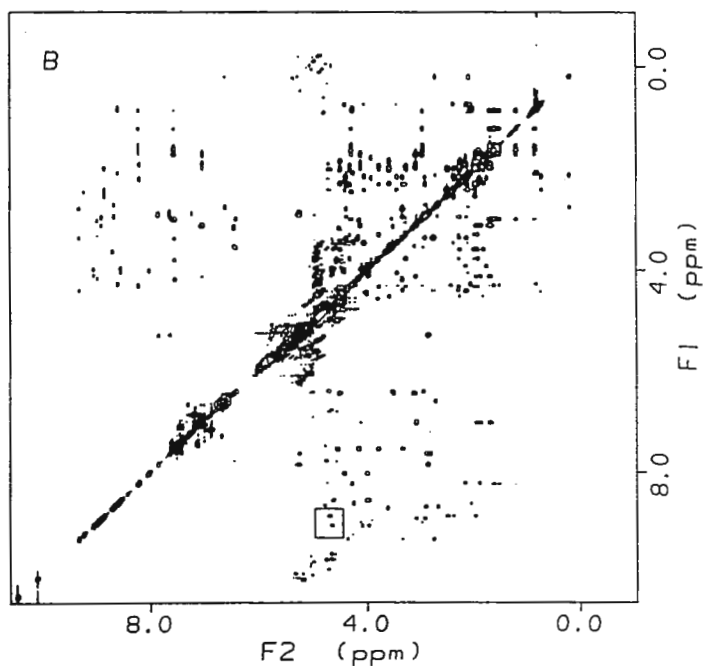
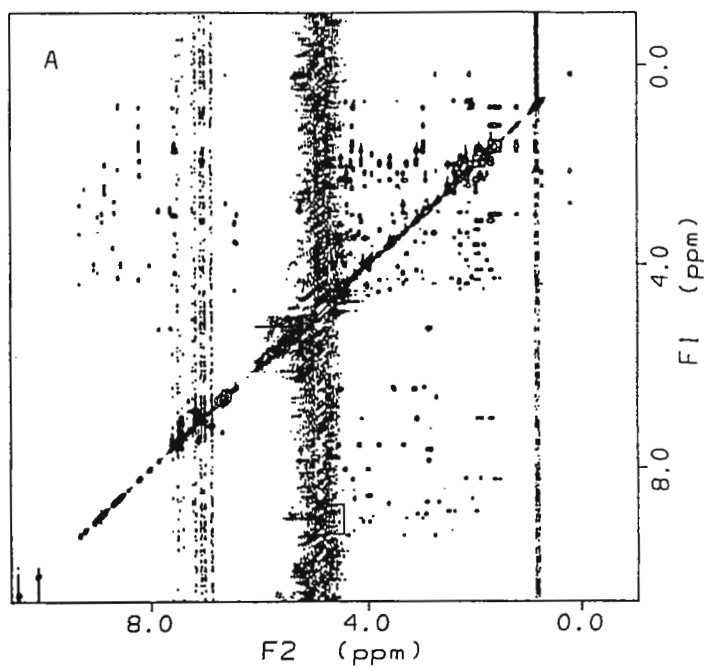
### **Suppression of $t_1$ noise and solvent artifacts in 2D NMR spectra of proteins**

Firstly my apologies for provoking the dreaded Utimatum, the threats in which hopefully will be offset by this contribution. One reason for the delayed contribution is my move from the University of New South Wales to the Biomolecular Research Institute in Melbourne. The BRI is a government funded initiative focussing on structural biology and molecular design. The NMR Laboratory is equipped with Bruker AMX-500 and -600 spectrometers and a network of UNIX workstations, supported by a dual processor Convex.

To matters scientific, where I wanted to describe briefly some spectral processing routines written by a PhD student in my group at the University of NSW, Nick Manoleras. The first is a baseline correction routine in which valid baseline segments are identified by their lower slope relative to regions containing peaks. The properties of these known baseline sections are then used to predict the baseline in areas occupied by peaks or bad  $t_1$  noise. The operation of BFX can be visualized as tracing out a baseline from the data similar to that which an operator would define by following the curve of the baseline with a cursor. It extracts a baseline from the data, then subtracts it to produce a flat baseline. In our experience it gives baseline correction superior to that achievable with polynomial or cubic spline routines.

The other technique is used to reduce  $t_1$  noise artifacts in 2D spectra. To begin with, a  $t_1$  noise profile is produced by measuring the average noise in each column. This profile is then used to determine weighting coefficients for a sliding weighted smoothing filter that is applied to each row, such that the amount of smoothing each point receives is proportional to both its estimated  $t_1$  noise level and the level of  $t_1$  noise of neighbouring points. Thus, points in the worst  $t_1$  noise bands receive the greatest smoothing, whereas points in low noise regions remain relatively unaffected. In addition, weighted smoothing allows points in low noise regions to influence neighbouring points in noisy regions. This method is also effective in reducing the noise artifacts associated with the solvent resonance in spectra of biopolymers in aqueous solution.

The effects of applying the  $t_1$  noise suppression routines to the TOCSY spectrum (recorded on an AM-500) of a polypeptide in  $H_2O$  are illustrated in the Figure. (A) Matrix after baseline correction in  $\omega_2$ . (B) Same as A (and plotted at the same level), but after the application of the  $t_1$  noise suppression routines.



A manuscript describing these procedures has been submitted recently. At present they operate in conjunction with FELIX, but we plan to make them more generally usable.

Yours sincerely,

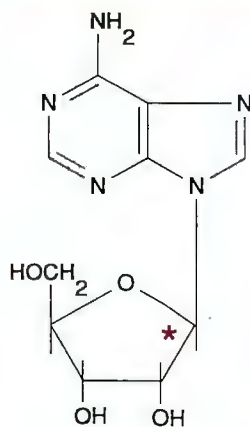
*Ray Norton*

Raymond S. Norton  
Head, NMR Laboratory

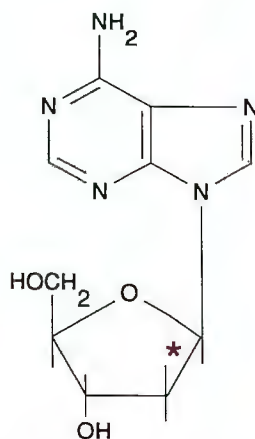


***NEW from CIL***

# **RIBONUCLEOSIDES & DEOXYRIBONUCLEOSIDES**

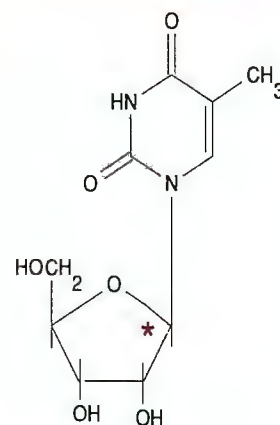


**Adenosine**  
(1'-<sup>13</sup>C, 99%)



**2'-deoxyadenosine**  
(1'-<sup>13</sup>C, 99%)

**New carbon-13 labeled  
Ribonucleosides & Deoxyribonucleosides  
providing <sup>13</sup>C probes for your  
biophysical NMR applications.**

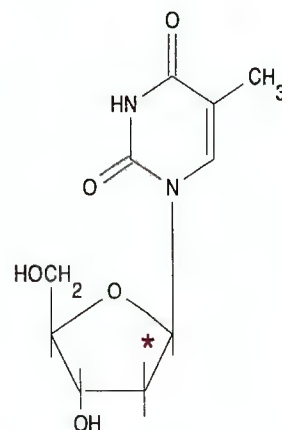


**Ribothymidine**  
(1'-<sup>13</sup>C, 99%)

**These products are currently  
under development.**

**Available Summer 1992.**

**Please call for more information.**



**2'-Thymidine**  
(1'-<sup>13</sup>C, 99%)

**CIL**

**CAMBRIDGE ISOTOPE LABORATORIES**

**20 Commerce Way, Woburn, Massachusetts 01801**

**800-322-1174 or 617-938-0067 Fax: 617-932-9721**

**and introducing...**

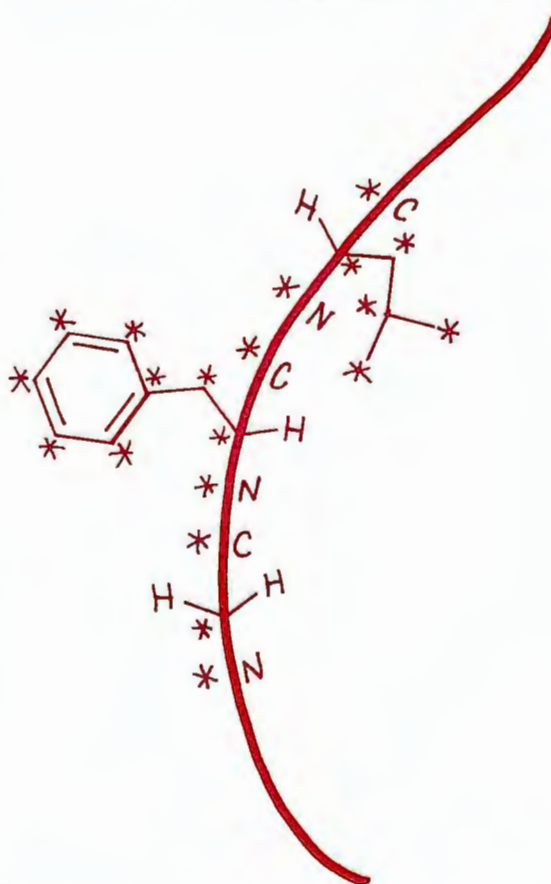
# **AN ISOTOPE LABELED POLYPEPTIDE STANDARD FOR NMR**

An  
Octapeptide with a  
 $^{13}\text{C}$ ,  $^{15}\text{N}$  labeled sequence  
to aid in setting up your  
NMR spectrometer for  $^1\text{H}$  ( $^{13}\text{C}$ ,  $^{15}\text{N}$ )  
triple resonance experiments.

**Tyr-Gly- $^{*}\text{Gly-}^{*}\text{Phe-}^{*}\text{Leu-Arg-Arg-Ile}$**   
 **$^{*}\text{U-}^{13}\text{C}$ ,  $^{15}\text{N}$  labels**

In collaboration with  
**Dr. Jonathan Lee,\***  
CIL is pleased to offer  
- ready to use -  
NMR samples of  
1 mM peptide in  $\text{DMSO-}D_6$   
\* Harvard Medical School

This octapeptide offers an easy  
solution to the difficult task of  
properly setting up your NMR  
spectrometer to perform today's  
heteronuclear multidimensional  
triple resonance experiments.



**Please call CIL for pricing and delivery.**  
**1-800-322-1174**



Conseil national  
de recherches Canada

National Research  
Council Canada

Institut de recherche  
en biotechnologie

Biotechnology Research  
Institute

6100, avenue Royalmount, Montréal, Québec, Canada H4P 2R2

Tel.: (514) 496-6100

Dr. B. L. Shapiro  
TAMU Newsletter  
966 Elsinore Court  
Palo Alto, California 94303

Référence File

April 8, 1992

(received 4/13/92)

## Sensitivity-Enhanced 3D NOESY-TOCSY: Applications to Transferred NOEs

Dear Dr. Shapiro,

In the usual pulse sequence for 3D NOESY-TOCSY, spin-locked coherence transfers are achieved by use of a trimmed MLEV-17 sequence. We replaced the MLEV-17 sequence by a z-filtered WALTZ-16 sequence (Figure 1) to obtain sensitivity enhancement (*Ni, JMR 1992, in press*). This method involves post-acquisition combinations of the FIDs acquired from subgroups of the full phase cycle utilized for the pulse sequence. The two detected FIDs are stored in separate memory blocks for subsequent processing. Adequate combinations of these FIDs would restore the two orthogonal components,  $I_{iy}$  and  $I_{ix}$ . If both the  $I_{iy}$  and  $I_{ix}$  FIDs are processed to yield absorptive spectra, they can be combined to produce a spectra with peaks doubled in size compared to each individual spectrum. The key to sensitivity enhancement lies in the fact that noise components in the two spectra are statistically independent and the post-processing combinations are then equivalent to signal averaging, reducing noise in the process (*Cavanagh & Rance, JMR 88, 72, 1990*).

Sensitivity-enhanced NOESY-TOCSY was applied to an anticoagulant peptide, acetyl-Asp-Phe-Glu-Glu-Ile-Pro<sub>60</sub>-Glu<sub>61</sub>-Glu-Tyr<sub>63</sub>-Leu-Gln-COOH at a peptide concentration of 6 mM and a thrombin concentration of 0.5 mM in an aqueous solvent of 90% H<sub>2</sub>O and 10% D<sub>2</sub>O at pH 5.5. Figure 2A is the  $F_1$ - $F_2$  plane sliced through the frequency of one of the well-resolved  $\delta\text{CH}_2$  protons of Pro along the  $F_3$  dimension of the  $I_{iy}$  3D spectral matrix. The sensitivity-enhanced ( $I_{iy}+I_{ix}$ ) spectrum is presented in Figure 2B. For some peaks sensitivity enhancement is less than the  $\sqrt{2}$  factor expected theoretically. This is probably due to the fact that the  $I_{ix}$  components travel through different transfer pathways and are much more sensitive to prolonged delays both before and after the WALTZ-16 spin-lock pulse (Figure 1).

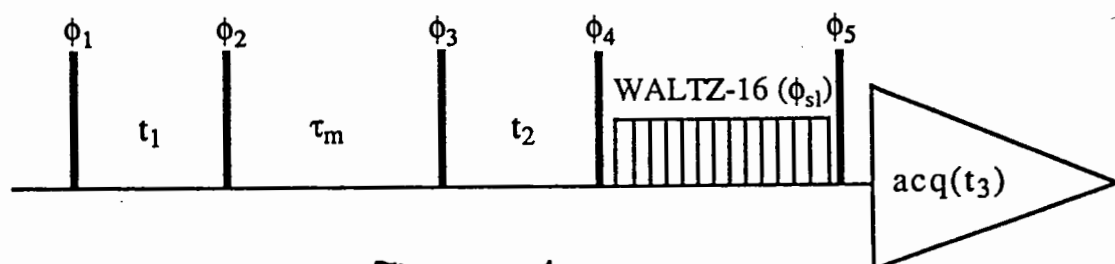


Figure 1



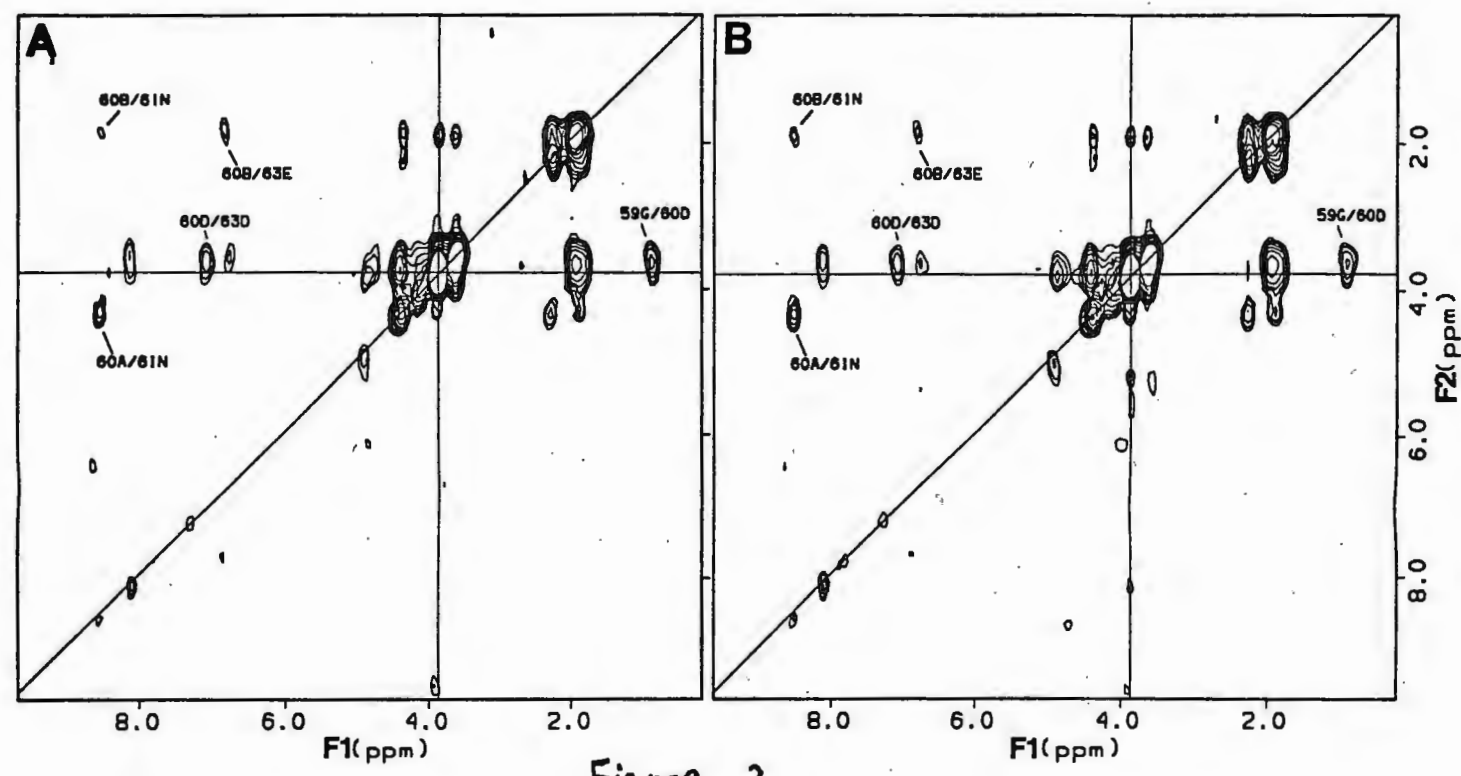
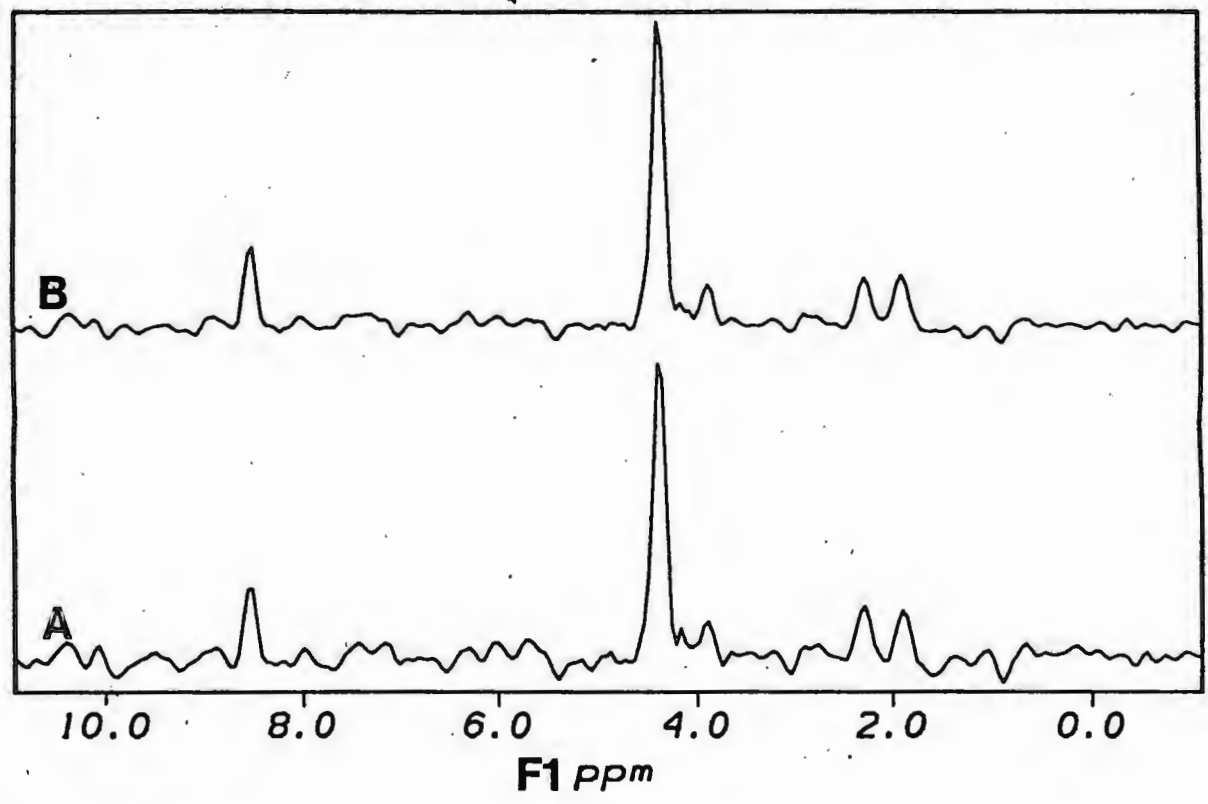


Figure 2



*Feng Ni*  
Feng Ni, Ph.D  
Protein Engineering

H A R V A R D M E D I C A L S C H O O L  
D E P A R T M E N T O F B I O L O G I C A L C H E M I S T R Y  
A N D M O L E C U L A R P H A R M A C O L O G Y

Professor Gerhard Wagner

Tel. (617) 432-3213 or 4366

Fax: (617) 432 4383



240 Longwood Avenue  
Boston, Massachusetts 02115

April 16, 1992  
(received 4/20/92)

Dr. Barry Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

Mapping of Spectral Densities of NH Motions in Proteins


Dear Barry:

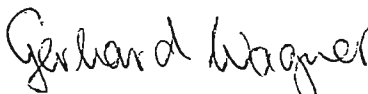
We have developed a strategy for direct mapping of spectral density functions from measurements of relaxation parameters of the NH groups in proteins. Previous strategies for interpretation of relaxation parameters were based on mechanistic models of internal motions, such as the "wobbling in a cone" model (1, 2). Alternatively, the "model-free approach" was developed (3,4) which makes, however, the assumption that the autocorrelation function  $G(t)$  can be described as a sum of decaying exponentials. As a consequence, the shape of the spectral density function is restricted to a sum of Lorentzians. Such assumptions about mechanistic models or about a functional dependence of the functional dependence of  $J(\omega)$  on certain parameters were necessary since the relaxation rates depend on five values of the spectral density functions,  $J(0)$ ,  $J(\omega_N)$ ,  $J(\omega_H + \omega_N)$ ,  $J(\omega_H)$  and  $J(\omega_H - \omega_N)$ , while fewer experimental  $^{15}\text{N}$  relaxation parameters were measured, such as  $T_1$ ,  $T_2$  and the heteronuclear NOE. Thus the problem is underdetermined, and model assumptions have to be made. We added some additional experiments to be able to calculate the values of the spectral density functions (5). We measure six relaxation parameters: the longitudinal relaxation rate of  $\text{N}_z$ , the transverse relaxation rates of in-phase and anti-phase coherence,  $\text{N}_{x,y}$  and  $2\text{N}_{x,y}\text{H}_z$ , the relaxation rate of longitudinal two-spin order,  $2\text{N}_z\text{H}_z$ , the heteronuclear cross relaxation rate and the longitudinal relaxation rates of protons. The pulse sequences to measure these parameters for an  $^{15}\text{N}$  enriched protein yield 2D  $^{15}\text{N}$ - $^1\text{H}$  correlated spectra in which the peak intensities can be measured as a function of a relaxation delay  $\tau$ . The analysis includes relaxation by dipole-dipole interaction and CSA relaxation. Crosscorrelation between dipole-dipole and CSA is minimized by appropriate decoupling sequences (6,7). A complete set of data was recorded on a AMX 500 spectrometer for the protein eglin c, and spectral densities were derived (8). The spectral densities decay from  $\omega=0$  to  $\omega_H + \omega_N$ . For many N-H groups, the spectral density increases significantly from  $\omega_H + \omega_N$  to  $\omega_H - \omega_N$  (due to the negative sign of  $\gamma_N$ , the latter is the larger frequency). Should this unexpected observation prove to be real, our common picture of how an autocorrelation function should look like had to be revised.

## References

1. Woessner, D.E. (1962) *J. Chem. Phys.* 69, 1723-1736.
2. Kinoshita, K., Kawato Jr. W., & Ikegami, A. (1977) *Biophys. J.* 20, 289.
3. Lipari, G., & Szabo A. (1982a) *J. Am. Chem. Soc.* 104, 4546-4559.
4. Lipari, G., & Szabo A. (1982b) *J. Am. Chem. Soc.* 104, 4559-4570.
5. Peng, J.W., & Wagner, G. (1992) *J. Magn. Reson.*, in press.
6. Palmer, III, A. G., Skelton, N. J., Chazin, W. J., Wright, P. E., & Rance, M. (1991) *Mol. Phys.*, 75, 699-711.
7. Boyd, J., Hommel, U., & Campbell, I. D. (1990) *Chem. Phys. Lett.* 175, 477-482.
8. Peng, J.W., & Wagner, G. (1992), submitted to *Biochemistry*.

Sincerely

  
Jeffrey W. Peng

  
Gerhard Wagner

\* \* \* \* \*

**The Newsletter's fiscal viability depends very heavily on the funds provided by our Advertisers and Sponsors. Please do whatever you can to let them know that their support is noted and appreciated.**

\* \* \* \* \*

## Mailing Label Adornment: Is Your Dot Red?

If the mailing label on your envelope of this issue is adorned with a large red dot or circle: this decoration means that you will not be mailed any more issues until a technical contribution has been received by me.

## Page Length Instruction

**Attention overseas subscribers:** If you must use paper which is longer than 11", *please* take care that all material (including signatures, addresses - everything!) ends no more than 10" from the top of each of your pages. It is costly to make reductions, and henceforth I reserve the right to chop the excess length off any page, no matter what the result. Beware of the dreaded guillotine! Your cooperation in this matter will be greatly appreciated.

### All Newsletter Correspondence

Should Be Addressed To:

Dr. Bernard L. Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303, U.S.A.

(415) 493-5971

### DEADLINE DATES

No. 406 (July)----- 19 June 1992  
No. 407 (August)----- 24 July 1992  
No. 408 (September)----- 21 August 1992  
No. 409 (October) -----18 September 1992



# Gradient Enhanced Spectroscopy

## Phase Sensitive DQF COSY

The selection of multiple quantum coherence with gradients is an effective method for suppressing the water resonance in aqueous solutions and for reducing  $t_1$  noise and other artifacts. A further enhancement is the use of selective water excitation using crafted RF pulses followed by gradient dephasing to attenuate the water signal prior to the coherence selection sequence. This technique has been applied to the phase sensitive gradient enhanced DQF COSY experiment for a 5mM lysozyme sample in 90%  $H_2O$ . The data were collected on an Omega PSG 500 equipped with the S-17 Gradient Enhanced Spectroscopy accessory using a 5mm inverse probe.

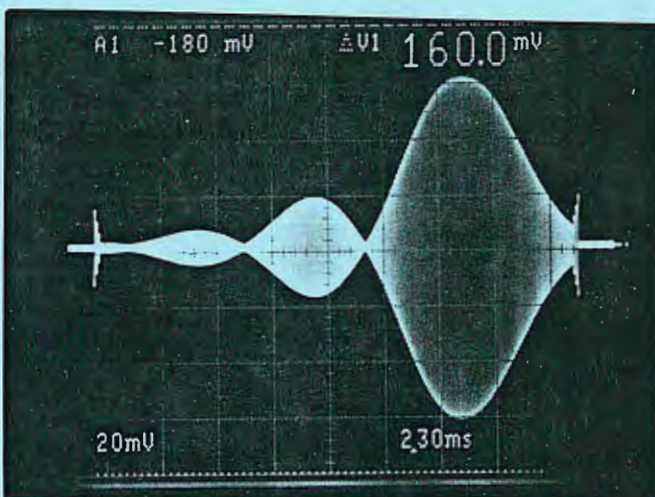


Figure 2

The crafted RF pulse used in this sequence. This pulse was designed using the "hard pulse approximation" method. It is characterized by a flat amplitude response in the selected region and minimal excitation in the out of band region. The duration of the selective RF pulse was set to 20 ms, corresponding to an excitation bandwidth of 175 Hz.

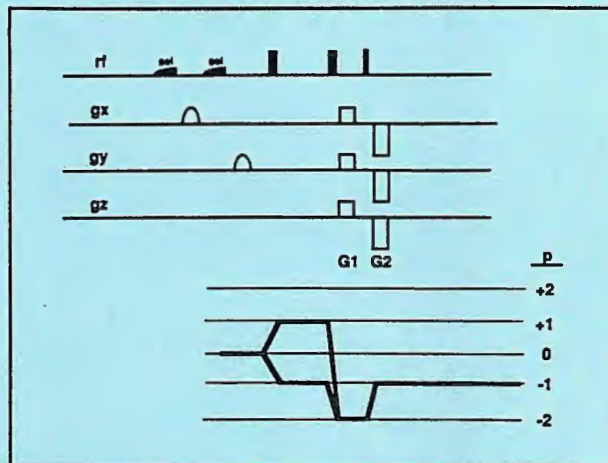


Figure 1

The pulse sequence and the corresponding coherence level diagram for the phase sensitive GE-DQF COSY experiment. The water resonance is selectively excited using a crafted RF pulse followed by a shaped gradient pulse along the X axis which dephases the transverse magnetization. A second selective RF pulse is applied with a dephasing gradient along the Y axis to avoid gradient recalled echoes. This is followed by a phase sensitive GE-DQF COSY sequence.

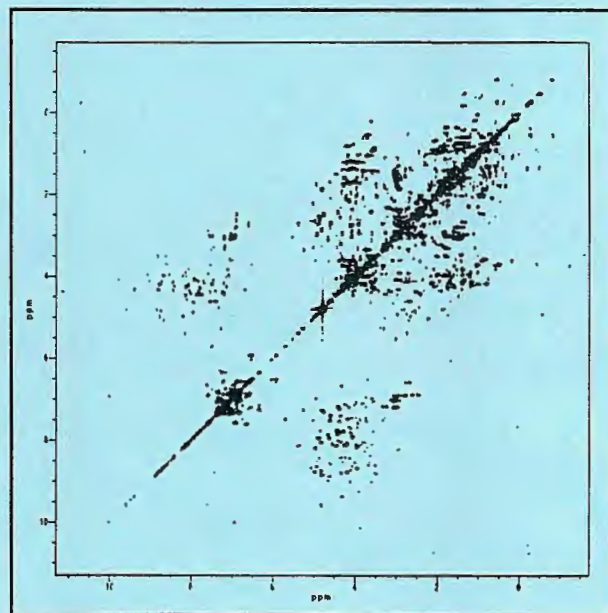


Figure 3

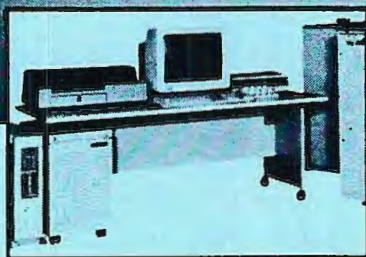
A phase sensitive GE-DQF COSY spectrum of 5 mM lysozyme in 90%  $H_2O$ . Thirty-two scans were accumulated for each of the 700  $t_1$  increments resulting in a total data acquisition time of approximately 9.7 hours. Half-sinusoidal gradient pulses of 20 ms duration with an amplitude of 10 G/cm were used to dephase the excited water signal. Coherence selection was achieved using 2 ms gradient pulses of 17 and 34 G/cm amplitude.

**GE NMR Instruments**



Of all the advanced technology on this research-level NMR, this may be the most important piece of hardware.

**JEOL**



JEOL's Alpha series FT NMR system offers a research-level NMR spectrometer that sets a new standard of performance and reliability.

The Alpha combines event bus architecture, experiment definition language, dynamic RF control, pulse shaping and matrix shims into an extremely flexible, high speed precision machine with exceptional sensitivity.

One of the Alpha's most important features isn't listed on

a technical data sheet, however. It's the reputation for quality and service that JEOL has earned over the years.

All of our machines are designed for reliability, flexibility and durability. And the outstanding service and applications support provided by our customer service staff makes sure that our high-performance

equipment always performs to your satisfaction.

For a demonstration or more information about the JNM-A400/A500/A600 Alpha series of FT NMR systems and JEOL's customer service organization, call 508-535-5900 or write to JEOL USA, 11 Dearborn Rd., Peabody, MA 01960.

**JEOL**

Analytical Instruments Division

M S • N M R • E S R