TEXAS A&M UNIVERSITY

NMR NEWSLETTER

NO. 307

APRIL 1984

Wasylishen, R.
Sulfur-33 Chemical Shifts and a Proposed Absolute Sulfur Shielding Scale 1

Barcza, S., Di Cataldo, S.N., Kolpak, M. X., and **Shapiro, M.J.**
The Sandoz, Inc. Structure-CMR Retrieval System at Work. 3

Harris, R.K., Cox, I.J., and **Belton, P.S.**
Taken for a Ride: Sulfur-33 NMR 5

Buchanan, G.W.
^{15}N Spectra of N-Methylnucleoside cis-Platinum Complexes. 7

Fraser, R.R.
Interim Report: Weak Nitrogen Acids . . . 10

Carr, T.M.
New Chip-Capacitor 16mm Broadband Probe . . 11

Edlund, U.
Simplified NMR Parameters in Structure-Activity Studies; Multipurpose Solid-Liquid Instrument, MSL-100. 13

MacFadden, K.O.
Position Available. 14

Hajek, M. and **Trska, P.**
^{19}F Relaxation Times 15

James, T.L., Gonzalez-Mendez, R., and **Litt, L.**
A 5.6T, Horizontal Bore Magnet System Used to Study Hypoxic Hypoxia in Rat Brain . . . 17

Robert, D., Bardet, M., and **Foray, M.F.**
Use of the DEPT Pulse Sequence to Facilitate the ^{13}C NMR Structural Analysis of Lignins. . 19

Hase, T., Pihlaja, K., and **Nurmi, T.**
2D Approach May Help to Analyze Even a Relatively Simple ^{1}H NMR Spectrum: The Case of 2-S-Butyl-2-Trimethylsilylmethyl-1,3-Dithiane . 21

Meyers, B.L. and Loo, J.
Cis and Trans Vinyl Methyls in Spin Echo Spectra 23

Abraham, R.J.
Proton Shifts in Porphyrins 25

Freeman, R.
Very Soft Pulses 27

Maciel, G.E. and **Hawkins, B.L.**
New Type of Approach to Zero-Field Zero-Abundance NMR for ^{15}N at 20 MHz . . . 29

Wong, T.C. and **Rutar, V.**
A New ^{13}C-^{1}H Chemical Shift Correlation Technique 31

de Bie, M.J.A. and **van Leest, P.M.**
The Effect of Multiple Quantum Coherences in ^{7}Li Relaxation: A Warning. . . 33

Storm, C.B. and **Turner, A.H.**
Deuterium Substitution Effects on Relaxation Times and Inter-Ligand NOE's for Assignment of Ligand Resonances in $(NH_3)_5CoL^{3+}$ Complexes. . 37

van Haverbeke, Y., Muller, R.N., di Rienzo, B., and **Vander Elst, L.**
Fast Characterization of Stability and Relaxativity of Short Lived Nitroxides Free Radicals 39

Smith, I.C.P., Geoffrion, Y., Deslauriers, R., Butler, K.W., and **Pass, M.A.**
Foie Raw: NMR Measurement of Drug Metabolism in Intact Mouse Livers 42

Smith, W.B.
Book Review 45

Levy, G.C.
Position Available. 46

Barfield, M.
Position Available. 47

DeLuca, H.F.
Position Available. 48

Bradbury, E.M. and **La Mar, G.N.**
Position Available. 49

DEADLINE DATES

No. 309 ----- 4 June 1984

No. 310 ----- 2 July 1984

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.

WILMAD REFERENCE STANDARDS We supply Reference Standards to major instrument manufacturers and, in practically every case, our standards meet or exceed the instrument manufacturer's specifications.

For Reference Standards not shown in the listings, please inquire directly to the plant about price, packaging and availability.

When ordering Wilmad Reference Star **the tube size** and **don't forget to include t**

Wilmad Reference Standards are **sea** high-resolution, Wilmad sample tubes ac otherwise indicated in the listing).

Now Available to NMR Investigators...

TUBE O	TUBE LENGTH	MATERIAL LENGTH
5mm	7"	2.5"
8mm, 10mm, 12mm	7"	3.0"
15mm	7"	4.0"
2.5mm	178mm	50mm

TUBE STYLE

* If st[illegible] ngths and/or m[illegible] vels are nee[illegible] ple[illegible] ctly to ur [illegible] location.

A NEW, UP-TO-THE-MINUTE LISTING OF WILMAD NMR REFERENCE STANDARDS.

WILMAD REFERENCE STANDARDS

Page No.	Catalog Number	PROTON SIGNAL	PARAMETER SET-UP	5mm
38	WGH-01	Acetaldehyde + 1% TMS	Resolution	$ 32.00
	WGH-02	Acetaldehyde + 2% TMS	Resolution	32.00
	WGH-[illegible]	[illegible]% Acetaldehyde + 2% TMS in Benzene-d,	Resolution	33.00
	WGH-[illegible]	[illegible]% Acetaldehyde in Benzene-d,	Resolution	33.00
	WGH-22	20% Acetaldehyde in Benzene-d,	Resolution	33.00
	WGH-24	20% Acetaldehyde + 2% TMS in Acetone-d,	Resolution	33.00
	WGH-17	Orthodichlorobenzene (Neat)	Resolution	32.00
	WGH-33	30% Orthodichlorobenzene + 5% TMS in Acetone-d,	Resolution	33.00
	WGH-55	20% Orthodichlorobenzene + 5% TMS in Acetone-d,	Resolution	33.00
	WGH-61	95% Orthodichlorobenzene + 5% TMS	Resolution	
	WGH-[illegible]	[illegible]% Orthodichlorobenzene in [illegible]	Resolution	33.00
	WGH-69	30% Orthodichlorobenzene in Acetone-d,	Resolution	33.00
	WGH-[illegible]	[illegible]% Orthodichlorobenzene + 5% TMS in Acetone-d,	Resolution	31.00
	WGH-64	50% Chloroform in Acetone-d,	Resolution	33.00
	WGH-36	Methyl Formate (Neat)	Res./Sens.	32.00

WRITE OR CALL FOR BULLETIN BD-102 TODAY. WE'LL SEND IT TO YOU BY RETURN MAIL.

Reference standards for use in NMR spectroscopy are an important and integral part of this investigative procedure. Our reference standards are sealed and degassed in ultra-precision, high resolution Wilmad sample tubes. We supply them to many of the major instrument manufacturers and, in practically every case, our standards meet or exceed the manufacturer's specifications.

Our last published listing of our reference standards was more than four years old and, since that time, we have deleted and added some new standards based on usage requirements. In our Bulletin BD-102, we have regrouped them and provided you with descriptions . . . and prices . . This bulletin is all you need to place your order for more than 130 items, including our new 2.5mm tubes.

WILMAD GLASS COMPANY, INC.

Rt. 40 & Oak Road, Buena, New Jersey 08310, U.S.A.
Phone: (609) 697-3000 • TWX 510-687-8911

"Position Available" Notices

Recent issues of the Newsletter have contained a substantial and growing number of "Position Available" notices. While this is most heartening in terms of the implied vigor of the field, the amount of space these notices are taking up has become a burden. In this, as elsewhere, we are trying to keep costs down.

Therefore, all "Position Available" notices should be constructed so as to fit within a space bounded by the frame line drawn around this notice. This space will allow for notices which have a **maximum size of 4.5 inches high x 7.5 inches wide (11.4 cm high x 19.0 cm wide).** Notices which do not meet this space restriction will be returned for reworking, resulting in a delay in their appearance in the Newsletter.

Please understand that we do not intend for these space restrictions to diminish the number of position available notices which appear in the Newsletter. This number should self-regulate. We must, however, deal with the economic aspects of the issue. Position available notices dated June 15 or later will be expected to meet this new space consideration policy. If you send longer notices between May 1 and June 15, we would appreciate your airmailing us smaller, replacement versions if this is appropriate.

B. L. Shapiro

May 1, 1984

ADVERTISERS

General Electric Company, Medical Systems Group, NMR Instruments . . . inside back cover
IBM Instruments, Inc. 36
JEOL Analytical Instruments . . . . (i), outside back cover
Varian Instrument Division. 8
Wilmad Glass Company, Inc. . . . . inside front cover

SPONSORS

Abbott Laboratories
The British Petroleum Co., Ltd. (England)
Bruker Instruments, Inc.
Eastman Kodak Company
E. I. du Pont de Nemours & Company
General Electric Company, Medical Systems Group - NMR Instruments
IBM Instruments, Inc.
JOEL (U.S.A.) Inc., Analytical Instruments Division
Dr. R. Kosfeld, FB 5 Physikalische Chemie, University of Duisburg, D-4100 Duisburg 1, West Germany
The Lilly Research Laboratories, Eli Lilly & Company
The Monsanto Company
The Procter & Gamble Company, Miami Valley Labs
Programmed Test Sources, Inc.
Shell Development Company
Unilever Research
Union Carbide Corporation
Varian, Analytical Instrument Division

CONTRIBUTORS

Chemagnetics, Inc.
Intermagnetics General Corporation

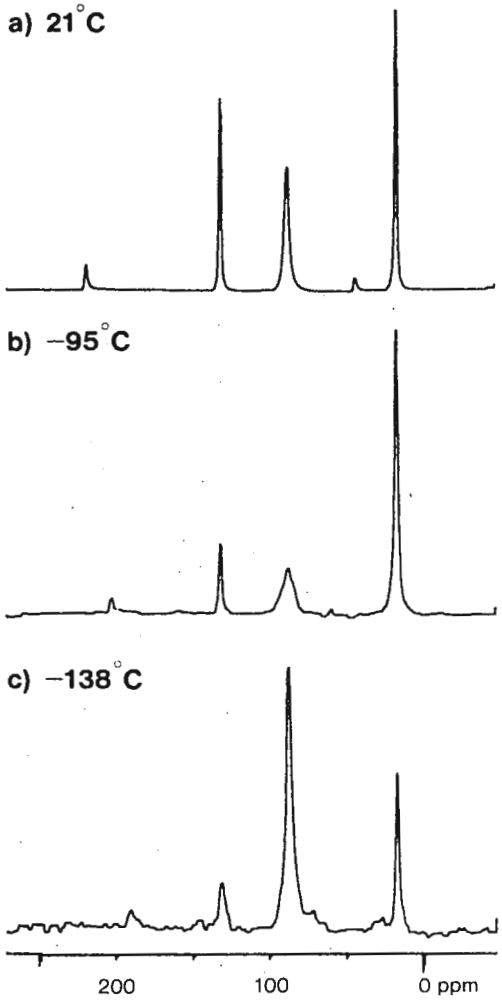
All Newsletter Correspondence
Should be Addressed to:

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

AUTHOR INDEX ----- TAMU NMR NEWSLETTER NO. 307, APRIL 1984

Abraham, R.J. 25
Barcza, S. 3
Bardet, M. 19
Barfield, M. 47
Belton, P.S. 5
de Bie, M.J.A. 33
Bradbury, E.M. 49
Buchanan, G.W. 7
Butler, K.W. 42
Carr, T.M. 11
Cox, I.J. 5
DeLuca, H.F. 48
Deslauriers, R. 42
Di Cataldo, S.N. 3
Edlund, U. 13
Foray, M.F. 19
Fraser, R.R. 10
Freeman, R. 27
Geoffrion, Y. 42
Gonzalez-Mendez, R. . . . 17
Hajek, M. 15
Harris, R.K. 5
Hase, T. 21
van Haverbeke, Y. 39
Hawkins, B.L. 29
James, T.L. 17
Kolpak, M.X. 3
La Mar, G.N. 49
van Leest, P.M. 33
Levy, G.C. 46
Litt, L. 17
Loo, J. 23
MacFadden, K.O. 14
Maciel, G.E. 29
Meyers, B.L. 23
Muller, R.N. 39
Nurmi, T. 21
Pass, M.A. 42
Pihlaja, K. 21
di Rienzo, B. 39
Robert, D. 19
Rutar, V. 31
Shapiro, M.J. 3
Smith, I.C.P. 42
Smith, W.B. 45
Storm, C.B. 37
Trska, P. 15
Turner, A.H. 37
Vander Elst, L. 39
Wasylishen, R. 1
Wong, T.C. 31

Variable Temperature CP-MAS with the GX Series FT NMR Spectrometers



^{13}C (50.1 MHz) VT/MAS spectra of hexamethylbenzene. a) and c) ^{1}H-^{13}C cross polarization. b) Bloch decay. The peak at ~ 90ppm is due to the Delrin rotor.

JEOL

235 Birchwood Ave., Cranford, NJ 07016
(201) 272-8820

DEPARTMENT OF CHEMISTRY
TELEPHONE 902-424-3305

DALHOUSIE UNIVERSITY
HALIFAX, CANADA
B3H 4J3

February 7, 1984

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

Dear Barry:

We have recently measured ^{33}S chemical shifts for a number of relatively simple compounds, eg. SF_6, SO_2, CH_3SH, H_2S and OCS. The nmr measurements have permitted us to propose an absolute sulfur shielding scale based on the ^{33}S nuclear spin-rotation constant of OCS (1). Using this spin-rotation constant, 870 ± 50 Hz, and the procedure of Flygare (2), that is, equation [1],

$$\sigma = \sigma^{d} \text{ (free atom)} + \left(\frac{2\Pi}{3\ mhc}\right) R_{\perp} I_{\perp} \qquad [1]$$

$$\sigma(OC^{33}S) = 842 \pm 12 \text{ ppm.}$$

The results of our measurements and calculations are summarized in figure 1. Few theoretical calculations of ^{33}S shielding constants have been reported, the most recent on H_2S predict σ = 735 ppm (3) which is in good agreement with our experimental value of 752 ppm. Our experimental results for SO_2 extend the ^{33}S chemical shift scale by more than 300 ppm.

Best wishes from Canada's ocean playground.

Yours sincerely,

Rod Wasylishen

Rod Wasylishen

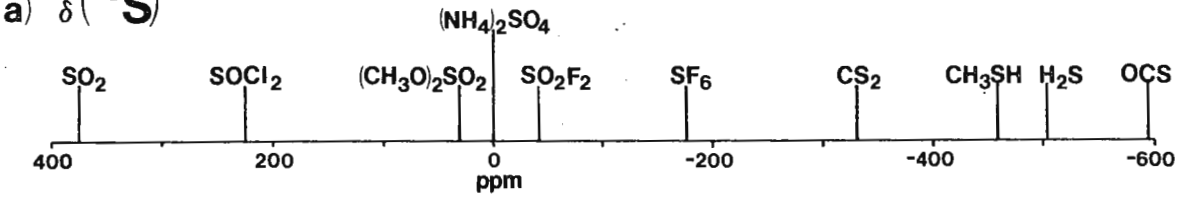
RW/djc

(1)J. Reinartz, A. Dymanus. Chem. Phys. Lett. 24 346 (1974).

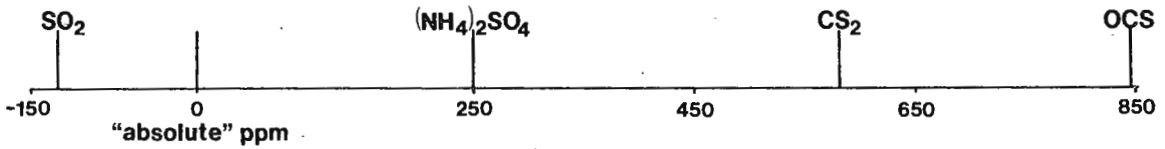
(2)W.H. Flygare, Chem. Rev., 74 353 (1974).

(3)J. Ridard, B. Levy, and P. Millie. Mol. Phys. 36 1025 (1978).

a) $\delta(^{33}S)$



b) $\sigma(^{33}S)$



c) $\delta(^{77}Se)$

SANDOZ, INC.

SANDOZ

PHARMACEUTICAL DIVISION
RESEARCH & DEVELOPMENT

EAST HANOVER, N. J. 07936

TELEPHONES
201 - 388 - 7500
212 - 349 - 1212
TWX: 710 - 986 - 8208

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

Febuary 29, 1984.

Dear Barry,

THE SANDOZ, INC. STRUCTURE-CMR RETRIEVAL SYSTEM AT WORK.

At this point about 1000 hand picked compounds are in the database, and we would like to summarize its workings.

The compounds were selected for their value in meeting current and future needs, and for covering broad structural types. Such a collection is equivalent to a higher number of automatically or randomly taken structures.

The configuration of the database was described: S. Barcza, TAMUN 291, p13, Dec. 1982. Briefly: The Maccs program is used to store structures and data organized as a conceptual matrix of compounds x datatypes. The compounds are (sub)structure searchable, and the data are range and text searchable. The SEMA atom numbering generated by the program is used to label the assigned chemical shifts. References, when available are stored and are also searchable.

The main purpose of this letter is to show that the system works well, and to provide illustrations of some search hit counts and times.

The accompanying table shows typical examples of how the database is searched. First one isolates the compounds having cmr shifts. After this narrowing all searches are quite fast. One major type of search is for a combination of chemical shifts. Each shift range is searched on the previous hitlist, amounting to an intersection. A second search type isolated all compounds with references and these were searched by author, year range, journal or combinations of these (can be consecutive or simultaneous). Finally, one of the most important searches, a search for all compounds having a certain substructure, can be followed by finding data on these.

After the search one takes the hitlist of the final desired compounds into the Margen report generator program, and plots out reports showing structure, atom numbering, chemical shifts and references, etc. (Already shown in previous Newsletter).

Of course, an interactive session would have the added typing time of the user, and all the freedom to make on-the-spot decisions.

We conclude that this database is well worth the work of feeding it.

S. Barcza, S. N. DiCataldo, M. X. Kolpak, M. J. Shapiro

Sandor Sue DiCataldo M. X. Kolpak MJShapiro

ACTION, SEARCH (* all times are in seconds)	NO OF HITS	TIME * SHARED	TIME ALONE
Initialization		27	9
Compounds in database	24114		
Search for all compounds having cmr shifts, store file subsequent searches are done on this hitlist or subsets thereof	939	142	41
Search these for having peaks 90-95 ppm	47	80	26
" " " " 158-180 ppm	40	9	5
" " " " 40-45 "	6	5	<3
File of hitlist was written in each case (included in time)			
Show atom number-shift pairs for these (about 100 lines displayed)		27	9
Find all cmr compounds having Reference	553	24	14
Search these for author Jackman (sorry, no offence, more later).	0	16	8
Search for author Wenkert	13	16	7
" " all Ref years 79-85	283	20	11
" " journal JACSAT	14	9	8
" these for years 79-84 (intersection)	4	~5	~3
Simult search all 553 Ref: JACSAT & years 79-84	4	15	7
Substructure search the 553 hits with query Indole	18	30	9
Intersecting file of these with file Wenkert	3	<3	<3
Entire process was run as command procedure, included writing files on most hitlists, capturing the entire session, including who is logged in (about 20 live users + 10 "phantoms" sharing) at beginning and end:			
Wall clock time		488	180
CPU time		88	85
I-O time		117	81

PERFORMANCE OF TYPICAL SEARCHES FOR CMR SHIFTS, REFERENCES AND (SUB)STRUCTURES.

University of East Anglia

Professor R.K. Harris

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

Telephone Norwich (0603) 56161
Telegrams UEANOR NORWICH

2nd March 1984

Dear Barry,

Taken for a RIDE - Sulphur-33 NMR

For the last two and a half years we have been exploring the potential and the limitations of solution-state ^{33}S NMR, using Bruker CXP 200 and CXP 300 spectrometers. Sulphur-33 is, on the face of it, a rather poor nucleus for magnetic resonance. It has a low natural abundance (0.76%), a low magnetogyric ratio (2.055×10^7 rad T^{-1} s^{-1}) and a moderate quadrupole moment (-5.5×10^{-30} m^2). Signals are frequently broad and weak, so spectrometer "dead-time" is often a severe problem. We have had some success in minimising the effects of dead-time by using a pulse sequence (an extension of ones already in the literature), suggested to us by Paul Ellis. This pulse sequence is of the form:

90°_x-FID-T_d-90°_{-x}-FID-T_d-180°_x-τ-90°_{-x}-FID-T_d-180°_x-τ-90°_x-FID-T_d-

where alternate FID's are added and subtracted to memory. We call this sequence RIDE (RIng Down Elimination). Figure 1 shows an example of its effectiveness.

We are now able to see acceptable signals from neat liquids in a single pulse, as shown in Figure 2. We have also observed what we believe to be the first (S,H) coupling constant (see Figure 3).

We hope this contribution satisfies TAMUNMR requirements for another year.

Best wishes

Robin Jane PSBelton

R.K. HARRIS I.J. COX P.S. BELTON

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

RKH/KP

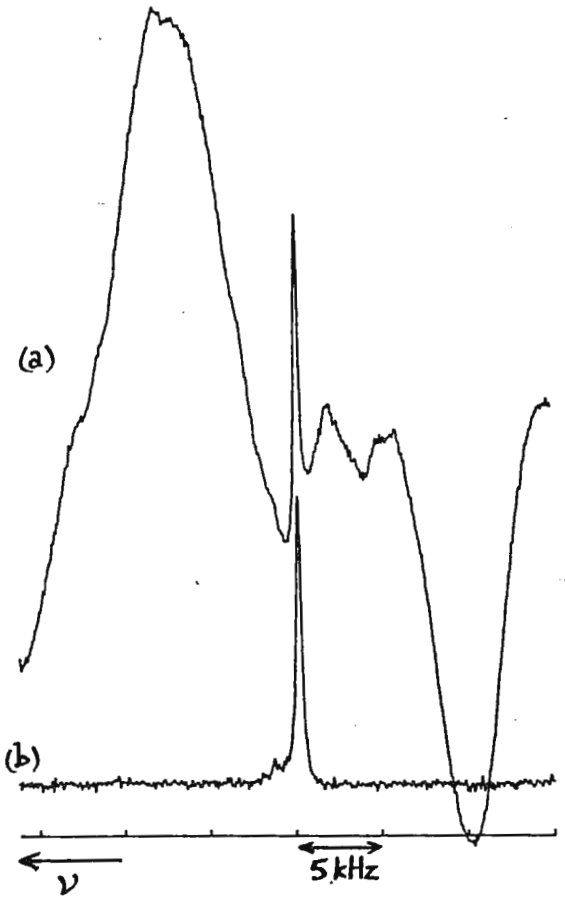


FIGURE 1: ^{33}S SPECTRUM of THIOPHENE
(a) without RIDE
(b) with RIDE

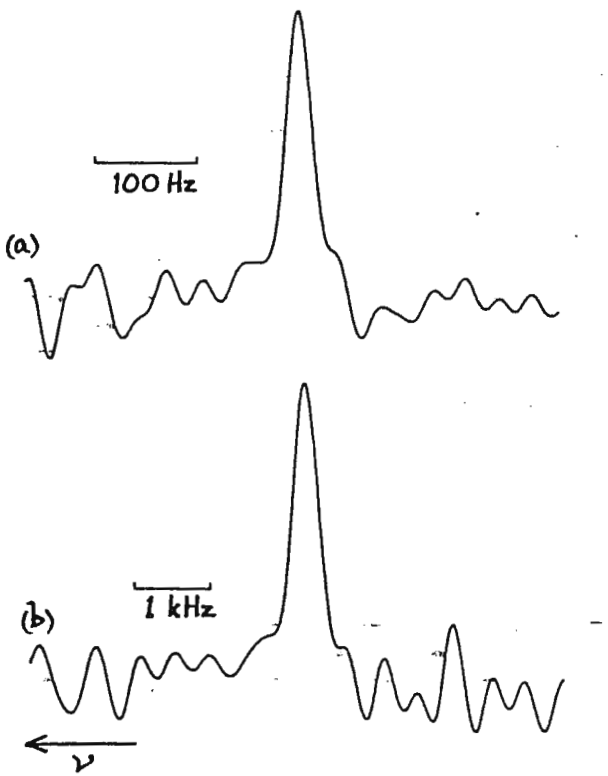


FIGURE 2: SINGLE-PULSE ^{33}S SPECTRA
(a) Sulpholane (b) carbon disulphide

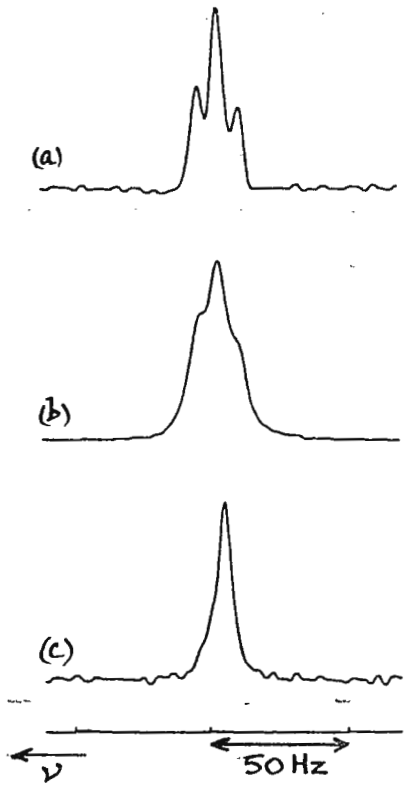


FIGURE 3: ^{33}S SPECTRA
of BUTADIENE SULPHONE
(a) coupled, resolution-enhanced
(b) coupled
(c) decoupled.

Carleton University
Ottawa, Canada K1S 5B6

March 1, 1984.

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

"^{15}N Spectra of N-Methylnucleoside cis-Platinum Complexes"

Methylnucleosides are important materials in the study of mutagenesis. Considerable literature exists on the NMR characterization of complexes of cis-platinum with "normal" naturally occurring nucleosides (1), but little is known regarding N-CH_3 and O-CH_3 nucleoside analogs.

Gene Florio in my lab has recently prepared and characterized a number of the title complexes. The platinum binding site can be determined nicely by n.O.e. suppressed ^{15}N spectra, reminiscent of mercuration phenomena (2). The platinated nitrogen shows coupling to the 33.8% abundant ^{195}Pt, and a concommitant reduction in centre band intensity.

Shift data for the symmetrical bidentate cis-Pt complex with 1-methylguanosine are as follows (δ_N relative to NH_3 at 0): NH_3, -37.7; NH_2, 82.9; N-1, 147.7; N-3, 161.4; N-9, 173.3 and N-7 (Platinated) at 144.2. The N-7 shift is ca. 100 ppm upfield from N-7 of the free nucleoside!

Sincerely,

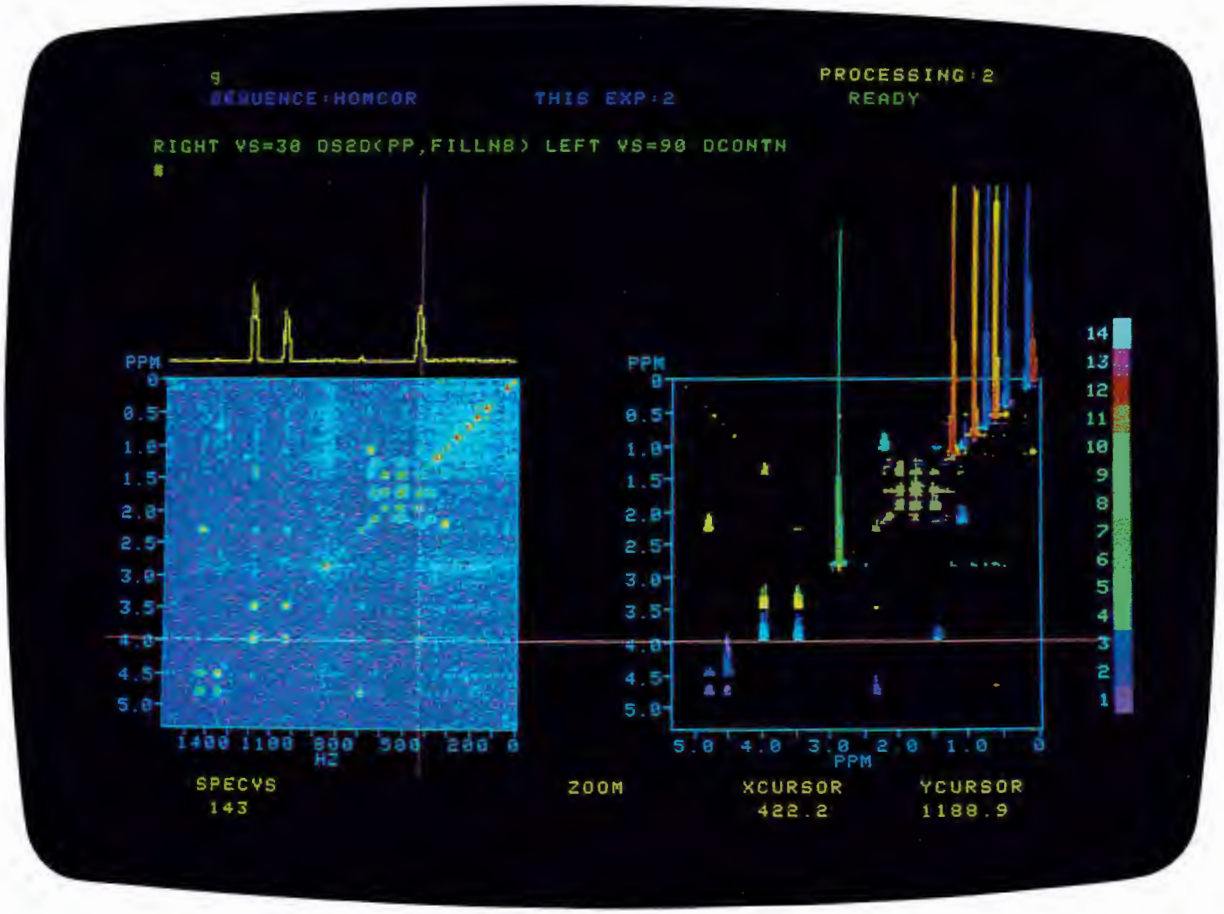
G.W. Buchanan,
Professor of Chemistry.

References: (1) Roberts et. al. Biochem. 21 4920 (1982).

(2) Buchanan et al. Can. J. Chem. 60 787 (1982).
ibid 61 2445 (1983).

mcs

Varian's new XL Series Data System is so advanced...



You'll have to see it to believe it!

Here's what the experts are saying:

Dr. Byron Arison, Merck & Co.
"You can select and display individual slices with the cursor, so it's no longer necessary to plot every contour spectrum... the whole system is overwhelming."

Dr. George Slomp, The Upjohn Co.
"The use of color in the stacked displays is more than just artistic. It helps correlate peaks in the individual areas."

Dr. Jake Stothers, University of Western Ontario
"The number of colors gives you greater dynamic range for contour plots."

Dr. Robert Santini, Purdue University
"It does Fourier transforms so fast that data manipulation is no longer a barrier to the routine use of 2-D... I want one."

Dr. Josef Dadok, Carnegie-Mellon University
"Finally, a company that makes NMR instruments has incorporated the advances that computers have made over the past decade."

Dr. Gheorghe Mateescu, Case Western Reserve
"What amazes me is the speed of the FT. This is essential for opening up new possibilities for research in two-dimensional NMR."

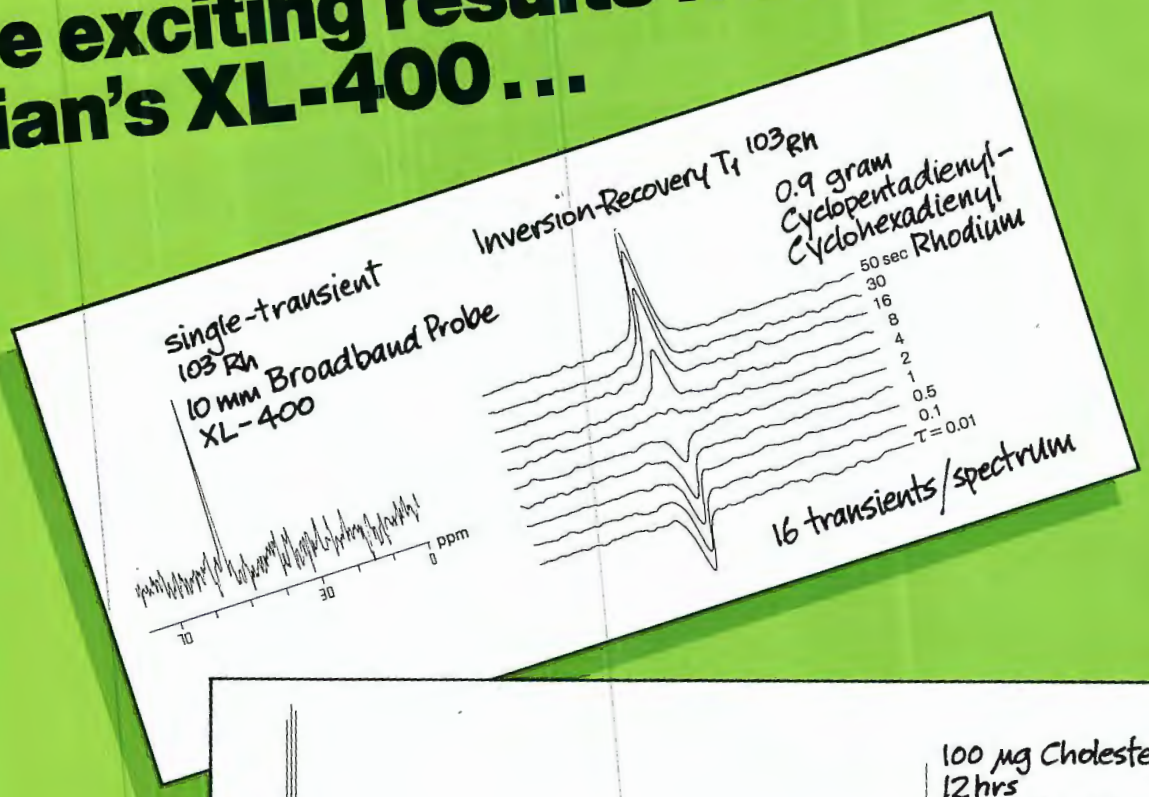
Now showing in an application lab near you.
Call today for a demonstration or literature at the offices listed below. Or write Varian NMR, Varian Associates, 611 Hansen Way, Palo Alto, CA 94303.

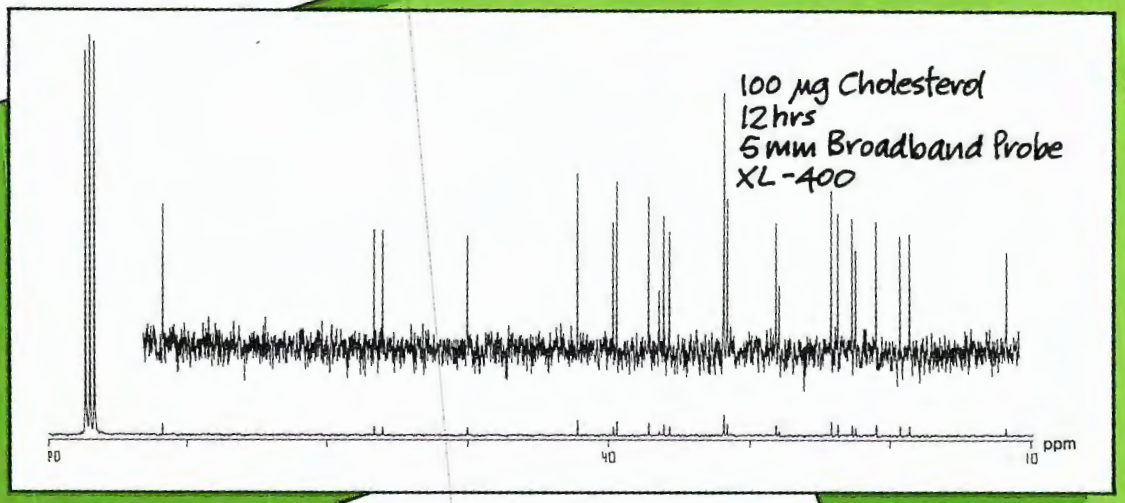
varian

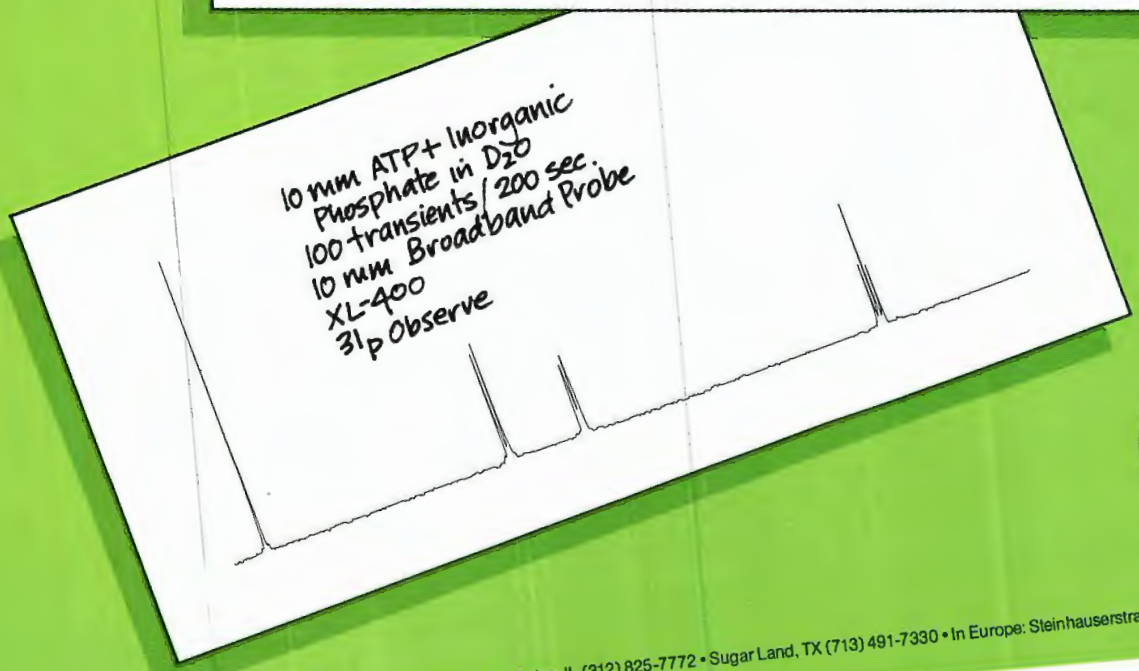
Another advance in NMR ...from Varian

For assistance contact: • Florham Park, NJ (201) 822-3700 • Park Ridge, IL (312) 825-7772 • Sugar Land, TX (713) 491-7330
In Europe: Steinhauserstrasse, CH-6300 Zug, Switzerland.

More exciting results from Varian's XL-400...







Write or call today to receive new literature on the ADVANCE NMR Data System and the XL-400 Spectrometer.

varian

For assistance contact: • Florham Park, NJ (201) 822-3700 • Park Ridge, IL (312) 825-7772 • Sugar Land, TX (713) 491-7330 • In Europe: Steinhauserstrasse, CH-6300 Zug, Switzerland.

UNIVERSITÉ D'OTTAWA UNIVERSITY OF OTTAWA
OTTAWA ONTARIO
CANADA

March 1, 1984

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

INTERIM REPORT - WEAK NITROGEN ACIDS

Dear Barry:

My excuse for being late can only be used on rare occasions but is currently valid as we are still in the process of testing and familiarizing ourselves with a new XL-300.

For those interested in performance checks, I can perhaps briefly summarize its sensitivity capabilities as meeting or exceeding specs by 10, 20 and 40% on ^{13}C (10 mm BB) ^{13}C (5 mm BB) and ^{1}H (5 mm high frequency) probes. All of the probes gave resolution performances far in excess of specs, always 50% of quoted line-width or better.

The magnet dewar system also performs very well having a N_2 loss of 14 ℓ per week (spec. at 20, without refrigerator) and a He loss of less than 2 ℓ per week (spec. at 2.3) which is obviously economically very important.

As a result of time spent in this installation, our productivity has been less than normal. Nevertheless, we have just completed another series of pKa measurements in tetrahydrofuran using ^{13}C with our FT-80. We have been able to synthesize amines having pKa's ranging from 30 to 40 which now allows us to measure pKa's of weak acids between the limits 27-43 units.

If anyone wishes a preprint of this work it should be available in a few weeks.

Best regards,

Bob.

RRF:rk

Robert R. Fraser

Département de chimie
Faculté des sciences et de génie

365 Nicholas
K1N 9B4

Department of Chemistry
Faculty of Science and Engineering

307-11

DOW CORNING

March 6, 1984

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

Dear Professor Shapiro:

Because of the number and extent of the various research projects conducted here at Dow Corning, there is always a demand for instrument time on our Varian XL-200 NMR spectrometer. Accordingly, anything that enhances our ability to process samples is a valuable asset.

Recently, we have taken delivery of one of the new chip-capacitor 16mm broadband probes that Varian has developed. In comparison to the 125:1 S/N obtained on the ^{13}C ASTM standard (60% C_6D_6 - 40% Dioxane) with our old 10mm broadband probe, we have enjoyed vastly increased sensitivity with our new probe. In practice, this has resulted in a factor of ca. 3-4 decrease in experimental time to obtain a useable NMR spectrum for our routine ^{13}C and ^{29}Si NMR work, which has pleased us greatly.

We have noted your "colorful" reminder of "impending doom" and hope this will return us to your good graces.

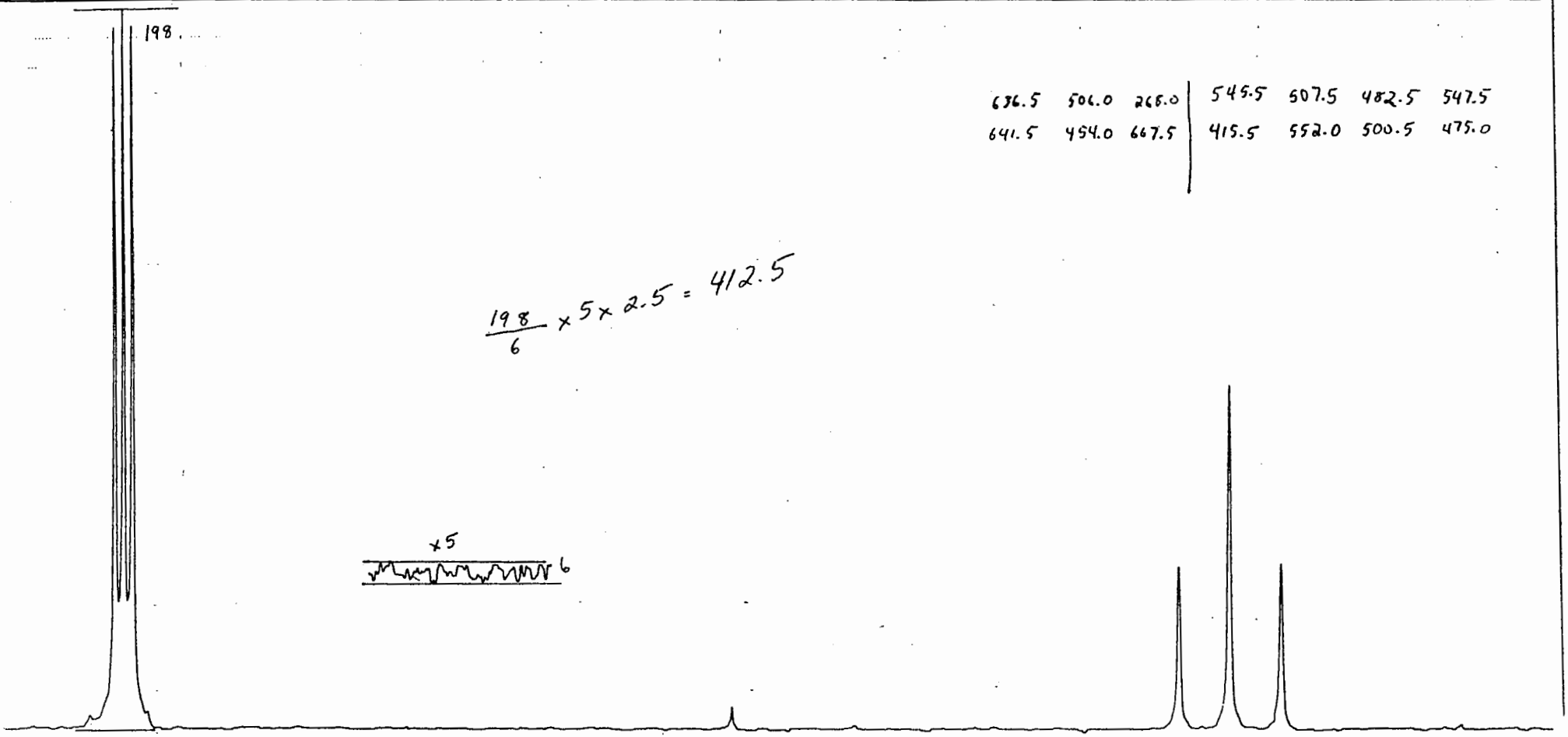
Sincerely yours,

Thomas M. Carr

Thomas M. Carr
Analytical Research

TMC:eld

Attachment



636.5	506.0	268.0	545.5	507.5	482.5	547.5
641.5	454.0	667.5	415.5	552.0	500.5	475.0

$\frac{198}{6} \times 5 \times 2.5 = 412.5$

UMEÅ UNIVERSITET
Avdelningen för organisk kemi

Telefon
090 - 16 50 00

UNIVERSITY OF UMEÅ
Department of Organic Chemistry

Telephone
46 - 90 - 16 50 00

March 6 1984

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

Simplified NMR Parameters in Structure-Activity Studies; Multipurpose Solid-Liquid Instrument, MSL-100.

Dear Barry,

The possibility that ^{13}C n.m.r. chemical shifts may correlate with the carcinogenic activity of alternant hydrocarbons is certainly not any new idea. But due to the fundamental difficulty of making spectral assignments, such projects are normally postponed until one has more money/ more hard-working students or postdocs to synthesize the labeled compounds.

A lazy man's approach to this problem would be to find regularities in simplified n.m.r. parameters. In this way we reduce the collection of data to the much simpler task of getting a ^{13}C n.m.r. spectrum, that separates between protonated and non-protonated carbons. Thereafter each compound is described by eight variables, four for each type of carbon, such as 1. δ;chemical shift mean 2. s^2; variance of signal distribution 3. μ_3; third moment or degree of skewness. 4. μ_4; fourth moment or kurtosis or degree of "peakedness".

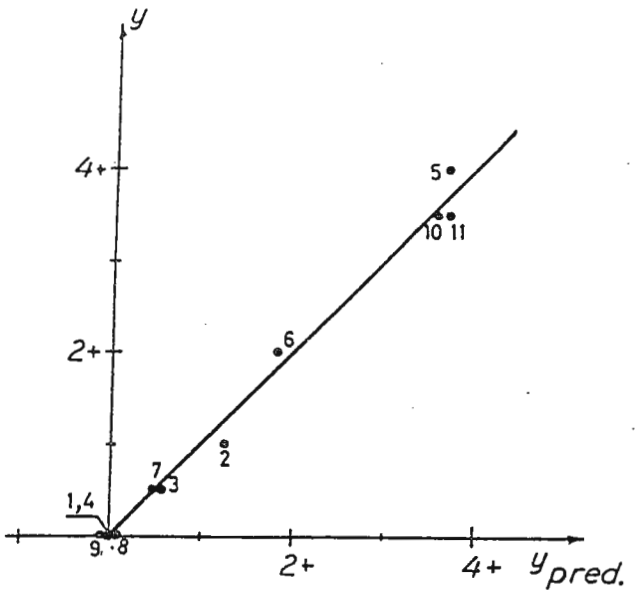
In a multivariate data analysis (partial least squares data analysis), we recently used such a matrix for eleven bay-region PAH's.[1] The first plot shows the correlation between the biological activities and the activity predictions using traditional PAH indicies. The second scheme illustrates the same plot but using the reduced n.m.r. variables as input data. Obviously, the reduced n.m.r. variables contain information of similar predictive ability as the more well-known descriptors (Pullman indicies, ΔE, superdelocalizability etc.).

Thanks to our physical chemists, we will get a new supercon to our n.m.r. lab this summer. A Bruker multipurpose solid-liquid machine (MSL 100) mainly designed for diffusion and CP/MAS studies will complement our high-resolution instrument, WM-250.

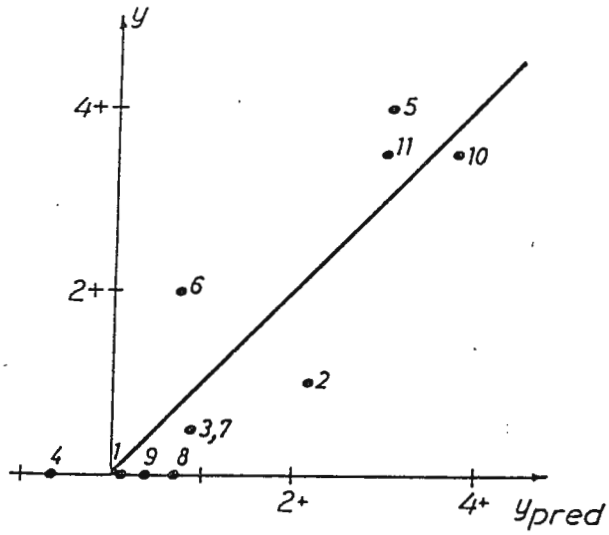
Best regards

Ulf Edlund

1. B. Norden, U. Edlund, D. Johnels, and S. Wold, Quant. Struct.-Act. Relat. **2**, 73 (1983)



Scheme 1



Scheme 2

POSITION AVAILABLE

W. R. Grace and Co. is now accepting applications for a Ph.D. level NMR Spectroscopist. The focus of the position is analysis of liquid state spectra of organic compounds and bioproducts. Familiarity with modern FT-NMR techniques, including decoupling sequences and procedures for analysis by two-dimensional NMR experiments is essential. A thorough knowledge of organic reactions and chemistry is also important. It is anticipated that the main nuclei of interest will include ^{1}H, ^{13}C, and ^{31}P as well as some studies involving ^{29}Si. Considerable contact with researchers in various areas of chemistry should be expected, and good communication skills will be an advantage.

W. R. Grace, Washington Research Center, is located in Columbia, Maryland, about half way between Baltimore and Washington, D.C. Columbia is a community which currently has a population near 100,000.

Interested parties should send resumes to: Dr. Kenneth O. MacFadden, Director; Analytical Research Department; 7379 Route 32; Columbia, Maryland 21044.

VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ
Laboratoř syntetických paliv
166 28 PRAHA 6 - DEJVICE, SUCHBÁTAROVA 5
Telefon 332/4168, 32 15 04
Dálnopis 122 744 - VSCH/C
Dr. Milan Hájek

Praha 5.3.1984

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

Title: ^{19}F Relaxation Times

Dear Professor Shapiro,

In TAMU NMR Newsletter No. 301(Lambert,Simpson) and No. 303(Sweeting) we have read the interesting discussion on ^{19}F relaxation times. In our laboratory we have also measured ^{19}F relaxation times of different fluorinated compounds. First,we measured T_1 of the CF_3 group of hexafluoroacetone(HFA) and its adducts with alcohols and some petrochemical and carbochemical products. We are using HFA to determine the content of -OH groups in fossil fuels samples and because the number of pulses used for the quantitative measurement varies in the range from 10 to 10^3, it was very interesting to know the values of T_1 for the optimisation of the NMR experiments (see Table 1).
The second group of relaxation times which we have measured were T_1 of simple fluorinated 2-4 carbon atoms containing molecules. Preliminary measurements of the temperature dependence of relaxation times T_1 of CCl_3-$CFCl$-CF_2Cl (I), CCl_3-CF_2-$CFCl_2$ (II) and CF_3-$CFCl$-CF_2Cl (III) (Table 2) show the changes indicating the important contribution of spin-rotational relaxation for all fluorine atoms containing groups. We hope to be able to finish these temperature experiments at different frequencies to exclude the possibility of the significant contribution to the relaxation rates via chemical shift anisotropy relaxation.

Sincerely yours

Milan Hájek
Petr Trška
Prague Institute of Chem. Technol.
Czechoslovakia

Table 1

The relaxation times of CF_3 groups of :a) free HFA; b)adduct HFA-phenol; c) adduct HFA-propanol; d) adduct HFA-H_2O; e) CF_3group of internal standard CF_3-CCl_2Br; f) adduct HFA-brown coals phenolic fraction. Temperature of measurement 25°C, $CDCl_3$- ethylacetate solution.

CF_3 signal in :	a	b	c	d	e	f
T_1(s)	2.3 (4.7)+	2.7 (3.8)+	2.6 (4.7)+	3.0 (5.0)+	3.0 (7.0)+	2.2-3.1

+degased samples

Table 2

Temperature dependence of T_1relaxation times (^{19}F) for compounds (I)-(III). The compounds(I) and (II) were measured in DMSO-d_6, the compound (III) in $C_6D_5CD_3$ (degased samples).

compound	t °C	T_1(s) $-CF_3$	$-CF_2Cl$	$-CFCl_2$	$-CF_2-$	-CFCl-
(I)	25		8.1			14.4
	50		11.6			16.3
	75		5.0			5.4
(II)	25			13.5	8.6	
	50			14.7	12.8	
	75			5.4	5.1	
(III)	25	6.9	7.3			12.0
	50	5.4	5.4			10.0

UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

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

SANTA BARBARA • SANTA CRUZ

SCHOOL OF PHARMACY
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

March 7, 1984

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

Re: **A 5.6T, Horizontal Bore Magnet System Used to Study Hypoxic Hypoxia in Rat Brain**

Dear Barry:

We finally got our 5.6 Tesla, horizontal bore magnet (from Nalorac, with 8.4 cm useful bore after shims) delivered in December, so we have been successfully running in vivo NMR experiments on it since the first of the year. The spectrometer was built here by Joe Murphy-Boesch, Mike Moseley and Greg Young using emitter-controlled logic circuitry designed by Joe. Performance has been all we expected, and the advantages of the horizontal bore for animal experiments was amply experienced after our earlier work using a vertical bore magnet (e.g., 1).

One example of studies in progress is an examination of hypoxic hypoxia (as redundant as it sounds, that's the medical term) in the brain. The figure shows the results of an experiment (repeated thrice) on adult rat brain in vivo under controlled hypoxic conditions. We can see the phosphocreatine peak decrease before the ATP level diminishes. This is in accord with the observation of Norwood et al. (2) on hypoxia/ischemia in perfused rat brain, but contrary to earlier reports that ATP and PCr decreased similtaneously in the adult brain. We note that most of the few NMR studies reported on brain hypoxia have not listed the O_2 level and none have varied the O_2 level. In addition, it would appear that published studies reporting hypoxia entail ischemic conditions as well, as in the top series of spectra in the figure. The lower set of spectra in the figure were obtained under conditions of hypoxia without ischemia since the blood pressure was maintained by administration of epinephrine; recovery from hypoxia is also shown. Not evident in the earlier studies is the large increase in sugar-P peak with hypoxia (see Fig.). The experiment utilized 1% isofluorane as anesthetic. At a level of 2% isofluorane (same pO_2), a rat required more than twice as long for hypoxia to be manifest. Careful physiological monitoring and control are necessary. Anesthetic $/O_2/N_2$ levels are metered and administered to the animal with mechanical ventilation via tracheal intubation. Fluids are administered through catheters into the femoral artery and vein. The arterial line is also connected to a pressure transducer which generates oscilloscope and recorder tracings, as well as digital display, of the blood pressure and heart rate. Blood gases are also analyzed. The animal probe has a water jacket for temperature control.

Sincerely,

Tom

Thomas L. James
Professor of Chemistry
Pharmaceutical Chemistry
and Radiology

Ricardo R. Gonzalez-Mendez
Post-doctoral Associate

Lawrence Litt
Assistant Professor
of Anesthesia

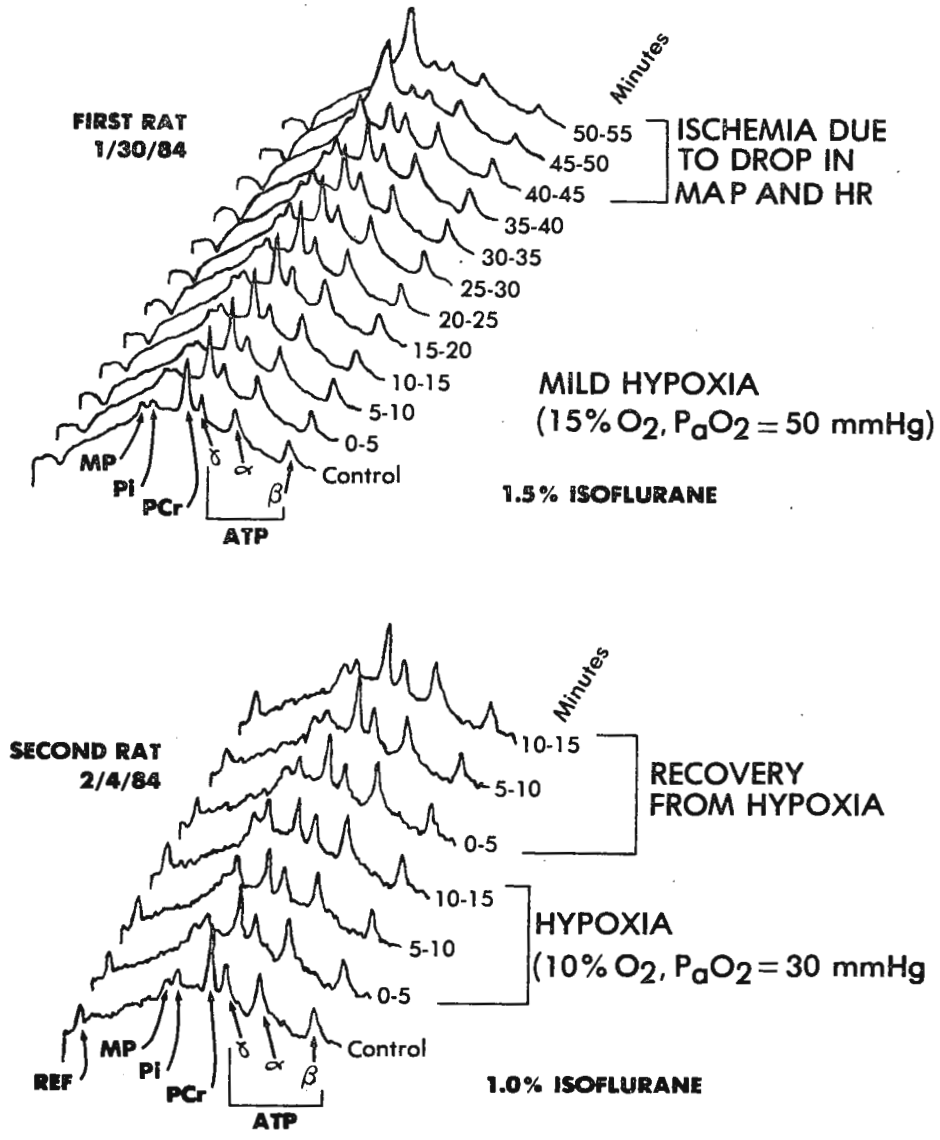


Figure Caption: Top: Hypoxia and ischemia. Bottom: Hypoxia without ischemia. 97.2 MHz ^{31}P NMR spectra of rat brain in vivo. Each spectrum is the result of 128 transients obtained with a 2.1 s repetition time. Data massage consisted solely of 30 Hz exponential multiplication. The probe contained a balanced matching circuit which yields better S/N with high dielectric samples (3).

1. Koretsky, A.P., Wang, S., Murphy-Boesch, J., Klein, M.P., James, T.L. and Weiner, M.W., Proc. Nat. Acad. Sci. USA 80, 7491 (1983).

2. Norwood, W.I., Ingwall, J.S. Norwood, C.R. and Fossel, E.T., Am. J. Physiol. 244, C205 (1983).

3. Murphy-Boesch, J. and Koretsky, A.P., J. Mag. Reson. 54, 526 (1983).

307-19

RÉPUBLIQUE FRANÇAISE

COMMISSARIAT A L'ÉNERGIE ATOMIQUE

CENTRE D'ÉTUDES NUCLÉAIRES DE GRENOBLE

AVENUE DES MARTYRS – 38 - GRENOBLE

ADRESSER LA CORRESPONDANCE
85 X
38041 GRENOBLE CEDEX
TÉLEX : ENERGAT GRENO N° 320.323

TÉL. (76) 97-41-11

Dr. D. ROBERT.
C. E. N. G.
DRF - Laboratoires de Chimie
85 X
38041 GRENOBLE Cédex France

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

RÉFÉRENCE A RAPPELER : G/ DRF/CH/84-113/mjc

VOTRE RÉF.

VOTRE LETTRE DU

GRENOBLE, LE 9 mars 1984

Dear Professor Shapiro,

USE OF THE DEPT PULSE SEQUENCE TO FACILITATE THE ^{13}C NMR STRUCTURAL ANALYSIS OF LIGNINS

By editing subspectra for CH, CH_2 and CH_3 signals, the DEPT pulse sequence appears to be a suitable method to facilitate the structural assignments of some signals in the ^{13}C NMR spectra of such polymeric natural products as Lignins. The chemical structure of these polyphenols, which are with cellulose and hemicelluloses, the main constituants of wood, is still not clearly elucidated (1). The DEPT experiments were generated using the Bruker WM.200 spectrometer's microprogramming facilities, with the pulse sequence for a J coupled heteronuclear ^{13}C-^{1}H system (2).

D2 = 1/2J has been selected for an average value of $^{1}J(^{13}C\text{-}^{1}H) \sim$ 150 Hz ; the ^{1}H pulse length ($\Theta = \pi/2$) which gives the best nulling for the $-CH_2-$ signals corresponds to 33 µsec ± 2. In the case of a milled wood lignin (MWL) extracted from a hardwood species "Betula verucosa" (Birch) the edited CH, CH_2 and CH_3 subspectra are shown respectively on Fig. Ia), b), and c). Spectrum d) is the total spectrum (^{1}H decoupled), where about thirty signals can be assigned (3).

In addition with the unambiguous assignment of the multiplicity of the different signals, it clearly shows, among others, the presence of two types of representative structures :

- the cinnamaldehyde structure (A), the vinylic carbons of which, C-α and C-β appears respectively at 152.6 and 129 ppm.
- the pinoresinol structure (B) which is demonstrated by the presence of the signal at 71 ppm on subspectrum b) corresponding to the C-γ carbon in this structure.

Up to now, these signals (cf. spectrum d) were totally or partially overlaped by other signals. One can notice that the large enhancement of the signal intensity due to the polarization transfer makes possible the observation of very small signal, (C-β in A), which otherwise could not be detected.

Sincerely yours,

D. ROBERT M. BARDET M.F. FORAY

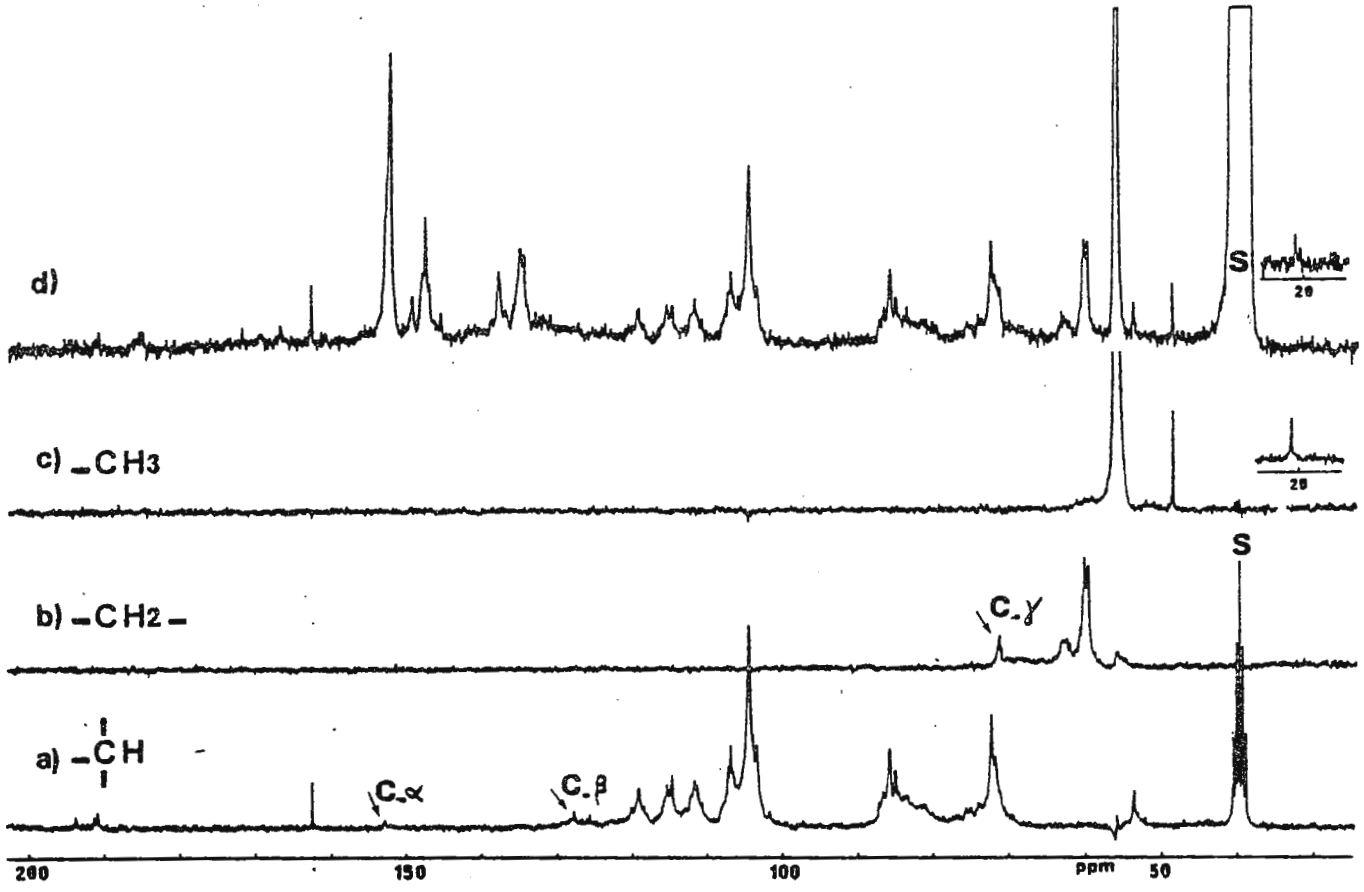
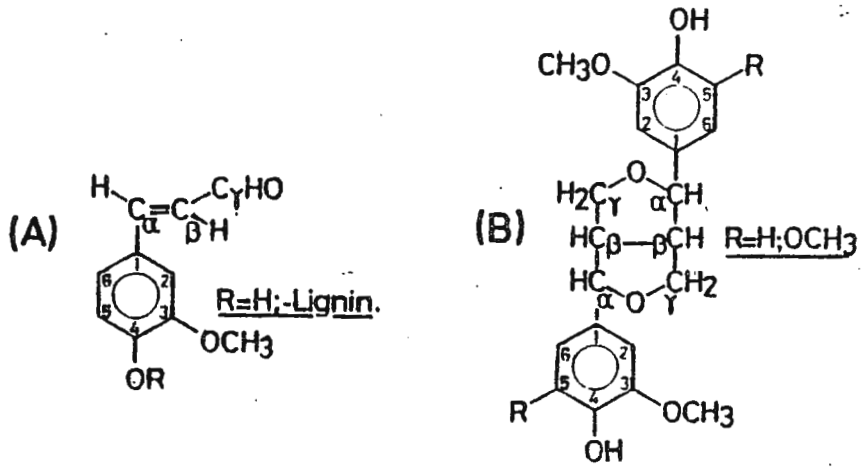


Fig.I a) b) and c) DEPT Edited ^{13}C spectra of lignin from Birch (S = $DMSOd_6$; Ref:TMS ; 50°C) at 50.3 MHz with 4000 transients at $\Theta = \pi/4$ and $3\pi/4$ and 8000 transients at $\Theta = \pi/2$; spectrum d) total decoupled spectrum with 10000 transients.



1 K.V. Sarkanen and C.H. Ludwig, "Lignins, Occurrence, Formation, Structure and Reactions, Wiley Interscience (1971).
2 M.R. Bendall, D.T. Pegg, D.M. Doddrell and W.E. Hull, DEPT-Bruker Information Bulletin, Bruker Analytische messtechnik, Karlsruhe (1982).
3) H.H. Nimz, D. Robert, O. Faix and M. Nemr, Holzforschung 35, 16 (1981).

307-21

KEMIAN JA BIOKEMIAN LAITOS
TURUN YLIOPISTO
20500 TURKU 50

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
UNIVERSITY OF TURKU
SF-20500 TURKU 50 FINLAND

Turku, March 12, 1984

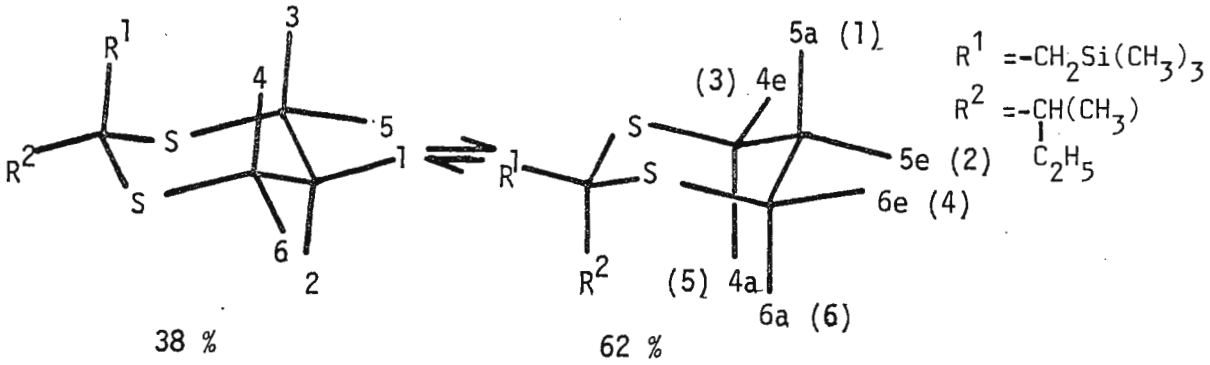
Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Dear Professor Shapiro,

2D Approach May Help to Analyze Even a Relatively Simple ^1H NMR Spectrum: The case of 2-s-Butyl-2-trimethylsilylmethyl-1,3-dithiane

When determining the ring conformations of some 2-alkyl-2-trimethylsilylmethyl-1,3-dithianes the ^1H NMR spectrum of the title compound was recorded in $CDCl_3$ on a Bruker WM-500. However, in contrast to the spectra of the corresponding 2-methyl and 2-ethyl derivatives which were easy to analyse at 400 (Jeol FX-400) and at 200 MHz (Jeol FX-200), respectively, it exhibits a complex looking multiplet close to 2.80 ppm which we could not solve by a simple simulation.

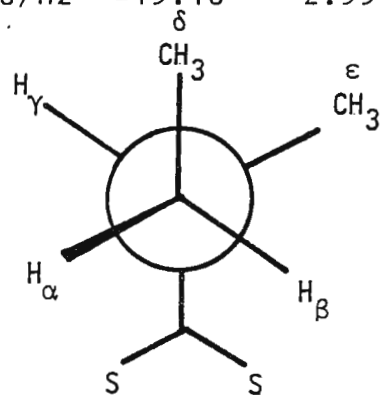
Since the s-butyl group is asymmetric one can, at least in principle, expect that eg the 4/6 axial protons do not have equal chemical shifts. Obviously the difference is small, however, since the visual inspection of the spectrum did not help much. Accidentally we used 2-s-butyl-2-trimethylsilylmethyl-1,3-dithiane also to test Varian XL-200 and its 2D software. And indeed the 2D spectrum showed that the chemical shifts of the 4/6 axial protons do differ by ca 4 Hz (ca 10 Hz at 500 MHz). Taking this into account the complete solution of the spectrum at 500 MHz was relatively easy using the LAME program and gave the following results:



	1	2	3	4	5	6
δ/ppm	1.90	1.92	2.72	2.72	2.82	2.84
	12	35≈46	13≈14	15≈16	23≈24	25≈26
J/Hz	-13.7	-14.5	3.25	9.34	7.47	3.07
	34	56				
J/Hz	0.88	0.38				

The s-butyl group cannot rotate freely even if the ring itself is a mixture of two interconverting chair forms. This can be easily seen from the ^{1}H NMR spectrum of the s-butyl group and especially from the values of $J_{gauche} = J_{\alpha\gamma}$ and $J_{trans} = J_{\beta\gamma}$.

	α	β	γ	δ	ε	
δ/ppm	2.03	1.12	1.96	0.94	1.09	
	αβ	αγ	αδ	βγ	γε	αε
J/Hz	-13.18	2.35	7.56	10.29	6.72	0.72



The methylene protons of the trimethylsilylmethyl group have almost equal chemical shifts (1.335 and 1.345 ppm) and exhibit a geminal coupling of -15.3 Hz.

Sincerely yours,

Tapio Hase
Professor
Department of Chemistry
University of Helsinki

Kalevi Pihlaja
Professor
Department of Chemistry
University of Turku

Timo Nurmi
Dr.
Department of Chemistry
University of Turku

UNIVERSITY OF CALIFORNIA, SANTA CRUZ

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

DIVISION OF NATURAL SCIENCES
THIMANN LABORATORIES

SANTA CRUZ, CALIFORNIA 95064

March 20, 1984

Professor B.L. Shapiro

Department of Chemistry

Texas A&M University

College Station, Texas 77843

Subject: Cis and Trans Vinyl Methyls in Spin Echo Spectra

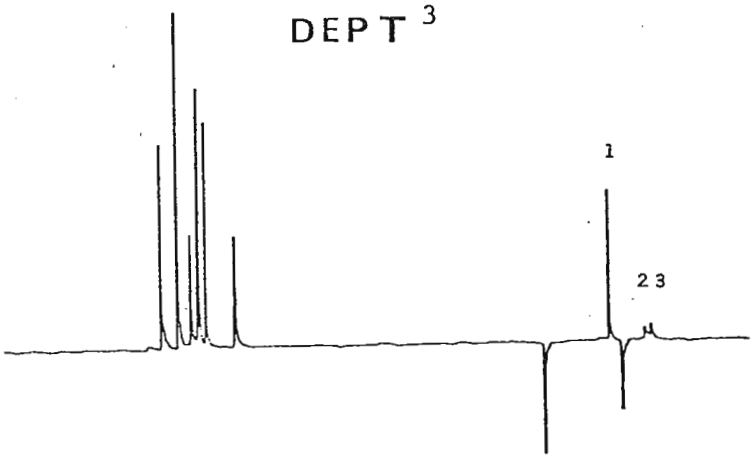
Dear Barry,

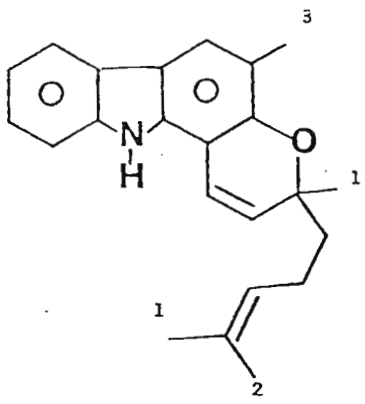
We have observed that vinyl methyls are broadened* in the DEPT[1] (Distortionless Enhancement by Polarization Transfer) pulse sequence with the variable ^{1}H pulse set to 135°. This sequence should be phased and printed before spectral editing to distinquish vinyl methyls from other quartet carbons.

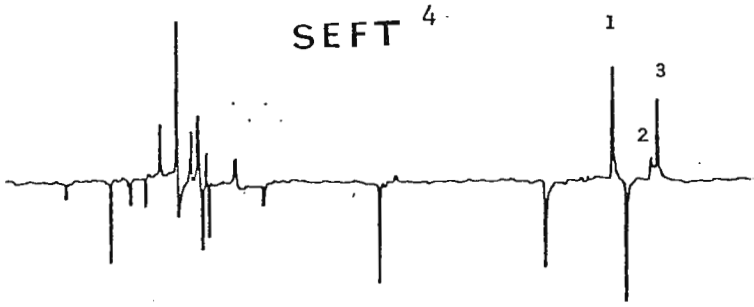
We have also observed broadening* of vinyl methyls, which have a trans proton, in modified SEFT[2] (Spin Echo Fourier Transform) spectra. Vinyl methyls which have a cis proton are observed to be sharp.

These observations may allow assignment of methyls in cases where model shift data is not available.

* or have reduced intensity







Sincerely,

Barbara L. Myers

Jim Loo

1) (a) Pegg, D.T.; Doddrell, D.M.; Bendall, M.R. *J. Chem. Phys.* *77*, 2745 (1982). (b) Doddrell, D.M.; Pegg, D.T.; Bendall, M.R. *J. Mag. Res.* *48*, 323 (1982).

2) Brown, D.W.; Nakashima, T.T.; Rabenstein, D.L. *J. Mag. Res.* *45*, 302 (1981). The modification of the SEFT sequence consists of simply turning the ^{1}H-decoupler off during the first half of the spin echo, rather than the second half.

3) Doublet and quartet carbons have been phased with positive intensity, while triplet carbons have been phased with negative intensity.

4) Doublet and quartet carbons have been phased with positive intensity, while singlet and triplet carbons have been phased with negative intensity. The compound was synthesized by Y.Kodo and V.V. Kane.

DEPARTMENT OF ORGANIC CHEMISTRY
THE ROBERT ROBINSON LABORATORIES P.O. BOX 147 LIVERPOOL L69 3BX
TEL: 051 – 709 · 6022
TELEX NO: 627095

1983
THE QUEEN'S AWARD FOR
TECHNOLOGICAL ACHIEVEMENT

The University of Liverpool

21st March 1984

RJA/AS
BLS/RRK

Dr. Bernard L. Shapiro,
Editor,
TAMU NMR Newsletter,
Texas A and M University,
Department of Chemistry,
College Station,
TEXAS

Dear Barry,

In reply to your letter requesting my periodic subscription to TAMU NMR, readers may be interested in some results on porphyrin NMR which Kevin Smith and I obtained recently.

The meso (methine) substituent chemical shifts (SCS) of a range of common functional groups have been obtained, both for the neutral porphyrin molecule and for the corresponding dications, in substituted octaethylporphyrin (OEP), etioporphyrin-I, and pyrroetioporphyrin-XV derivatives. The SCS are discussed in terms of both ring current variations and specific effects at the neighbouring beta-substituents and the meso-proton opposite the perturbing substituent, using a ring current model to quantify the former. In the neutral molecules, meso substitution in OEP (Me, NO_2, CN, CHO) causes a 10% decrease in the macrocyclic ring current, and marked anisotropic shifts at the beta-positions flanking the meso function. The meso-NH_2 group introduces a much larger decrease (ca. 35%) in the main ring current, due to conjugation of the amino group with the porphyrin π-system. In the porphyrin dications, SCS are much larger and there is some evidence of a concomitant decrease in the ring current of the adjacent pyrrole subunits. The meso-NMe_2 substituent at the γ-meso-position in pyrro-etioporphyrin-XV has only small SCS in the neutral molecule, but a large shift (similar to that of NH_2) in the dication, due to the different orientation of the substituent with respect to the porphyrin plane in each case. The meso-OH substituent in the oxophlorin from etioporphyrin-I behaves as a conjugated OH group in the dication. The anomalous position of the meso-proton opposite to the perturbing substituent is noteworthy, and this could be due to electronic (resonance) effects, or to some protonation at this position.

The proton NMR spectra of the free base porphyrins γ-meso-dimethylamino-pyrroetioporphyrin-XV (1) and the corresponding γ-diethylamino compound (2) show no temperature dependence, and are interpreted as due

RJA/AS
BLS/RRK
21st March 1984

to an essentially orthogonal conformation of the γ-NR_2 substituents. However, the corresponding dications (1A) and (2A), in $CDCl_3$/TFA solution, both give temperature dependent proton NMR spectra. Nuclear Overhauser enhancement difference spectra allow complete assignment of the spectrum of (1A), and hence the interpretation of the temperature dependence. The spectra arise from a skew conformation of the -NR_2 groups in which the barrier to rotation through the orthogonal conformation is ca. 13.6 kcal/mole, and the barrier to rotation through the planar conformation is somewhat greater than this.

This work has currently been submitted for publication and Preprints of the papers are available on request.

I trust this will reinstate my subscription to TAMU NMR.

With best wishes,

Yours sincerely,

DR. R.J. ABRAHAM

Physical Chemistry Laboratory, Oxford University

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

26 March 1984.

Dear Barry, 'VERY SOFT PULSES'

Recently we had occasion to try some experiments with very soft rectangular pulses in an attempt to obtain very high frequency selectivity. As a rule of thumb, one naturally tends to assume a Fourier transform relationship between the pulse envelope (in the time domain) and the excitation pattern (in the frequency domain) although this is known to be only an approximation. In this case the approximation breaks down in a quite serious way - where we expect an excitation spectrum with many sinc function sidelobes, we find only a monotonic fall-off in signal amplitude as a function of offset from resonance (Fig. 1a). By contrast, when the width t_p of the rectangular pulse is reduced (from 1.3 seconds to 10 milliseconds) the customary sinc function sidelobes are much in evidence (Fig. 1b).

One way to rationalize the appearance of sidelobes is to calculate magnetization trajectories for suitable resonance offsets, for example in regions where $\Delta B >> B_1$, so that the effective field makes only a small angle θ with respect to $O\bar{Z}$. For relatively short pulses a typical vector might rotate as shown in Fig. 2a, leaving finite absorption and dispersion components after the pulse. However, for pulses comparable in length to T_2^* (inverse of the inhomogeneous line width) the isochromats representing different volume elements of the sample are dispersed around a circle (Fig. 2b). Note that the spatial inhomogeneity of B_o introduces a variation of B_{eff} values and the precession angles $\gamma B_{eff} t_p$. (There are also small variations in θ but these can be neglected for the sake of simplicity). For really long pulses ($t_p >> T_2^*$) the dispersion of the different vectors is almost uniform around the circle, and only the component along B_{eff} contributes to the net detected signal. This is therefore a pure dispersion signal and falls off monotonically with offset according to $M_o \sin\theta \cos\theta$, at large offsets. This accounts for the smooth offset dependence noted in Fig. 1, and because near exact resonance there is quite severe signal cancellation (1,2), the selectivity in the frequency domain is surprisingly poor. This is a situation where Gaussian-shaped pulses afford a very important improvement in selectivity (3).

Yours sincerely,

Ray

R. Freeman

(1) D.I. Hoult, J. Magn. Reson. 26, 165 (1977); 35, 69 (1979).

(2) P. Mansfield, A.A. Maudsley, P.G. Morris and I.L. Pykett, J. Magn. Reson. 33, 261 (1979).

(3) C. Bauer, R. Freeman, T. Frenkiel, J. Keeler and A.J. Shaka, J. Magn. Reson. (in press).

Fig.1

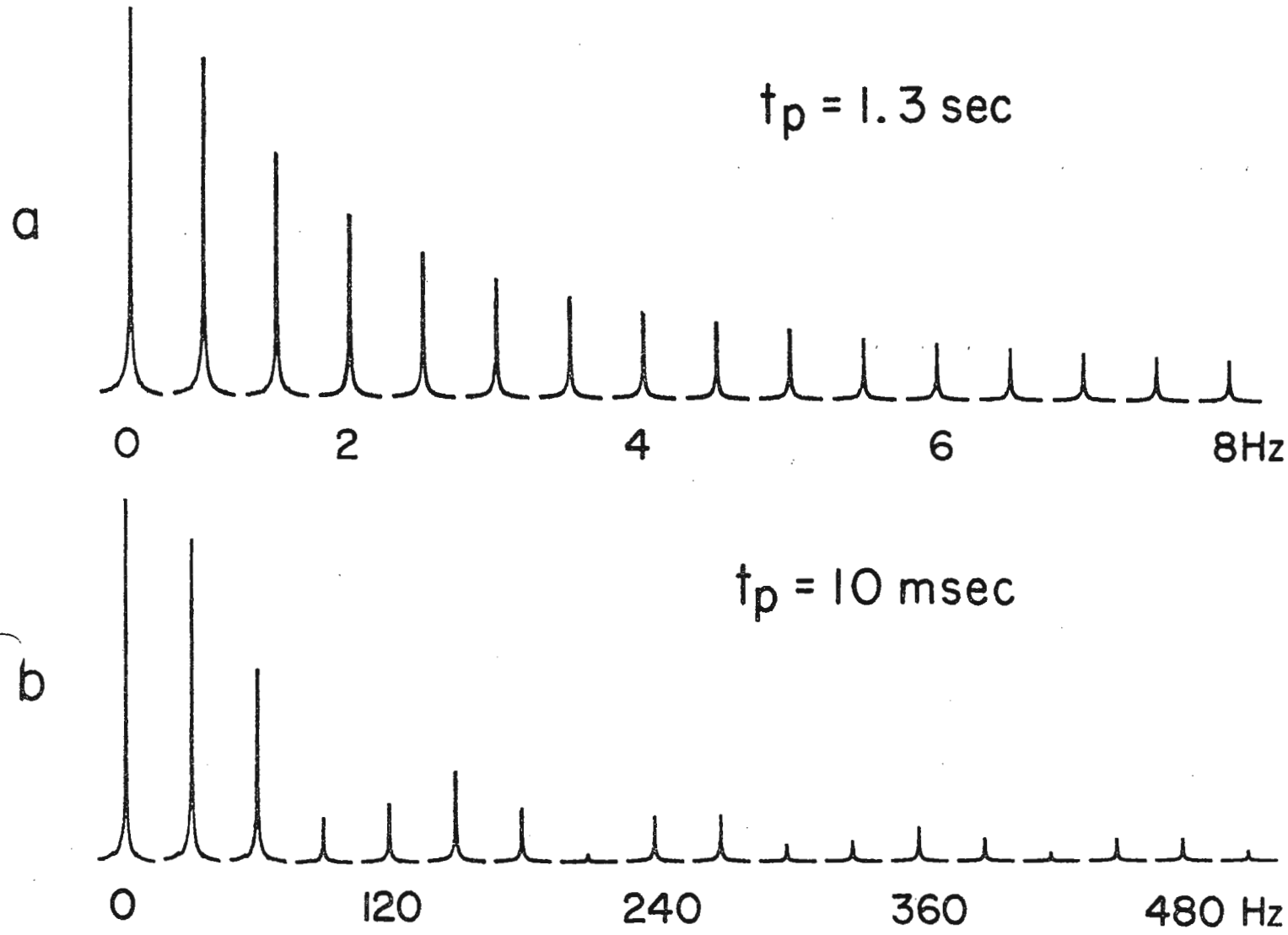
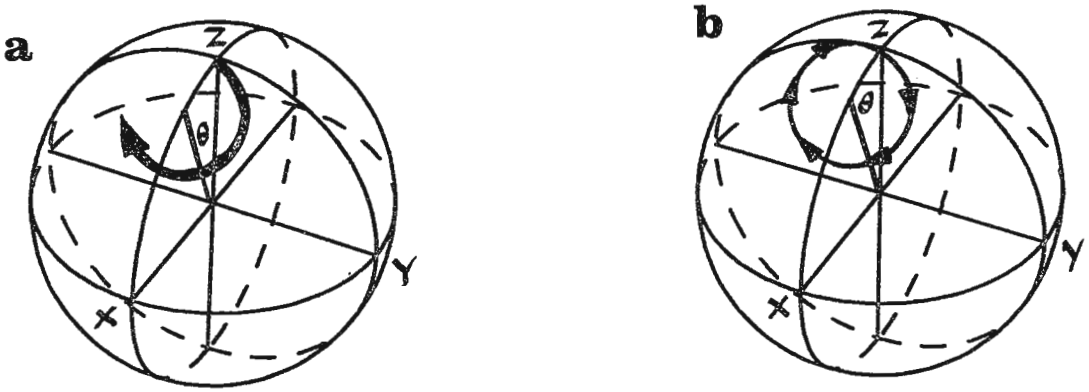


Fig.2



307-29

Department of Chemistry

Colorado State University
Fort Collins, Colorado
80523

New Type of Approach to Zero-Field Zero-Abundance NMR for ^{15}N at 20 MHz

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

Dear Barry:

In the accompanying figure you will see the spectacular richness of 20 MHz signals we have observed recently in connection with our active pursual of ^{15}N CP/MAS NMR. The most remarkable feature of these spectra is that, unlike much of our ^{15}N work requiring ^{15}N-enriched samples, these spectra can be obtained without any ^{15}N present in the sample at all, even without a sample or a magnet! All that is necessary for successful observation of these remarkable signals is to have a reasonably sensitive receiver system and a nearby Nicolet 1180 data system that is operating.

In the course of ^{15}N CP/MAS studies of pyridine adsorbed on surfaces we had to be on guard constantly against a plague of "gliches". Finally, after suspecting that one or more of the six Nicolet 1180 data systems in the Regional Center and adjacent laboratory might be the culprit(s), a pick-up coil was placed in various locations in the laboratories (rooms B206 and B208 in the figure) near the various suspected data systems (in the figure dubbed: Enterprise, Columbia, NT 360, NT 200, NT 150, data station). The single-scan magnitude "spectra" collected in the attached figure were obtained, with a "peak" associated with each Nicolet 1180 (just like assigning chemical shifts in a real spectrum!).

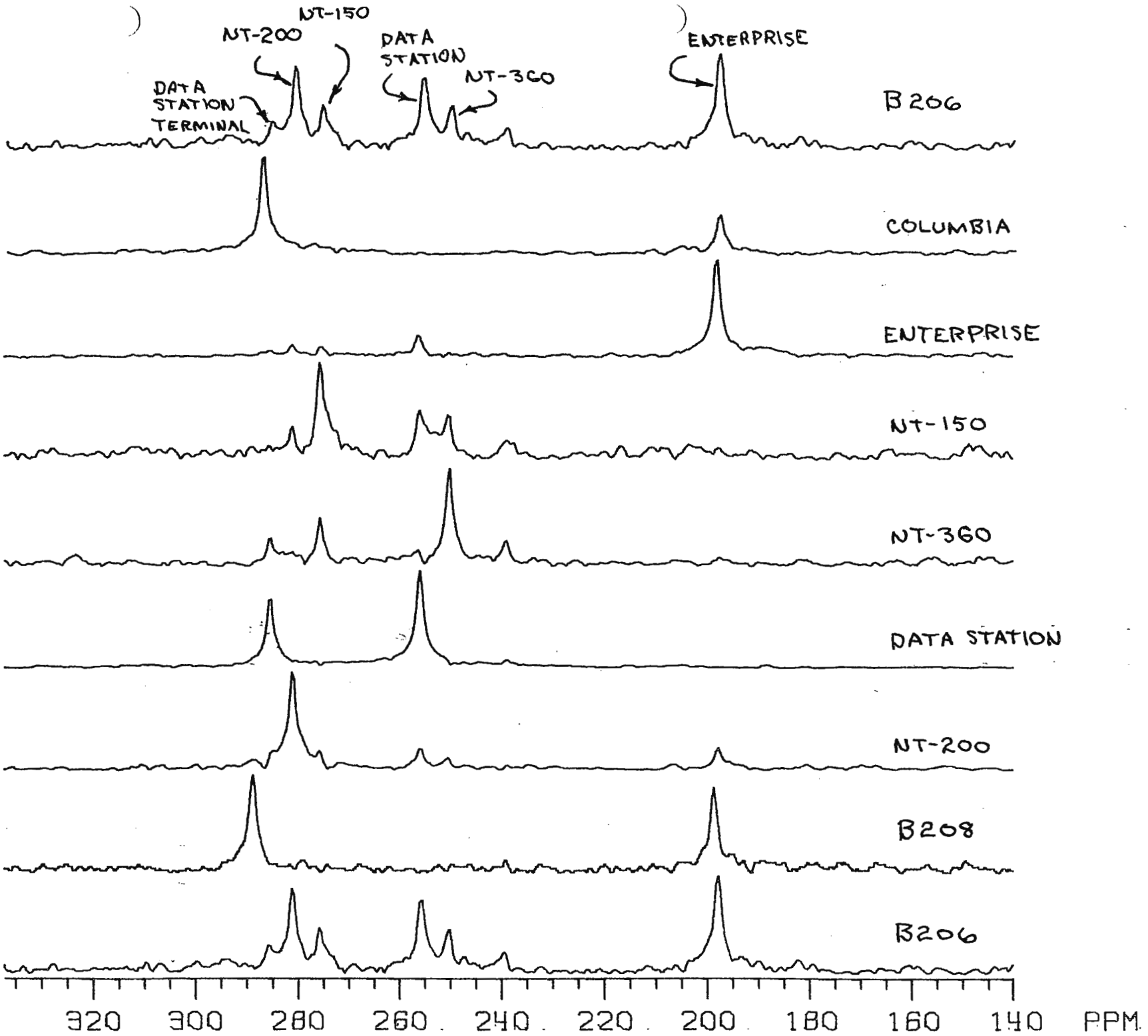
The offending component turned out to be the Slow I/O board of each 1180 (used for communicating with paper tape readers, teletypes, etc, which we don't have). The problem was eliminated by suppressing the third harmonic of the 6.7584 MHz oscillator, disabling a string of digital dividers for the unused teletype interface, and disconnecting the punch and reader connectors on the board.

Fortunately, we were cognizant of the glich problem before we understood it, so we were able to avoid mistaking these gliches for real ^{15}N resonances in our earlier work.

Sincerely,

Gary E. Maciel

Bruce L. Hawkins


NT-200
NT-150
DATA STATION
NT-360
ENTERPRISE
DATA STATION TERMINAL
B206
COLUMBIA
ENTERPRISE
NT-150
NT-360
DATA STATION
NT-200
B208
B206
320
300
280
260
240
220
200
180
160
140
PPM

307-31

UNIVERSITY OF MISSOURI-COLUMBIA

College of Arts and Science

Department of Chemistry

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

March 29, 1984

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

Dear Professor Shapiro:

Recently we have devised a new ^{13}C-^{1}H chemical shift correlation technique which combines DEPT with a selective spin flip at the middle of the evolution period

^{1}H: $\pi/2(\phi_1)$-$t_1/2$-$\pi/2(\phi_2)$-τ-$\pi(\phi_1)$-τ-$\pi/2(\phi_2)$-$t_1/2$-τ-$\pi(\phi_1)$-τ-$\theta(\phi_3)$-τ-dec.

^{13}C: $-\pi(\phi_3)-$ $-\pi/2(\phi_2)$ $-\pi(\phi_2)-$ -acq.(±)

| evolution | mixing |

where $\tau = 1/2^{1}J_{CH}$. The 4-step phase cycle is as follows:

Step	ϕ_1	ϕ_2	ϕ_3
1	-y	x	x
2	-x	-y	-x
3	y	-x	x
4	x	y	-x

The selective flip of non-attached protons results in homonuclear decoupling (except for coupling between nonequivalent protons attached to the same carbon) in the F_1 dimension. In addition to better signal to noise ratios and better resolution, this CSCM technique facilitates measurement of ^{1}H-X (X = heteronucleus, e.g. ^{19}F, ^{31}P) couplings (magnitude and relative signs). We have now applied this pulse sequence to steroids, fluorinated steroids and fluorinated oligosaccharides, and the results show that they can be applied routinely to generate CSCM.

The following are two examples on simple model compounds to demonstrate how the sign and magnitude of the ^{1}H-X coupling can be determined from the correlation map.

Sincerely yours,

Tuck C. Wong

V. Rutar

TCW:jcc

Enclosure

an equal opportunity institution

UNIVERSITY OF MISSOURI-COLUMBIA

307-32
College of Arts and Science

Department of Chemistry

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

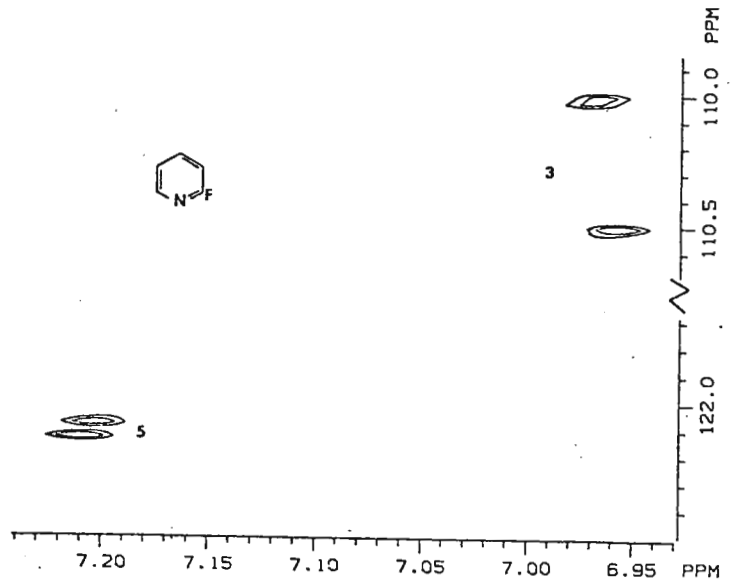


Fig 1 A part of the ^{1}H-^{13}C CSCM of 2-fluoropyridine. Since homonuclear J couplings have been eliminated by the selective flip of distant protons, positions of peaks are determined by chemical shifts and heteronuclear J couplings with the ^{19}F spin. The map clearly shows that J_{H_5F} and J_{C_5F} have the same sign, while J_{H_3F} and J_{C_3F} are of opposite signs.

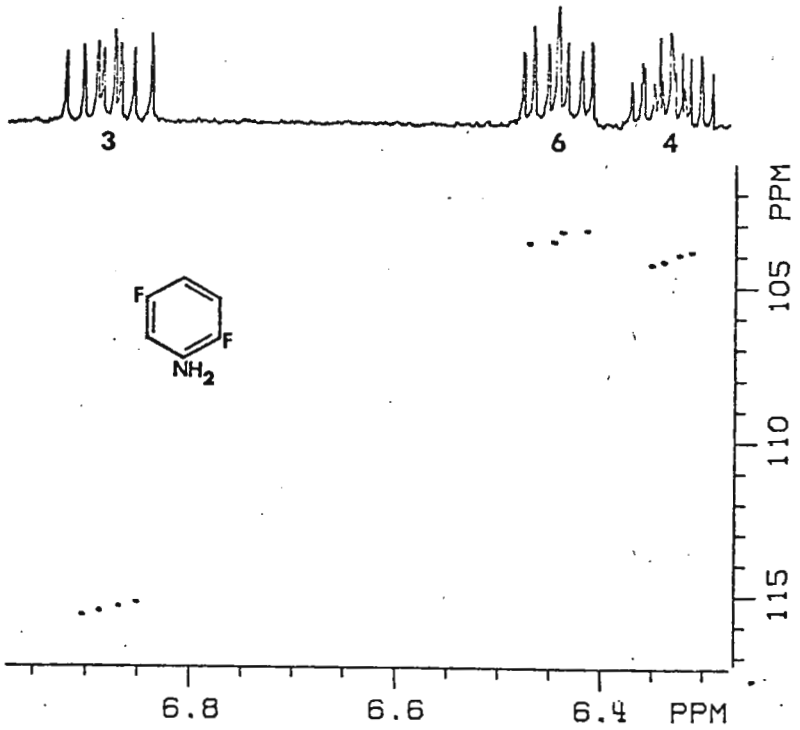


Fig 2 ^{1}H-^{13}C CSCM of 2,5-difluoroaniline where ^{13}CH spin pairs are coupled to two nonequivalent ^{19}F spins. Suppression of homonuclear J couplings simplifies determinations of heteronuclear couplings with ^{19}F. The upper trace shows 1-D ^{1}H spectrum for comparison.

an equal opportunity institution

Rijksuniversiteit Utrecht

Organisch chemisch laboratorium

Croesestraat 79
3522 AD Utrecht
Telefoon 030 - 882311

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

Datum
Uw kenmerk
Ons kenmerk
Onderwerp

The effect of multiple quantum coherences in ^{7}Li relaxation; a warning!

Dear professor Shapiro,

Recently we began a study on ^{6}Li and ^{7}Li relaxation (T_1 as well as T_2) in organolithium compounds in order to correlate the information on quadrupolar relaxation rates with the bonding situation in terms of the aggregation of the lithium compound and covalency of the Li-C bond.

As a start we decided to try and reproduce the results of Wehrli[1] on the relaxation of ^{6}Li and ^{7}Li, as in that study approximately 50% of the total ^{6}Li relaxation could not be attributed to either dipolar or quadrupolar relaxation mechanisms, thus, the total relaxation mechanism remained unclear.

A first T_1 modified inversion recovery experiment with a composite 180° inverting pulse and a 90° monitoring pulse, showed a nonexponential decay. This may be expected for a spin $^{3}/_{2}$ nucleus, because of the different relaxation rates for the $|^{3}/_{2}| \leftrightarrow |^{1}/_{2}|$ and the $^{1}/_{2} \leftrightarrow -^{1}/_{2}$ transitions[2,3].

We observed that the signal consisted of a narrow and a broad component (fig. 1). This was quite unexpected, since the effect could not be ascribed to different species being present in the solution because it is safe to assume that n-BuLi exists only as hexameric aggregates in the concentration used.

A literature survey showed that the effect might be due to a second order frequency shift, as described by Werbelow et al.[3]. In case the system is *not* in the extreme narrowing limit, the degeneracy between the narrow-($^{1}/_{2} \leftrightarrow -^{1}/_{2}$ transition) and the broad-component ($|^{3}/_{2}| \leftrightarrow |^{1}/_{2}|$ transitions) is removed, expressing itself in both the width and the position of the signals.

Clarification in this case might be obtained by running the MIR sequence with various "magic" monitoring pulses α (e.g. $\alpha = \arcsin(^{2}/_{3}^{\frac{1}{2}})$, $^{\pi}/_{2}$, $\arcsin((^{2}/_{3})^{\frac{1}{2}})$, 10°). In this way

"separation" may be achieved for the two components to a certain extent.

However, this part of our study did not simplify the problem; instead it became more complicated. With a progressively shorter monitoring pulse, an oscillation in the amplitude of the observed signal, became increasingly manifest. This oscillation is superposed on the recovery curve, expected on the basis of the experiments with a 90° monitoring pulse. The magnitude of the oscillation with small monitoring pulses α (see fig. 2) is so large that the observed inverted equilibrium magnetization, extrapolated to $\tau=0$ ($-M_z^{\infty}(\alpha)$) is much larger than the observed $M_z^{\infty}(\alpha)$ for the same flip-angle.

A two-dimensional transform of the $S(\tau,t_2)$ array points out that the observed phase modulation arises from two frequency components (fig. 3). We spent some time looking for an explanation before it became clear that the oscillatory behaviour could arise from multiple quantum coherences, excited by the single inverting pulse (it does not make a difference whether a composite or a simple inverting pulse is used, also BB-decoupling of the protons does not change the response). As soon as we realized this, (with the help of dr. J.A.B. Lohman, Bruker Nederland BV) the explanation was proved to be correct by using phase cycling techniques to suppress the MQ-coherences. By suppressing the MQ-coherences, an exponential response is obtained for all monitoring pulse angles.

Presently, we are studying the MQ-relaxation behaviour of the ^{7}Li nucleus in different systems in more detail.

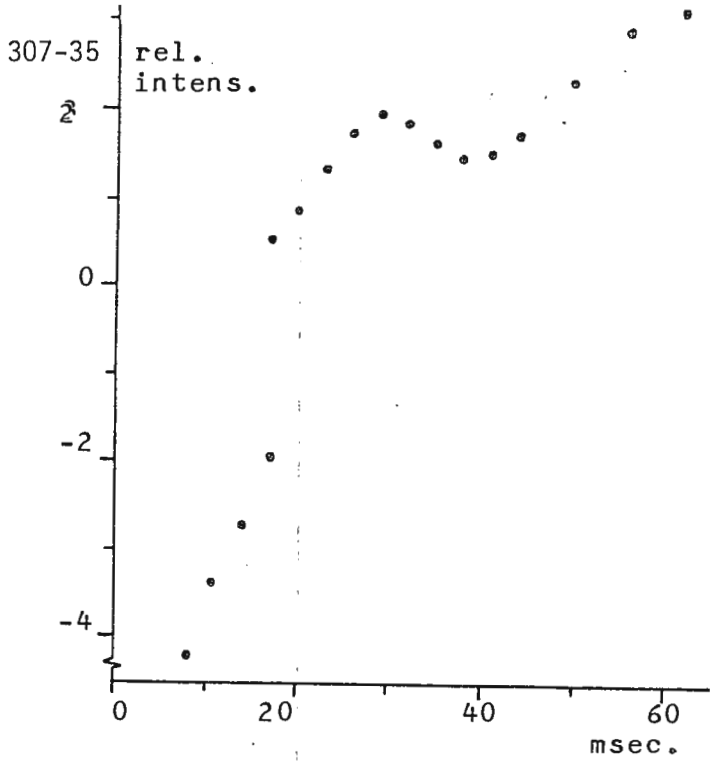
We hope that this communication may serve as a warning for those who have become conditioned to the responses expected for spin-$^1/_2$ systems and who use MQ-NMR only as an Inadequate tool for Cosmic studies, in order that they may be aware of this pitfall in studying the relaxation of quadrupolar nuclei.

References

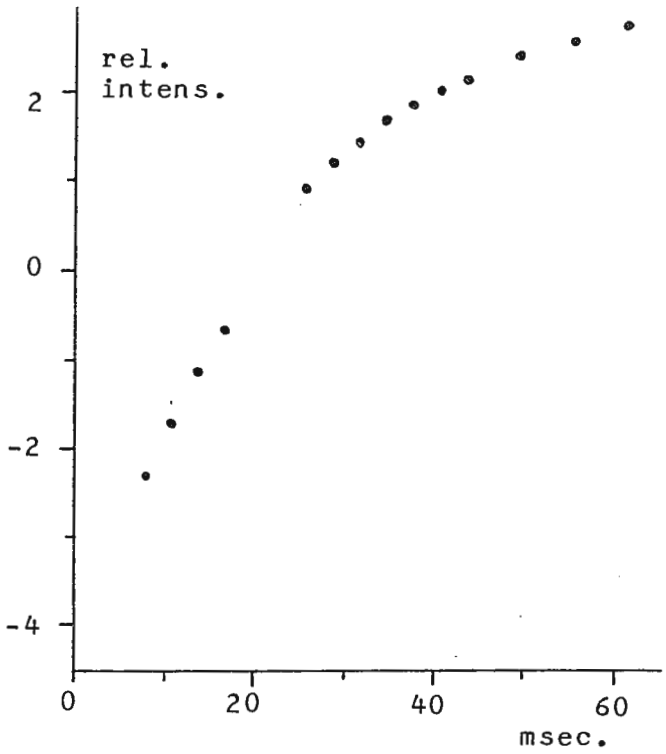
1. F.W. Wehrli, Org. Magn. Reson., 11, 106 (1978)
2. C. Fouques and L. Werbelow, Can. J. Chem., 57, 2329(1979)
3. L. Werbelow and A.G. Marshall, J. Magn.Reson. 43,443(1981)

Yours Sincerely

M.J.A. de Bie
P.M. van Leest



MIR experiment, $\alpha = \pi/4$



MIR experiment, $\alpha = \pi/2$

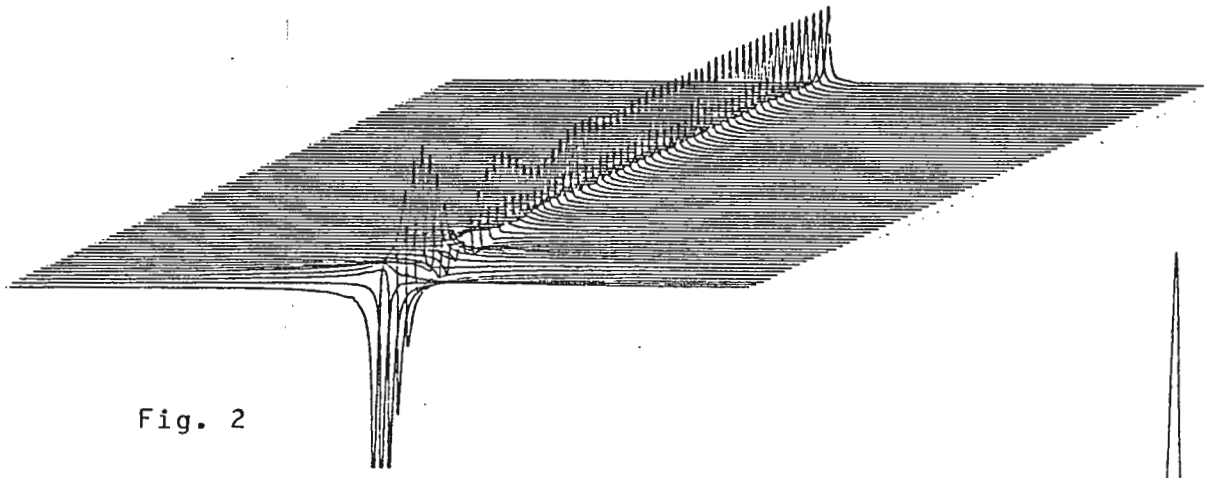


Fig. 2

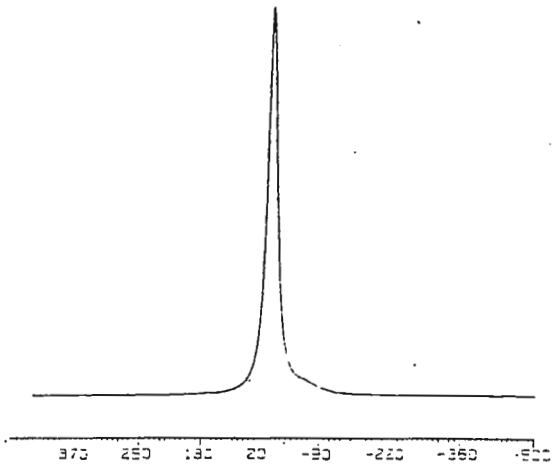
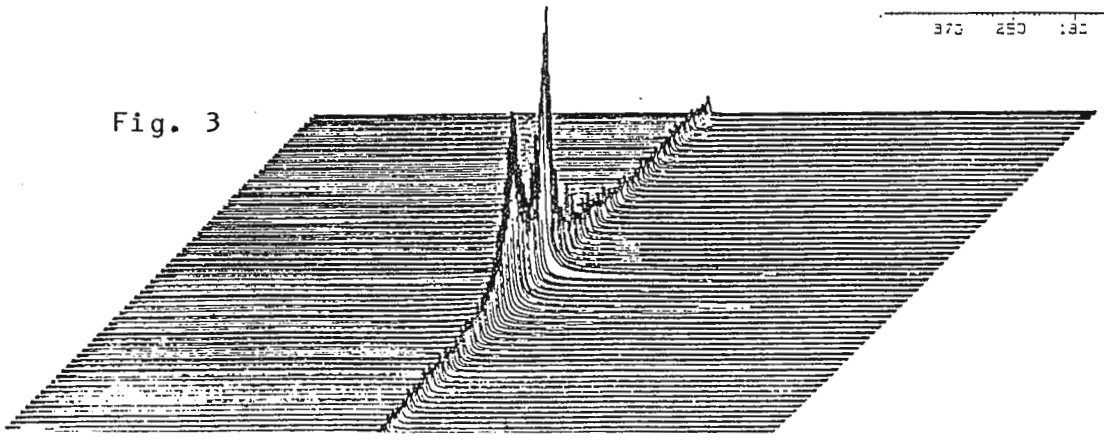


Fig. 1

Fig. 3



Determine oil, fat or moisture content in seconds

PC 10/20 NMR Analyzers from IBM Instruments

The PC 10/20 Analyzer produces fast, accurate readouts in routine quality control, process control and monitoring operations. In addition, the PC 10/20 is a sophisticated pulsed NMR analyzer with microprocessor and advanced electronics that you can use for complex experiments such as T_1 and T_2 relaxation studies.

A PC 10/20 can provide the information you need in seconds; on an LED display, printed on paper tape or transmitted to a remote data base for process control or a permanent record.

Easy to use

Operation is simple. The sample substance is placed in a container and inserted in the PC 10/20. Parameters are set by a pre-programmed module for routine work or by a keypad for experimental work. The PC 10/20 Analyzer can give accurate results on almost any substance that contains hydrogen.

Choice of models

Two models are available in two pulse frequencies each. The Development model has both a pre-programmed module and keypad control. It can be used for both routine analysis and sophisticated experiments.

The Monospec model is designed for routine repetitive use either in the lab or on the plant floor. It is controlled by a pre-programmed module which can be changed quickly and easily in the lab when a new set of parameters is desired.

Let us tell you more

For more information on PC 10/20 NMR Analyzers, please call our toll-free number, 800-243-7054. In Connecticut, 800-952-1073. Or write IBM Instruments, Inc., Orchard Park, PO Box 332, Danbury, CT 06810.

The Monospec model with pre-programmed module control for routine repetitive analysis.

IBM Instruments Inc.

HOWARD UNIVERSITY

WASHINGTON, D.C. 20059

DEPARTMENT OF CHEMISTRY

March 30, 1984

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

Dear Barry:

Deuterium Substitution Effects on Relaxation Times and Inter-Ligand NOE's for Assignment of Ligand Resonances in $(NH_3)_5CoL^{3+}$ Complexes.

The assignment of ^1H ligand resonances in coordination complexes of heterocyclic ligands is complicated by the combination of metal ion sigma polarization, paramagnetic anisotropy resulting from the temperature independent paramagnetic moment of the metal atom, anisotropic effects in the metal-ligand bond, quadripolar effects of metal centers and back bonding (1). It usually necessary to have an x-ray crystal structure to identify closely related structures (2).

We have found that interligand relaxation effects between ammine ligand protons and imidazole ligand protons in $(NH_3)_5CoImH^{3+}$ complexes can be used to make unambiguous assignments. The ammine ligand protons do not undergo exchange with deuterium solvent under acid conditions and exchange readily at neutral conditions, enabling one to use the DESERT technique reported by Akasaka et al. (3) to assign resonances due to nearby protons. In addition a clean NOE is obtained on adjacent ligand protons when the (NH_3) ammine protons are irradiated. The results are summarized in the Figure.

1. R. D. Foust and P. C. Ford, J. Am. Chem. Soc., 94, 5686-5696 (1972)
2. M. F. Hoq, C. R. Johnson, S. Paden and R. E. Shepard, Inorg. Chem. 22, 2693-2700 (1983).
3. K. Akasaka, T. Imoto, S. Shibata and H. Hatano, J. Mag. Res., 18, 328-343 (1975).

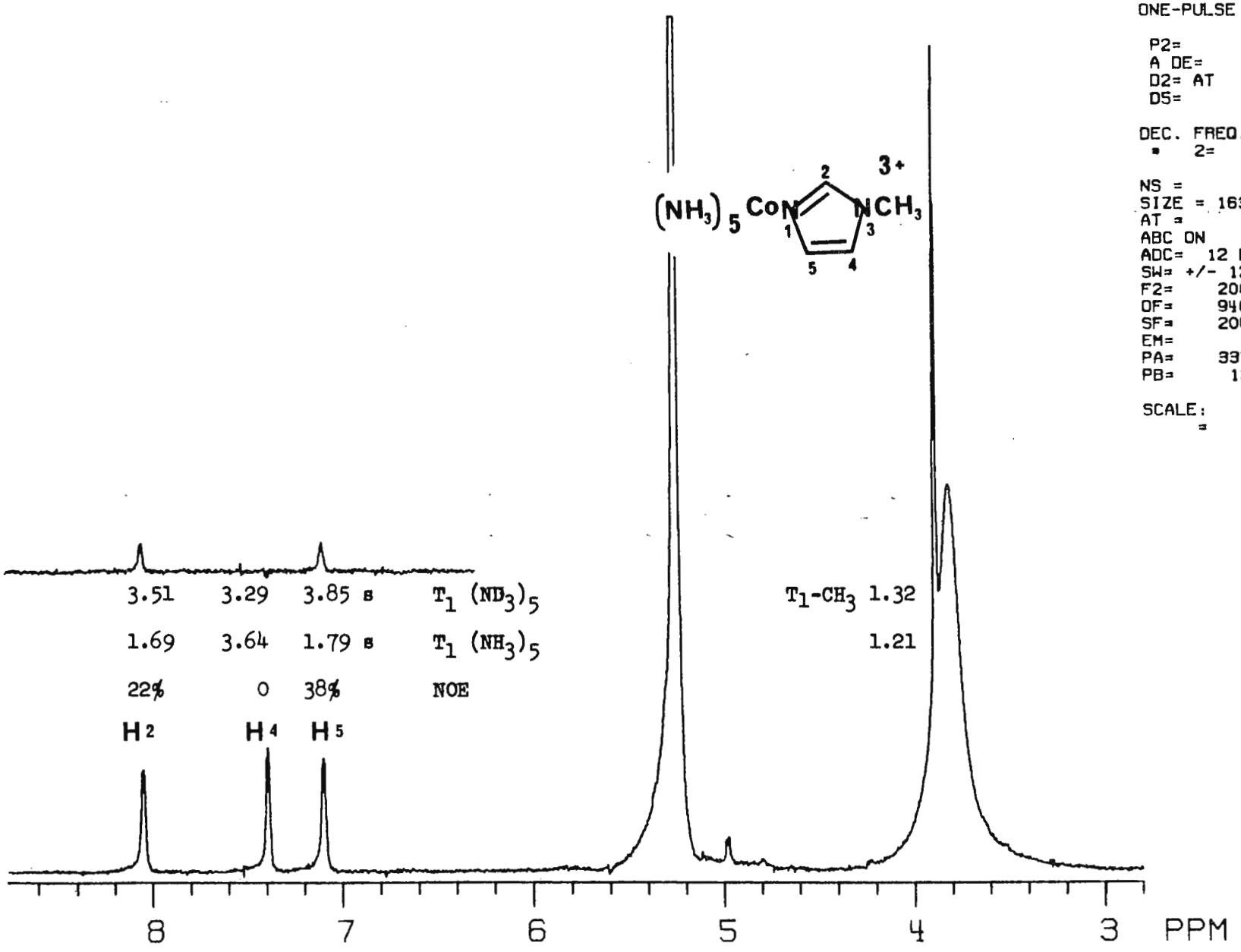
Sincerely yours,

C. B. Storm

A. H. Turner

MIM . 002 CARL 28MAR84
NH3-5,NMEIM,NOE

NIC



ONE-PULSE SEQUENCE

P2= 6.00 USEC
A DE= 416 USEC
D2= AT
D5= 8.00 SEC

DEC. FREQ.= -556.7
* 2= .0

NS = 32
SIZE = 16384
AT = 3.41 SEC
ABC ON QPD ON = 1
ADC= 12 BITS AI= 4
SW= +/- 1201.92 DW= 416
F2= 200.067782
OF= 946.92
SF= 200.067782
EM= .30
PA= 337.3
PB= 13.1

SCALE: 59.55 HZ/CM
= .2976 PPM/CM

MINISTERE DE L'EDUCATION NATIONALE
ET DE LA CULTURE FRANÇAISE

UNIVERSITE DE L'ETAT A MONS
FACULTE DE MEDECINE
Avenue du Champ de Mars, 24
7000 MONS (Belgique)
Tél. (065) 31 51 71

Department of Organic Chemistry

FAST CHARACTERIZATION OF STABILITY AND RELAXATIVITY OF SHORT LIVED NITROXIDES FREE RADICALS.

Dear Professor Shapiro,

Short lived free radicals are sometimes hard to characterize especially without the help of an ESR spectrometer.
Formation, stability and relaxativity (relaxation rate/concentration) of nitroxides free radicals have been assessed semi-quantitatively by measuring their paramagnetic contribution to proton relaxation rates in aqueous reactions media.
The experimental technique used has been previously applied to monitor, *in vivo*, and " in real time " relaxation rates alterations[1].
Oxidation of secondary amines by hydrogen peroxide in presence of phosphotungstic acid is carried out in water. The amount and the relaxativity of free radical formed are monitored by observing the amplitude of the water protons signal when the system is submitted to repetitive 180°-τ-90°-T pulse sequences. The length of time delay τ is chosen such as the magnetization amplitude is negative at the beginning of the reaction (before addition of the amine) and reflects the variations of solvent relaxation rate induced by changes of free radical concentration.

Fig. 1 shows the signal amplitude recorded during the first 90 minutes of the reaction of three different systems (delay τ = 800 ms ; T=4,500 ms).
Fig. 2 represents the relaxation rates measured during a period of ca. 7 hours.
As expected, triradicals are obviously more active than mono- and biradicals and compounds characterized by a lower steric hindrance in the vicinity of the N-O$^{\cdot}$ group are less stable but their formation rate is higher.

Sincerely,

Prof. Yves VAN HAVERBEKE Dr. Robert N. MULLER Dr. Barbara DI RIENZO

Ms. Luce VANDER ELST

(1)
M.H. MENDONÇA-DIAS, P.C. LAUTERBUR and E.J. BROWN. Proceedings of the First Annual Meeting of the Society of Magnetic Resonance in Medicine. Boston, 16-18 Aug. 1982, p. 105.

Fig. 1.

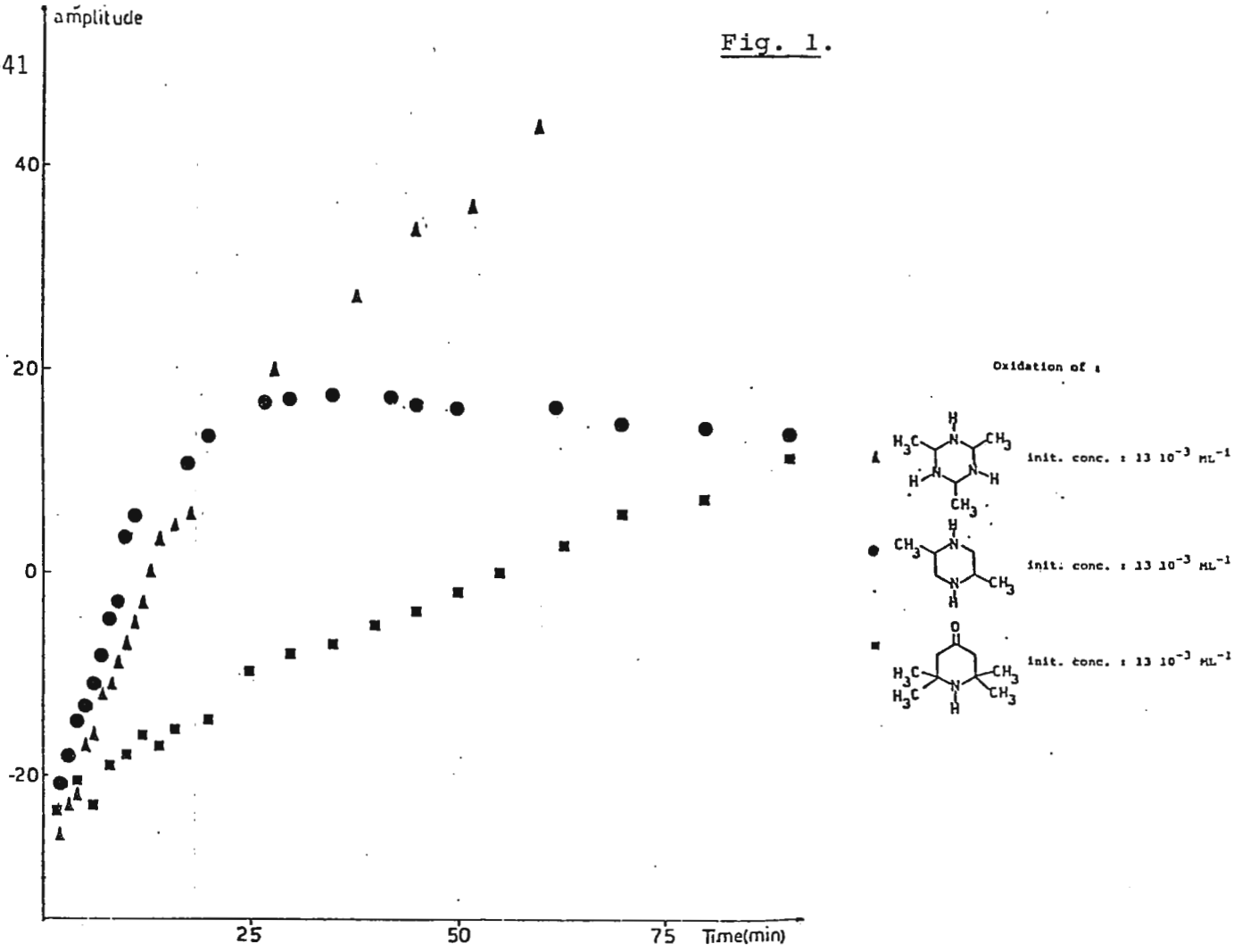
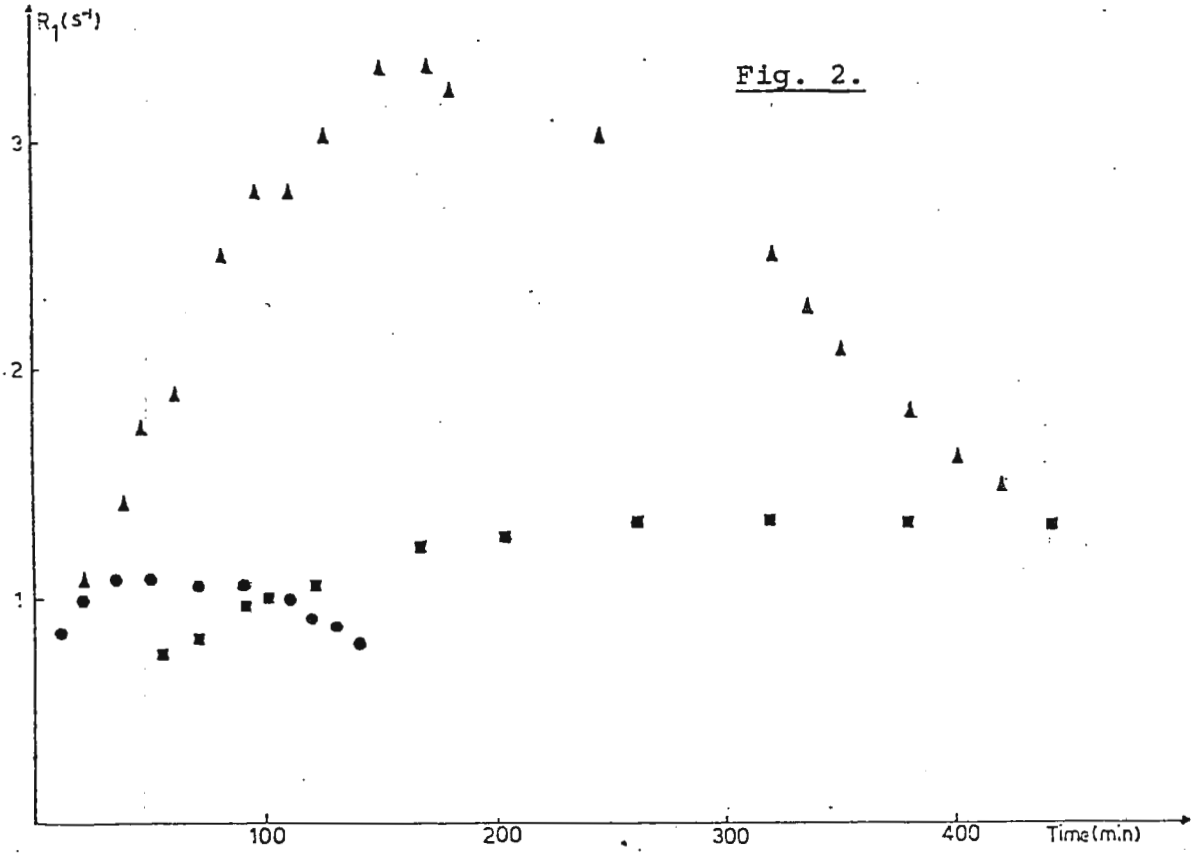

amplitude
40
20
0
-20
25
50
75
Time(min)
Oxidation of :
init. conc. : 13 10⁻³ ML⁻¹
init. conc. : 13 10⁻³ ML⁻¹
init. conc. : 13 10⁻³ ML⁻¹

Fig. 2.


R1(s⁻¹)
3
2
1
100
200
300
400
Time(min)

National Research Council Canada
Conseil national de recherches Canada

Division of Biological Sciences
Division des sciences biologiques

Ottawa, Canada
K1A 0R6

March 28, 1984

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

FOIE RAW: NMR MEASUREMENT OF DRUG METABOLISM IN INTACT MOUSE LIVERS

Dear Barry:

Our studies of mouse malaria and the effects thereon of various drugs (1,2) have led us to attempt to follow drug metabolism in a functioning liver (3). More conventional methods involve such things as mincing up livers and using the supernatant from centrifugation as a source of liver enzymes.

Up to now we have used perfused mouse livers in a standard 15 mm NMR tube and probe, on a CXP-300. The perfusion system has been described elsewhere (4). The ^{13}C-labelled drug is added to the perfusion medium and is quickly accumulated by the liver. The figure shows spectra for the analgesic, aminopyrine. The bottom spectrum is that for the liver "sans drogue". The next spectrum up was obtained during the 30 minutes after addition of labelled aminopyrine; notice the excellent S/N on the peak at 43.8 ppm. Successive scans show a steady diminution of the peak due to labelled drug, and kinetic constants can be readily measured. The peaks between 20 and 35 ppm are due to liver lipids - our foie is also somewhat gras! The reference peak is due to tubing used in the perfusion setup, and provides a good intensity monitor throughout the experiment. Liver viability is checked by obtaining ^{31}P spectra to show maintenance of ATP levels.

This looks to be a rather good way to follow drug metabolism. With some attention to probe design we should be able to reduce the observation time significantly. Using surface coils we hope to be able to do similar experiments on whole and happy mice. Labels on positions other than those metabolized directly to CO_2 should give us a good shot at the metabolic products as well.

With many thanks for your patience,

Yours sincerely,

Ian C.P. Smith, Yves Geoffrion, Roxanne Deslauriers

Keith W. Butler Michael A. Pass*

*Now back home at Univ. of Queensland, St. Lucia, Australia.

References:

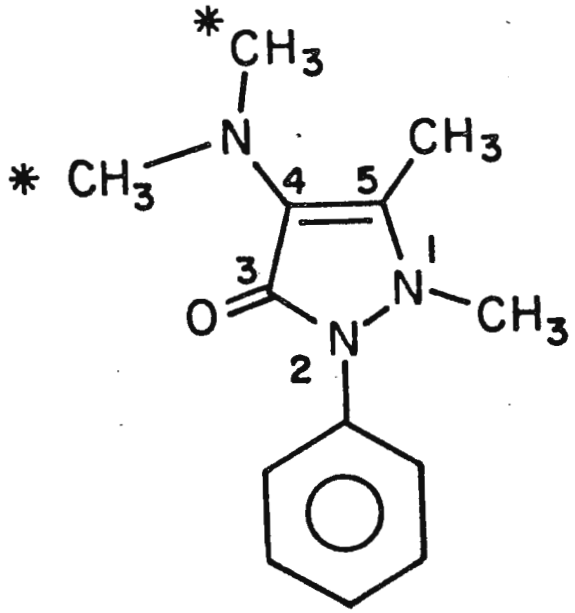
1. R. Deslauriers et al., Biochim. Biophys. Acta 721, 449 (1982).

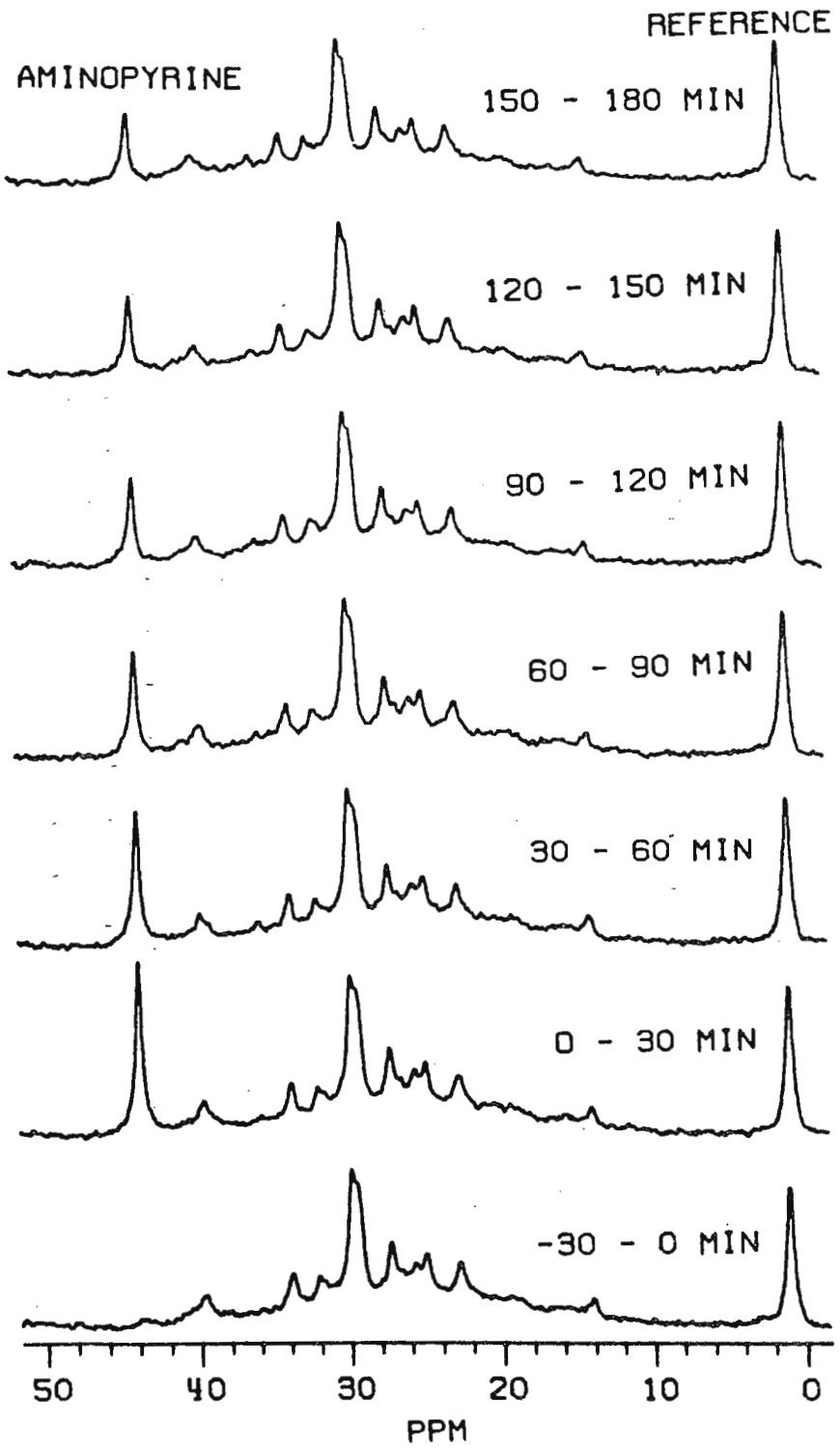
2. R. Deslauriers et al., Tetrahedron 39, 3543 (1983).

3. M.A. Pass et al., Submitted for publication.

4. Y. Geoffrion et al., also submitted.

Figure caption: ^{13}C NMR spectra (75 MHz) of a perfused mouse liver before, and at different times after, addition of ^{13}C-labelled aminopyrine.


*CH3
N
CH3
* CH3
4
5
3
O
N
1
N
CH3
2


REFERENCE
AMINOPYRINE
150 - 180 MIN
120 - 150 MIN
90 - 120 MIN
60 - 90 MIN
30 - 60 MIN
0 - 30 MIN
-30 - 0 MIN
50
40
30
20
10
0
PPM

Book Reviews

Editor: W. B. Smith
Texas Christian University
Fort Worth, Texas

NMR and Chemistry, 2nd Edition

by J. W. Akitt (School of Chemistry, University of Leeds, Leeds LS2 9JT England)

Associated Book Publishers Ltd.
11 New Fetter Lane
London EC4P 4EE England

Methuen, Inc.
733 Third Avenue
New York, New York 10017

1983, 263 pages, $16.95

Spring must be in the air somewhere. The campus bookstore has just asked for textbook orders for summer school. Since I let myself get conned into offering a short introductory course in NMR this summer, my interest in NMR textbooks has waxed somewhat warmer than usual. Happily, NMR and Chemistry by J. W. Akitt of the University of Leeds came my way, and it looks like a text well worth considering. Subtitled "An Introduction to the Fourier Transform-Multinuclear Era," it appears that it might be just the item to use with a group of first year graduate students who face the prospect of being introduced later in the summer to a new Varian XL-300 with all its attendant capabilities.

This volume, a paperback, is a new version of a text which first appeared in 1973. If the earlier version was available in this country, I was not aware of it. Consequently, I can't compare the new version with the earlier version. Chapter headings are: 1. The Theory of Nuclear Magnetization; 2. The Magnetic Field at the Nucleus; 3. Internuclear Spin-Spin Coupling; 4. Nuclear Magnetic Relaxation and Related Phenomena; 5. Modern Spectrometer Systems; 6. The Sample; 7. Multiple Resonance Experiments; 8. Some New and Exciting Techniques in NMR; 9. Some Examples of the Use of NMR in Chemistry. These examples are followed by a few exercises for which answers are given. Unfortunately, no such exercises are given at the ends of the various chapters.

The first four chapters are the requisite introduction to the subject. While well written, it took me a while to get used to looking at the spin ensemble with the z-axis laying on the side rather than pointed upward as is usually represented. The treatment of spin coupling and spectral analysis follows the current trend in being rather superficial. We are bringing up a generation who will only be able to deal with first order spectra or those with two or three spins. I found no reference to computer simulation. Of course, this information is available in older texts for those who need it, but will the student realize this? I found Chapter 5 a particularly well written introduction to the modern spectrometer with a good account of the FT-process, data collection, and processing. The new and exciting techniques are each given a few brief paragraphs and one or two examples. The material covered involves 2D NMR, whole body imaging, in vivo biological investigations, high resolution solids NMR, and high pressure NMR. Numerous examples are given throughout of nuclei other than protons and carbon, and the last

half of Chapter 9 is devoted to that subject (i.e. other nuclei) as well.

In the end, I concluded that the Akitt text fell somewhere in between the more mathematical, physical chemistry approach of Robin Harris' new edition (reviewed in TAMU NMR Newsletter #300, p. 37) and the text on carbon and proton NMR by Abraham and Loftus. The latter has more material relating NMR parameters and molecular structure for the organic chemist. Since my class will be a mix of organic and inorganic students, I decided to let each group buy the text most appropriate to their perceived needs. The class split 50:50 between the Akitt and the Abraham & Loftus books.

---

nmr/specnet

SYRACUSE UNIVERSITY

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

NEW FACULTY POSITION IN BIOMEDICAL NMR RESEARCH

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

Dear Barry.

I am writing to let you know of a new faculty position in medical magnetic resonance (spectroscopy and imaging) at Upstate Medical Center in Syracuse, New York. The Radiology Department at Upstate and the Syracuse University NMR Laboratory are establishing a new Biomedical Magnetic Resonance Research Laboratory, located in one of the Upstate Buildings, approximately 300 yards from my current laboratory. Initially in early 1985 we expect to have a GE NMR multinuclear 2.0 Tesla 12" chemical shift imager for animal research studies. Upstate has received one of 13 State Certificates of Need for clinical NMR Demonstration sites; we hope funding will materialize to allow initial human 1.5 Tesla imaging here by early 1986.

I believe that this is an outstanding opportunity for a physicist or chemist with NMR experience and an interest in medical imaging and spectroscopy. The new Magnetic Resonance facilities will be administered by Professor Stephen Kieffer, chairman of the Upstate Radiology Department. Scientific direction will come from a distinguished radiological scientist. John McAfee, and myself. Substantial resources have been committed to the laboratory and we also anticipate an active extramural grants program. My group has special ties with GE Medical systems in the area of software development, and this provides an additional dimension. The Upstate Magnetic Resonance Scientist will be expected to help design collaborative studies with Radiologists, Physiologists and others at Upstate. as well as with Biophysicists from Syracuse University and possibly nearby institutions.

(continued on p. 47)

We will consider either junior or senior appointments, as appropriate. An adjunct faculty appointment at Syracuse University can be added for an appropriate candidate. The resources of the Syracuse University NMR Laboratory will be available, including access to substantial NMR and data processing equipment and involvement with S.U. NMR Laboratory staff and graduate students.

This position is available immediately, but a starting date as late as September, 1984 is acceptable. I would very much appreciate if you would inform prospective candidates about this opportunity. Alternatively, if you think of specific possibilities, please call me and share your ideas; I will follow up, personally.

Candidates should contact Dr. D. A. Bassano or Dr. S. A. Kieffer, Department of Radiology, Upstate Medical Center, Syracuse, New York 13210, or me, at this address. I will be pleased to discuss our plans in more detail with you or with any candidate.

Yours sincerely,

George C. Levy
Professor and Director

Research Specialist in Radiofrequency Electronics. To design and construct state-of-the-art radiofrequency electronics including high power transmitters amd low-level, low noise amplifiers for frequencies up to 400 MHz. Minimum requirements are a doctorate degree or equivalent and at least 6 years of documented experience. The salary base for this career staff position is approximately $37,000. Send a resume, summary of accomplishments and three letters of reference to Dr. Michael Barfield, Department of Chemistry, University of Arizona 85721 before June 15, 1984. EEO/AA

Department of Biochemistry

College of Agricultural & Life Sciences
University of Wisconsin-Madison

420 Henry Mall
Madison, Wisconsin 53706 USA

Founded in 1883

March 16, 1984

Professor B. L. Shapiro
TAMU NMR Newsletter
Texas A & M University
College Station, TX 77843

Dear Professor Shapiro:

Please bring the following job opening to the attention of TAMU NMR Newsletter readers:

INSTRUMENTALLY ORIENTED NMR SPECTROSCOPIST

The Biochemistry Department of the University of Wisconsin-Madison, is searching for a Ph.D. level scientist to serve as the instrumentation specialist of its NMR facility. The salary and responsibilities will be competitive and will depend on the experience and qualifications of the applicant.

The ideal candidate will have had extensive experience in RF and digital electronics and will have published on the design of NMR instrumentation and the implementation and evaluation of new NMR techniques. This new position, which is supported by University funds, should provide an excellent opportunity for independent and collaborative research at the frontiers of experimental NMR. Equipment available at present includes a Nicolet NT-200 wide-bore spectrometer with a 1280 computer and 293C pulse controller. Upon completion of the new wing of the Biochemistry Building (projected date: August, 1985), the NMR laboratory will be housed in spacious new quarters. The first floor of this new wing has been designed to house state-of-the-art instrumentation for biophysical and physiological investigations; it also contains electronics laboratory, computer, and office space. The Department has pending a proposal to establish a national NMR resource based on a wide-bore 400 MHz spectrometer and a narrow-bore 500 MHz spectrometer (the latter to be upgraded as soon as a practical persistent solenoid is commercialized which operates in the 600 - 700 MHz range). The facility is to be directed by Professor John L. Markley who will be joining the Department in September, 1984. If funded, the grant will provide staff to carry out the day-to-day operation of the laboratory so that the instrumentation specialist can concentrate on research. We desire to fill this position well in advance of the projected starting date of the grant (January, 1985) so that the instrumentation specialist can participate in the specification and evaluation of NMR instrumentation and associated test and design equipment. The instrumentation specialist will also have the opportunity to interact with the NMR imaging group in the Medical School which has a General Electric 1.5 T whole-body NMR imaging spectrometer on order.

Telephone: 608-262-3026, 262-3040
Telex: 26 54 52

(continued on p. 49)

Women and minority candidates are especially encouraged to apply. Interested candidates should send a complete resume and have three letters of recommendation forwarded to: Professor H. F. DeLuca, Chairman, Department of Biochemistry, University of Wisconsin-Madison, 420 Henry Mall, Madison, WI 53706, before June 15, 1984. The University of Wisconsin is an Equal Opportunity Affirmative Action employer.

Sincerely,

H. F. DeLuca
Professor and Chairman

UNIVERSITY OF CALIFORNIA, DAVIS

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

SANTA BARBARA • SANTA CRUZ

OFFICE OF THE DEAN

SCHOOL OF MEDICINE
DAVIS, CALIFORNIA 95616

Dear Colleague:

The UCD NMR Facility has an opening for a staff spectroscopist at the Ph.D. level, to be hired as an Assistant Research Spectroscopist. This is a full-time, non-tenured track research position, with a salary range of $25,100 to $33,100, depending on experience and qualifications. Duties include aiding Facility users in spectrometer operation and in interpretation of data, as well as spectrometer operation and maintenance activities. The ability to interact well with researchers in the physical and biological sciences is essential, and electronic expertise would be helpful, but is not required.

The UCD NMR Facility is equipped with superconducting spectrometers operating at proton frequencies of 500, 360, and 200 MHz, and a Topical Magnetic Resonance spectrometer operating at a proton frequency of 80 MHz. The 500 MHz instrument currently does deuterium as well as proton observation, while the 360 instrument is equipped for proton, phosphorus, carbon, and deuterium operation. The wide-bore 200 MHz instrument is fully broadbanded, and the TMR spectrometer has proton, fluorine, phosphorus, and carbon capabilities in its 200 mm bore magnet.

Needless to say, the research making use of the Facility's spectrometers spans a broad range, and contains a growing interest in the use of NMR for biological and in vivo research. Collaboration with faculty members is expected, and the opportunity for independent research exists as well. The closing date for this position is May 15, 1984. Interested persons may send a resume and three letters of reference to G. B. Matson, Ph.D., Operations Manager, UCD NMR Facility, University of California, Davis, CA 95616.

Sincerely,

E. M. Bradbury, Ph.D.
Co-Director
UCD NMR Facility

G. N. La Mar, Ph.D.
Co-Director
UCD NMR Facility

Find out how friendly and versatile NMR can be.

The QE-300 spectrometer was specifically developed for high efficiency, high-throughput carbon and hydrogen NMR. It provides a complete range of routine and high resolution capabilities with a 300 MHz (7 Telsa) superconducting magnet, synthesizer based frequency control, quadrature phase detection, high-speed pulse programming, and a dual $^{13}C/^{1}H$ switchable probe. To make operation dramatically simple, the QE-300 also features auto-locking, auto-shimming, and auto-spectral phasing plus an incredible menu driven software package called CHARM.

And now, to make the QE-300 even more versatile, we've added a number of accessories to make your work faster and more efficient than ever before.

Around-the-clock data acquisition and processing

First, there's the QE-300 Automatic Sample Changer for unattended, sequential analysis of up to 100 samples. It lets you collect spectra continuously—overnight and even over weekends. So, instead of facing a stack of samples when you walk into your lab in the morning, you have a stack of results, completely phased and annotated to your specifications.

Multiple megabyte speed and power

Winchester and other optional hard disk accessories for the QE-300 dramatically expand your data handling capacity. And to speed up Fourier Transforms and spectral phasing, you can add a high-powered array processor as well.

Remote data stations for multi-user productivity

Increased data requires more data processing capability. To meet that need, you can add a remote, interactive data station to the QE-300. It communicates directly with the QE-300 as well as other Nicolet 1280-based NMR spectrometers and enables you to process NMR data off-line while the main spectrometer is being used to acquire spectra.

VT capability for temperature dependent studies

A new microprocessor controlled Variable Temperature accessory for the QE-300 allows acquisition of experimental data at differing sample temperatures. The controller ranges from +160C to −100C with ±0.1C precision.

Enhanced ^{13}C sensitivity

An optional dual 10mm ^{13}C/5mm ^{1}H switchable probe increases ^{13}C sensitivity to more than three times that of the standard $^{13}C/^{1}H$ probe.

Broadband console electronics and X nucleus probes

Broadband console electronics and X nucleus probes for the QE-300 are offered for observing nuclei other than ^{13}C and ^{1}H, including a dual 5mm $^{31}P/^{1}H$ switchable probe for analyzing phosphorous in biological, medical, and related applications.

Call or write today for complete information on the QE-300. We'll help you select the accessories to meet your NMR needs.

The QE-300 with CHARM. Friendly, *versatile* NMR for the laboratory that has alot of work to do.

You've never had NMR like this before.

General Electric Company NMR Instruments*

255 Fourier Avenue
Fremont, California 94539
(415) 490-8310/TWX 910 381 7025

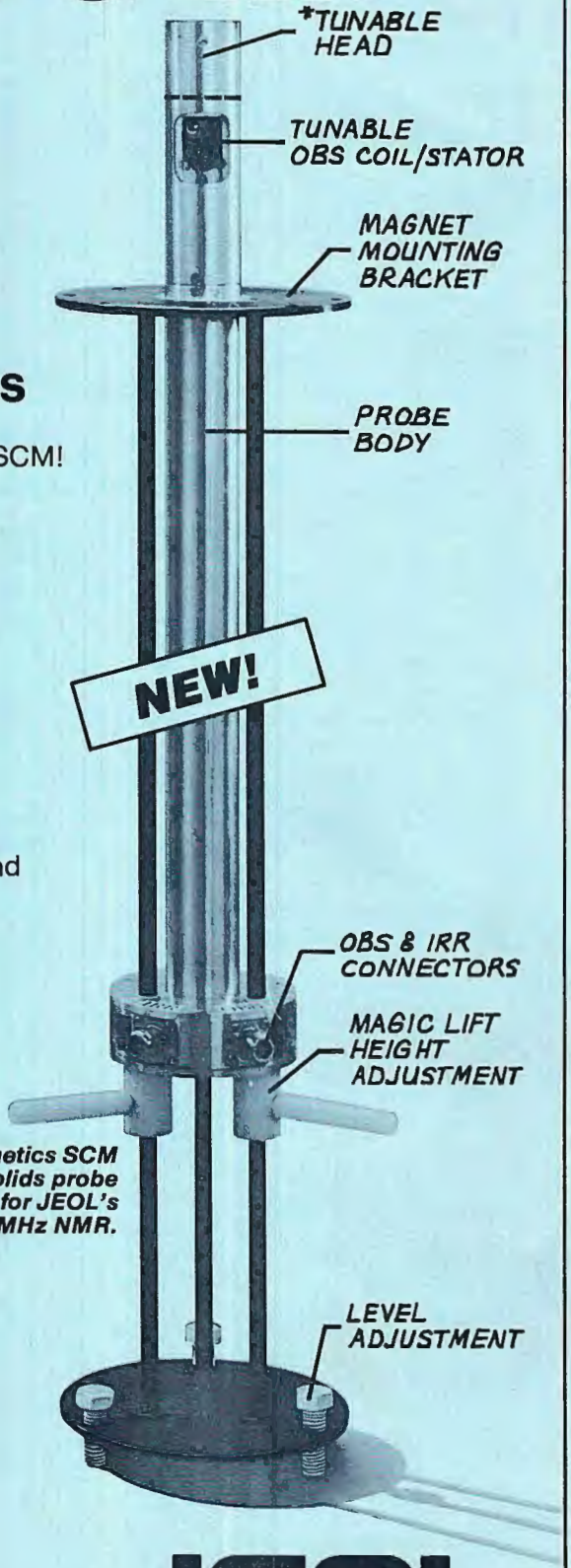
GENERAL ELECTRIC

*A business formerly operated by Nicolet Magnetics Corporation.

THE GX SOLID LEADER in NMR

With Multi-Nuclear/ Multi-Field Solid State Probes

- **High field** solid sample probe for JEOL's 270 MHz SCM!
- ***Tunable heads** — interchangeable plug-in matching units for observation of
  ^{13}C (~67.8 MHz)
  ^{31}P (~109.2 MHz)
  ^{29}Si (~53.6 MHz)
  with one probe!
- Self-starting rotor/stator design!
- High Speed magic-angle double air bearing sample spinning **(>4.0 KHz)!**
- **"Magic lift probe"** for quick sample change and probe insertion!
- All this, in addition to a full line of dual and broad-band high resolution liquid sample probes!



Chemagnetics SCM Solids probe for JEOL's 270 MHz NMR.

SOLIDS UPDATE – NOW AVAILABLE

- MULTI-NUCLEAR SOLIDS PROBE FOR THE GX-270
- WIDE BORE MAGNET WITH VARIABLE TEMPERATURE SOLIDS FOR THE GX-270/89

JEOL

235 Birchwood Ave., Cranford, NJ 07016
(201) 272-8820