TEXAS A&M UNIVERSITY NMR NEWSLETTER

No. 289

October, 1982

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.

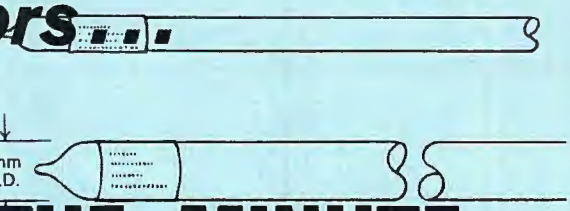
For Reference Standards not shown in the listings, please inquire directly to the plant about prices, packaging and availability.

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 STYLE



TUBE O.D.	TUBE LENGTH	MATERIAL SPEC.
5mm	7″	2.5″
8mm, 10mm, 12mm	7″	3.0″
15mm	7″	4.0″
2.5mm	178mm	50mm

* If special tube lengths and/or material levels are needed, please inquire directly to our plant location.

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

WILMAD REFERENCE STANDARDS

Page No.	Catalog Number	PROTOCOL	PARAMETER SET-UP	5mm
38	WGH-01	Acetaldehyde + 1% TMS	Resolution	$ 32.00
	[illegible]	[illegible]	[illegible]	32.00
	[illegible]	[illegible]	[illegible]	33.00
	[illegible]	[illegible]	[illegible]	33.00
	WGH-22	20% Acetaldehyde in Benzene-d_6	Resolution	33.00
	WGH-24	20% Acetaldehyde + 2% TMS in Acetone-d_6	Resolution	33.00
	WGH-17	Orthodichlorobenzene (Neat)	Resolution	32.00
	WGH-33	30% Orthodichlorobenzene + 5% TMS in Acetone-d_6	Resolution	33.00
	WGH-55	20% Orthodichlorobenzene + 5% TMS in Acetone-d_6	Resolution	33.00
	WGH-61	95% Orthodichlorobenzene + 5% TMS	Resolution	
	[illegible]	[illegible]	[illegible]	33.00
	WGH-69	30% Orthodichlorobenzene in Acetone-d_6	Resolution	33.00
	[illegible]	[illegible]	Resolution	31.00
	WGH-64	50% Chloroform in Acetone-d_6	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

TAMU NMR NEWSLETTER - ADVERTISERS

TAMU NMR NEWSLETTER - SPONSORS

Abbott Laboratories
The British Petroleum Co., Ltd. (England)
Bruker Instruments, Inc.
Eastman Kodak Company
IBM Instruments Inc.
JEOL Analytical Instruments, Inc.
Dr. R. Kosfeld, FB 5 Physikalische Chemie, University of Duisburg, D-4100 Duisburg 1, Germany
The Lilly Research Laboratories, Eli Lilly & Co.
The Monsanto Company
Nicolet Magnetics Corp.
The Procter & Gamble Co., Miami Valley Labs
Programmed Test Sources, Inc.
Shell Development Company
Unilever Research
Union Carbide Corporation
Varian, Analytical Instrument Division

TAMU NMR NEWSLETTER - CONTRIBUTORS

E. I. DuPont DeNemours & Company
Intermagnetics General Corporation
The NMR Discussion Group of the U. K.

DEADLINE DATES:	No. 290	1 November 1982
	No. 291	6 December 1982

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

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 289

ABBOTT
289-1

Pharmaceutical Products Division

Abbott Laboratories
North Chicago, Illinois 60064

August 24, 1982

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

Dear Barry,

Assignment of Some ^{13}C NMR Chemical Shifts

A compound with beta-lysine was submitted for ^{13}C NMR analysis. In an attempt to assign all carbons a sample of beta-lysine 1 was also titrated in D_2O. Table I shows the titration values of 1. The titration curve does not clearly assign C-4 and C-5 of 1 since they both have beta shifts. A literature search notes conflicting assignments. In[1] C-4 is assigned to the 23 ppm resonance and C-5 to the 29 ppm resonance. In[2] these assignments are reversed. Recently an acylated derivative of the original compound was submitted for analysis. Since ^{13}C NMR chemical shifts are now available for the compound without beta-lysine, a titration curve of the sample showed that the acetyl group was attached to the amino group at C-3 of beta-lysine. The titration values for the 3-N-acetyl-beta-lysine group are shown in Table II. Since C-2 and C-4 showed no beta shifts, it is now clear that in beta-lysine C-5 is the resonance at 23 ppm and C-4 is the resonance at 29 pm at an acid pD. Therefore the assignments in[2] are the correct ones.

Sincerely yours,

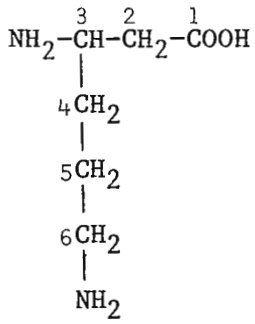
Ruth

Ruth Stanaszek

RS:dmh

[1]JOC 43, 1282 (1977).
[2]Chem. Pharm. Bull, 25, 280 (1977).

August 24, 1982



1

Table I

Titration Values for Beta-Lysine

Assignment	pD	9.8	9.6	8.9	4.4	3.8	Beta Shift
C-2		43.2	42.1	40.4	38.9	38.8	-4.9
C-3		49.3	49.4	49.5	49.6	49.4	
C-4		32.3	31.6	30.7	29.9	29.9	-2.3
C-5		25.0	24.6	24.1	23.7	23.7	-1.3
C-6		40.3	40.2	39.9	39.8	39.8	

Table II

Titration Values for 3-N-Acetyl-Beta-Lysine

Assignment	pD	12.3	9.6	8.0	6.3	2.0	Beta Shift
C-2		42.3	42.1	42.0	41.9	41.9	
C-3		48.1	47.7	47.7	47.8	47.9	
C-4		32.1	31.8	31.8	32.0	32.0	
C-5		28.3	24.7	24.2	25.4	25.6	-2.7
C-6		40.9	40.0	39.9	40.0	40.0	

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD,
CAMBRIDGE,
CB2 1EW
TELEPHONE (0223) 66499

14 September 1982

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

Dear Professor Shapiro

A RABBIT for breeding NOE's

It is my privilege to announce a new advance in animal husbandry which will be of interest to all those who do nOe experiments on small molecules.

We have been using kinetic nOe's to measure interatomic distances and to probe conformational equilibria,[1] but the long T_1 values and slow nOe growth rates (ρ_{dd}) demanded painfully long relaxation delays. It took all night to do a simple kinetic nOe experiment. The reason is clear from eqn. 1 which shows that ρ is proportional to the rotational correlation time τ_c:

$$\rho_{dd} \propto \tau_c . r^{-6}$$

Small molecules have short τ_c and so breed nOe's slowly.

Much impressed by the fecundity of rabbits we have attempted to emulate their example in the nmr tube. The necessary genetic engineering is indicated below.

short τ_c
slow ρ

long τ_c
fast ρ

In practice this transformation is most easily achieved by binding the molecule of interest to a diamagnetic reagent such as $La(FOD)_3$, metallopoprhyrin, cyclodextrin, etc. τ_c in the adduct is longer, ρ is bigger and T_1 is shorter. As a result the nOe's grow faster and sometimes end up larger because ρ competes better against O_2 and rust particles. The figure below shows one example : the time saving for a given S/N for the nOe after 1 second irradiation is sixfold.

We hope to publish more examples soon. RABBIT is Relaxation Aided By BInding Tightly.

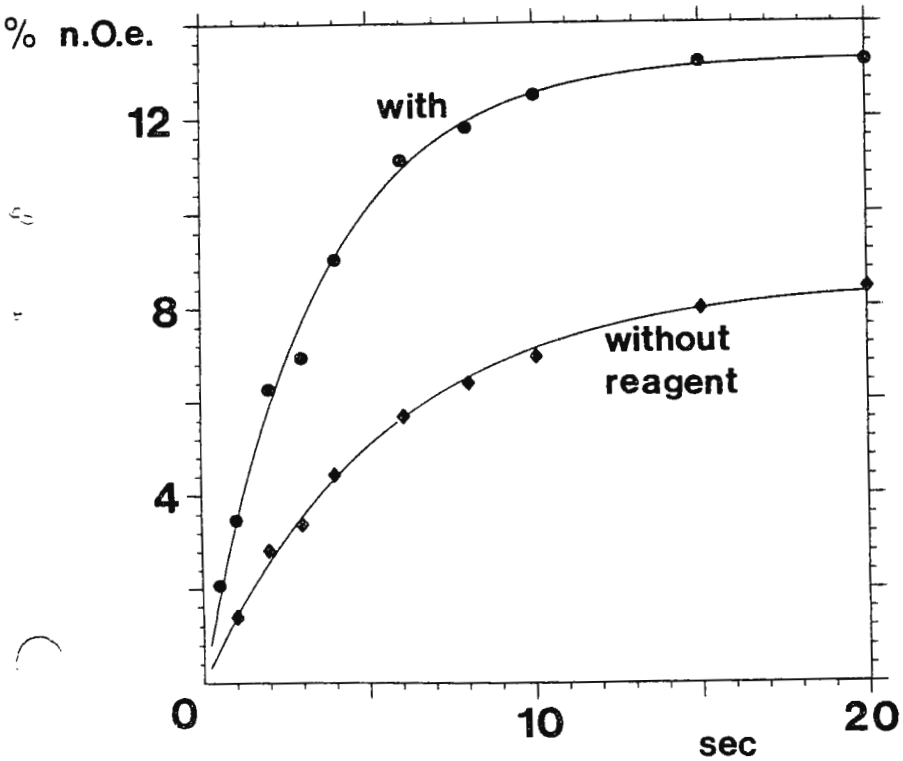
As usual,[1-3] the work was done by John Mersh.

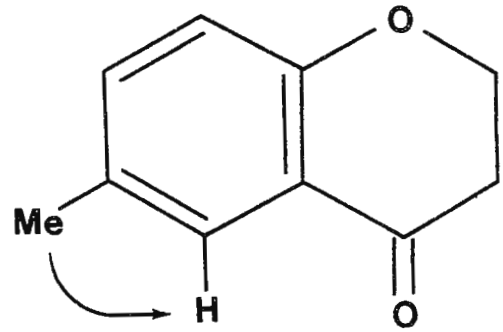
Yours sincerely

Jeremy Sanders

J K M Sanders

1. J. D. Mersh & J. K. M. Sanders, Tetrahedron Letters, 1981, 4029
2. SUDSY : TAMUNMR, January 82 & J. Magn. Reson., Nov. 82
3. Snopake in 2D NMR : J. Magn. Reson. Oct. 82





UNIVERSITY OF CALIFORNIA, DAVIS

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

DEPARTMENT OF CHEMISTRY DAVIS, CALIFORNIA 95616

13 September, 1982

Dr. Barry L. Shapiro
Department of Chemistry
Texas A and M
College Station, TX 77843

PARAMAGNETIC EFFECTS ON DEUTERIUM RELAXATION

Dear Barry,

Sorry about the delay, and the dreaded pink sheet.

We have been applying deuterium NMR to protein dynamics in solution, by studying motional narrowing of ^2H resonances. Since we are primarily interested in paramagnetic proteins, nonquadrupolar ^2H relaxation must be accounted for and excluded. Quadrupolar relaxation should be least effective for a deuterated methyl group, due to fast internal motion, and the quadrupolar spin-lattice relaxation should be much slower than the spin-spin relaxation as $\omega_0\tau_m > 1$ (@ 55 MHz). We measured the ^2H T_1 of the deuterated methyls in 1,3 - d_6 sperm whale metaquo myoglobin to be 49 ms; the corresponding proton T_1 is 3.8 ms. Upon addition of CN^- to yield the low spin form of the protein, the ^2H T_1 was 73 ms; the proton T_1 is 100 ms. Simply scaling the T_1 rates by 1/42.4 and subtracting yields quadrupolar T_1's that are with 4% of each other. Thus scaling proton relaxation rates by the ratio of the γ's, to get the deuterium nonquadrupolar rates, seems to work well in this system.

We are interested in protein side chain dynamics in heme proteins; the deuterated hemins are synthesized by Professor Kevin Smith and his group.

Sincerely,

Robert D. Johnson

Robert D. Johnson

Gerd

Gerd N. La Mar

GX Report #2

Introducing the JEOL Theory of NMR Productivity: Multi-terminals are better than one.

Finally! A spectrometer that helps you do more research and less running around.

Increased throughput! It's the name of the game in NMR spectrometers. And while some people will tell you sensitivity equals throughput, at JEOL we know that's only half the story. Increase the speed of the data generation and you increase your need for data manipulation. Lots of companies can offer you sensitivity. But, our GX Plexus System can offer you sensitivity plus the throughput power of multi-terminals.

Multi-terminals mean the end of waiting in long lines to "get on" to the spectrometer. What's more, to prove our data system is a cut above the rest, each of our terminals are interactive, giving you direct access to the spectrometer at all times. You just can't get that kind of throughput from non-interactive satellite stations.

Add it all up and you'll see that multi-terminals give you more of what a spectrometer's for: more operators working at one time, more tasks accomplished . . . and less system dead time.

But the reasons for choosing the GX Series don't stop here. There are lots more:

- 270, 270W/B, 400, 400W/B, 500 and 600 MHz magnets
- 32 bit high speed data processor, JEC-32
- High density memory up to 1M Byte (4M Byte available in 1983)
- Light pen and keyboard/keypad control
- SIC diagnostics (status integrity check)
- Fiber optics link to eliminate cross-talk
- PGX-300 pulse programmer

Find out the difference a multi-terminal system can make in your operation. Write or call for our brochure today.

JEOL
235 Birchwood Avenue
Cranford, NJ 07016
201 — 272-8820

JEOL

Serving Advanced Technology

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SOUTHAMPTON
SO9 5NH

TEL. 0703-559122
TELEX 47661

JWE/HN

27th September, 1982.

Professor B.L. Shapiro,
Department of Chemistry,
TEXAS A and M UNIVERSITY,
College Station,
Texas,
UNITED STATES OF AMERICA.

Dear Barry,

N.A.T.O. ADVANCED STUDY INSTITUTE ON N.M.R. OF LIQUID CRYSTALS

The above Advanced Study Institute will be held from 26th July to 7th August at San Miniato, a Tuscan village about 40 kms from Florence and Pisa. We aim to cover the whole range of the application of N.M.R. to studying oriented liquids including the determination of geometries of small molecules dissolved in liquid crystals, the characterization of order and structure in pure mesophases (thermotropics, lyotropics, discotics, membranes), and the study of dynamical behaviour.

The lectures will be given by N. Boden, J. Charvolin, P. Diehl, J.W. Doane, G.R. Luckhurst, Z. Luz, A. Pines, I.C.P. Smith, R.L. Vold, R.R. Vold, C. Zannoni and the two directors (myself and Carlo Veracini). Attendance at the Institute will be limited to about seventy students, who should preferably be engaged in the study of oriented systems. The cost of food and accommodation for the school will be of the order of $450.

Intending participants from N.A.T.O. countries may apply for a grant to cover a part of the accommodation costs. Those interested in receiving further details of the Advanced Study Institute should write to me.

Best wishes,

Jim.

J.W. EMSLEY.

Prof. Dr. R. Kosfeld
Physikalische Chemie
Universität Duisburg

D-4100 Duisburg, 20.09.82
Bismarckstr. 90
Telefon:0203/379-3320

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

J-modulated spin echo on chloralkanes

Dear Barry,

the well known spin echo experiment can be applied with various types of broad band decoupling. We used to following sequence:

C-13: Delay - $\frac{\Pi}{2}$ - τ - Π - τ - AQUISITION

H-1: BB(-15dB)| | BB(-5dB)

The J-modulated spin echo (JMSE) transforms signal multiplicities due to heteronuclear coupling to intensity modulations of the entire BB-decoupled resonance signal. Many applications with $^1J_{CH}$ = 125 Hz have been reported. In special systems e.g. chloroalkanes, with $^1J_{CH}$ = 125 Hz and $^1J_{CHCl}$ = 150 Hz intensity modulations of resonance signals can be calculated as shown in fig. 1 for -CH- and -CHCl- JMSE enables selective assignments of structural moieties by resonance signals of zero intensity. This procedure is time saving in comparison to a full 2D-experiment. However, it is limited to systems with definite coupling constants different by at least 5 Hz. Application is demonstrated in fig. 2 by JMSE spectra of 2,4-dichloro pentane taken at suitable τ.

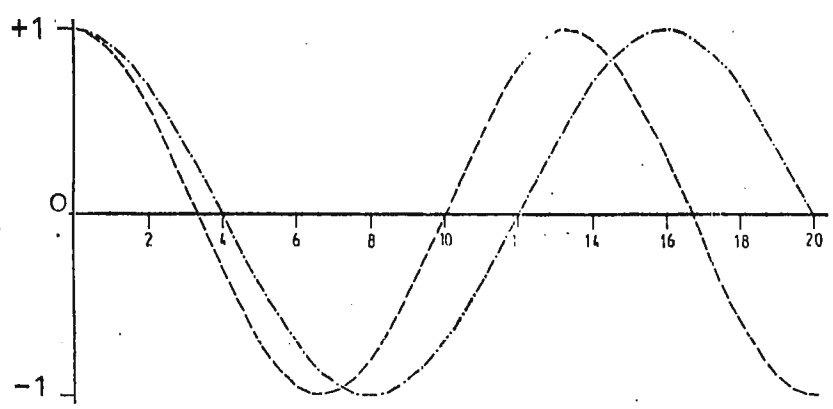


Fig. 1 Intensity modulations of resonance signals by JMSE
-.- = -CH- -- = -CHCl-

Best regards
Your sincerely

(Prof. Dr. R. Kosfeld)

(Dr. K.-F. Elgert)

a)

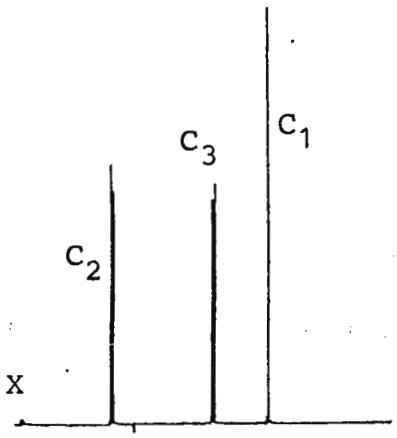
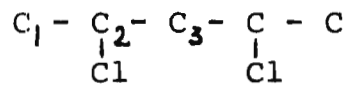


Fig. 2

C-13 nmr spectrum of 2,4-dichloro pentane



(mixture of diastereomers)

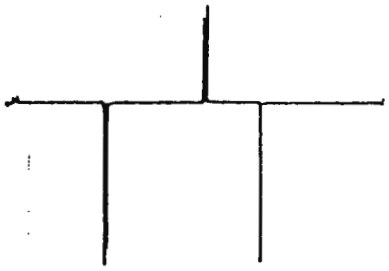
a) broad band decoupled

b) - e) JMSE spectra with τ = 8, 10, 12, 20 msec, resp.

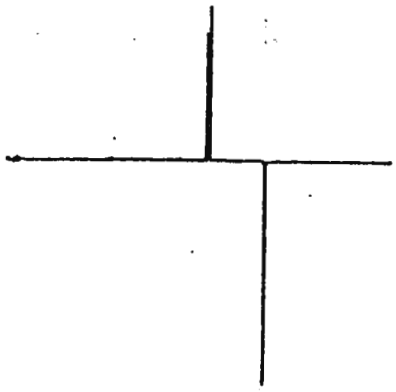
X = solvent, $CDCl_3$

BRUKER WM 300, pulse repetition: 60 sec, pulse width: 17.3 µsec, pulse sequence generated by multi-pulser unit

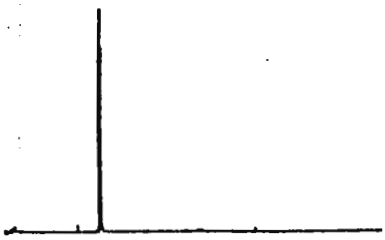
b)



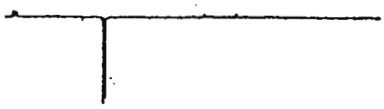
c)



d)



e)



UNIVERSITÉ RENÉ DESCARTES (PARIS V)

UER DES SCIENCES PHARMACEUTIQUES ET BIOLOGIQUES

DÉPARTEMENT DE CHIMIE ORGANIQUE
ERA 613 DU CNRS
SCN 21 DE L'INSERM
PROFESSEUR B. P. ROQUES

PARIS, LE September, 17th, 1982

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

^{15}N antisymmetric T_1 measurements by the INEPT method.

Dear Professor Shapiro,

The great sensitivity gain of the INEPT sequence (1) is now well established and looks very attractive for the relaxation measurements of insensitive nuclei such as ^{15}N. We have developped a method derived from INEPT (2) leading to the "antisymmetric" $^{15}NT_1$ a new parameter usefull for peptides conformational analysis. The models choosen are ^{15}N enriched (90%) enkephalin derivatives : Tyr-*Gly-*Gly-*Phe, I, Boc-Tyr-*Gly-*Gly-*Phe-OCH_3, II, and Tyr-*Gly-*Gly-*Phe-*Leu, III. If one consider in the peptide backbone each ^{15}N and its ^{1}H linked nucleus as independant AX spin-systems (A = ^{15}N, X = ^{1}H), three observable parameters can be measured for each one : the total magnetization related to the symmetric T_1^s for both nitrogen, M_N, and proton, M_H, and the intensity difference within each doublet M_{NH}, related to the antisymmetric T_1^a (3).

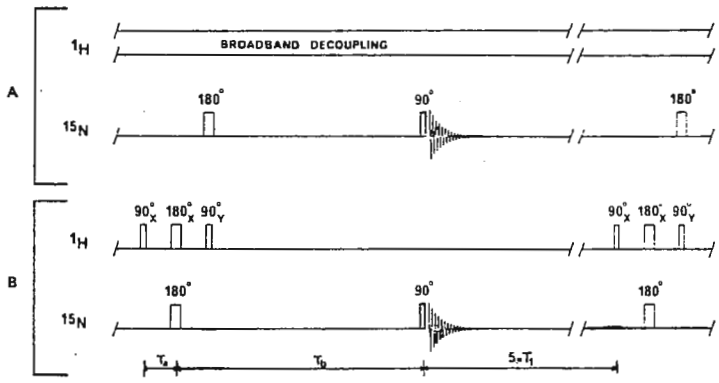


Figure 1.

Pulse sequence used for relaxation measurements.
A : Symmetric T_1 (Freeman-Hill method).
B : Antisymmetric T_1 (slightly modified INEPT sequence).
- ^{15}N 180° pulse = 42 µs ; - ^{1}H 180° pulse = 400 µs.

4, AVENUE DE L'OBSERVATOIRE. 75270 PARIS CEDEX 06 · TÉL. 329.12.08

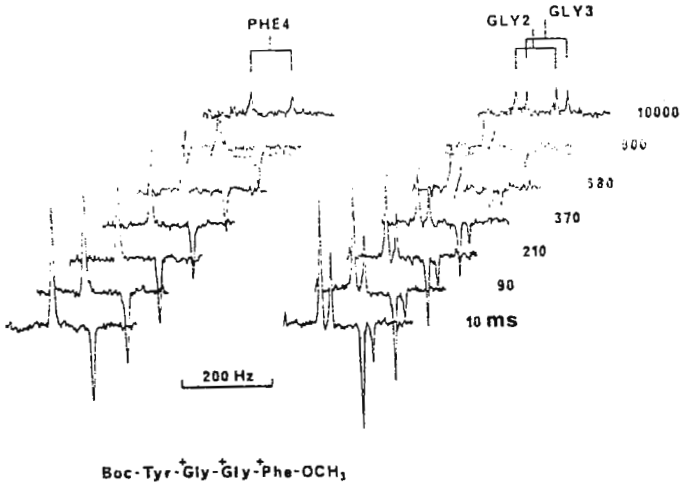


Figure 2.

Antisymmetric T_1 measurement for Boc-Tyr-*Gly-*Gly-*Phe-OCH_3 in Me_2SO (0.1 M) at 310°K (50 scans).

A sequence excitation (B) is proposed to measure T_1^a and compared with the sequence for measurement of the conventional T_1^s (A). The sequence A is characterized by ^1H broad-band irradiation during the evolution period τ_b whereas such irradiation does not occur in the sequence B. By contrast the T_1^a are obtained by using an excitation sequence based on the spin-echo polarization transfer method (INEPT) firstly described by Morris and Freeman . The original INEPT sequence which creates a ^{15}N magnetization in the x-y plane by a ^{15}N modulated proton spin-echo is just altered by suppressing the second ^{15}N 90° pulse (Figure 1.).

After the INEPT excitation the two components of the ^{15}N doublet are enhanced but in the opposite direction. Therefore the modified pulse excitation allows to observe the recovery (along the x-axis) of the magnetization-difference between the two components of the doublet for τ_b (Figure 2.). As expected, in each peptide models T_1^s and T_1^a values differ one from each other as shown in Table 1. Moreover a large variation range in the T_1^a appears in free peptides what is not the case of the protected one according to large differences in conformational flexibility occuring in these compounds (4).

Table 1. ^{15}N symmetric T_1^s and antisymmetric T_1^a spin-lattice relaxation times (in sec) at 310 K for compounds : Tyr-*Gly-*Gly-*Phe, I, Boc-Tyr-*Gly-*Gly-*Phe-OCH_3, II, and Tyr-*Gly-*Gly-*Phe-*Leu, III.

Compound	Residue	T_1^s	T_1^a
I	Gly^2	0.95	0.028
	Gly^3	0.95	0.34
	Phe^4	0.85	0.22
II	Gly^2	1.35	0.54
	Gly^3	1.40	0.61
	Phe^4	1.60	0.78
III	Gly^2	1.15	0.028
	Gly^3	1.15	0.52
	Phe^4	0.90	0.47
	Leu^5	0.90	0.41

a) T_1 have internal estimated error less than 10% (90% confidence interval), except for the Gly^2T_1's in the free peptides (∿20%).

Sincerely yours.

D. Marion

Dominique MARION

Christiane GARBAY-JAUREGUIBERRY

B. R

Bernard P. ROQUES

(1) G.A. Morris, R. Freeman, J. Amer. Chem. Soc. (1979), 101, 560-563.

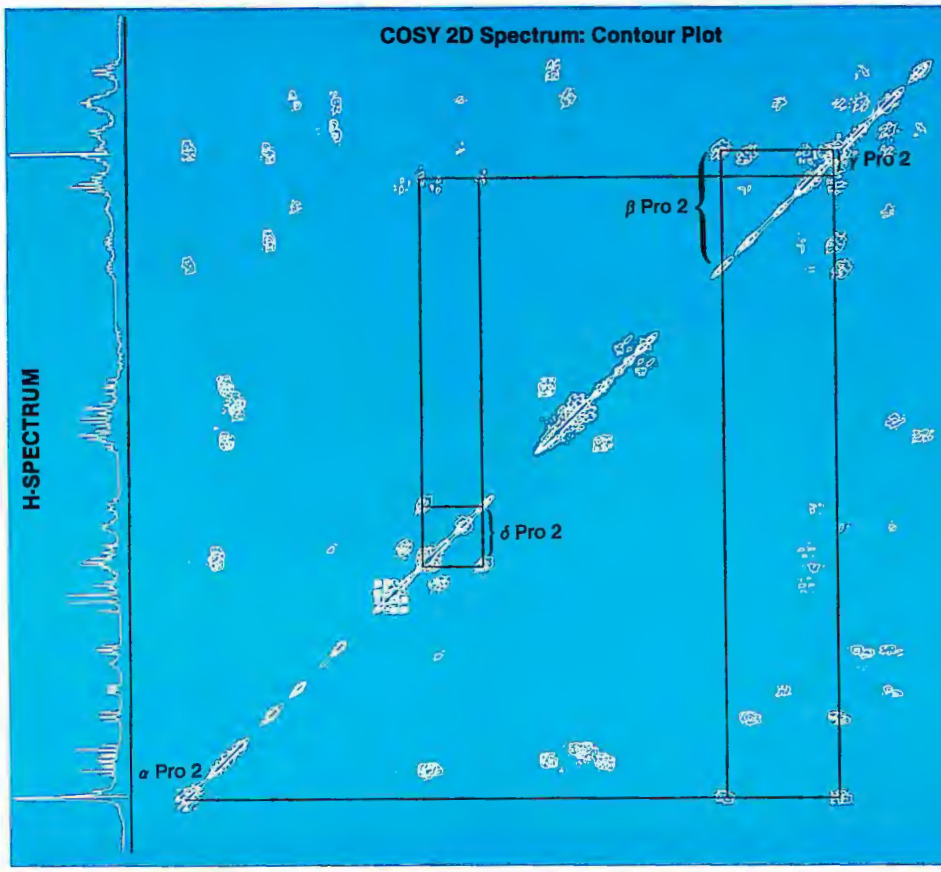
(2) D. Marion, C. Garbay-Jaureguiberry and B.P. Roques, J. Amer. Chem. Soc. (1982) in press.

(3) L.G. Werbelow, D.M. Grant, Adv. Magn. Reson. (1979), 9, 189-299.

(4) D. Marion, C. Garbay-Jaureguiberry, B.P. Roques, J. Magn. Res. (1982) in press.

$C_{50}H_{73}N_{15}O_{11}$ by 2-D NMR

When complex molecules are submitted to analysis—e.g. the oligopeptide Bradykinin sample in this experiment—two-dimensional spectra such as proton correlated spectroscopy (COSY) can often produce dramatic simplification of seemingly intractable spectra, even at high magnetic field. Here is evidence:



Chemical Shift Assignments Using 2D Proton Correlated Spectroscopy (COSY).

The pulse sequence for COSY is given by:

$$90°_x - t_1 - 90° \pm x - \text{Acq}(t_2) \pm y \quad (1)$$

The chemical shifts of mutually coupled protons can be extracted from over-lapping multiplets by means of a contour plot obtained from the COSY Experiment Data. The normal Proton Spectrum is represented along the diagonal axis, and the symmetrical off-diagonal cross peaks provide the clue to any coupled protons.

The COSY Contour Plot of Bradykinin triacetate (Arg-Pro*-Pro- Gly - Phe - Ser - Pro - Phe-Arg), illustrates the technique on the aliphatic moiety. With the known position of the Hα-Pro 2 (*), the chemical shifts of all the six remaining protons (2β; 2γ; 2δ) can easily be located as shown by the connecting lines.

(1) Ad Bax and Ray Freeman, JMR 44, p. 542-561 (1981)

Q.E.D. Both spectrum and contour plot of this COSY experiment were produced on a WM 400 at the Bruker Applications Laboratory. The WM Series of high-field NMR spectrometer systems comes with an extensive software system, including programs for 2-D processing display and plotting. A full-color graphic display processor further facilitates speed and clarity of stack and contour plots.

Please tell us your particular application and ask for more information with the coupon below: Bruker Instruments, Inc., Manning Park, Billerica, MA 01821.

BRUKER

My NMR application is: _____

Tell me more about
- ☐ High-Field NMR (WM Series)
- ☐ NMR in Solids (CXP Series)
- ☐ NMR Imaging Systems

Name/Title: _____
Dept.: _____
Company/Institute: _____
Address: _____
City _____
State/Zip _____

New Literature Available from BRUKER

NMR-Tomography

– A simple introduction into a fascinating NMR technique –

The "NMR-Imaging" technique is without any doubt a revolutionary new method for obtaining pictorial information about internal structures e.g. of the human body. The evolution of this method has now reached the state were non-specialists have recognized the extraordinary power of this technique and consequently BRUKER has now available an introductory six-page brochure for those not familiar with this new method. In order to facilitate the understanding of the physical background to this method the basic principles are given in a simplified manner and are illustrated by a large number of figures.

In a short survey it is shown that for the last twenty years the instrumental development in the pulsed NMR field has been synonymous with the name of BRUKER and it is pointed out that the first commercially available Fourier Transformation (FT) spectrometers were developed by BRUKER in 1969. Since NMR tomography is based on both "pulsed" and "FT"-NMR, the unique experience of BRUKER in these fields represents the ideal basis for the recently developed imaging systems.

After a short introduction, the principles of NMR are described in the brochure followed by a short representation of the "Projection-Reconstruction-Technique". Due to the expected extraordinary importance of NMR tomography in the field of diagnostic medicine a comparison of the average X-ray tissue contrast with NMR data is given as well as some remarks about theoretically possible risks for patients. At the end of this brochure an "outlook" is given into new applications and of the expected development of NMR tomography.

The three new BRUKER brochures.

With the general title "BRUKER Info", periodically illustrations of BRUKER's latest results are added to the NMR Tomography brochure.

If you wish to obtain the new brochure containing two "BRUKER Info" illustrations please return the reply card.

Two-Dimensional NMR *aspect 2000*

A practical introduction into this new technique by an experienced spectroscopist.

The common 2-D experiments are described, measuring conditions and microprograms are given. Application examples on various spectrometers demonstrate the capabilities of the method and naturally the outstanding performance of BRUKER spectrometers in 2-D spectroscopy.

DEPT

Distortionless Enhancement by Polarization Transfer

A new method with significant advantages over other polarization transfer techniques is described in a new brochure.

This method developed at the Griffith University by Drs. Bendall, Doddrell and Pegg can be performed on any BRUKER Spectrometer equiped with a CXP or high speed pulse programmer. Using this sequence the sensitivity in coupled spectra can be significantly increased or the multiplicity selection in ^{13}C spectra can be performed without the critical adjustments required for other polarization transfer pulse sequences.

For Your Copy, Please Write to Your Nearest BRUKER Sales Office

Wayne State University
College of Liberal Arts

Department of Chemistry
Detroit, Michigan 48202

289-16

September 20, 1982

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

^{13}C NMR Spectra of Polyethylene Oxide Derivatives

Dear Professor Shapiro,

We have been studying ionophores which can be "switched on" and "switched off" by closure and cleavage of disulfide bonds. We have found ^{13}C spectra of great utility in making structural assignments and following reactions. In the course of our work we have made a number of spectral assignments on final ionophores and intermediates, some of which are given in the table. Spectra were measured on an FX-60 spectrometer at 15 MHz. Of special interest are the shifts which follow closure ot the disulfide: + 15 ppm and -3.5 ppm for the α + β carbons, respectively, due to the β + γ effects of the second sulfur atom.

	C_1	C_2	C_4	C_5	C_7	C_8
$HO(CH_2CH_2O)_3CH_2CH_2OH$	61.4	72.7	70.0*	70.5*		
$HO(CH_2CH_2O)_4CH_2CH_2OH$	61.4	72.5	70.1	70.4	70.4	
$HO(CH_2CH_2O)_5CH_2CH_2OH$	61.6	72.5	70.5	70.5	70.5	70.5
$Br(CH_2CH_2O)_3CH_2CH_2Br$	30.3	71.1	70.5	70.5		
$Br(CH_2CH_2O)_4CH_2CH_2Br$	30.3	71.2	70.6	70.6	70.6	
$Br(CH_2CH_2O)_5CH_2CH_2Br$	30.3	71.2	70.6	70.6	70.6	70.6
$HS(CH_2CH_2O)_3CH_2CH_2SH$	24.2	72.8	70.2*	70.6*		
$HS(CH_2CH_2O)_4CH_2CH_2SH$	24.3	72.9	70.2	70.6	70.6	
$HS(CH_2CH_2O)_5CH_2CH_2SH$	24.2	72.8	70.2	70.6	70.6	70.6
$\overline{S(CH_2CH_2O)_3CH_2CH_2S}$	39.1	69.3	70.9*	71.0*		
$\overline{S(CH_2CH_2O)_4CH_2CH_2S}$	39.1	69.5	70.3	70.6	70.6	70.6
$\overline{S(CH_2CH_2O)_5CH_2CH_2S}$	39.2	69.2	70.2	70.8	70.8	70.8

*assignments may be reversed

Sincerely

Morton Raban
Professor of Chemistry

Farouk Kandil
Visiting Professor of Chemistry
(on sabbatical leave from the University of Aleppo, Syria)

289-17

U.S. Department of Energy
Laramie Energy Technology Center
P.O. Box 3395, University Station
Laramie, Wyoming 82071

September 23, 1982

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

Dear Barry:

RE: Hydrocarbon Type Analysis of Fossil Fuels Using Spectral Editing Techniques.

We have been examining the feasibility of utilizing ^{13}C NMR spectral editing techniques to quantitate hydrocarbon types found in fossil fuel. Several methods for spectral editing are given in the literature (1-4), but only the Gated Spin-Echo Technique (GASPE)[3] and the Distortionless Enhancement by Polarization Transfer (DEPT)[1] are applicable to quantitative hydrocarbon type analysis.

In order to compare the GASPE and DEPT methods, a test mixture was prepared. The composition of this mixture and its method of preparation are given in Table I (attachment).

The GASPE, Conventional Spin/Echo (CSE) and DEPT sequences were written with modifications of the literature for the JEOL FX-270 NMR spectrometer. By appropriate combination of addition and subtraction of GASPE and CSE spectra at τ values of 1/J, 1/2J, 1/4J, and 3/4J, spectra containing only C, CH, CH_2, and CH_3 were obtained. From the integration of this spectra, the percent carbon types were calculated for the mixture. Table II lists the percent of aliphatic carbon types using the GASPE method. An examination of the data in Table II indicates that quantitation of carbon types present in minor amounts is not accurate.

We are now completing the work using the DEPT sequence. Hopefully a full paper discussing the pros and cons of the two methods will be published in the near future.

Sincerely,

Ed Clennan

Daniel A. Netzel and Ed Clennan
LETC Chemistry Dept.
Univ. Wyoming

Attach.

TABLE I: TEST MIXTURE[a]

COMPOUND	Moles used	#C	#CH	#CH_2	#CH_3
toluene	.01	1	5	0	1
2,2,4-trimethylpentane	.01	1	1	1	5
o-ethyltoluene	.01	2	4	1	2
acenapthanene	.01	4	6	2	0
2,3-dimethylnapthalene	.01	4	6	0	3
1-methylnapthalene	.01	3	7	0	1
1,2,3,4-tetrahydro-napthalene	.01	2	4	4	0
hexane	.01	0	0	6	0
heptane	.01	0	0	5	2
tetradecane	.01	0	0	12	2
TOTAL		17	33	31	15
% TOTAL		17.71	34.38	32.29	15.63

[a]The samples were prepared by taking this mixture and diluting it to 25 ml with $COCl_3$. The samples were sealed in 5 and 10 mm NMR tubes. Some of the samples were also .04 M in $Cr(AcAc)_3$.

TABLE II: QUANTITATION OF ALIPHATIC CARBONS WITH THE GASPE METHOD

	EXPERIMENTAL CARBONS		EXPERIMENTAL % CARBON		CALCULATED CARBONS	CALCULATED % CARBON
CH_3	14.06[a]	(15.52)[b]	29.31	(32.34)	15	31.25
CH_2	31.96	(31.93)	66.58	(66.53)	31	64.58
CH	10.48	(3.98)	21.84	(8.30)	1	2.08
C	1.24	(5.01)	2.6	(10.44)	1	2.08
	57.74	(56.44)	120.33	(117.61)	48	99.99

aFirst Attempt

[b]Second Attempt

REFERENCES

1. Bendall, M. R., D. M. Doddrell, D. T. Pegg, and W. E. Hall. Brochure by Bruker, 1982.
2. Patt, S. L. and J. N. Shoolery. J. Magn. Resonance 46, 535 (1982).
3. Cookson, D. J. and B. E. Smith. Org. Magn. Resonance 16, 111 (1981).
4. Bendall, M. R., D. M. Doddrell, and D. T. Pegg. J. Am. Chem. Soc. 103, 4603 (1981).

289-19 **ROSKILDE UNIVERSITETSCENTER**
MARBJERGVEJ 35

Poul Erik Hansen, Institut I
POSTBOX 260 DK-4000 ROSKILDE TELEFON 02 - 75 77 11
Denmark

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

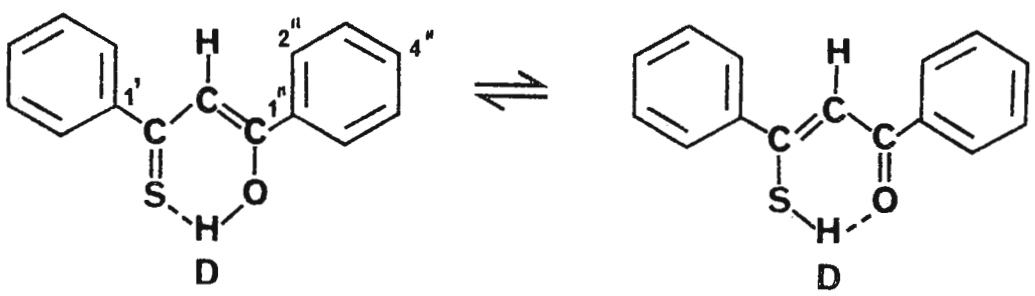
DATO/REFERENCE JOURNALNUMMER DERES REFERENCE/JOURNALNUMMER
September 16 1982

Dear Professor Shapiro

DOES THE BORN-OPPENHEIMER APPROXIMATION BREAK DOWN IN THE CASE OF LONG-RANGE ISOTOPE EFFECTS?

In response to your colorfull reminders a short description of some results from my latest visit to Harald Günther at Siegen.

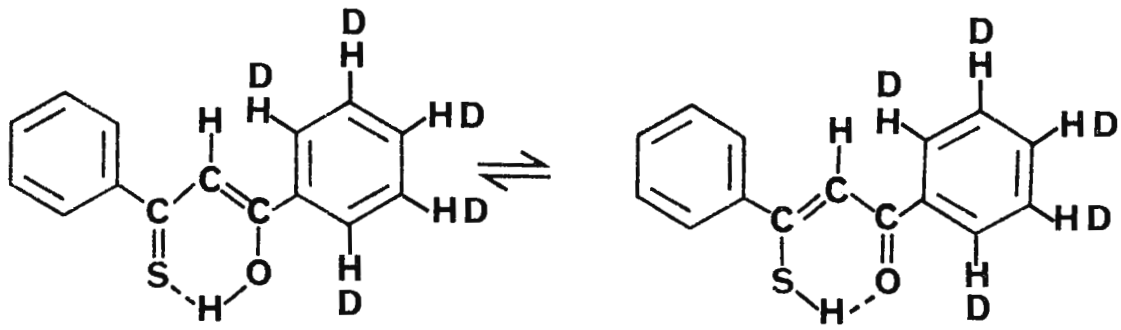
From our results in a previous paper[1] it is clear that substituents at one of the phenyl rings in the β-thioxoketonesystem may change the enol-enethiol equilibrium, but also that deuterium substitution at the S or O may perturb the equilibrium (I) giving rise to long-range equilibrium isotope effects on ^{13}C as shown in Table 1.



(I)

What we did this time was to look at the pentadeuteroderivative as shown in II. As seen from table 1, did this derivative also show small, but significant isotope effects(large for

long-range isotope effects). As the effects furthermore are proportional to those observed when the equilibrium is perturbed by other means (D on S or O) we do not hesitate to claim that the pentadeuteration leads to a change in the equilibrium.



(II)

Table 1. Deuterium isotope effects on ^{13}C nuclear shielding in ppm

	CS	CO	CH	C-1'
I	-4.69	+1.69	+0.32	-0.59
II	-0.11	+0.04	+0.01	-0.01

The change in the equilibrium shows that the β-thioxoketo-system is a very sensitive gauge of substituent effects. However, the remaining question is why does the equilibirum change.

The magnitude of the isotope effects in case II does not depend upon the ration of H and D compound in the mixture and it is not changed upon a ten fold dilution.

We consider two possibilities. The first is that the COH-C_6H_5 part not is planar and as the five H are exchanged with five D the steric interaction between the COH group and the phenyl ring is reduced. The other possibility is that the C_6D_5 radical is slightly more electronegative than the C_6H_5 radical. This however means that the Born-Oppenheimer approximation not is valid in this case. A heretic thought among theoreticians. Nevertheless, many other data in the litterature point towards a break down at least for the very small effects observed in long range isotope effects.

I hope some theoretician would like to comment on why they believe so strongly in the B-O app. and what experimental evidence on the same level as long range isotope effects support the B-O approximation.

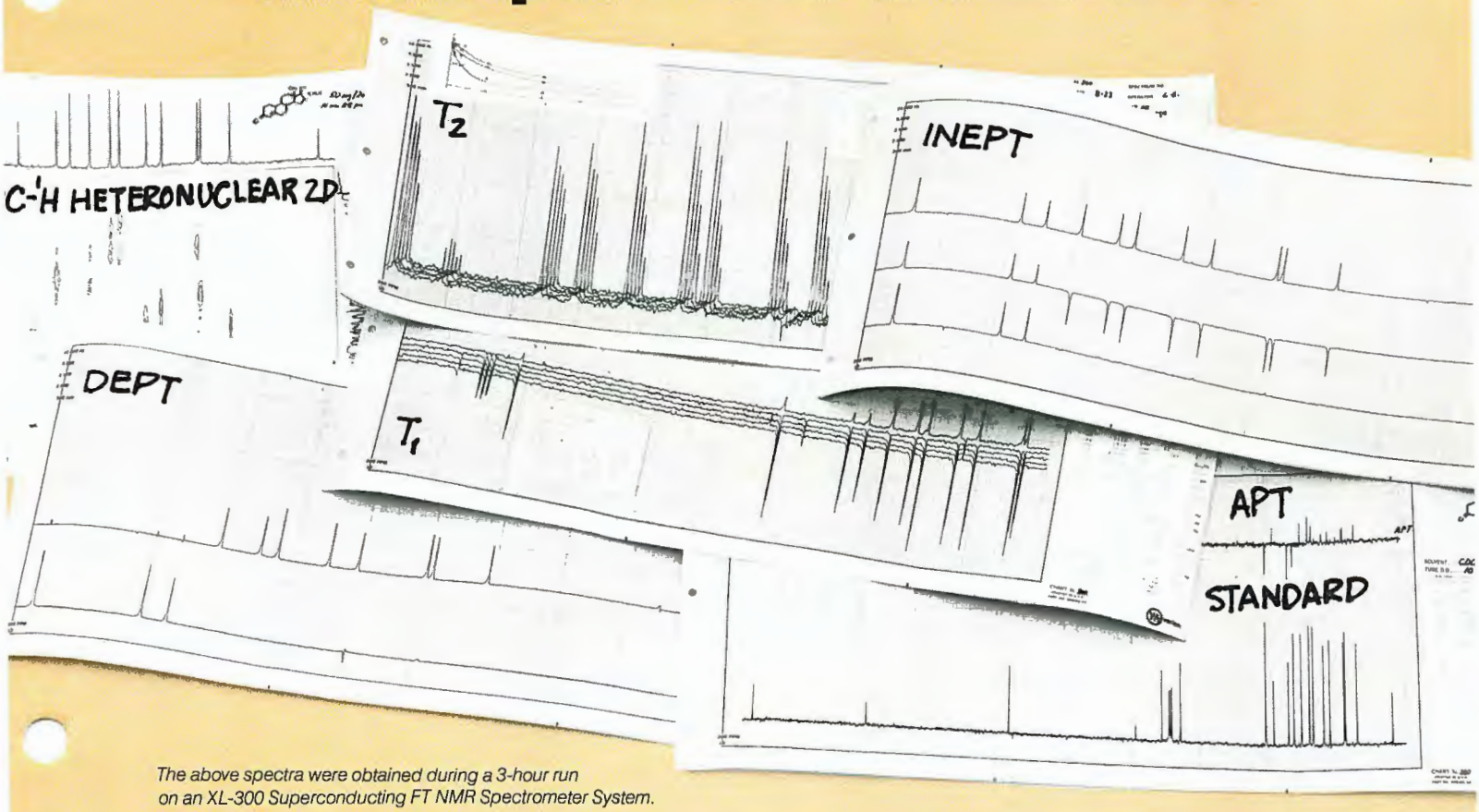
1. P.E.Hansen, F.Duus and P.Schmitt, OMR 18,58(1982)

Yours sincerely

Poul Erik Hansen

PS! The isotope effect is defined as $\Delta^n = \delta C(H) - \delta C(D)$

Some manufacturers claim these experiments are difficult



The above spectra were obtained during a 3-hour run on an XL-300 Superconducting FT NMR Spectrometer System.

Varian owners perform them all before lunch

Here's what one XL Series owner says:
Dr. Peter Rinaldi is a chemist at the ***Major Analytical Instruments Facility,*** *Greenwood, Ohio. MAIF is a research and testing facility serving Case Western Reserve University and scientists throughout the Ohio Valley region. All quotes are from the* MAIF NEWSLETTER, *Vol. I, Issue 3, March 1982, reprinted courtesy of MAIF.*

Software written for chemists: "Special experiments are a standard part of the XL-200 NMR software package," says Dr. Rinaldi. "We have been routinely running experiments such as INEPT, APT, solid state cross polarization, and most of the commonly used 2D-FTNMR experiments. Having run many of these myself, I can personally vouch for the tremendous advantage they offer."

Multi-tasking capabilities: "We need not be concerned about idling the instrument while time-consuming data processing and plotting is being performed; a long acquisition can be run simultaneously. It is not uncommon for the more experienced users to have the XL-200 occupied doing three or even four tasks simultaneously for extended periods of time."

More information in less time: "In the rare instance that a new experiment is needed for which the pulse program does not exist, it can easily be written in convenient Pascal language, and no hardware modifications are required. Thus, most of the barrier to utilizing new NMR techniques has been eliminated."

Here's what Varian software can do for you: To receive your free copy of "Software: New Ways to Solve Difficult Problems," write **NMR Software**, Varian Associates, D-070, Palo Alto, CA 94303; or call the sales office nearest you today.

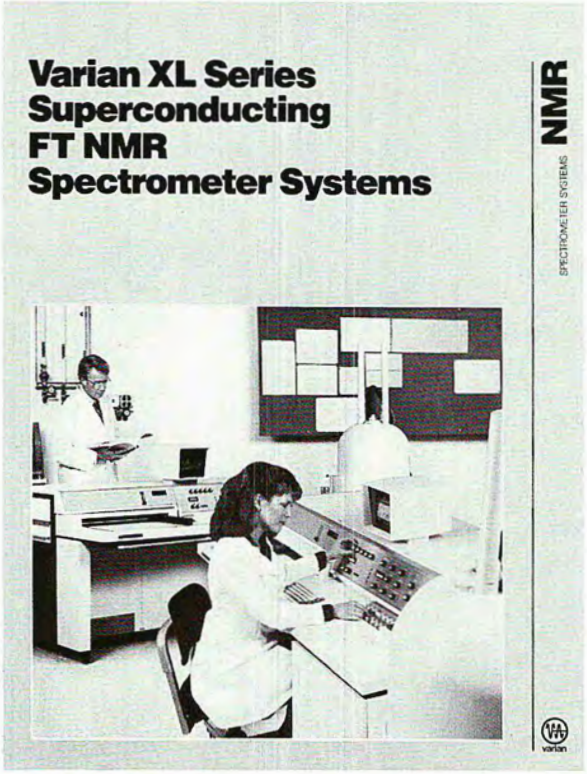
Varian performs while others only promise.

varian

For assistance contact: • Florham Park, NJ (201) 822-3700 • Park Ridge, IL (312) 825-7772 • Houston, TX (713) 491-7330 • Los Altos, CA (415) 968-8141
In Europe: Steinhauserstrasse, CH-6300 Zug, Switzerland.

VARIAN AD No. MAG-2787(A)
TAMU NMR Newsletter — Oct/Nov/Dec 1982

Send today for this XL Series brochure.



Call or write now to receive your copy of the XL Series brochure on Varian Superconducting FT NMR Spectrometer Systems. This publication includes information concerning 2-D NMR, pulse sequence generation, dot matrix displays, new software capabilities, user programming and other valuable input for NMR spectroscopists.

To receive your copy, or to have a Varian Sales Representative call on you, please contact the Varian Sales Office nearest you. A listing of both U.S. and international offices appears below.

varian

Varian U.S. Sales Offices

California
9901 Paramount Blvd.
Downey, CA 90240
(213) 927-3415

375 Distel Circle
Los Altos, CA 94022
(415) 968-8141

Colorado
4665 Kipling, Suite 1
Wheatridge, CO 80033
(303) 425-0413

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

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

Maryland
4701 Lydell Drive
Cheverly, MD 20781
(301) 772-3683

Massachusetts
83 Second Avenue
Burlington, MA 01803
(617) 272-4152

Michigan
3721 W. Michigan
Suite 300
Lansing, MI 48917
(517) 321-5000

New Jersey
25 Hanover Road
Florham Park, NJ 07932
(201) 822-3700

New York
6489 Ridings Road
Syracuse, NY 13206
(315) 437-6464

Texas
505 Julie Rivers Road
Suite 150
Sugar Land, TX 77478
(713) 491-7330

Varian International Sales Offices

Australia
Varian Pty. Ltd.
679 Springvale Road
Mulgrave, Victoria,
Australia 3170

Brazil
Varian Industria e Comercio Ltda.
Av. Dr. Cardosa de Melo, 1644
CEP 04548, Sao Paulo, SP, Brazil

Canada
Varian Canada, Inc.
45 River Drive
Georgetown, Ontario,
Canada L7G 2J4

Europe/Near East/Africa
Varian AG
Steinhauserstrasse
CH-6300 Zug, Switzerland

Japan
Analytica Corporation
3rd Matsuda Building
2-2-6 Ohkubo
Shinjuku, Tokyo 160,
Japan

Mexico
Varian S.A.
FCA Petrarca 326
Mexico City, Mexico 5, DF

Southeast Asia
Varian Pacific
East Commercial Center
Room 1103
393-407 Hennessy Road
Wanchai, Hong Kong

United States
Varian Instrument Group
611 Hansen Way
Palo Alto, CA 94303

UNIVERSITÄT TÜBINGEN
PHYSIKALISCHES INSTITUT
Prof. Dr. O. Lutz

D-7400 TÜBINGEN 1, den 24.9.82
Morgenstelle
Telefon (0 70 71) 29 67 14

289-24

Physikalisches Institut, Morgenstelle, D-7400 Tübingen 1

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

Ihr Zeichen | Unser Zeichen Lu/Ja | Ihre Nachricht vom

Shielding Constants of Copper and Gallium

Dear Barry,

as addition to the fruitful discussions on "shielding" and "screening" during the summer school at Stirling, I would like to direct the attention on further available shielding constants in the free atomic shielding scale (σ^*):

1) For copper σ^* is given in the following paper:
O. Lutz, H. Oehler, and P. Kroneck,
Z. Physik A 288, 17 (1978); in the meanwhile further shielding data are available on copper compounds:
O. Lutz, H. Oehler, P. Kroneck, Z. Naturforsch. 33a, 1021 (1978), P. Kroneck, O. Lutz, A. Nolle, H. Oehler, Z. Naturforsch. 35a, 221 (1979); K.O. Becker, H.P. Schäfgen, Sol. State Comm. 32, 1107 (1979)

2) For Gallium $\sigma^*(^{71}Ga^{3+}$ in $H_2O) = -880(45)\cdot 10^{-6}$ was found:
J. Kodweiß, O. Lutz, W. Messner, K.R. Mohn, A. Nolle, B. Stütz, D. Zepf, J. Magn. Res. 43, 495 (1981)

From the figure given there, the influence of the different halides ligands is very obvious.

Sincerely yours

Otto

(Otto Lutz)

CONCORDIA
UNIVERSITY

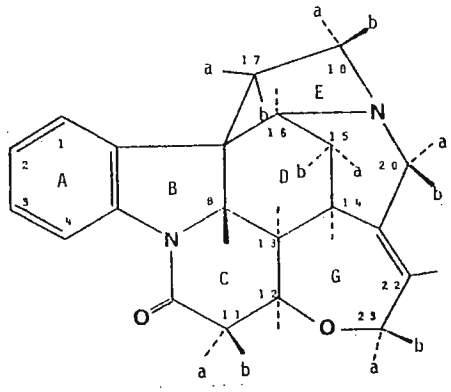
September 23, 1982

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

Dear Barry,

APPLICATION OF NOED MEASUREMENTS TO STRYCHNINE

In the course of some work with Jack Edward, of McGill University, on the application of ^1H spin-lattice relaxation measurements to the structure and stereochemistry of some strychnine sulfonic acids, we turned up some apparently anomalous relaxation rates. These anomalies seemed to disappear if some of the previously reported (1) ^1H chemical shifts for strychnine (I) were re-assigned. We therefore undertook a re-examination of the assignments, using nuclear Overhauser effect difference (nOed) measurements at 400 MHz.



I

Those who attended the 1982 ENC meeting in Madison will recall that Dr. Suzanne Wehrli displayed in the Bruker suite two examples of applications of 2D techniques to strychnine - ^1H-^{13}C and ^1H-^1H shift correlation (COSY). We are indebted to Dr. Wehrli for copies of her plots. Her work provides an elegant verification of the assignment of the ^1H signals to specific sites through scalar coupling connectivities. Our nOed work has determined the dipolar relaxation connectivities which establish the stereochemical relationships among the protons.

Strychnine is a good molecule on which to apply nOed measurements, since the spectra at 400 MHz (0.1 M in $CDCl_3$ or DMSO-d_6) are well dispersed. We used a slight modification of

SIR GEORGE WILLIAMS CAMPUS
1455 DE MAISONNEUVE BLVD. WEST
MONTREAL, QUEBEC H3G 1M8

the nOed procedure reported by Hall and Sanders (2). Degassing was unnecessary, since intramolecular relaxation is efficient in a molecule of the size and rigidity of strychnine. The data were interpreted with the aid of molecular models and calculated enhancements.

From irradiation of the H-8, 13, 15a, 15b, 18a, 18b, 20a, 20b, and 22 transitions we established that the assignments for the geminal pairs of protons at C-15, C-18, and C-20 should be reversed. The use of both $CDCl_3$ and DMSO-d_6 solutions to modify chemical shifts, and computer simulations using LAOCOON III led to a revised set of coupling constants for the four spin system H-17a, 17b, 18a, and 18b. The revised chemical shifts and coupling constants are listed in the Table.

Best regards,

Yours sincerely,

Walter

Walter J. Chazin

Laurie

Laurie D. Colebrook

LDC/dg

---

1. J.C. Carter, G.W. Luther, and T.C. Long, J. Magn. Reson., 15, 122 (1974).
2. L.D. Hall and J.K.M. Sanders, J. Am. Chem. Soc., 102, 5703 (1980).

Table. Revised ^1H chemical shifts and coupling constants for strychnine[a]

Proton	δ[b]	Coupling constants, J (Hz)[c]		
15a	2.36	15a,15b = -14.5	15a,16 = 4.9	15a,14 = 4.0
15b	1.46	15b,16 = 2.0	15b,14 = 1.0	
17a	1.88	17a,17b = -15.5	17a,18a = 8.4	17a,18b = 11.7
17b	1.89	17b,18a = 0.1	17b,18b = 6.9	
18a	3.19	18a,18b = -10.2		
18b	2.87			
20a	3.70	20a,20b = -14.7	20a,22 = 0.9	
20b	2.72			

[a]The remaining assignments were in agreement with those in Ref. 1.
[b]Ppm from TMS, $CDCl_3$ solutions.
[c]Negative signs were assumed for geminal coupling constants.

ES 3178 REV. 1/81

DU PONT
ESTABLISHED 1802
E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED
WILMINGTON, DELAWARE 19898

CENTRAL RESEARCH & DEVELOPMENT DEPARTMENT
EXPERIMENTAL STATION

1982 September 27

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

Dear Professor Shapiro,

Selenium-77 NMR of Some Fluorinated
Alkenylphenyl and Alkylphenylselenides

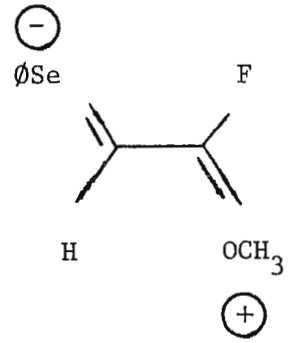
Organoselenium compounds have received much attention as reagents in organic synthesis.[1] Despite this interest, relatively little has been reported on the use of selenium-77 NMR as a tool for structural elucidation of organoselenium compounds[2] and only one article appeared in the area of fluoro-organoselenides where the fluorines are on the hydrocarbon portion.[3] The selenium-77 isotope has a natural abundance of 7.58% and has approximately 3 times the receptivity of carbon-13. In this note we wish to report the ^{77}Se chemical shifts and ^{77}Se-^{19}F coupling constants for a few fluorinated alkylphenyl and alkylphenylselenides.[4]

The proton decoupled ^{77}Se spectra were recorded on a Varian FT80A spectrometer at 15.167 MHz in $CDCl_3$. The ^{77}Se chemical shifts, measured relative to phenylvinylselenide (i.e. 395.5 ppm downfield from dimethylselenide) and the ^{77}Se-^{19}F coupling constants for the alkenylphenyl and alkylphenyl selenides studied are listed in Tables I and II.

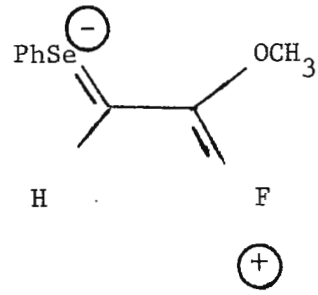
From Tables I and II we see the following:

1. Trans Se-F coupling constants are larger than cis in the fluorinated alkenylphenyl selenides.

2. A selenium trans to a fluorine, as in compound 2, is 20 ppm upfield relative to the cis fluorine compound. However, when a resonance electron donor is trans to a selenium, such as methoxy, then the selenium trans to the fluorine is downfield relative to the cis, due possibly to greater contribution of resonance structure A than resonance structure B.



A



B

3. An alkyl group geminal to a selenium (compd 7) deshields the selenium and also reduces the trans $^3J_{Se-F}$ coupling constant while increasing the cis.

4. A chlorine atom γ to a selenium in the case of alkyl selenides causes a 24 ppm downfield shift relative to a fluorine and methoxy group. This may be due to some conformational or electronic effect.

References

1. H. J. Reich, Accts Chem. Res. 12, 22 (1979);
D. L. J. Clive, Tetrahedron, 34, 1049 (1978).

2. J. P. Fackler and W. H. Pam, J. Amer. Chem. Soc. 101, 160 (1979).
W. H. Pam & J. P. Fackler, ibid, 100, 5783 (1978) and references therein.

3. W. Gombler, Z. Naturforsch, 36b, 535 (1981).

4. Preparation of compounds 4, 5, 6, 8, 10, 11: A. E. Feiring, J. Org. Chem. 45 1958 (1980); compounds 7, 12, 13: ibid 45, 1962 (1980). Compound 9 was prepared by addition of PhSeCl to vinyl fluoride; treatment of 9 with methanolic KOH gave compounds 2 and 3 which were separated by careful spinning band distillation (A. E. Feiring, unpublished results).

We hope this limited amount of data can generate further study of selenium-77 NMR by your readers.

Sincerely yours,

F. Davidson

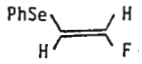
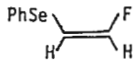
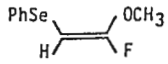
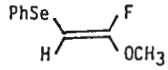
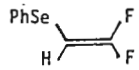
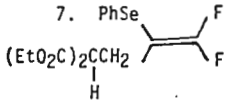
A. E. Feiring

FD:AEF/dew

Please credit this contribution to the account of D. D. Bly

Table 1

Selenium-77 Chemical Shifts and ^{77}Se-^{19}F Coupling Constants for Fluorinated Alkenylphenyl Selenides

Compounds	δ^a	$^3J_{SeF}$
1. $PhSeCH{=}CH_2$	0	
2. 	-125.4	51.1
3. 	-105.4	7.1
4. 	-143.7	40.0
5. 	-154.0	<1
6. 	-141.7	3.3 (cis) 41.0 (trans)
7. 	- 95.5	5.9 (cis) 19.5 (trans)

a - negative sign is upfield from phenylvinyl selenide.

b - absolute value of coupling constants are given.

Table II

^{77}Se Chemical Shifts and ^{77}Se-^{19}F Coupling Constants for Fluorinated Alkylphenyl Selenides

	Compounds	δ^a ppm	$^3J_{Se-F}{}^b$(Hz)
8.	$PhSeCH_2CF_2Cl$	-101.5	3.9
9.	$PhSeCH_2CHFCl$	-102.0	7.6
10.	$PhSeCH_2CF_2OCH_3$	-125.1	3.2
11.	$PhSeCH_2CF_3$	-125.0	3.9
12.	$PhSeCH(CF_3)CH_2Cl$	- 25	3.5
13.	$PhSeCH(CF_3)CH_2OCH_3$	- 49.2	1.7

a. negative sign is upfield from phenylvinyl selenide.

b. absolute value of coupling constants are given.

WASHINGTON UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY
Campus Box 1134

September 20, 1982

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

Dear Barry:

We currently have a position available within the Departments of Chemistry and Medicine at Washington University for a postdoctoral research associate in the field of NMR of intact biological systems. I am soliciting applications and ask that you make this letter available to any qualified individuals whom you feel might be interested.

The primary focus of this position will be the hormonal regulation of liver metabolism as studied by H-1, C-13 and P-31 NMR experiments with rat liver in vivo and in vitro. The studies in vivo will make use of surface coil and chemical shift spin-imaging techniques while studies in vitro will utilize both perfused liver and isolated hepatocytes (liver cells). Time will also be available for independently motivated research within the context of our group interests.

The applicant should have a Ph.D. in chemistry, physics, biochemistry or other related field with extensive hands-on experience in magnetic resonance and a keen interest in biomedical applications. The initial appointment will be for a period of one year with additional extensions if mutually agreeable.

The NMR instrumentation available within our group for this project includes two state of the art Bruker NMR spectrometers, the WH-360 and CXP-200. Both spectrometers are fully multinuclear and employ widebore superconducting magnets of 72 mm and 85 mm inner diameter bores (inside room temperature shims) for the WH-360 and CXP-200 respectively. Extensive radio frequency design and test equipment is also available for NMR probe development and construction.

This position offers an exciting opportunity to gain extensive experience in the rapidly expanding field of intact tissue NMR while also becoming acquainted with the biomedical techniques needed to support such experiments. All interested applicants are invited to submit a letter detailing their background and interests along with a curriculum vitae; two letters of professional recommendation should also be submitted. Washington University is an Equal Opportunity, Affirmative Action Employer.

Sincerely,

Joe

Joseph J. H. Ackerman, Ph.D.
Assistant Professor of Chemistry
Research Assistant Professor of Medicine

UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

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

SCHOOL OF MEDICINE
DEPARTMENT OF RADIOLOGY
EXPERIMENTAL NUCLEAR INSTRUMENTATION

UCSF Radiologic Imaging Laboratory
400 Grandview Drive
South San Francisco, California 94080
(415) 952-1366

September 27, 1982

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

University-Industry Collaboration; Positions Open

Dear Dr. Shapiro,

Since 1975 the Department of Radiology has had an NMR imaging program that has resulted in two imagers operating at 3.5 KGauss, one using a Varian 12-in pole tip magnet having a useful aperture of 6.5cm and a second incorporating an Oxford superconducting magnet and a useful aperture of 55cm. The small unit has been used to image rats, mice, gerbils, guinea pigs and phantoms that model disease conditions in humans (1,2) and the large unit has been used to evaluate the technology in volunteers and patients (3,4). Two examples of such images are shown below. An upgrading of this unit, as well as construction of additional ones, is now in progress. The University R & D program is supported by Diasonics, a medical imaging company based in South San Francisco. The UCSF effort is a continuing program designed to improve hardware, develop imaging techniques, study their clinical effectiveness, and understand the reasons behind the tissue characteristics observed in images. The Diasonics program involves the commercialization of this technology. We are interested in hearing from people interested in R & D or production responsibilities, either at the University or in Diasonics. Positions are open for NMR spectroscopists, digital, RF or software engineers, or technologists. Resumes should be sent to our attention.

Larry Crooks

Larry E. Crooks, Ph.D.
Associate Professor of Electrical Engineering
Assistant Director, UCSF Radiologic Imaging Laboratory

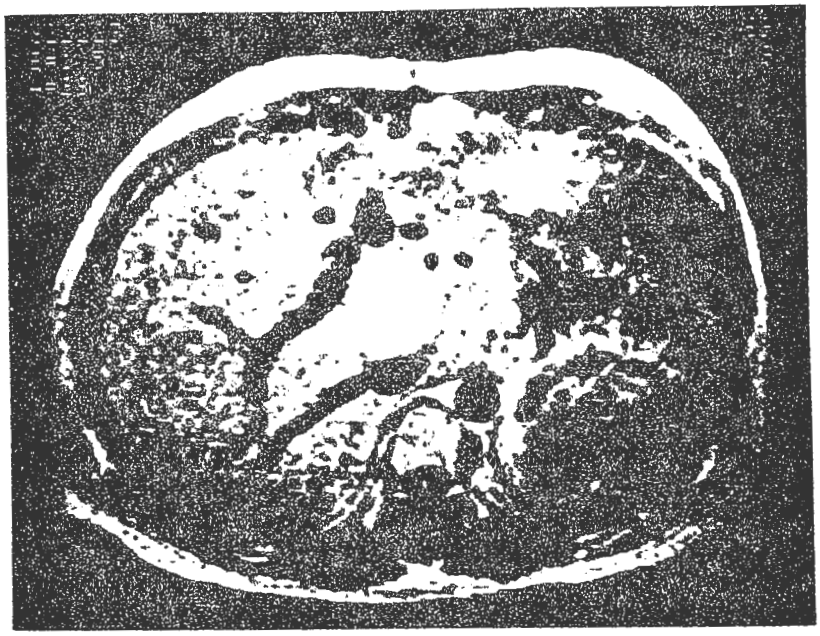
Leon Kaufman, Ph.D.
Professor of Physics and
Director, UCSF Radiologic Imaging Laboratory

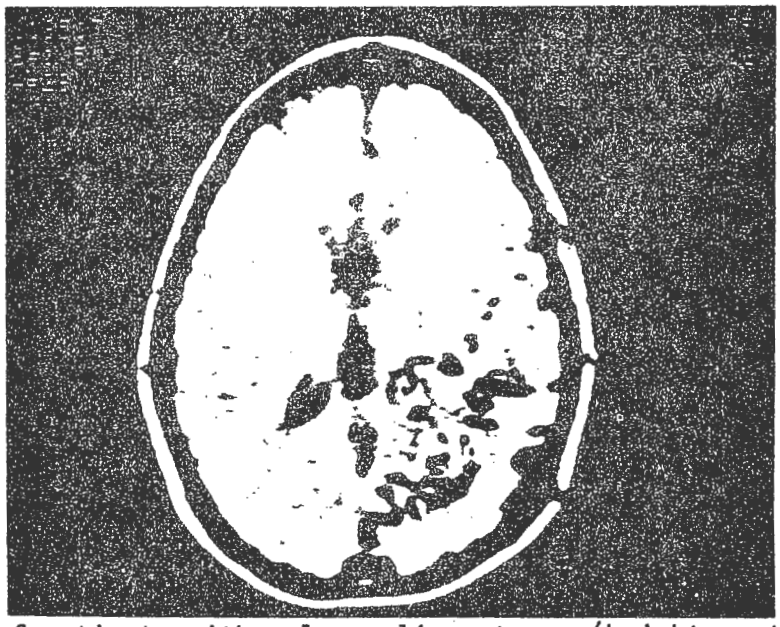
1. Herfkens R, Davis PL, Crooks LE, Kaufman L, Price DC, Miller RT, Margulis AR, Watts J, Hoenninger JC, Arakawa M and McRee R. NMR Imaging of the Abnormal Live Rat and Correlation with Tissue Characteristics. Radiology 141:211, 1981.

2. Davis PL, Kaufman L, Crooks LE, Margulis AR and Miller TR. Detectability of Hepatomas in Rat Livers by Nuclear Magnetic Resonance. Investigative Radiology 16:354, 1981.

3. Crooks LE, Arakawa M, Hoenninger JC, Watts JC, McRee RW, Kaufman L, Davis PL and Margulis AR. NMR Whole Body Imager Operating at 3.5 KGauss. Radiology 143: 169, 1982.

4. Crooks LE, Mills CM, Davis PL, Brant-Zawadzki M, Hoenninger JC, Arakawa M, Watts JC and Kaufman L. Visualization of Cerebral Abnormalities by NMR Imaging: The Effects of Imaging Parameters on Contrast. Radiology 144:843, 1982.





NMR images of patients with a large liver tumor (bright central region in the top image), and an arteriovenous malformation (bottom image). Vasculature is seen dark because of flow. In the head image the dark regions of the brain demonstrate the abnormal vasculature.

289-33

STANFORD MAGNETIC RESONANCE LABORATORY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

Director: Oleg Jardetzky, M.D., Ph.D.
Professor of Pharmacology

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

September 27, 1982

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

Dear Barry,

Two positions at the Research Associate or Postdoctoral Fellow level will become available at SMRL in early 1983 as the laboratory inaugurates a new program with the installation of a 600 MHz spectrometer, which is currently on order. We are looking for highly competent, highly motivated individuals with an active interest in biological applications of NMR, willing to learn and to function as members of an interdisciplinary team in this rapidly growing field. Proficiency in NMR electronics, hardware and software and familiarity with probe design and construction are essential. Readiness to accept challenges and spearhead new developments highly desirable. Experience with in vivo NMR and imaging technology helpful, but not mandatory. Rank and salary dependent on qualifications. All inquiries should be addressed to me at the above address.

With best regards,

Yours sincerely,

Oleg

Oleg Jardetzky

OJ:reh

P.S. Stanford is an Equal Opportunity Affirmative Action Employer.

Examine its capabilities. Think of yours.

Advanced Nicolet Data System

The new 1280 Data System and its predecessors are the most popular spectroscopy computer systems ever designed. The 1280 comes complete with 128K/20-bit RAM memory expandable to 256K. It also includes the Model 293C Pulse Programmer and the most comprehensive FT-NMR software available today.

Magnets/Probes

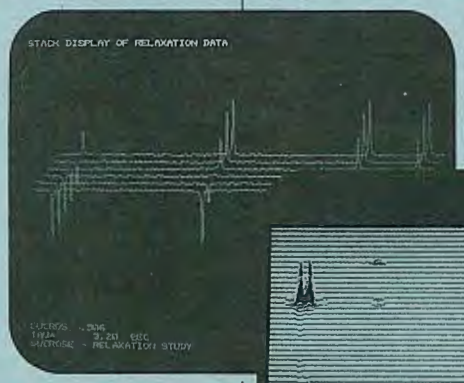
Magnets range from 4.7T to 11.7T (200, 300, 360 and 500 MHz) in both wide and narrow bore. Probes available include fixed-tune, broadband, special cross-polarization/magic angle spinning and the new sideways-spinning solenoidal.

Compu-Shim

Performs fast, efficient, automatic shimming of all spin and non-spin gradients, using the lock level or FID response. Available as an option.

^{13}C Library & Search Programs

A library of 8,960 ^{13}C spectra is available, known as the EPA/NIH/NIC CNMR Data Base. Three different routines are provided to search for spectra.

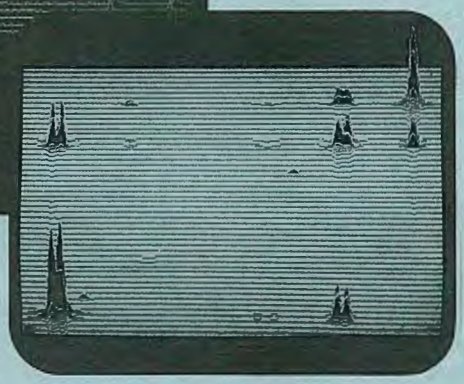


Color raster-scan stacked display of data measured at different delay times for an inversion-recovery T_1 determination.

New solenoidal sideways-spinning probes provide enhanced sensitivity.

New Color Raster-Scan Display

Optional feature provides simultaneous display of up to seven colors and full alphanumerics. Particularly valuable for displaying 2D-FT data and multiple spectra.



Raster-scan display of 2D-FT data.

"LOG IN PLEASE"

Now update your software by phone!
If you have a NIC-1180 or 1180E/1280 Data System with a 300 baud modem, we can update your software with our Telephone Software Distribution Network.

With a Nicolet NMR, you'll do more work and do it better.

NICOLET MAGNETICS CORPORATION

255 Fourier Avenue, Fremont, CA 94539
(415) 490-8300

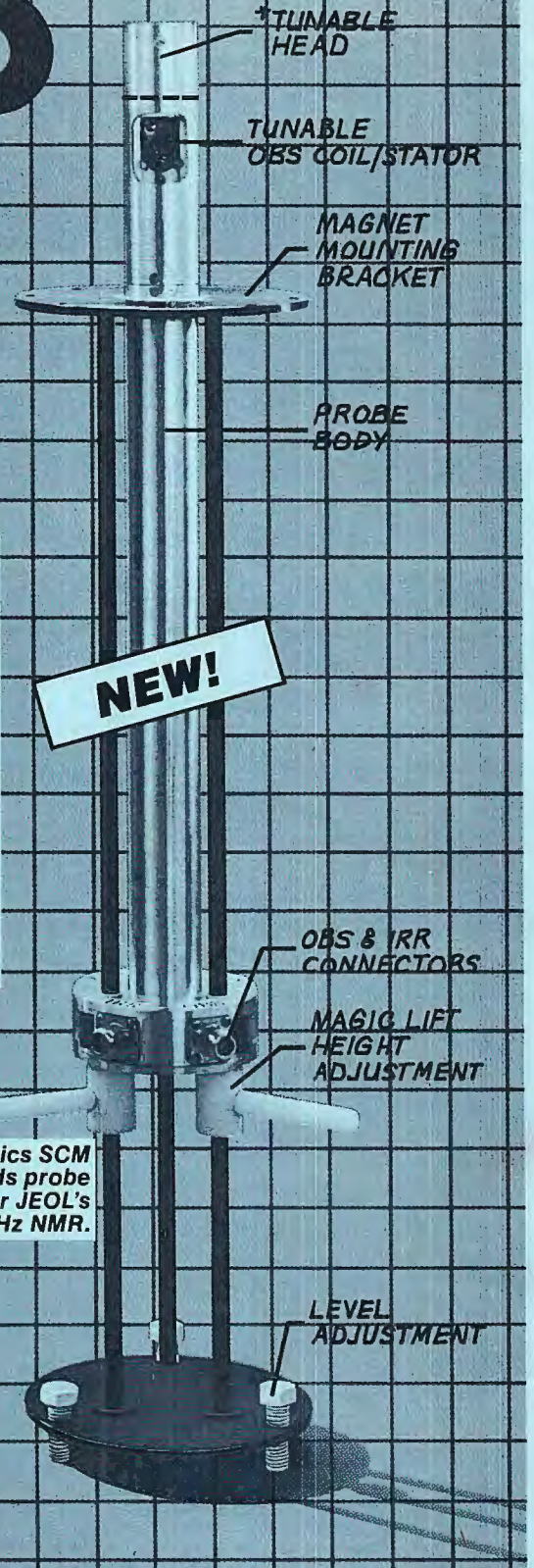
The Nicolet NMR

THE SOLID LEADER in NMR

With Multi-Nuclear/ Multi-Field Solid State Probes

- **High field** solid sample probe for JEOL's 200 MHz SCM!
- ***Tunable heads** — interchangeable plug-in matching units for observation of
  - ^{13}C (~50 MHz)
  - ^{31}P (~80 MHz)
  - ^{29}Si (~40 MHz)

  with one probe!
- Self starting rotor/stator design!
- High speed magic-angle 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 200 MHz NMR.

SOLIDS UPDATE – NOW AVAILABLE

- MULTI NUCLEAR SOLIDS PROBE FOR THE FX 270
- WIDE BORE MAGNET WITH VARIABLE TEMPERATURE SOLIDS FOR THE FX 200

JEOL

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