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NMR NEWSLETTER

FEB 7 1983

No. 291

December, 1982

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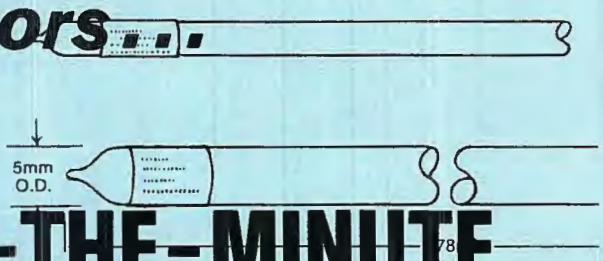

* If sp[illegible] t[illegible]ngs [illegible]d/or m[illegible]vels a[illegible] nee[illegible] ple[illegible]ctly to [illegible] location.

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DEADLINE DATES: No. 292 3 January 1983
No. 293 7 February 1983

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.

A U T H O R I N D E X - TAMU NMR NEWSLETTER NO. 291

THE JOHNS HOPKINS UNIVERSITY
SCHOOL OF MEDICINE
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DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

TELEPHONE 955-5000
AREA CODE 301

October 25, 1982

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

Dear Barry:

CONFORMATIONAL SEARCH ON ENZYME-BOUND LACTOYL-GLUTHATHIONE

We have been using the paramagnetic effects of Mn^{2+} on T_1 to measure Mn^{+2} to proton distances on the tripeptide product, S-(D-lactoyl)glutathione, bound to the enzyme Glyoxalase I (Figure 1) (1). In order to more objectively build molecular models based on these measured distances and to better evaluate the uniqueness of the model, we are using a distance geometry algorithm (2) which computes a structure consistent with known intermolecular bond distances, bond angles, Van der Waals radii, and experimentally measured Mn^{2+} to proton distances.

After more than twenty runs, our best fit structures fall into two families (Fig. 2) both of which show little variation about their respective means (Fig. 3). We hope to distinguish between these two sets of solutions by further distance measurements using interproton Overhauser effects.

With apologies for lateness,

Albert S. Mildvan, Paul Rosevear and
Joe Schaffer

Paul Rosevear
Al Mildvan
Joe Schaffer

1. Sellin, S, Rosevear, P., Mannervik, B. and Mildvan, A.S. J. Biol. Chem. 257 10023 (1982)

2. Kuntz, I.D., Crippen, G.M., and Kollman, P.A. Biopolymers 18, 939 (1979)

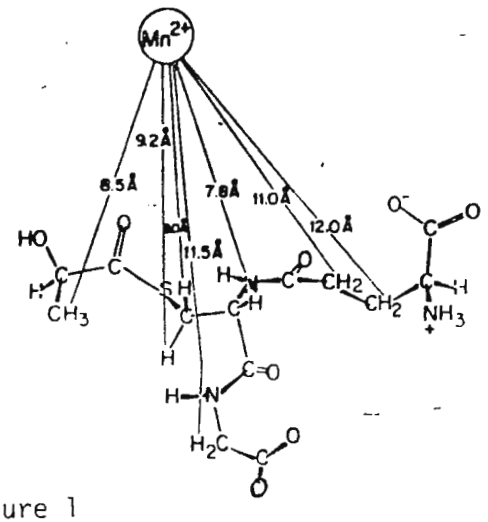

Figure 1

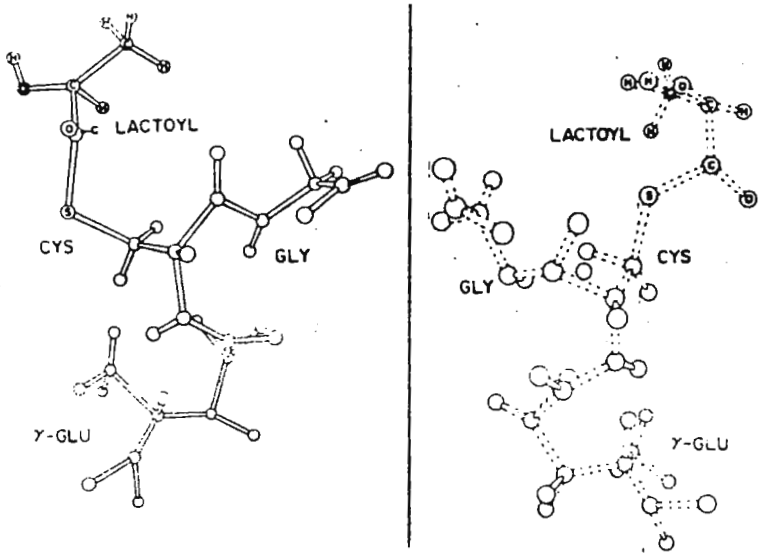

Figure 2

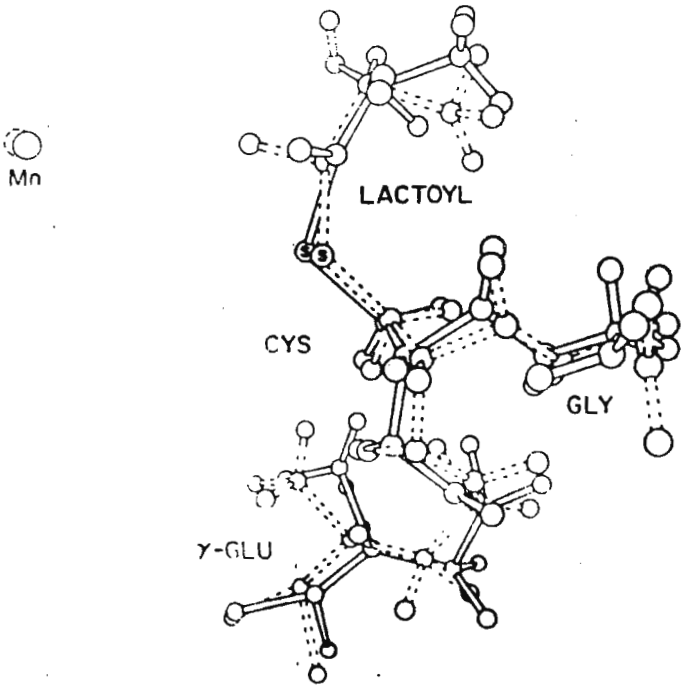

Figure 3

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October 26, 1982

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

Dear Barry:

Spectral Properties of a Hydroquinone: Triethylenediamine Complex.

Recently an unexpected precipitate, filtered from a known oligomer formulation, was submitted to this laboratory for identification. The material was poorly soluble in organic solvents and water but very soluble in either dilute aqueous base or acid. No melting point was found; the material decomposed on heating. It could be recrystallized from methanol. Elemental analysis (C, 64.70%; H, 8.23%; O, 14.73%; N, 12.52%) indicated the empirical formula: C_6H_9NO.

With the aid of C-13 and proton NMR, infrared, and mass spectroscopy, the unknown was identified as the 1:1 complex of hydroquinone (HQ) with triethylenediamine (TEDA), having the molecular formula $C_{12}H_{18}N_2O_2$. TEDA was known to be present in the formulation; HQ was an additive whose presence was not known at the time. This identification was confirmed by comparison of the IR and C-13 NMR spectra of the precipitate with material synthesized by direct reaction of HQ with TEDA in this laboratory.

This HQ:TEDA complex was first reported over 25 years ago. A fairly recent paper by Ilczyszyn, et al. (1) reports C-13 chemical shift data for salts of substituted phenols with triethylamine. We are unaware of any previous report on the NMR spectra of salts of dihydroxy benzenes and dibasic amines.

The C-13 and proton NMR spectra of the HQ:TEDA complex have only three signals each. These signals and their assignments are tabulated below; assignments were made using the positions of the signals, the multiplicities in the SFORD C-13 spectrum and the relative intensities of the proton signals. Olefinic or carbonyl structures were ruled out by the infrared spectrum.

OBSERVED CHEMICAL SHIFTS IN NMR SPECTRA OF HQ:TEDA COMPLEX

C-13 Spectrum[a]		Proton Spectrum[b]		Assignment
δ(from TMS)	SFORD Multiplicity	δ(from TMS)	Rel. Int.	
149.6	singlet	-	-	Aromatic ipso carbon
115.5	doublet	6.61	2	Aromatic CH groups
46.8	triplet	2.73	6	$R-CH_2-N-$ groups
-	-	4.5	1	Exchangeable H

a) Obtained from a saturated solution in DMSO-d_6.

b) Obtained from a saturated solution in methanol-d_4.

The mass spectrum of the precipitated material did not show a molecular ion for a $C_{12}H_{18}N_2O_2$ compound. Instead there were two strong peaks for m = 110 and m = 112 (molecular ions of HQ and TEDA) and the remainder of the spectrum was the superposition of the fragmentation patterns of HQ and TEDA. These probably formed by thermal decomposition of the original solid.

In our spectra, obtained in DMSO-d_6 solution, the C-13 signals of the material have the same chemical shifts as the corresponding signals observed for pure HQ and TEDA. The reported data of Ilczyszyn et al. indicated downfield shifts for the carbon signals in chloroform solutions of substituted phenol: triethylamine complexes due to either strong hydrogen bonding or charge transfer between phenol and base. It is postulated that in DMSO-d_6 solution competition with the polar solvent suppresses this bonding and the HQ and TEDA moieties of the complex exist as neutral rather than charged species. In the solid state the IR spectrum of the HQ:TEDA complex shows peaks for the NH^+ species and may indicate that the solid complex has either an ionic crystal lattice or a hydrogen-bonded polymeric structure.

We hope that this contribution will satisfy our subscription obligations for TAMU Newsletter.

Sincerely Yours,

Jessie L. Gove Donald J. Clancy William E. Killinger

(1) M. Ilczyszyn, Z. Latajka, and H. Ratajczak, Org. Magn. Reson. 16, 173 (1981).

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Professor B. L. Shapiro

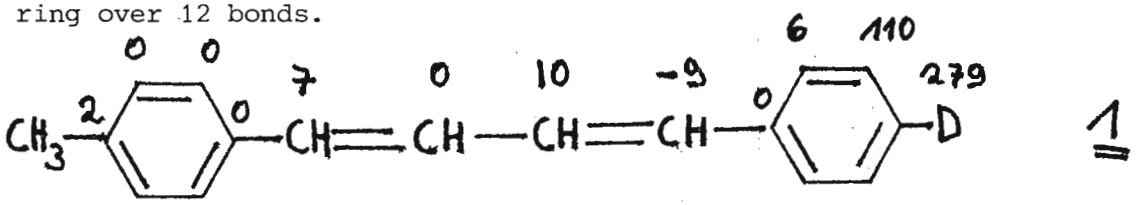
Texas A & M University
College Station, TX - 77843

USA

Dear Professor Shapiro,

Deuterium Isotope Effect on ^{13}C Chemical shift over 12 bonds

In the current race for long range deuterium isotope effects on ^{13}C chemical shifts (see TAMU 276/34, 277/23, 278/8, 280/3, 281/5) we would like to mark a distinct point. We have recently synthesised a series of compounds with a single deuterium atom at the end of a growing chain of conjugated carbon atoms. The last compound of this series, 1-phenyl-4-tolyl-butadiene 1, shows a deuterium isotope effect from the single deuterium in the phenyl ring over 12 bonds.



1

The values given in the formula are in ppb and have been obtained on our WH-400 spectrometer from a mixture of both the labelled and unlabelled species. Even more interesting than the deuterium effect over 12 bonds is the behaviour of the carbon atoms within the butadiene bridge, which do show a polarisation as if the deuterium would be a real substituent.

Sincerely yours

(S. Berger) (H. Künzer)

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October 26, 1982

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

Dear Professor Shapiro:

The second New Mexico Regional NMR ($\equiv[NMR]^2$) meeting held at the Los Alamos National Laboratory NMR Facility on September 25, 1982, was attended by 27 people from five institutions in New Mexico as well as representatives from corporate sponsors Cryomagnet Systems, JEOL, Nicolet, and Wilmad. The meeting featured a number of posters in addition to invited talks by Paul Lauterbur (SUNY-Stoney Brook) and Bill Earl (Los Alamos). The next meeting will be March 1983 at New Mexico Institute of Mining and Technology in Socorro and will be organized by Larry Werbelow.

Sincerely,

E. Fukushima
for the $(NMR)^2$
Steering Committee

EF/nb

Cys: CRM (2), MS A150
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E. Fukushima

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Prof. B.L. Shapiro
Texas A&M University

29 October 1982
4073/82

re.: assignment of ^{29}Si chemical shifts in silylated methyl β-D-xylopyranoside derivatives

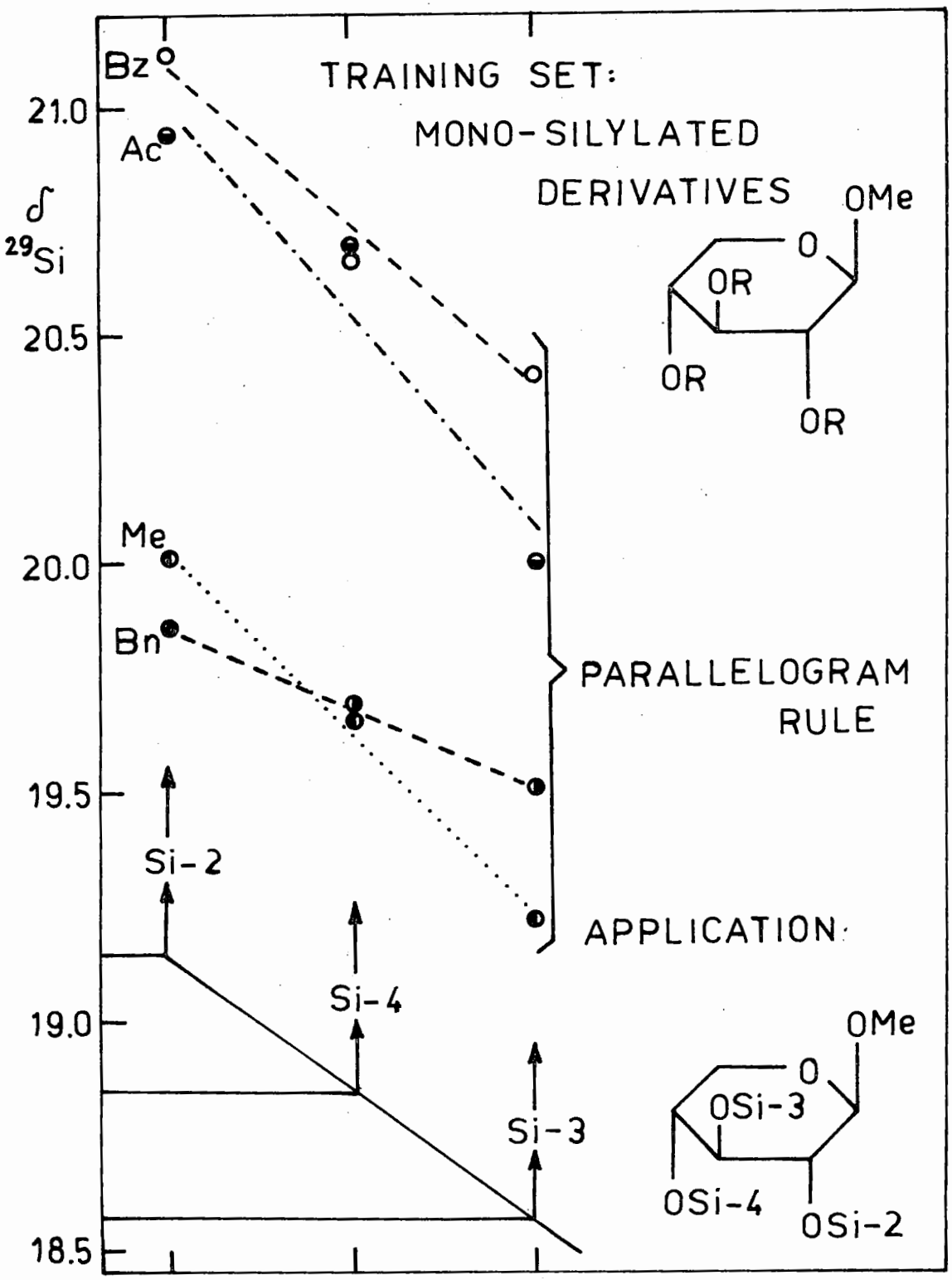
Dear Barry,

we are still involved with applications of ^{29}Si NMR to analytical problems. When polyfunctional compounds are silylated the number of ^{29}Si lines gives the number of functional groups; the assignment of these lines is a problem. Though it can be made in a rigorous way by 2D techniques, we are looking for empirical rules (^{29}Si 2D experiments are extremely time demanding as good resolution in both dimensions is required).

Recently, we have investigated (with Dr. Petráková of Bratislava) an extensive series of all possible mono- and di-O-methylated (Me), O-benzylated (Bn), O-benzoylated (Bz), and O--acetylated (Ac) methyl β-D-xylopyranosides. The results are schematically depicted in the Figure. Using the simple one-line ^{29}Si NMR spectra of trimethylsilylated di-O-substituted compounds as a training set, we established a "parallelogram rule" that the silicon shifts are always in the indicated order. Using this rule, lines in more complex spectra could be assigned as demonstrated for the case of pertrimethylsilylated methyl β-D-xylopyranoside. The assignment can be verified by the 2D techniques or by heteronuclear ^{13}C - ^{29}Si INADEQUATE experiments developed (see TAMU-NMR-N 287,p.35) for this purpose.

Sincerely yours,

Jan Schraml


TRAINING SET:
MONO-SILYLATED
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Professor B.L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station,
Texas 77843,
U.S.A.

Dear Barry:

Molybdenum Relaxation

Since we have been working with ^{95}Mo chemical shifts for a number of years, we have started using the same compounds for relaxation studies.

We have been carrying out relaxation studies of ^{95}Mo nucleus in various compounds. ^{95}Mo is a spin 5/2 nucleus, and so its relaxation would be expected to be dominated by the quadrupolar mechanism. Under motional narrowing conditions ($\omega_o \tau_c << 1$)

$$\frac{1}{T_{1q}} = \frac{1}{T_{2q}} = \frac{3\pi^2}{10} \frac{(2I+3)}{I^2(2I-1)} \chi^2 (1 + \frac{1}{3}\eta^2) \tau_c$$

where χ is the nuclear quadrupole coupling constant = $\frac{e^2 q_{zz} Q}{h}$

η is the assymetry parameter, τ_c is the rotational correlation time.

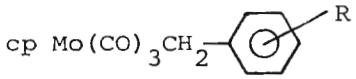
T_2 can be obtained from the ½ height linewidth if the inhomogeneity broadening is negligible ($T_2 = \frac{1}{\pi \omega_{½}}$). Since ^{95}Mo linewidths range from a few Hz to thousands of Hz, T_1's ranging from hundreds of milliseconds to microseconds are expected.

T_1's are measured using the inversion recovery $(180^o - \tau - 90^o_T)_n$ pulse sequence, with the time (τ) and intensity data $S(\tau)$ fitted to a 3 parameter equation of the form

$$S(\tau) = S(\infty) \quad (1 - B \exp^{-\left(\tau / T_1\right)})$$

Exponential fitting is preferred to the usual method of obtaining the T_1 from the slope of the logarithmic equation, since it is not dependent on the accuracy of the $S(\infty)$ measurement. The broad lines and rapid decay of the FID in many compounds make acquisition of the FID after about 30 msec unnecessary, allowing quite rapid determination of T_1's.

Table 1 shows some relaxation data for the class of compounds



(cp = cyclopentadienyl anion)

TABLE 1.

	$W_{\frac{1}{2}}$(Hz)	T_2 (msec)	T_1 (msec)
P-H	66.9±1.2	4.76±0.1	4.92±0.13
P-CF_3	62.0±1.2	5.13±0.1	5.29±0.09
P-OMe	63.2±1.2	5.04±0.1	5.11±0.12
O-Me	68.1±1.2	4.67±0.1	4.86±0.12
2,4,6 Me	126.3±1.2	2.52±0.02	2.51±0.04
$(Me)_5$cp P-H	97.4±1.2	3.27±0.04	3.39±0.04

T_1's are the average of several measurements; uncertainties are standard deviations. C ≈ 0.5M in $CHCl_3$. Temp. = 20°.

The results in Table 1 show good agreement between T_2's calculated from linewidths and inversion recovery T_1's, indicating a 1 or 2 Hz inhomogeneity contribution to linewidths. Addition of extra methyl groups to the benzyl or cp. ligands results in longer correlation times and shorter T_1's.

Table 2 shows the results for another class of compounds; (arene) $Mo(CO)_3$. The π bonded arenes are toluene, xylene and mesitylene. The ^{95}Mo linewidths are too narrow (3-6Hz) for T_2 calculations to be meaningful, but this also means that the ^{97}Mo linewidths are narrow enough to be accurately measured. If only quadrupolar relaxation is significant, then the quadrupole moment ratio can be calculated ($^{97}Q/^{95}Q = (^{95}T_1/^{97}T_1)^{\frac{1}{2}}$). The results are in excellent agreement with the value of 11.4±0.4 obtained by the same method for aqueous molybdate. [1]

TABLE 2

	toluene	o-xyl	m-xyl	p-xyl	mes
^{95}Mo T_1 (msec)	165.4±3.2	88.2±2.2	115.0±0.5	103.6±2.2	77.6±2.0
^{97}Mo $W_{\frac{1}{2}}$ (Hz)	252 ±3	466 ±3	358 ±3	398 ±3	532 ±3
^{97}Mo T_1 (msec)	1.26	0.683	0.889	0.800	0.598
$^{97}Q/^{95}Q$	11.5	11.4	11.4	11.4	11.4

C ≈ 0.5M in CH_2Cl_2. Temp. = 20°

Again, a decrease in T_1 is apparent with increasing methyl substitution, but the order of the xylyl T_1's may indicate an effect of increasing metal-arene bond strength on the quadrupole coupling constant. Such an effect has been advanced as a possible explanation of chemical shift order in these compounds. [2]

Please credit this contribution to the Monash University account (Ian Rae, Mike Heffernan) who are kind enough to share the newsletter with us.

[1] R.R. Vold and R.L. Vold, J.Mag.Res., 19, 365 (1975).

[2] A.F. Masters, R.T.C. Brownlee, M.J. O'Connor, A.G. Wedd, Inorg.Chem., 20, 4183 (1981).

Rob Brownlee B Philip Shehan

R.T.C. Brownlee B.P. Shehan

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

October 18, 1982.

Dear Barry,

COMBINED C-13 SHIFT AND STRUCTURE STORAGE AND RETRIEVAL USING THE MACCS SYSTEM.

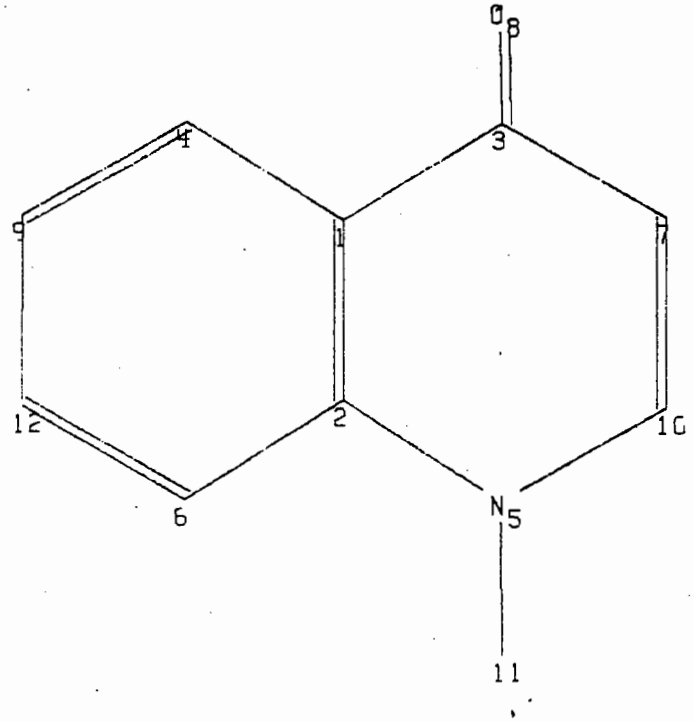
As part of a project to store and retrieve structures and associated chemical and biological data, a Datatype was Created (CMR.SHIFTS) in our in house Database. This Database is set up and Run using the MACCS (Molecular Access System, by Molecular Design Ltd., Inc.) program. The Datatype is Numeric, accepting two columns of numbers (atom number and shift) followed by comment fields of cca 110 characters, up to 300 lines per compound.

Input is as follows: The structure is Drawn with a light pen and Registered, if not already present in the Database. The system automatically creates a unique numbering of non-hydrogen atoms. The structure is Plotted out with Numbering turned On. With this plot and the CMR shifts in view, the Data are Registered under the compound into Datatype CMR.SHIFTS, one atom, one shift, one optional comment per line. The comments can include letters a, b etc for groups of interchangeable atoms.

Searching: After Filing, the information is immediately available to all authorized users. The shifts can be range Searched, and several ranges can be combined. Structures on the hitlist can be Viewed, or the Data CMR can be inspected, printed, the structures can be Plotted. The comments and other Data can be string Searched. Conversely, a structure or SubStructure Search will hit all the appropriate compounds, whose CMR data can then be inspected, printed or Searched.

INT.REG.NO	SAH.NO	SALTCODE	CHEM.NO	UNIT
67	SAH-300333	N	8888-777-66	BAR

CMR.SHIFTS



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7.0 - 109.8 REPTIME 1.8S
8.0 - -9999.0 IS OXYGEN
9.0 - 123.7 8K-->4K FT
10.0 - 144.0 +/- .1PPM
11.0 - 40.5 RT
12.0 - 132.3 TUBE 5-MM

MOL NAME CMR EG

C10 H9 N O	SPECTRUM.NO 12345C	INIT SB	CMR REF ETC G.M.COPPOLA, A.D.KAHLE AND M.J.SHAPIRO, ORG.MAGN.RESON., 17, 242 (1981). THIS IS A TEST OF MARGEN ON CMR DATA FROM PILOT.
M 159. W 189	NOTE FOR C-SHIFTS	DATE 8-3-82	

Reporting: Using FORGEN (Format Generator, by MDL), a report form was designed with the light pen, keyboard and CRT. Running the program MARGEN (Molecular Access Report Generator, by MDL) calls on a FORGEN Template and a Database. Getting (a) compound(s) from the database fills the structure and appropriate data into the form. Runtime information can be supplied (e.g. CMR.REF etc. Alternatively, a Datatype can be set up for the latter. The system accepts a large number of Text, Formatted or Numeric datatypes). 1000 characters per Box are handled, 200 Boxes, if necessary. Viewing or Copying of the reports on one or several compounds can be done automatically. The report form can be modified by an editing process. New Datatypes can be added. An example of a CMR shift report is enclosed.

Hardware: Prime 550 computer, Imlac II or VT100 graphic terminals, Versatec V-80 plotter, also runs others.

The main merit of this system is the combined structure, substructure and data search capability, speed and ease of use.

Yours truly,

Sandor

Sandor Barcza

Dr. Bernard L. Shapiro

October 26, 1982

The 74LS02 may be inserted in one of the empty IC locations on the board, but it is important to be sure both V_{CC} and ground are properly connected.

More details are available on request.

Sincerely,

Bill

W. E. Wageman
INC-4
Mailstop C346
(505) 667-5046

WW/nb

Cys: CRM (2), MS A150
INC-4 File

Los Alamos
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

October 26, 1982

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

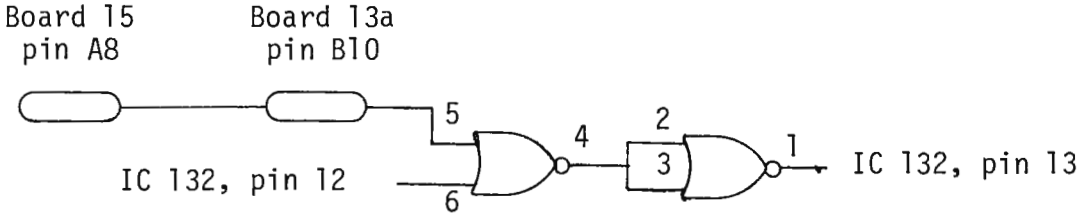
Subject: DECOUPLER DISABLE CIRCUIT FOR THE BRUKER ASPECT 2000 COMPUTER

Dear Dr. Shapiro:

Our group is part of the ICONs (Isotopes of Carbon, Oxygen, and Nitrogen) program at Los Alamos, and we frequently deal with labeled compounds that require a great deal of preparation. We also experience occasional power glitches that sometimes stop the computer on our WM-300 spectrometer, but leave the decoupler at a high power level (with only sufficient cooling for bi-level decoupling) until an operator intervenes by pushing the CLEAR button. As a result a sample gets cooked. Uninterruptible power supplies eliminate these problems, but they are expensive and add maintenance difficulties of their own.

We asked Bruker for a means of automatically shutting off the decoupler when the computer (an Aspect 2000) stops, but unfortunately their suggestion did not work. It involved putting an inverter from board 15, backplane pin A8 (labeled STOP on the schematic) to IC 101, pin 1 on pulser board 13A. Probably the 74LS00 that they furnished had insufficient drive capabilities to reset all the ICs on that line, which is labeled BINIT- (Board INITialize) on the schematic.

The source of BINIT- is two buffer-driver inverters (IC 132) in series fed by the INIT- signal. The logic to reset BINIT- can be easily inserted between the two inverters. It is necessary to cut the foil connecting pins 12 (mislabeled INIT- on our schematic) and 13 of IC 132 (it was on the component side of the board in our computer) and add the following circuit to shut off most of the functions of the pulser board when the computer halts.



74LS02 (J,N)

UNIVERSITÉ PARIS VII

ITODYS

INSTITUT DE TOPOLOGIE ET DE DYNAMIQUE DES SYSTEMES
1, rue Guy de la Brosse - 75005 PARIS - Tél. : 336 25.25, poste 36-15

LABORATOIRE DE CHIMIE
ORGANIQUE PHYSIQUE

J.-E. DUBOIS, *Directeur*

Ref.: BT/BA/ob N° 309

Paris, October 8, 1982

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

Dear Professor Shapiro,

Title: Acoustic Ringing Again: Pyrex against Quartz

In an earlier letter (TAMU 268,33) we reported acoustic ringing occurring at low frequency (i.e. 15 MHz for ^{33}S) on our Bruker WP 200 multinuclear spectrometer. Following a suggestion by R.L. and R.R. Vold (TAMU 270, 7), we tried to wrap an earthed lead foil inside the dewar of our low-frequency broadband probe. No significant improvement was found. A few months later, Dr. C. Brevard of Bruker-France suggested that the quartz used to build the glass parts of our probe might be responsible for most of the acoustic ringing. He kindly proposed to modify our probe. The replacement of all quartz parts by pyrex and also a shielding with an unknown metal in the same way as we put the lead shielding, but not earthed, reduces the length of the acoustic ringing by a factor of 5. Thus the actual delay needed to avoid ringing is ca. 200-300 µs instead of 1000-1500 µs before the probe modification. It is likely that the strong ringing previously observed was mainly related to the piezoelectric properties of quartz.

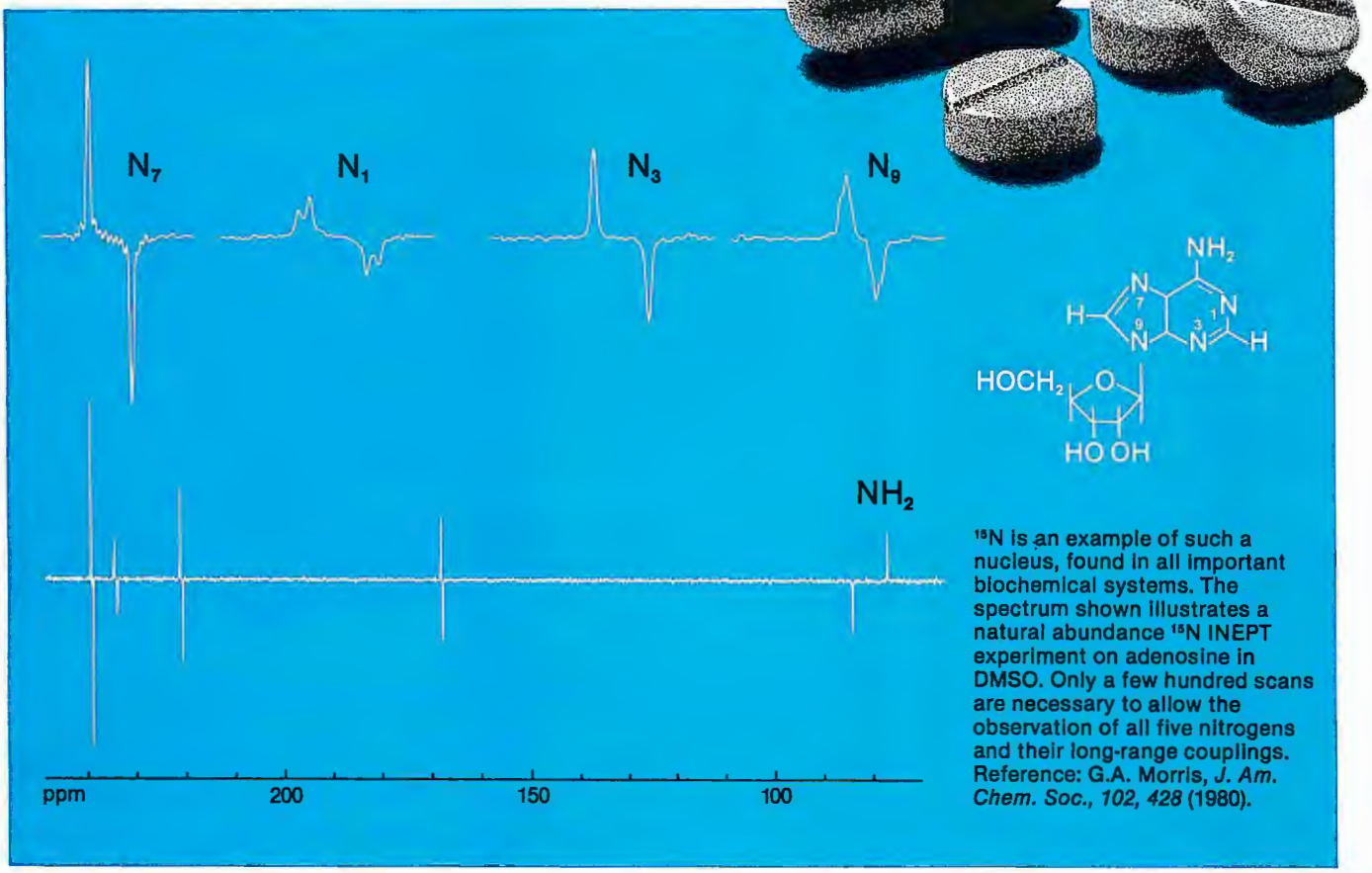
Sincerely yours,

B. TIFFON

B. ANCIAN

Efficient ^{15}N studies by NMR

Low gamma nuclei are often difficult to detect directly because of their low sensitivity, long T_1's, and unfavorable NOE's. However, using the INEPT technique, signal intensity can be borrowed from the abundant coupled proton spins through a process called "magnetization transfer," allowing their direct observation.



^{15}N is an example of such a nucleus, found in all important biochemical systems. The spectrum shown illustrates a natural abundance ^{15}N INEPT experiment on adenosine in DMSO. Only a few hundred scans are necessary to allow the observation of all five nitrogens and their long-range couplings. Reference: G.A. Morris, *J. Am. Chem. Soc., 102, 428* (1980).

Q.E.D. The above INEPT experiment was performed on a routine NMR spectrometer at the Bruker Applications Laboratory. The new AM Series of high-field NMR spectrometer systems comes with an extensive software system, including programs for INEPT processing, display and plotting. A new 8-color graphic display processor further facilitates speed of analysis and clarity of data presentation.

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

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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.

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The Ridgeway, Mill Hill
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Your reference

Our reference GCKR/JL

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

19th October, 1982

Dear Professor Shapiro,

^{15}N INEPT studies of trimethoprim binding to dihydrofolate reductase

One of the most useful applications of nmr to the study of protein-small molecule interactions is in establishing the ionisation state of the bound ligand (1) - something which cannot be done by X-ray crystallography. These experiments commonly involve chemical shift arguments. Thus in our study (2) of the binding of [2-^{13}C]-trimethoprim to dihydrofolate reductase, we observed the ^{13}C signal from the 2-carbon of the bound inhibitor at 89.26 ppm, compared to 87.97 ppm for free protonated and 95.06 ppm for free unprotonated trimethoprim. The chemical shift of the bound ligand is clearly much closer to that of the protonated than to that of the unprotonated molecule. The difference of 1.29 ppm between the shifts of the bound and the protonated molecules can readily be accounted for by the kind of environmental effects expected for a bound ligand, whereas the difference of 5.80 ppm between the shifts of the bound and unprotonated molecules is improbably large for such effects in a diamagnetic non-haem system. It is reasonable to conclude, therefore, that trimethoprim is protonated when bound to the enzyme, but this has not been demonstrated unequivocally.

An unequivocal demonstration is possible by using ^{15}N nmr, since the existence of a one-bond ^{15}N-^{1}H scalar coupling can give direct information on whether a proton is attached to a given nitrogen. Trimethoprim enriched with ^{15}N at N_1, N_3 and the 2-amino group was kindly synthesised for us by Dr. Lee Kuyper (Wellcome Research Laboratories). The Figure shows the ^{15}N signals from N_1 and the 2-amino group of trimethoprim bound to the enzyme. The spectra were obtained by using the INEPT method (3), using timings appropriate to a one-bond ^{15}N-^{1}H coupling (see Figure legend). The observation that both the N_1 and the 2-NH_2 resonances show signal enhancement by the INEPT procedure demonstrates that N_1 does have a one-bond coupling to a proton, and this can be seen directly as a splitting of the N_1 resonance in the absence of ^{1}H decoupling. This is therefore unequivocal proof that trimethoprim is protonated on N_1 when bound to dihydrofolate reductase.

Cont./

Professor B.L. Shapiro 19th October, 1982

The proton coupled to N_1 is of course potentially exchangeable with the aqueous solvent, and indeed no INEPT enhancement could be observed for free trimethoprim in aqueous solution. The observation of INEPT enhancement in the bound state reflects the relatively slow exchange of the N_1-proton with the solvent; from the crystal structure (4) it is seen to be involved in a hydrogen-bond to an aspartate residue. As the sample temperature is increased, so the $^{15}N_1$ signal decreases in intensity, until it becomes undetectable at 30°C. Model experiments with trimethoprim in DMSO confirm that, as expected, the INEPT enhancement disappears when the exchange rate is such as to collapse the ^{15}N-^{1}H doublet. Thus at 30°C, the N_1-proton exchanges with the solvent at a rate of about 80 s^{-1}; since the dissociation rate constant for the complex at this temperature is <6 s^{-1}, the proton exchange must be due to some degree of flexibility in the complex.

Yours sincerely,

Alan Bevan Gordon Roberts Jim Feeney

A.W. Bevan G.C.K. Roberts J. Feeney

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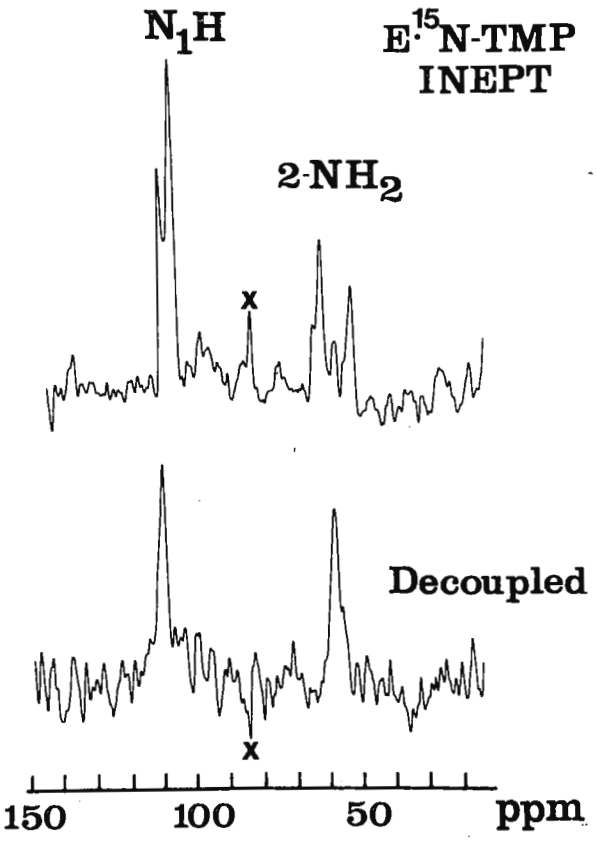


20.3 MHz ^{15}N INEPT spectra of the complex between [N_1, N_3, 2-amino-^{15}N] trimethoprim and L.casei dihydrofolate reductase. The solution contained 1.4 mM complex, 500 mM KCl, 50 mM phosphate pH 6.5, in 3 ml H_2O (containing 10% D_2O for field-frequency lock). Each spectrum was obtained using the 'refocussed' INEPT method on a Bruker WM200 spectrometer at a sample temperature of 5°C. The timings used were those appropriate to a triplet with a coupling constant of 90 Hz; signals from the N_1 doublet and the 2-amino triplet are clearly seen using triplet timing, whereas the 2-amino signal is not clearly seen using doublet timing. The bottom spectrum was obtained using noise-modulated ^1H decoupling during acquisition only. The top spectrum is the result of averaging 35000 FIDS, the bottom spectrum of averaging 15000 FIDS. 'X' denotes an instrumental artefact.

291-23

Weyerhaeuser Company

Tacoma, Washington 98477
(206) 924-2345

November 2, 1982

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

Dear Professor Shapiro:

Re: Is Your Surfactant Supplier Ripping You Off?

Certain surfactants are useful as softeners and defoamers and as additives in pulp products. When these are purchased for an industrial operation, a check should be made for identity, purity and compliance with purchaser's specifications. Three related surfactant types are amides, imidazolines and quaternized imidazoliniums of the general structures shown on the next page; R normally is a long, partially unsaturated chain. The cyclic compounds are made from amide precursors by dehydration to imidazolines, then quaternized with the appropriate dialkyl sulfate. Some suppliers seem less than conscientious in conducting all this chemistry and pass off amides as higher priced imidazolines.

Although the literature is devoid of comparative studies (1, 2), carbon-13 NMR easily differentiates these substances (see Table - my apologies for the carbon numbering system). The amide carbonyl carbon is always found at >173δ and imidazo C-2 at <170δ; the characteristic ring methylene shifts and those of alkyl carbons α and β to the ring amply differentiate the two cyclic forms. We have found several samples, supposedly the cyclic surfactants, to contain amide percursors in high purity. Some of these were in a Chem Service surfactant kit.

Another application has been the measurement of imidazoline content in liquid polyamide resins. In these, R' is an amide linkage and dehydration is only partial. The imidazoline and amide structures in the resulting polymer are conveniently quantitated from the imidazo and carbonyl carbon intensities in the NOE-suppressed spectrum.

Sincerely,

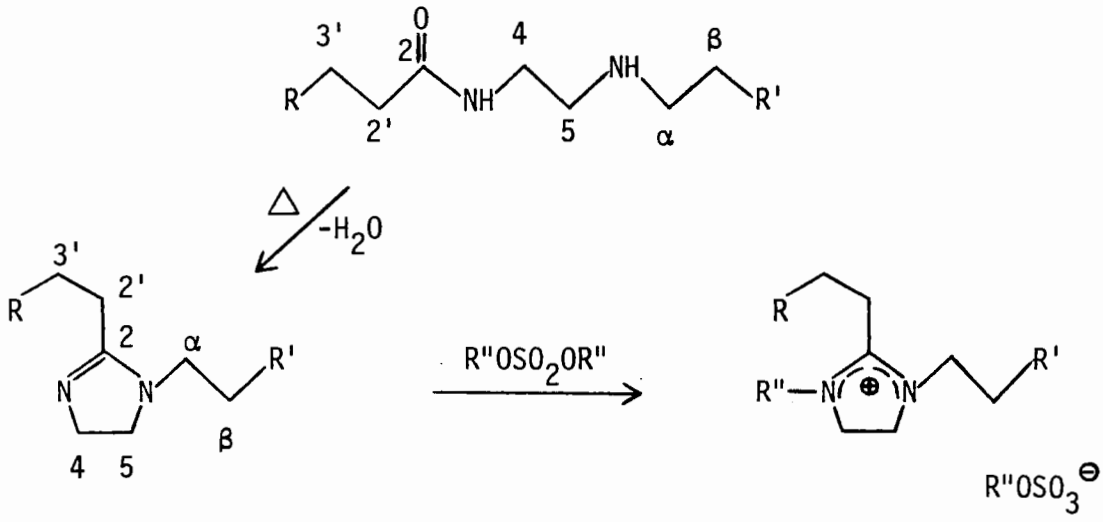
Larry Amos

Larry W. Amos

LA:jd 2C/D13

1/ B. C. Trivedi, A. J. Digioia and P. J. Menardi, J. Amer. Oil Chem. Soc., 58(6), 754 (1981).

2/ H. Kohn, M. J. Cravey, J. H. Arceneaux, R. L. Cravey and M. R. Willcott III, J. Org. Chem., 42(6), 941 (1977).



Chemical Shifts in $CDCl_3$ vs. Internal TMS

Carbon Number	Amide		Imidazoline		Imidazolinium	
	I[a]	II[b]	I	II	I	II
2	174.0	174.0	168.0	167.8,167.4	168.4	168.7
2'	36.7	36.7	27.7	27.9	24.0	23.8
3'	25.9	25.9	26.6	26.6	25.9	25.7
4	39.0	39.1	49.2	50.2	47.4/5	47.5/5
5	48.6	48.7	51.5	52.0	46.8/4	46.8/4
α	51.5	48.7	50.1	50.2	49.8	50.0
β	60.3	39.1	59.2	40.6	57.7	36.1
1"					42.0	33.9
2"					12.7	

[a]For series I, R' = OH and R" = CH_2CH_3.

[b]For series II, R' = $NHCOCH_2CH_2R$ and R" = CH_3.

Prof. Dr. F.H. Köhler
ANORGANISCH-CHEMISCHES INSTITUT
DER
TECHNISCHEN UNIVERSITÄT MÜNCHEN

D-8046 GARCHING, den 03.11.82
Lichtenbergstraße 4
Ruf-Nr. (089) 3209/3080/3081 (Prof. Fischer)
3110 (Prof. Fritz)
3130 (Prof. Schmidbaur)
3109 Prof.Köhler

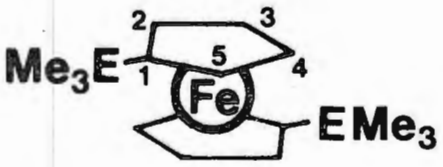
Prof. B.L. Shapiro
Department of Chemistry
Texas A.u.M. University
College Station, Texas 77 843

Title: ^{13}C problems with simple ferrocenes

Dear Professor Shapiro,

from time to time we have to look on ferrocenes such as 1 and 2 which are supposed to be simple. From these compounds we need reliably assigned and precise NMR data as diamagnetic reference values for paramagnetic NMR studies of the corresponding open shell metallocenes. I emphazise assignment and precision since we are interested also in temperature dependent studies. And with a reference error of ± 1 ppm the reduced shift $\nu(= \frac{\delta T}{298})$ is no longer constant in the ν/T^{-1} diagram; instead slopes of ± 0.0034 [ppm/deg] are introduced.

It is clear that a difficulty arises for the assignment of C2/5 and C3/4 in 1 and 2. There is no proton in the α-position which could couple specifically with C2/5[1,2]. $^3J(CH)$, which usually assures the assignment in monosubstituted benzenes, is very similar to $^2J(CH)$ so that $^{2/3}J(CH)$ multipletts (two even reduce to quartets) with no benefit for the assignment are obtained.



		(C1) [$^nJ(EC)$] in Hz	(C2-5) [$^nJ(EC)$]	
1	E = Si	72.00 [71.80]	73.07 [5.38]	71.33 [4.16]
2	E = Sn	68.91 [492.8]	74.20 [51.8]	71.98 [40.3]

Günther's "fingerprint" assignment of 1,2-disubstituted benzenes [3] appears to be not applicable for monosubstituted ferrocenes. Earlier a larger $^{1}J(CH)$ seemed to distinguish C3/4 from C2/5 in $(Rcp)_2Fe$ [1]; now the $^{1}J(CH)$ are equal for 1 and 2 within experimental error. None the less we hope to proceed without specific deuteration [4] since we have $^{n}J(EC)$.

From numerous monosubstituted benzenes with a spin-1/2 element in the α-position it is known that $^{2}J(EC) < ^{3}J(EC)$. The inverse comes out from Jakobsen's work on methylferrocene [5]. I would be glad if anybody could comment on this difference.

Please credit this letter to the subscription of H.P. Fritz.

Yours sincerely

Frank H. Köhler

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291-27

Université Libre de Bruxelles
Faculté des Sciences Appliquées
Service de Chimie Organique
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Avenue F.-D. Roosevelt, 50
1050 Bruxelles
Tél. : (02) 649 00 30 - Extension : 2048

Professeur J. REISSE

B-1050 Bruxelles, le November 5th, 1982.

to

Prof. Dr. B. SHAPIRO
Department of Chemistry
Texas A & M University
College Station
TEXAS 77843 (U.S.A.)

Dear Professor Shapiro,

Upgrading of a WP 60 NMR Spectrometer

These is no need for us to emphasize the advantages of methods like J modulated spin-echo(1) or INEPT(2) over traditional off-resonance decoupling for ^{13}C spectral assignments. Our purpose is to describe the upgrading of our 7 year old WP 60 multipulser-equipped spectrometer which, basically, is unable to make a spin-echo measurement or to switch the decoupler on and off rapidly.
Fig. 1 shows the block diagram of the circuits. As acquisition can only be triggered by PII, two PI pulses are generated by the micro-program and than transformed into a 180° and a 90° pulse respectively. For the purposes of security, this devider by two is reset by the sweep flag or manually. The decoupler is switched off between the pairs of PI pulses through the BU16 of "Lo PROTON".
As our first measurements revealed that the software was unable to generate VD delays as short as 2 or 3 msec properly (this defect is still under investigation) we checked our accessory with an external pulse generator. The pulse program was :

```
1  ZE
2  FD
3  PI      switched to 90°
4  VD      τ = 1/2J
5  PI      switched to 180°
6  VD
7  SC = 2  (pulse width = 0)
```

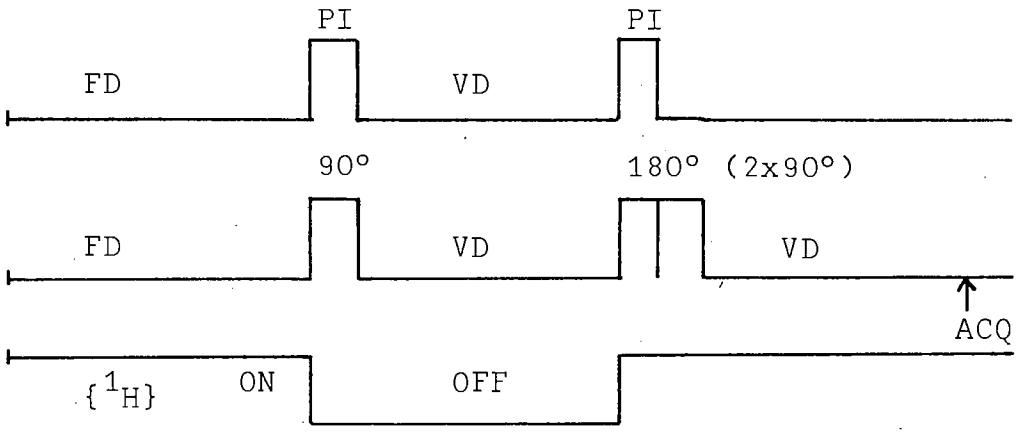
We can provide details of this modification to anyone who is interested.

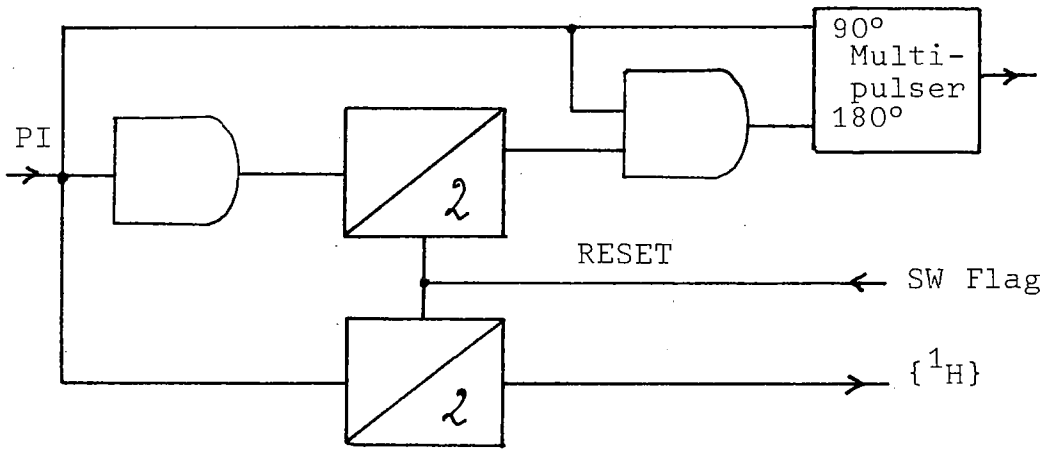
Sincerely,

O. FABRE

D. ZIMMERMANN

(1) C. Le Cocq, J.Y. Lallemand, J.C.S. Chem. Comm. 1981, 150
(2) D. Burum, R. Ernst, J. Magn. Res. 1980, 39, 163.





291-29

ISTITUTO SUPERIORE DI SANITA'
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Rome, September 30th 1982

Telegrammi: ISTISAN - ROMA
TELEX RM071 ISTISAN

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

Insulin action and compartmentation of glycolysis metabolites in tissues: a problem revisited by ^{31}P NMR.

Dear Professor Shapiro,

the non-invasive character of ^{31}P NMR approaches not only allows the simultaneous detection "in situ" of various metabolites in intact biological systems (cells, tissues, organs), but may also provide information on their intracellular compartmentation (1).

The role of a possible compartmentation of glycolysis metabolic pathways was widely investigated in the past (2). Only indirect evidence was however provided so far on the existence of distinct pools of Embden-Meyerhof intermediary hexose monophosphate esters (3, 4).

^{31}P NMR experiments recently carried out in our laboratory confirm the hypothesis of an intracellular compartmentation of glucose-6-phosphate (G6P).

The experiments were performed at 4 °C with a spectrometer Varian XL-100 (40.5 MHz) on rat diaphragm muscles preincubated in a Warburg respirometer with G6P (1%), either in the presence or in the absence of insulin (0.1 u.). The resonances of various intermediates of glycolysis in the tissue were identified on the basis of peak assignments in the spectra of their ethanolic extracts.

The action of insulin resulted in a downfield shift of the peak of intracellular inorganic phosphate (Pi), which monitored an increase of ~ 0.13 pH units in the average environment of this compound within the tissue. This result is in agreement with a similar finding reported by Moore and Gupta (5) in freshly-dissected and insulin-treated sartorius muscles from *Rana pipiens*. The concomitant average pH shift induced in insulin-treated diaphragms on the G6P signal was instead much smaller (~ 0.05 pH units).

The different pH variations induced by insulin on the respective environments of Pi and G6P are interpreted on the basis of the existence of at least two distinct sets of glucose metabolizing enzymes, with different physical location and physiological functions within the cell. This result represents, to our knowledge, the first direct evidence supporting the hypothesis of compartmentation of glycolytic intermediates in a tissue.

Sincerely yours,

Franca Podo — Franca Podo
Giulia Carpinelli — Giulia Carpinelli
Giuliano D'Agnolo — Giuliano D'Agnolo

References

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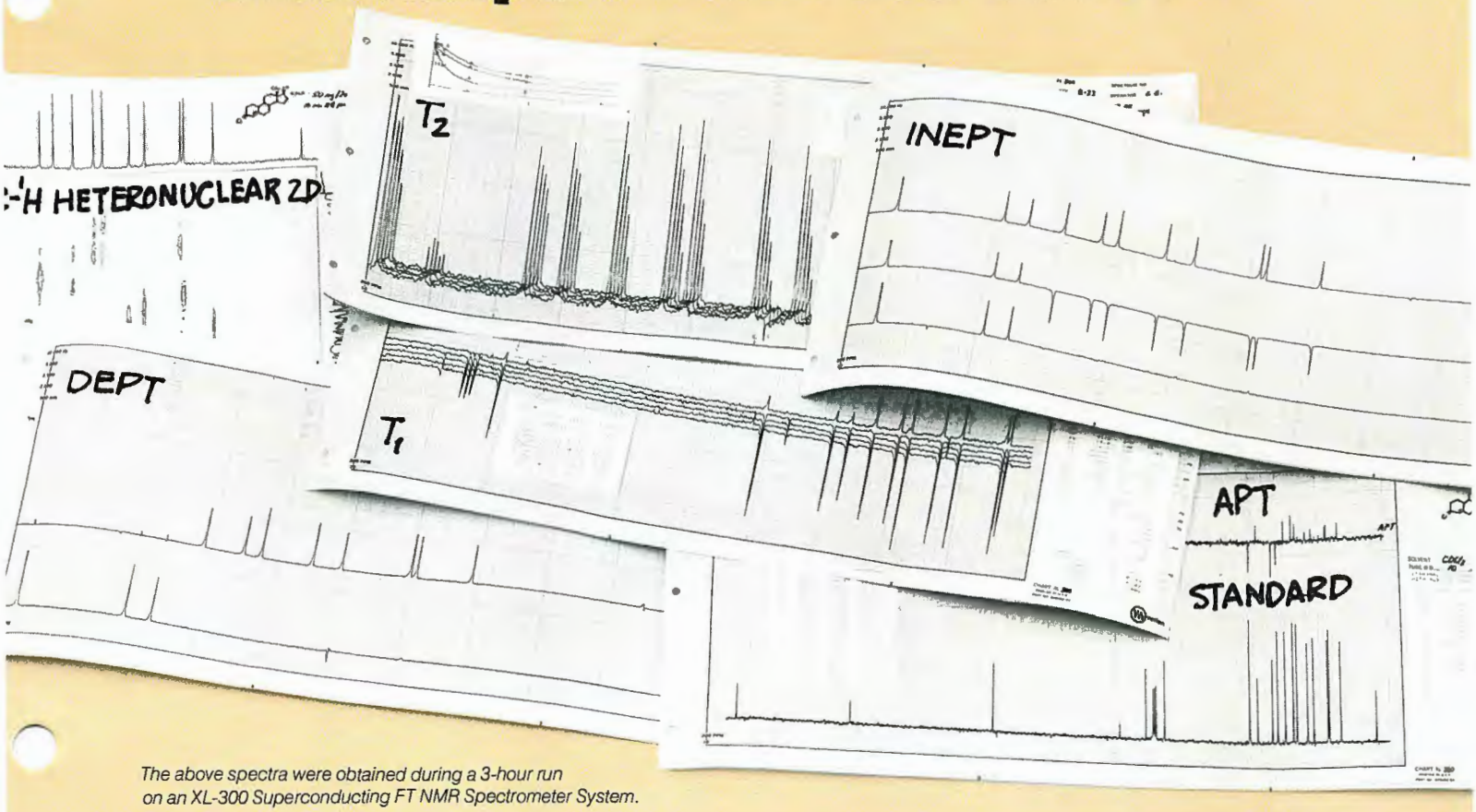
5. R.D. Moore and R.K. Gupta, Int. J. Quantum Chem., Quantum Biology Symposium n. 7, 83-92 (1980).

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.

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TAMU NMR Newsletter — Oct/Nov/Dec 1982

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PHYSICAL CHEMISTRY LABORATORY
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1st November, 1982

RF/ml

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

Dear Barry,

"Nostalgia"

Does anyone still yearn for the good old days when proton NMR spectra were all simple and signal-to-noise ratio was terrible? You can fix up your spectrometer with the following pulse sequence (see Figure 1):

(a) Presaturate all protons with repeated radiofrequency pulses and field gradient pulses.

(b) Excite a single chosen carbon-13 resonance with an on-resonance DANTE sequence.

(c) Allow free precession of carbon-13 vectors while coupled to protons for a fixed period Δ_1. $\Delta_1 = 1/(2\ J_{CH})$ for methine; $\Delta_1 = 1/(4J_{CH})$ for methylene groups.

(d) Transfer polarization to protons with a 90° carbon pulse applied along the Y axis of the rotating frame. This is similar to INEPT, but no 180°'s are needed since the carbon transmitter is at exact resonance. Alternate the phase of this pulse ($\pm$ Y).

(e) Excite the proton signals with a 90° pulse (the multiplet components are in antiphase).

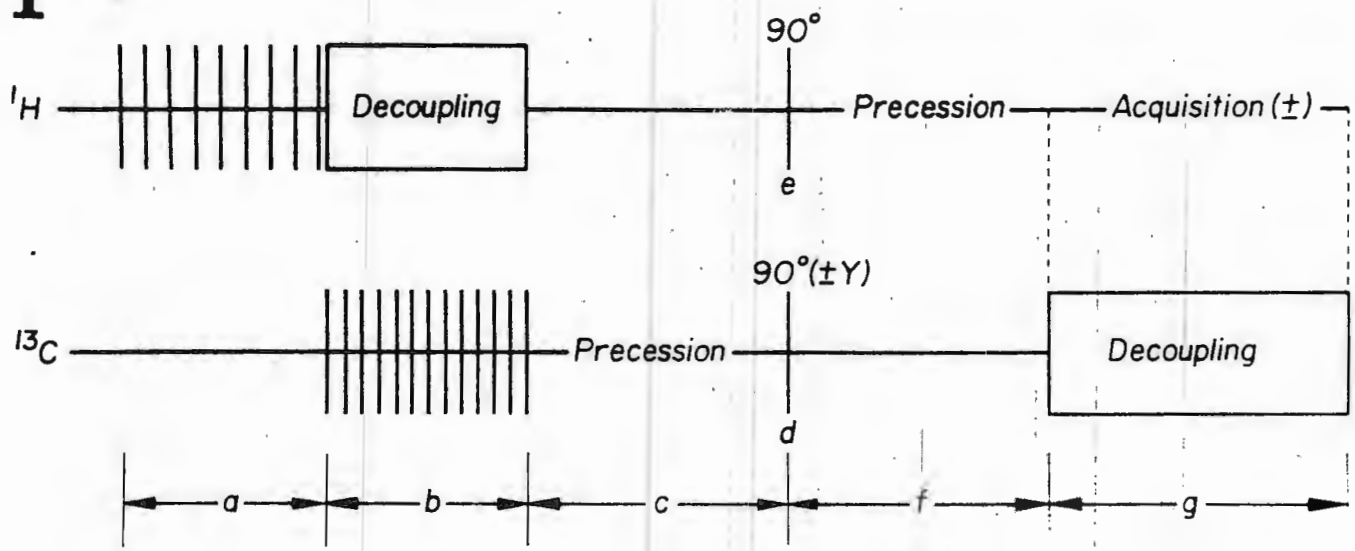
(f) Allow free precession for a period $\Delta_2 = 1/(2\ J_{CH})$.

(g) Acquire the proton signal decoupled from carbon-13. Any old decoupler mode will do, since this transmitter is at resonance. Alternate the receiver phase in step with the alternation in stage (d) so as to cancel all proton signals save those transferred from carbon.

We can guarantee a sensitivity loss of almost two orders of magnitude by this trick. Better still, most of the remaining spectrum disappears, leaving only the subspectrum from the protons at the chosen carbon site.

cont'd.....

1 291-33



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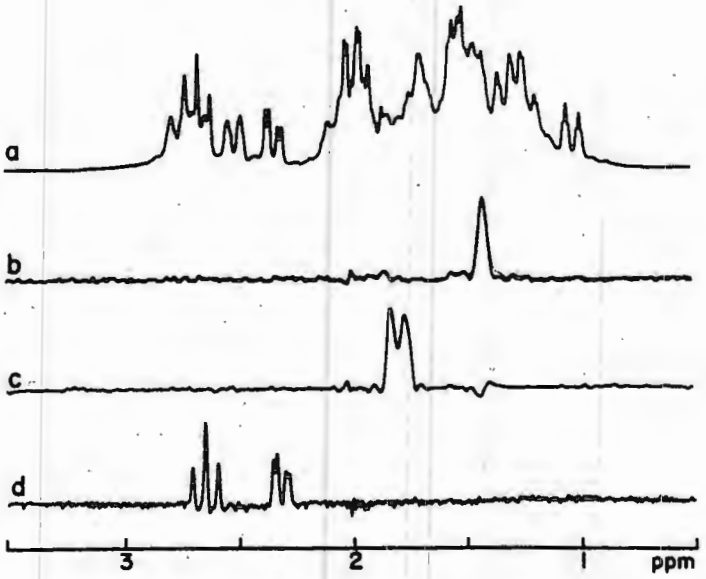
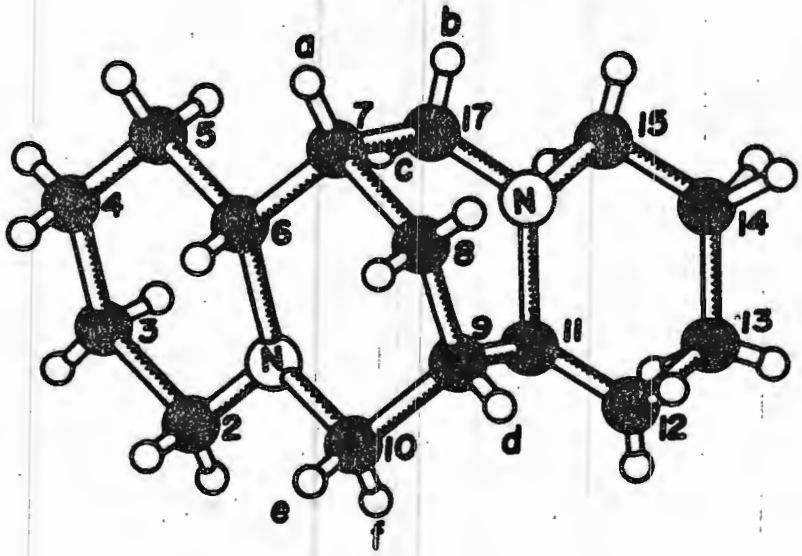


C9 → H_d

C7 → H_a

C17 → H_b , H_c



Occasionally this may solve a chemical problem. The conventional proton spectrum of sparteine (Figure 2a) can be simplified by such polarization transfer experiments. In particular Figure 2c shows a proton subspectrum obtained by transfer from C7. The large (12 Hz) vicinal coupling J_{ab} confirms that these CH bonds are nearly eclipsed, which is evidence that the third ring (C7, C8, C9, C11, N, C17) has a boat conformation.

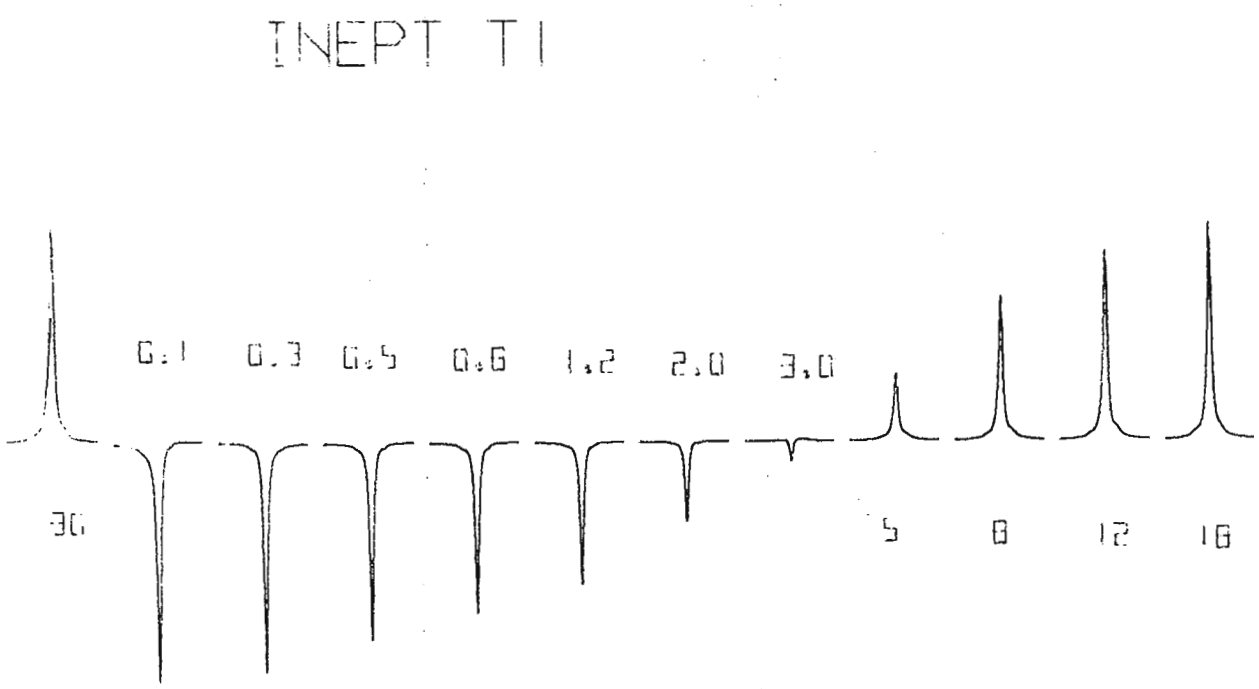
This work was conceived and carried out by A.J. Shaka in this laboratory and is to be published as a communication to the Journal of Magnetic Resonance.

Yours sincerely,

Ray

Ray Freeman

Figure for contribution by J. Kowalewski (page 291-35).



UNIVERSITY OF STOCKHOLM
Physical Chemistry

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

Stockholm, November 9, 1982

INEPT, T_1 and GX 400

Dear Professor Shapiro,

Our new JEOL GX 400 has recently been installed. Waiting for the multinuclear accessory (due to arrive this month) we have been exploring the possibilities offered by a pulse-programable spectrometer, which is a lot of fun for persons used to Varian XL 100.

As an introductory exercise, we have decided to write the pulse program for the recently described [1] T_1 experiment making use of the INEPT-type polarization transfer to prepare the magnetization of a low γ nucleus I in a far-from-equilibrium initial state along the z-axis. After that state is prepared, the rest of the experiment is analogous to most of other T_1 experiments: the I magnetization is allowed to relax under noise decoupling conditions during a variable delay after which the final 90° pulse gives a detectable signal.

The standard JEOL GX 400 software contains a modified version of the Burum-Ernst-Doddrell-Pegg [2,3] refocused and decoupled INEPT sequence. Further modifying the sequence by adding two 90° pulses with suitable phases and a variable delay in-between was easy and gave for the ^{13}C signal of the 50% dioxane-D_2O mixture the results shown in the figure. One should note the good efficiency of the polarization transfer: the signal corresponding to the short delay (100 msec) is in fact larger than the equilibrium, NOE enhanced signal corresponding to the delay of 30 seconds. The calculated T_1 is 4.4±0.1 sec.

Best wishes

Jozef Kowalewski

[1] J. Kowalewski and G.A. Morris, J. Magn. Res., 47, 331 (1982).
[2] P.D. Burum and R.R. Ernst, J. Magn. Res., 39, 163 (1980).
[3] D.M. Doddrell and D.T. Pegg, J. Amer. Chem. Soc., 102, 6388 (1980).

(Figure for contribution is on page 291-34.)

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMISTRY
CAMBRIDGE, MASSACHUSETTS 02139

November 29, 1982

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

Dear Barry:

Sample Prep for MAS of Polymer Films

We wish to report a sample preparation technique useful to practitioners of CP-MAS NMR. Polymers are frequently obtained in the form of films or sheets. These samples are commonly rolled into cylinders, or cut into round discs which are stacked into rotors of the Beams or Andrews variety. The resulting packed rotors are the nuclei for considerable frustration, as they do not always exhibit the desired dynamic balance for magic angle sample spinning.

We have observed that a small amount of virgin Teflon® powder (Dupont 7A), when tightly packed on top of stacked film discs, significantly increases rotor balance. The beneficial deformation of the soft Teflon® packing usually occurs within a short spinning time. The Teflon®, which also serves to compress the stacked discs, can be capped with an adhesive disc of Scotch Magic Tape®. The cohesive properties of Teflon® powder make it an ideal packing material consumming only 5-10% of the available sample volume. Finally, the totally fluorinated hydrocarbon material contributes no unwanted signal in proton decoupled ^{13}C or ^{31}P CP-MAS NMR.

Sincerely yours,

D. W. Kormos J. S. Waugh

PURDUE UNIVERSITY

SCHOOL OF SCIENCE
at INDIANAPOLIS

PHYSICS DEPARTMENT
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November 16, 1982

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

Title: NMR Lineshapes

Dear Barry:

We have made a numerical calculation (by the finite difference method[1]) of the low power line shape of a dipole coupled two spin system using the density matrix equation

$$\dot{\rho} = -i[H_Z + H_{DD}, \rho] - i[H_{rf}, \rho] + D_R \nabla^2_{\theta,\phi} (\rho - \rho_{equil})$$

For the condition $\omega_{DD} << 1/\tau_c << \omega_c$ $D_R = 1/6\tau_c$ the line shape is Lorentzian and agrees "perfectly" with the width derived from the standard

$$\frac{1}{T_2} = \frac{3}{5} \frac{\gamma^4 \hbar^2}{r_{12}^6} I(I+1)\tau_c$$

For the condition that $1/\tau_c$ is of the order of ω_{DD} the line width is no longer Lorentzian. For example given $\omega_{DD} = 9.4 \times 10^4$ rad/sec, $1/\tau_c = 1.2 \times 10^5$ sec^{-1} the line shape is as shown where the dotted points represent a Lorentzian line with a half width at half height the same as the calculated line (continuous line)

We plan to apply this treatment to problems where there maybe questions as to the range of validity of line shapes obtained from autocorrelation procedures where the motion is a complex one, as in the case of biological systems.

1. J. I. Kaplan, E. Gelerinter, and G. C. Fryburg, Mol. Cryst. and Liq. Cryst. 23, 69 (73); J. R. Norris and S. I. Weissman, J. Phys. Chem. 73, 3119 (1969).

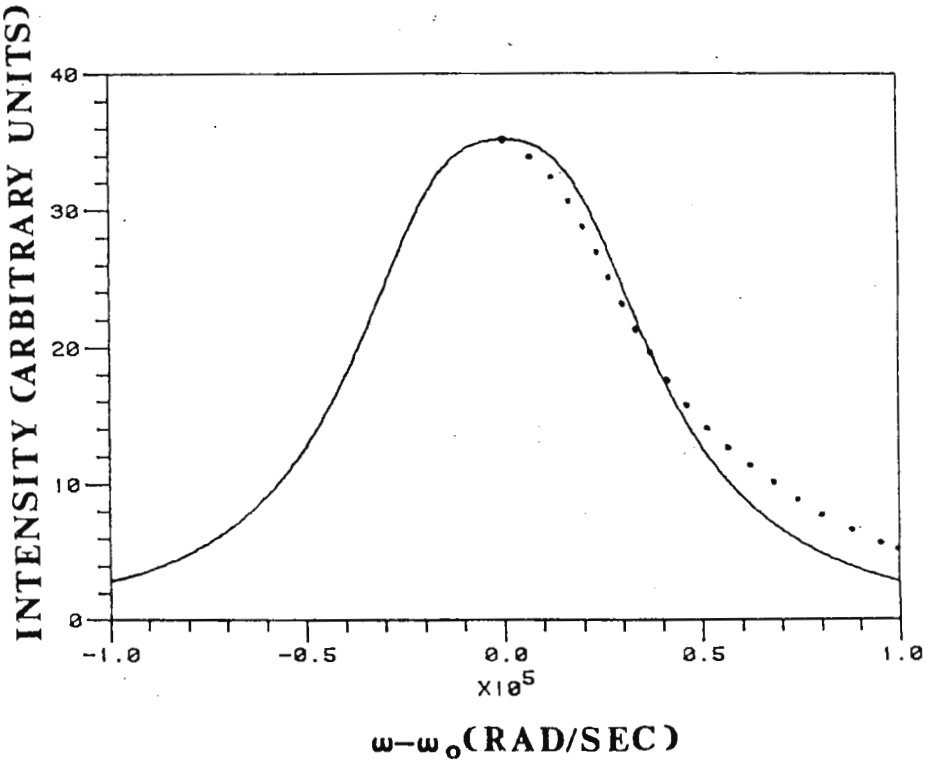
Sincerely

Jerome I. Kaplan
Professor of Physics

Kashyap V. Vasavada
Professor of Physics

JIK:KVV/flw

Enclosure



P.S. a) Please credit this note to B.D. Nageswara Rao's account

b) Thank you for your reminder.

Wesleyan UNIVERSITY

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MIDDLETOWN, CONNECTICUT 06457
TEL.: (203) 347-9411

DEPARTMENT OF CHEMISTRY

22 November 1982

Proton-Proton Chemical Shift Correlations via Double Quantum Coherence

Dear Barry:

The now familiar method of correlating the chemical shifts of protons is rather unsightly. There is this large ridge running along the diagonal which contains not a bit of useful information. Furthermore, the diagonal signals tend to obscure the more interesting cross peaks. It seems a shame that the signals which are typically the most intense contain the least information.

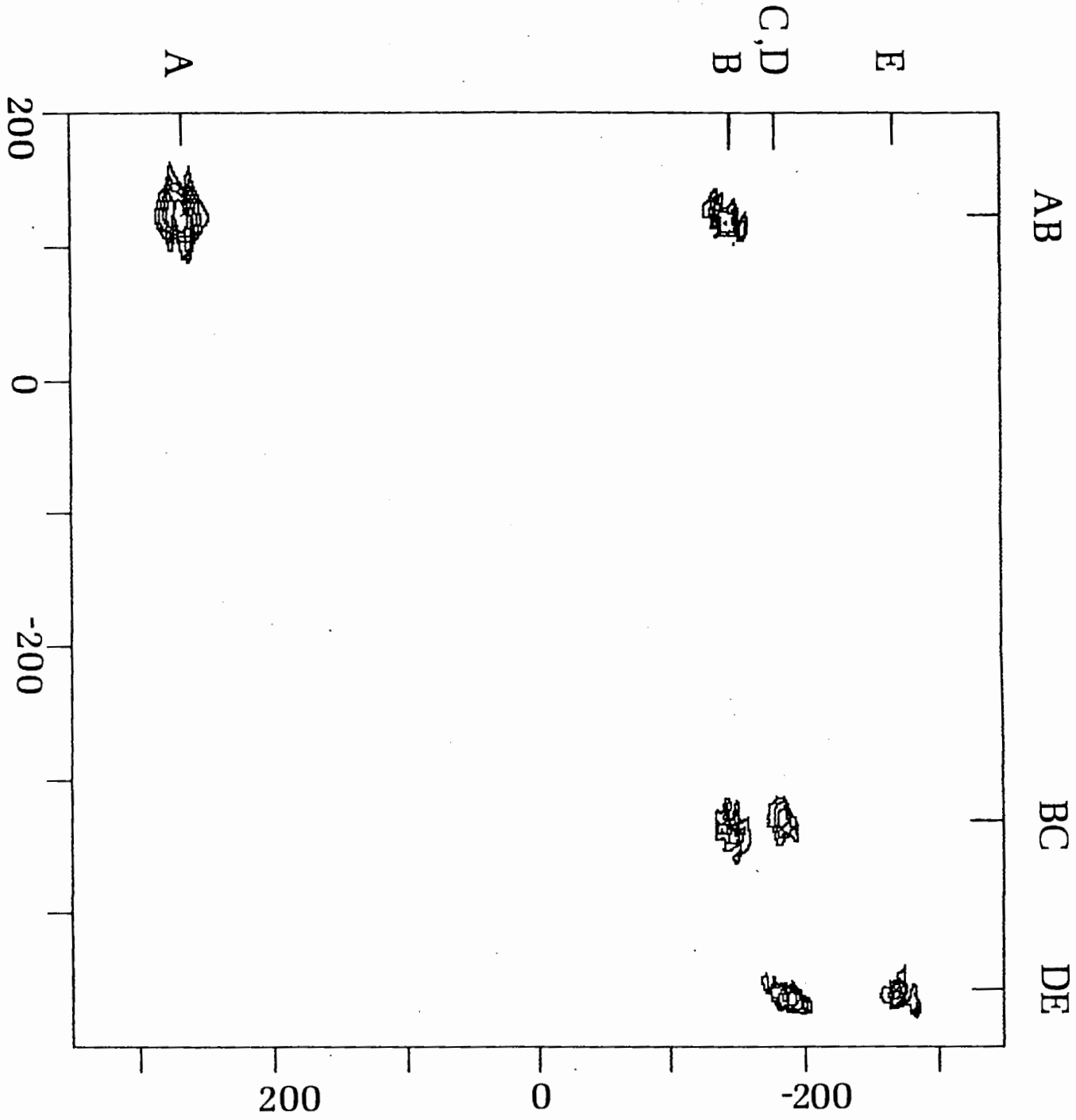
In an attempt to improve the aesthetics of the correlation of proton chemical shifts via scalar couplings I have adapated the double quantum experiment of Bax and friends to protons. Now, the experiment as applied to carbon works just fine for protons as long as there are no proton multiplets. The presence of multiplets gives rise to signals which contain little, if any, information. A contour map obtained for pentanol is shown. The double quantum based chemical shift correlation has no signals along the diagonal and no signals other than those telling which protons are coupled to which. There is no signal correlating sites C and D since they are very strongly coupled. The trick is to use a 45^{o} pulse for the conversion of double quantum to single quantum coherence. A more complete story is being prepared for the usual place.

Sincerely,

Philip Bolton

90 - τ - 180 - τ - 90 - t_1 - 45 - Acquisition

intricately phase cycled to only detect 2QT



Double quantum chemical shift correlation for 1-pentanol. The axes are labelled in Hz relative to transmitter frequency.

nmr/specnet

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

November 23, 1982

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

Subject: HIGH FIELD SOLENOID COIL PROBE PERFORMANCE

Dear Barry,

In much of our heteronuclei NMR work, especially that dealing with biologically significant samples, we must achieve the best possible efficiency. In these cases material availability or vulnerability can preclude use of large samples, or extended experimental observation times. Solenoid coil probes operating at moderate magnetic fields have been shown to gain a two to three fold advantage in sensitivity compared with Helmholtz coil designs for similar sample volumes that are used in most commercial probe designs.

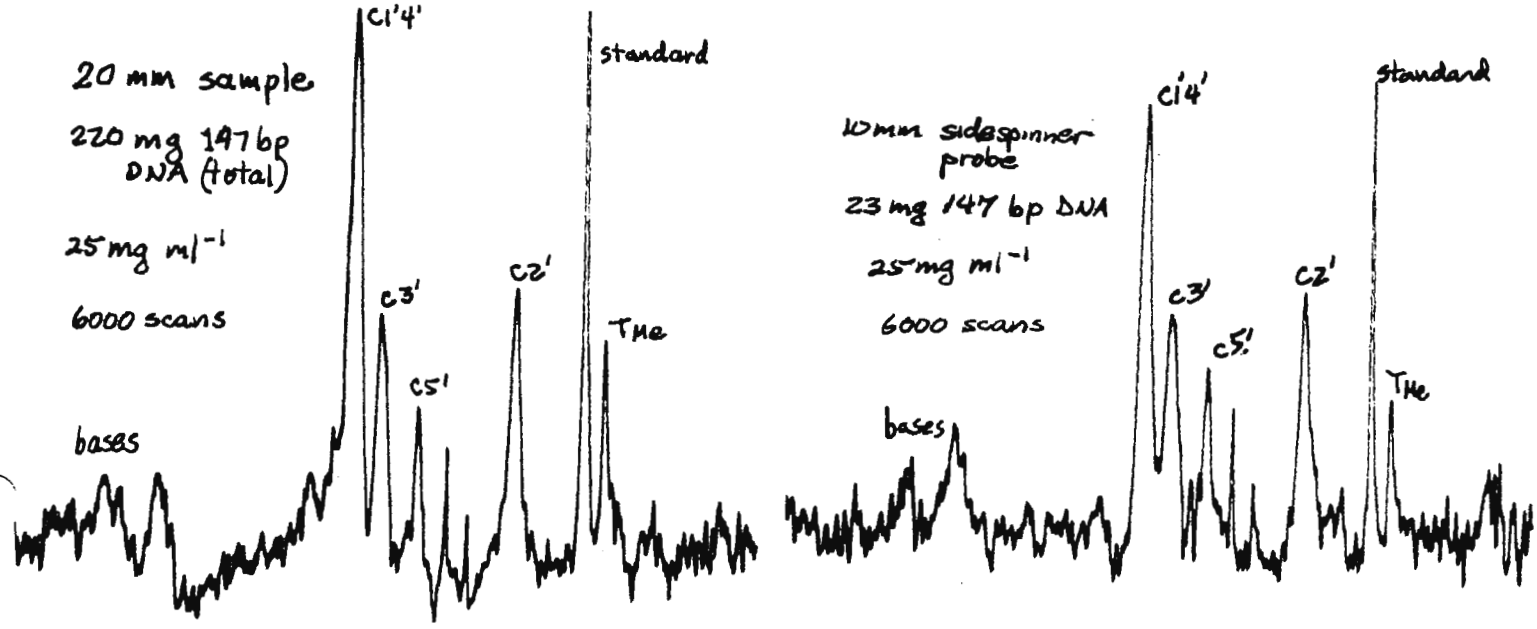
We utilize 20mm samples for ^{13}C and other nuclei NMR of 147 base pair double stranded DNA and other systems at 8.5 tesla on our Bruker WM-360 widebore spectrometer. Some of these experiments, and many runs for customers of our N.I.H. Resource, utilize samples of very limited availability.

We commissioned Cryomagnet Systems Inc. (Dr. Craig Bradley) to build an 8.5 tesla broadband sidespinner probe. While the design iteration process is not yet complete, we are currently obtaining results which may be of interest to TAMU NMR readers. This probe utilizes 10mm size samples of 0.5 to 1 ml; its frequency range covers ^{31}P down through ^{15}N (>145 MHz to below 35 MHz). Rf coupling is very efficient: a 90° pulse for ^{13}C requires 11 µsec, **with 3 db of attenuation on the output of the Bruker WM-360 observe channel** (the ^{1}H 90° pulse width on the decoupling coil is 5.5 µsec).

Initial tests of lineshape are not exceptional and we plan to modify the coil; nevertheless we can get more than 350:1 by the ASTM ^{13}C test **on 0.8 ml of sample.**

Professor B. L. Shapiro November 23, 1982

A more useful test at this point has been the performance of this probe with our DNA samples. Below are two spectra: one obtained on 8.8 ml of DNA solution (25 mg ml^{-1}) in a conventional 20mm probe which achieves ASTM ^{13}C sensitivity near 700:1 and the second spectrum obtained on **just under 1 ml of the same sample** (but only ca. 0.5 ml is in the active area -- we are making a smaller cell now).



As shown, we are getting ca. 70% of the sensitivity on less than 1/8 of the volume. This of course results from two factors: better coupling to the smaller coil and the solenoid geometry.

I hope to have more information soon. In the meantime, this probe is available for N.I.H. Resource users. Just call or write us with your problems!

Best regards,

George C. Levy
Director

Paul S. Marchetti
Resource Biochemist

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STANFORD, CALIFORNIA 94305

STANFORD MAGNETIC RESONANCE LABORATORY

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"RETRO-PEPTIDE SHIFTS"

December 1, 1982

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

Dear Barry,

In attempts to evaluate the relative contributions of the peptide backbone and various side chains to the biological activity of peptides, a number of chemical modifications like N-methylation or replacement of the amide bond with an ester bond (depsipeptide) have been undertaken. Many of these structural alterations cannot be considered as minor perturbations.

A novel attractive approach is the reversal of the direction of one or several peptide bonds in the backbone, while simultaneously maintaining the overall side chain topology of the extended peptide. Such modification yields the partially modified retro-inverso peptide analogs (retropeptide from hereon)[1]. The reversal of one peptide bond yields two adjacent non-amino acid residues - a gem-diaminoalkyl group on the N-terminal side of a malonyl residue (g and m).

-NH-CH(R)-NH-CO-CH(R)-CO-

(g) (m)

^{1}H NMR spectroscopy is an obvious choice to explore the conformational characteristics induced by these non-amino acid residues. The figure shows the spectrum of the retropeptide Boc-Tyr(Bzl)-D-gAla-mGly-OH in DMSO-d_6. The parent peptide is Boc-Tyr(Bzl)-D-Ala-Gly-OH. The Tyr NH, $C_\alpha H$, side chain and the blocking groups (Boc, Bzl) proton signals are in the usual shift positions seen in the parent peptide. The gAla residue shows the well-resolved NH doublets at 8.1 and 8.3 ppm and the $C_\alpha H$ multiplet at 5.4 ppm, while the mGly protons resonate at ∿3.1 ppm. The latter shifts are significantly down- and upfield from their usual position in the parent peptide.

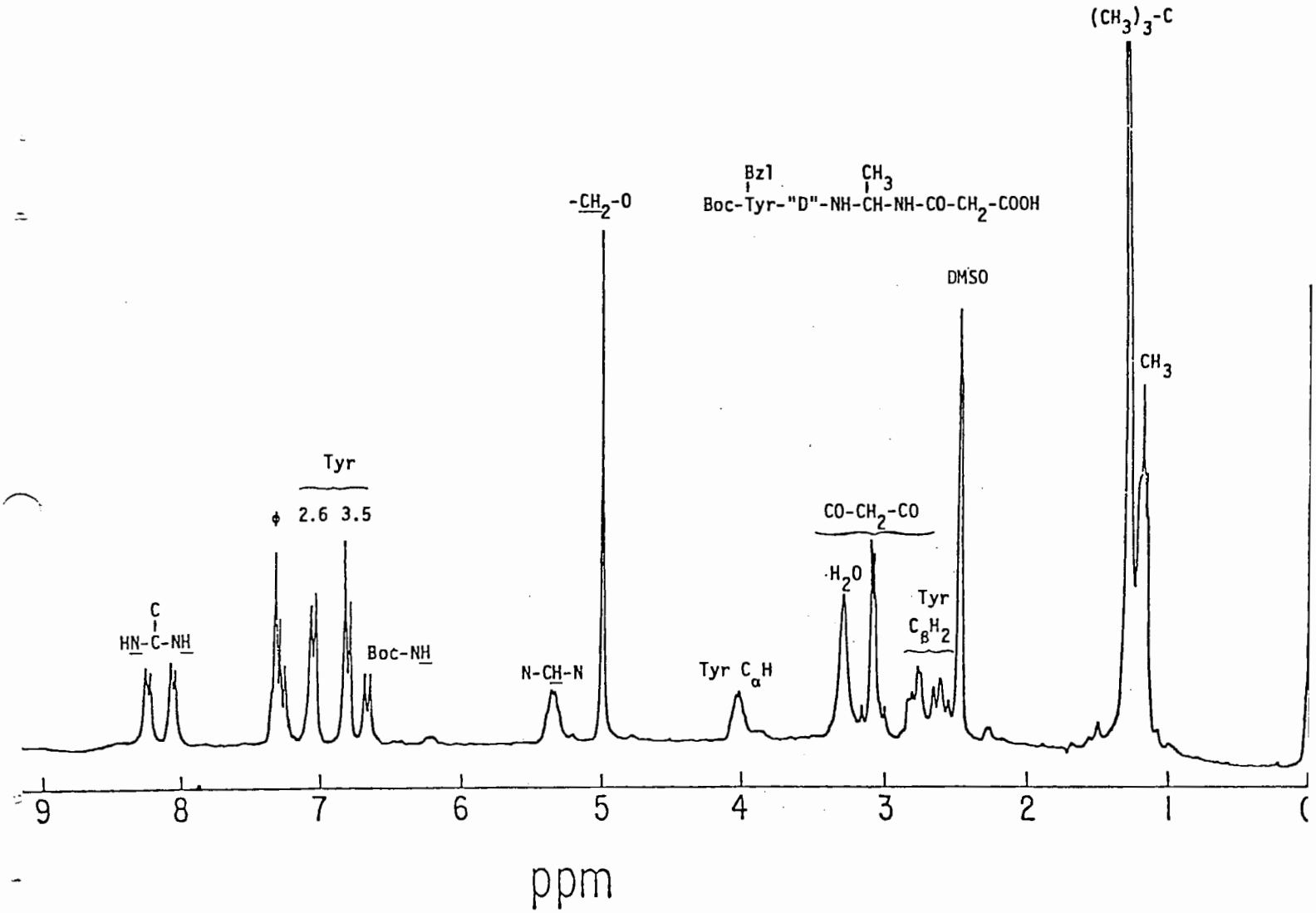
From studies with other analogs, it appears that the retropeptide modification does not significantly perturb the backbone and side chains of non-modified residues. At the same time, the deshielding of the $C_\alpha H$ of the gem-diamino group into a clearly resolved region of the ^{1}H NMR spectrum suggests this group should be most useful to probe complicated peptide structures.

Sincerely,

Anthony Ribeiro

Anthony Ribeiro

1. M. Goodwin and M. Chorev (1981) in "Perspectives in Peptide Chemistry"(Eberle, A., Geiger, R. and Wieland, T. eds). Karger Press, Basel, Switzerland, pp. 283-294.


(CH3)3-C
Bzl
CH3
-CH2-O
Boc-Tyr-"D"-NH-CH-NH-CO-CH2-COOH
DMSO
CH3
Tyr
2.6 3.5
CO-CH2-CO
H2O
Tyr
CβH2
HN-C-NH
Boc-NH
N-CH-N
Tyr CαH
9
8
7
6
5
4
3
2
1
ppm

UNIVERSITY OF NEW HAMPSHIRE
DURHAM, NEW HAMPSHIRE 03824

Department of Chemistry
College of Engineering and Physical Sciences
Parsons Hall (603) 862-1550

November 17, 1982

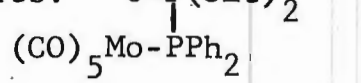
Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Dear Barry:

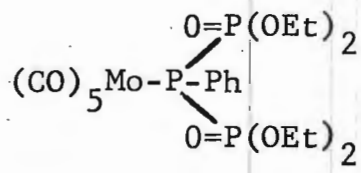
Some Not-so-impressive $^{1}J_{P-P}$ Values in Phosphoryl-phosphine Complexes

We were jolted out of our rockers upon receipt of your ultimatum. Please credit Ms. Kathleen S. Gallagher for this contribution.

We have observed some rather unimpressive values for direct-bonded P-P coupling constants in the P-31 spectra of several new phosphoryl-phosphine complexes of metal carbonyls. Usual J_{P-P} values are in excess of 100 Hz. We would like to present these data as antidote to the "biggest ever" reports.



44 Hz



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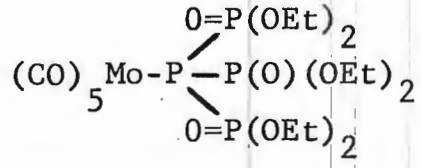

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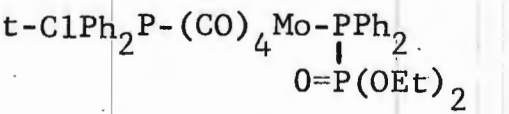

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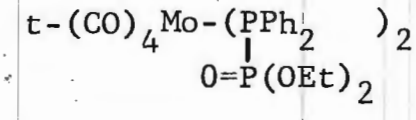

29

Best regards,

Ed Wong

RIJKSUNIVERSITEIT GENT

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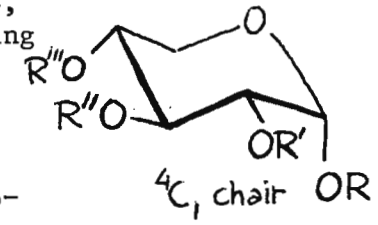
B-9000 GENT. 17 November 1982
KRIJGSLAAN 271 - S 4 Tel. 22 57 15
(België - Europa)

Prof. B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College Station TX 77843 (U.S.A.)

Dear Barry,

ABOUT COUPLING CONSTANTS IN α-D-XYLOPYRANOSIDES.

We found that in α-D-xylopyranosides $^3J(4,5eq) = \sim 5.5$ Hz, $^3J(4,5ax) = \sim 10.5$ Hz and $^2J(5eq,5ax) = \sim -10.5$ Hz. These data are considered to be diagnostic for $^4C_1$ chairs. The pattern of H-5ax in the ^1H spectrum of Me 2-O-Ac-α-D-xylopyranoside (1)(R = Me, R' = Ac, R'' = R''' = H) appeared as a triplet-like structure with a distance between the outer lines of 24.6 Hz and suggesting in a first order approximation that $^3J(4,5ax) = |^2J(5eq,5ax)| = 12.3$ Hz. Utille[1] and Gagnaire report for 1,2,3-tri-O-acetyl-α-D-xylopyranose (2) in $CDCl_3$ (R = R' = R'' = Ac, R''' = H) ($^3J(1,2) = 3.5$ Hz (pointing to a $^4C_1$ conformation), $^3J(4,5eq) = 2.5$ Hz, $^3J(4,5ax) = 12.5$ Hz and $^2J(5eq,5ax) = 12.5$ Hz. As H-5eq and H-4 both are found[1] at δ 3.90 degeneration of the system is expected. For (1) H-4 and H-5eq resonate respectively at δ 3.73 and δ 3.69.
We have simulated the isolated ABX-part (A is H-4, B is H-5A, X is H-5B) as a three spin system, using the coupling constants extracted from the other compounds in the α-D-xylopyranoside series (e.g. $^3J(4,5eq) = 5.6$ Hz, $^3J(4,5ax) = 10.5$ Hz and $^2J(5eq,5ax) = -10.5$ Hz) and have found excellent agreement with the experimental spectrum. The position of the lines of the X-part (H-5B) could easily be calculated from the table of energies[2]. It appears from these calculations that the outer lines are not the transitions representing $J_{AX} + J_{BX}$ (namely 2 → 1 and 8 → 7) but the lines from the transitions 6' → 3' and 5' → 4'. The distance between the outer lines of the X-part (H-5B) of 1 in benzene amounts to 21.0 Hz. Now the data measured by first-order approach agree very well with the real values.
In general, the patterns of H-5 protons in aldopentoses should be analyzed with care.



Sincerely yours,

André DE BRUYN. Luc SPIESSENS.

REFERENCES : 1) J.P. Utille and D. Gagnaire, Carbohyd. Res. 106, 43-57 (1982).
2) J.D. Roberts, "An introduction to the analysis of the spin-spin splitting in high resolution n.m.r. spectra" W.A. Benjamin, N.Y. 1961, p. 80.

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varian

December 2, 1982

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

Dear Barry:

NEW FACES AT VARIAN

We have had several excellent people join our staff recently and I thought that as well as your newsletter carrying "Help Wanted" letters it might be refreshing to see a follow-up report:

Applications Laboratory

We're happy to have David Foxall joining us in the Applications Laboratory. He conducted his graduate studies with Ian Campbell at Oxford using spin-echo methods to examine enzyme-catalyzed reactions in intact cells. He has recently been with Jack Cohen at NIH conducting research on cellular metabolism using NMR techniques. David will bolster our biochemical expertise and continue his intact cell work.

NMR Research

We welcome Lynne Batchelder to the Research Group. For the past three years she has been at the National Institute of Dental Research, first as a Post-Doctoral Fellow and then as a Staff Fellow. She worked with Dennis Torchia on the application of solid state NMR techniques to the study of molecular structure and dynamics in biological solids. She has considerable experience in building and modifying NMR spectrometers and this, together with her research interests, will significantly strengthen our capability in solid state NMR.

Digital Systems

The digital systems group has just recently expanded to include Peter Grimes. He has been working with Gerald Stockton at American Cyanamid, Princeton, NJ expanding their NMR capabilities by providing microprocessor and compter interfaces as well as applications software. His experience in both the digital systems and applications areas will further strengthen Varian's data systems.

Sincerely yours,

George Gray
Howard Hill
Steve Smallcombe

THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175
CINCINNATI, OHIO 45247

SYMPOSIUM ON HIGH-RESOLUTION NMR OF SOLIDS,

OXFORD, OHIO, MAY 24, 1983

Dear Barry:

Thank you for the yellow reminder. To continue receiving the Newsletter, which we find valuable, I would like to call attention to a Symposium on High-Resolution NMR of Solids: Techniques and Applications, of which I am chairman. This Symposium will be held May 24, 1983, at Miami University, Oxford, Ohio (about 40 miles from Cincinnati). It is part of the ACS Central Regional Meeting to be held there May 23-25. The Symposium speakers (indicated with an asterisk) are:

J. L. Ackerman* and R. Pratt, University of Cincinnati: "Magic-Angle Spinning of Quadrupolar Nuclei"

M. G. Munowitz, W. P. Aue, D. J. Ruben, and R. G. Griffin*, Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology: "Two-Dimensional NMR in Rotating Solids"

B. E. Hanson*, H. Dorn, and E. Motell, Virginia Polytechnic Institute and State University: "^{13}C NMR Studies of Solid-State Dynamics in Metal Carbonyls"

E. Oldfield*, University of Illinois: "High-Resolution NMR of Solids"

W. M. Ritchey*, D. Cory, and A. Cholli, Case Western Reserve University: "^{29}Si and ^{13}C MAS-NMR of Solid Polymers"

J. P. Yesinowski*, R. A. Wolfgang, and M. J. Mobley, Miami Valley Laboratories, The Procter & Gamble Co.: "^{19}F Magic-Angle Spinning NMR Revisited: Surface Applications"

Open papers/posters on a wider variety of subjects are also being solicited. Four copies of an abstract, with the original on a standard ACS form, should be submitted to the Program Chairman, Dr. Marion D. Francis, by January 15, 1983 (his address is that on this letterhead). Further details of the program have appeared in the November 15 issue of Chemical and Engineering News.

Very truly yours,

THE PROCTER & GAMBLE COMPANY
Research & Development Department

James Yesinowski

James P. Yesinowski
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DEPARTMENT OF CHEMISTRY, BOWNE HALL, SYRACUSE UNIVERSITY, SYRACUSE, NY 13210

December 1, 1982

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

Scientific Programmer: NMR Positions

Dear Barry,

My laboratory has two openings for scientific programmers who have extensive FORTRAN and assembly level programming experience. Primary responsibilities involve continuing development of **ORACLE®**, a uniquely powerful spectroscopic data analysis software system. Currently we are expanding **ORACLE®** to include quantitation of heavily overlapping complex spectral lines and to support powerful processing of large 2D NMR data sets. Aspects of this work involve interaction with outside academic and commercial laboratories.

Our laboratory programming facilities are excellent. Most program development takes place on a large Data General MV-8000 32 bit computer (5Mbyte MOS, 880Mbyte disk, 40 ports, two high speed color graphics processors) which implements FORTRAN77 under AOS/VS, a multiprogramming virtual memory operating system. Programming is facilitated by a high level language symbolic debugger.

Other computer systems which will be used include two powerful Motorola 68000-based laboratory computers and a large Data General Eclipse computer with integrated array processor and high speed color graphics.

The Scientific Programmers will report to Dr. Charles Dumoulin, Operations Director of the laboratory. Each programmer will have two to four assistants (usually undergraduates in Computer and Information Sciences, who work part time during sessions and full time in the summers). Much of our programming activity leads to publication in the scientific literature. Our software is modular and structured for ease of export.

We are especially anxious to fill at least one position as soon as possible. Interested parties should write to me or call (315-423-4026, collect) and have letters of recommendation forwarded directly.

Thank you.

Yours sincerely,

George C. Levy
Professor

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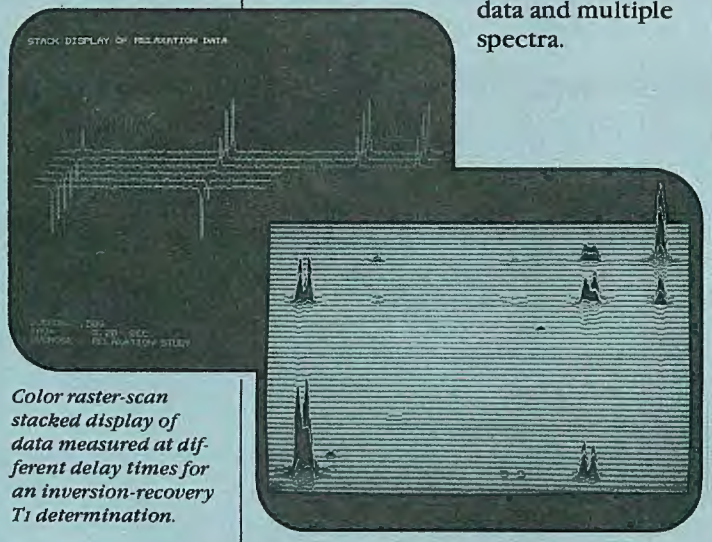

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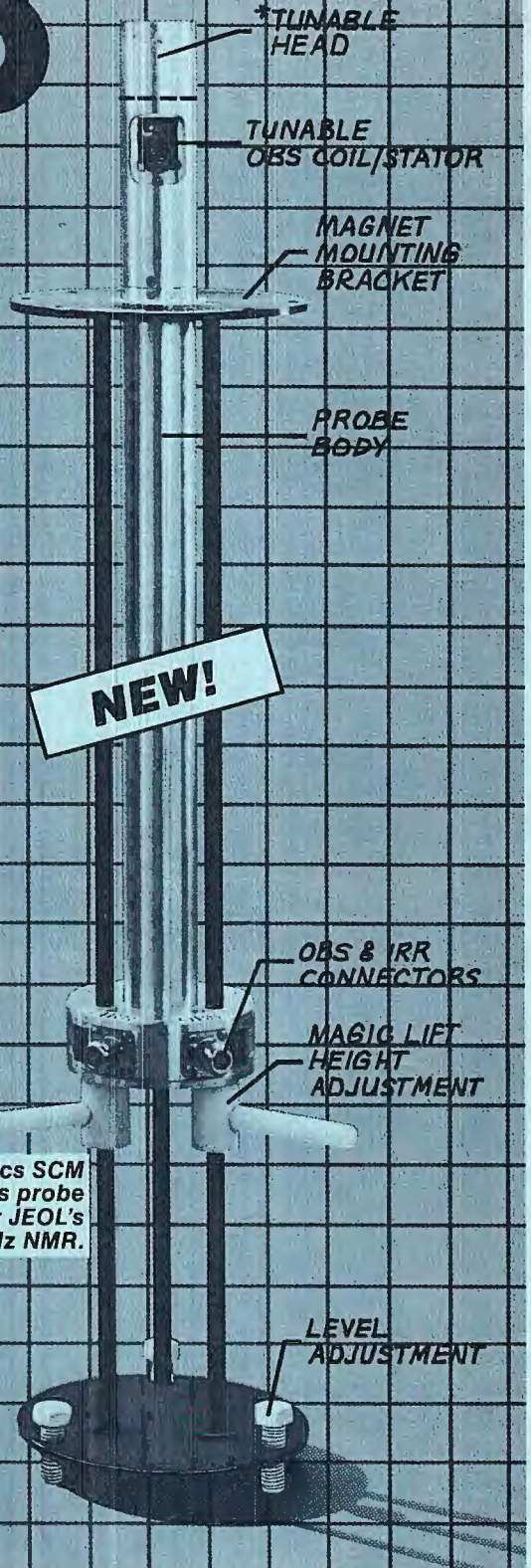

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