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NMR NEWSLETTER

NO. 336

SEPTEMBER 1986

TEXAS A&M UNIVERSITY

NMR NEWSLETTER

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CONTRIBUTORS

Cryomagnet Systems, Inc.
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AUTHOR INDEX --- TAMU NMR NEWSLETTER, NO. 336, SEPTEMBER 1986

ADVERTISERS

FORTHCOMING NMR MEETINGS

1986 Eastern Analytical Symposium - October 20-24, 1986; Hilton Hotel, New York; see Newsletter No. 329, p. 23 and No. 325, p. 27.

28th ENC (Experimental NMR Conference) - April 5-9, 1987; Asilomar; Pacific Grove, California; Chairman: Dr. Lynn W. Jelinski, (AT&T Bell Laboratories); For information, contact Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

8th International Meeting "NMR Spectroscopy" - July 5-10, 1987; University of Kent at Canterbury, England; For information, contact Dr. John F. Gibson, Royal Society of Chemistry, Burlington House, London W1V OBN, England.

29th ENC (Experimental NMR Conference) - April 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For information, contact Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence Should be Addressed to:

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

DEADLINE DATES

No. 338 (November) ---- 31 October 1986

No. 339 (December) --- 28 November 1986

OXFORD RESEARCH SYSTEMS

Oxford Research Systems Limited
Nuffield Way, Abingdon,
Oxon OX14 1RY,
England.
Telephone 0235 32421
Telex 83356

DATE: 21 July 1986
OUR REF:
YOUR REF: (Received August 5, 1986)

Microscopic Imaging of Maize Root-Sections

Dear Professor Shapiro

Recently we have applied microscopic NMR imaging to the interesting field of water exchange in plant tissue. Sections of the roots of freshly germinated maize seeds were inserted in a 1.5 mm id capillary glass tube and placed in a 3mm solenoid RF imaging coil. A constant flow through the tube of an aerated solution was maintained during the experiments.

Images were acquired using a Bruker AM200SY spectrometer with a standard bore (54mm) 4.7 T magnet and equiped with accessories for imaging. A standard 2DFT imaging technique was used with a TE of 14ms and a TR of 1.5 s. Data were collected in a matrix of 64 x 64 points and the pixel resolution was approximately 30 x 30 microns at a slice thickness of 2 mm. Because of the anatomy of the root sections these unconventional voxel dimensions gave an acceptable spatial resolution in the transverse images. Details of the epidermis, the cortex, and of the xylem vessels in the stele were clearly visible.

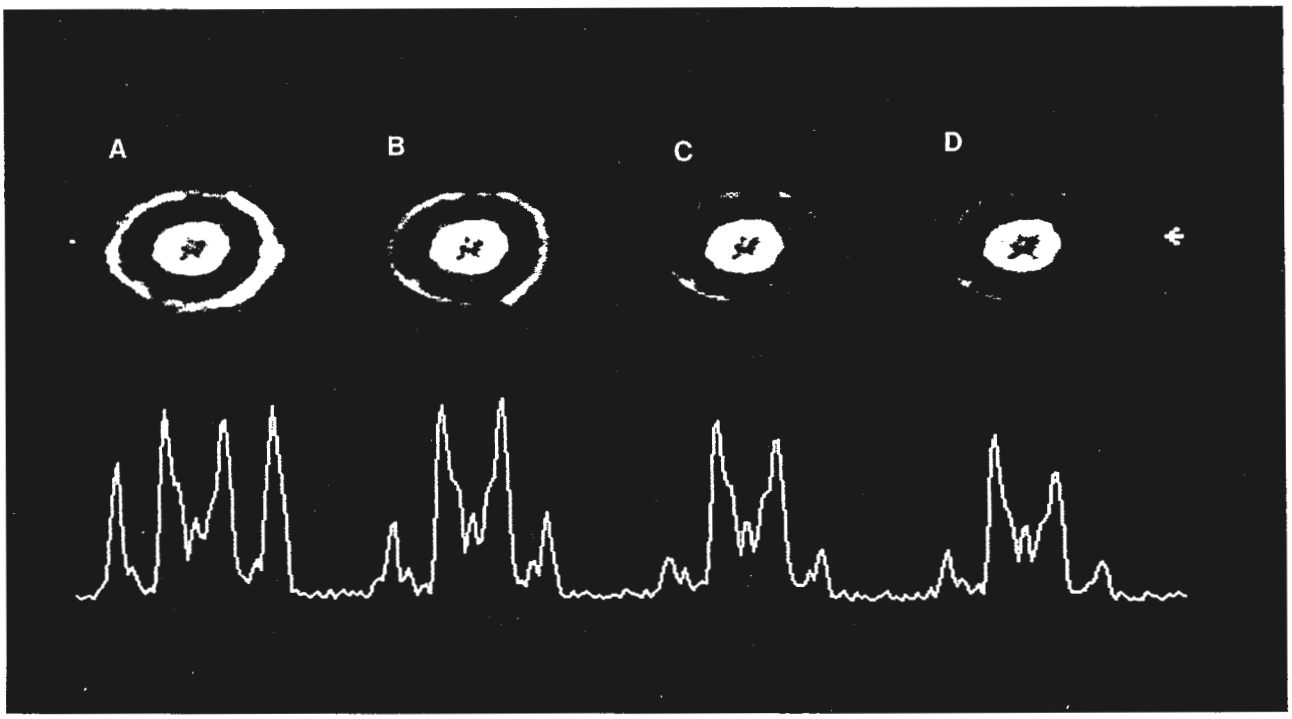
In the figure some results are shown of a time course study of the replacement of tissue water by D_2O. For this experiment the circulation system was filled with D_2O and images were obtained before the changeover (A), at the start of D_2O circulation (B), after 4 minutes (C), and after 14 minutes of circulation (D). For a more quantitative evaluation of the observed effects cross sectional profiles through the images taken at the position marked with an arrow are shown.

Yours sincerely

Joost A B Lohman
Oxford Research Systems

R George Ratcliffe
Department of Plant Sciences
University of Oxford, UK

Herve Quiquampoix
Department of Plant Sciences
University of Oxford, UK.
Visiting from CNRA, Station de Science du Sol,
Versailles, FRANCE



UNIVERSITY OF MISSOURI-COLUMBIA

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Professor Tuck C. Wong
314-882-7725

NMR SPECTROSCOPIST POSITION

An NMR Spectroscopist position is open in the NMR Facility of the University of Missouri-Columbia. The duties of the spectroscopist are to maintain the facility, advise and train users, and to engage in collaborative research. A Ph.D. in chemistry or related fields with experience in modern NMR techniques required. Salary commensurate with qualifications. Applicants please send inquiry, C.V., and names of 2 to 3 references to

Professor Tuck C. Wong
Department of Chemistry
University of Missouri
Columbia, MO 65211

or phone

314-882-7725, 882-3291

TOWSON STATE UNIVERSITY
TOWSON, MARYLAND, 21204

Department of Chemistry (301) 321-3058

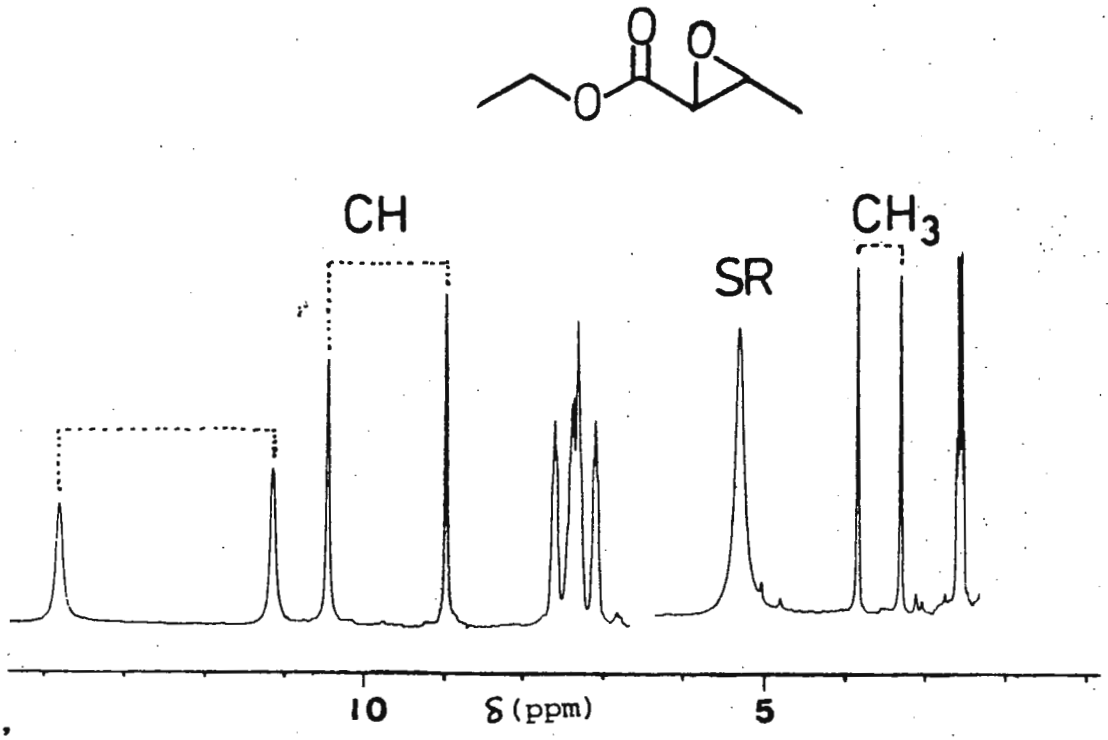
August 7, 1986
(Received August 15, 1986)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, TX 77843-3255

Dear Barry:

Large Enantiotopic Shift Differences

During a study of the effect of chiral europium shift reagents on polyoxygenated compounds, we were amazed by the 300 MHz spectrum below. In the presence of 0.2 M bis ((3-heptafluoropropylhydroxymethylene)-d-camphorato) europium (III) in $CDCl_3$, 0.2 M ethyl 2,3-epoxybutyrate exhibits $\Delta\Delta\delta$ for the epoxide C<u>H</u>'s of 2.7 and 1.4 ppm, and 0.5 ppm for the C<u>H</u>$_3$'s. The coupling is obscured by the line broadening. Note that the line widths (T_2's) of the enantiotopic CH's are observably different, a phenomenon expected but seldom seen. Is this a $\Delta\Delta\delta$ record?



Sincerely,

Linda

Linda M. Sweeting
George M. Whitesides

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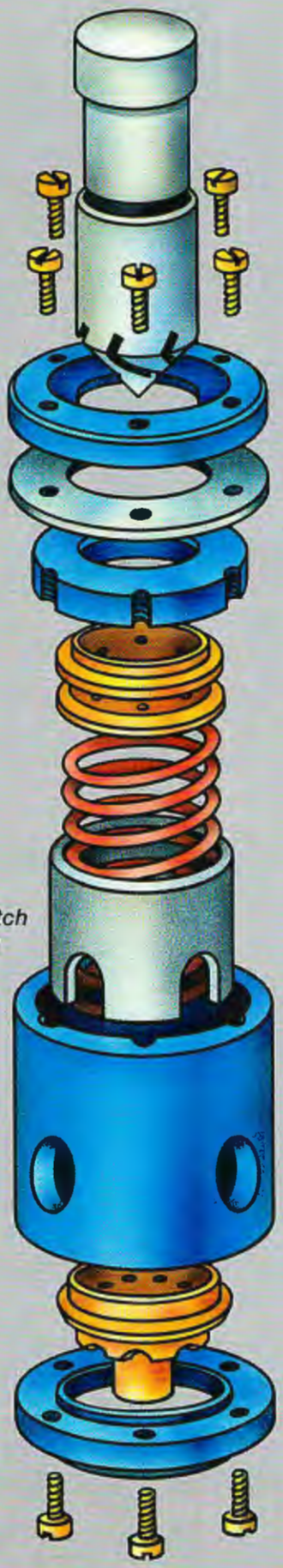

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M295C	12 gauss (5μsec)	4 KHz	2 KHz	only accepts Ceramic/KEL-F rotors
M275	20 gauss (3μsec)	10 KHz	5 KHz	fast spinning system, for non ^{13}C appl.
M275C	20 gauss (3μsec)	6 KHz	4 KHz	only accepts Ceramic/KEL-F rotors
M395	10 gauss (6μsec)	5.5 KHz	N/A	triple bearing system for wide bore
M375	15 gauss (4μsec)	8 KHz	N/A	flipper or VASS probes only

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295K	9.5mm	5.4mm	0.35ml	KEL-F®	3.8 KHz @ 15 psi	routine, no C13 background
295T	9.5mm	7.1mm	0.56ml	TORLON®	6 KHz @ 28 psi	multinuclear, dense materials
295C	9.5mm	7.9mm	0.78ml	CERAMIC	4 KHz @ 16 psi	highest sens., no C13 background
275T	7.5mm	3.6mm	0.13ml	TORLON®	10 KHz @ 40 psi	highest speed, Al, B and Si free
275T	7.5mm	4.5mm	0.21ml	TORLON®	8 KHz @ 35 psi	high speed, volume; Al, B, Si free
275C	7.5mm	6.0mm	0.45ml	CERAMIC	6 KHz @ 15 psi	highest speed, no C13 background
395D	9.5mm	7.1mm	0.56ml	DELRIN®	4 KHz @ 20 psi	highest stability, triple bearing
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July 28, 1986 (Received August 4, 1986)

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

TITLE: Solid State 31P NMR of Palladium-Phosphine Complexes Bound to Silica

Dear Barry:

I would like to re-initiate my subscription to the TAMU Newsletter by describing some work I did while still at B. F. Goodrich Company in collaboration with Drs. A. J. Magistro and P. P. Nicholas of that laboratory. The complete work will be published in Inorganic Chemistry in several months.

Our interest was in characterizing tertiary-phosphine-palladium complexes and their precursors bound to the surface of silica gel by cross-polarization, magic-angle-spinning (CPMAS) techniques along the lines pioneered by Colin Fyfe and co-workers. Phosphorus-31 NMR is a good probe of complex formation and geometry, whereas C-13 NMR is a good probe of ligand structure. Figure 1 shows some of our P-31 results for bis-ethyldiphenylphosphine palladium dichloride complexes. In Figure 1A is the spectrum of derivatized silica before complex formation, showing bound phosphine and phosphine oxide. Upon complex formation, two new peaks are seen at 21 and 30 ppm (Figure 1B), assignable to trans and cis geometries, respectively. If the trans-complex is preformed, then attached to the surface, the spectrum in Figure 1C results. Now no uncomplexed phosphine or phosphine oxide is observed, and the trans-configuration is not totally retained. Figure 1D is the spectrum of the crystalline trans-complex, whereas Figure 1E shows the shift positions reported by Grim and Keiter (Inorg. Chem. Acta 1970, 4, 56) for the model complexes trans-and cis-$[EtPh_2P]_2PdCl_2$.

The palladium dichloride chelate complexes of bis(diphenylphosphino)methane, -ethane, and -propane, all of which have an approximately square-planar configuration, were examind as solid state models for strained cis-complexes on the silica surface. As in solution, the solid state P-31 chemical shifts of these compounds occur over a range of 127 ppm while the P-Pd-P angle varies from 73 to 91 degrees. Hence the P-31 chemical shift is a very sensitive measure of strain in such complexes, and confirms that the structures in solution are similar to those in the solid state. Applying these models, we find that the surface-bound complexes have mainly unstrained, trans-configurations.

Other species that have been examined on surfaces or as models include dicyclohexylpropylphosphino-complexes, for which cis- and trans- surface-bound complexes are observed, trimethylsilyl-capped samples, and phosphine oxides. Evidence is found for hydrogen-bonding between bound phosphine oxide groups and silanol groups on the silica surface. Figure 2B shows a standard P-31 spectrum with the bound phosphine oxide peak occuring at about 43 ppm. Upon capping of the remaining silanol groups with CH3SiCl, the phosphine-oxide peak shifts upfield to about 38 ppm. We attribute this to breakup of P=O-silanol hydrogen bonds. The new peak at about 10 ppm is probably from phosphonium salt formation.

In summary, we found CPMAS to be a valuable technique for characterizing molecular structure and geometry at surfaces.

Sincerely,

Rich

Richard A. Komoroski, Ph.D.
Associate Professor of Radiology/Pathology

RAK:lm

Enclosures

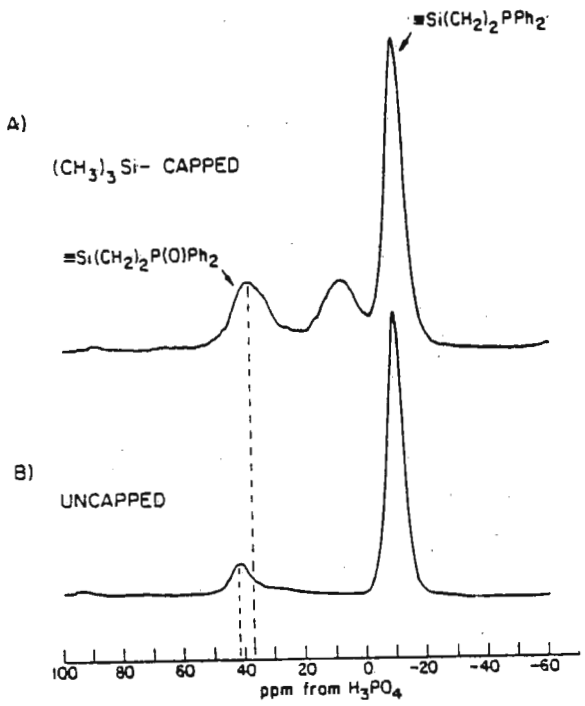

Figure 2

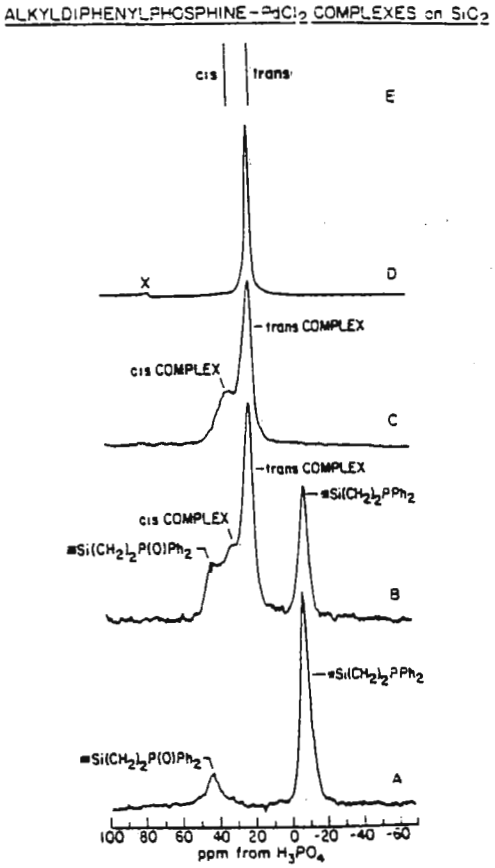

Figure 1

POSITIONS AVAILABLE

NMR/MRI ENGINEER. The NMR Spectroscopy Laboratory of the University of Arkansas for Medical Sciences is seeking an individual to design, build, and implement radio-frequency circuitry and NMR instrumentation, including imaging and surface coils/probes, in support of biomedical research. The successful candidate should have a degree or related experience in rf electronics with an interest in working in a research enviroment. He/she will have the opportunity to collaborate with users of the NMR Laboratory on projects relating to instrumentation and technique development. The Laboratory will have (November, 1986) a GE CSI-4.7 T, 33cm bore imaging/spectroscopy unit and a fully equipped GN-300 high resolution spectrometer. Also available will be a GE 1.5 T clinical imager with spectroscopy capability. Send resume and salary requirements to: Richard A. Komoroski, Ph.D., Department of Radiology, University of Arkansas for Medical Sciences, 4301 West Markham Street, Little Rock, AR 72205, (501) 661-5740.

POSTDOCTORAL. The position is with an established group of investigators in the Department of Pathology to develop applications of NMR imaging and spectroscopy to biomedical problems. The UAMS NMR Center will have a GE CSI-4.7T, 33 cm bore imaging/spectroscopy unit and a fully equipped GN-300 high resolution spectrometer. Also available will be a GE 1.5T clinical imager with spectroscopy capability. The fellow will participate in chemical pathology, toxicology, and psychopharmacology programs. Background in NMR desirable. Starting date negotiable. Salary competitive. Send C.V. and names of three references to: Richard A. Komoroski, Ph.D., Department of Pathology, Slot 517, University of Arkansas for Medical Sciences, Little Rock, AR 72205

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Please send resume or inquires and 2 letters of recommendation to: Dr. Lowell Kispert, Chemistry Department, The University of Alabama, Tuscaloosa, AL 35487-9671 (205) 348-7134 or (205) 348-8450.

UNIVERSITÉ D'OTTAWA UNIVERSITY OF OTTAWA
OTTAWA ONTARIO CANADA

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

August 1st, 1986
(Received August 11, 1986)

Dear Professor Shapiro,

K-39 NMR of K^+-crown complexes

With such a low gyromagnetic ratio as 1.248×10^7 rad.T^{-1}.s^{-1}, K-39 is not a very gifted nucleus for nmr applications. Even if its natural abundance is 93.1%, its receptivity relative to C-13 is only 2.69. Since, in addition, it is quadrupolar (I=3/2; Q=0.055 barn), and suffers from acoustic ringing problems, one can easily understands why applications have been so scarce (1).

Working at 13.997 MHz (Varian XL-300), we have followed the titration of K^+ by Dibenzo-30-crown-10 (DB30C10) in several non-aqueous solvents.

The figure shows the K-39 chemical shifts of 5.0×10^{-2}M KSCN solutions in four solvents (nitromethane-NM-; acetonitrile-AN-; acetone-AC-; Pyridine-PY-) as a function of ρ, the ratio [DB30C10]/[KSCN]. In the four cases, a plateau value is reached for $\rho > 1.0$, showing the presence of a 1:1 complex, characterized by an equilibrium constant of formation higher than 10^4. In the case of NM, where a curvature appear, more data have been collected and have been analyzed in terms of ion-pairing and of a 2:1 complex formation (2).

The striking result of this experiment is the evidence from K-39 nmr that, in solution, solvent molecules have been expelled from the first coordination sphere of K^+. The structure of the complex in solution could be similar to the structure in the crystal: DB30C10 wraps around K^+ (3). This result is in agreement with previous C-13 studies on the ligand (4).

Please, credit this contribution to the subscription of Professor R.R. Fraser.

Sincerely yours,

C. Detellier

(1) C. Detellier, in "NMR of Newly Accessible Nuclei", Vol. 2, Chapter 5, P. Laszlo Ed., Wiley, 1983.
(2) H.D.H. Stöver, M. Robillard, C. Detellier, Polyhedron, in press.
(3) M.A. Bush, M.R. Truter, J. Chem. Soc., Perkin Trans. II, 345, (1972); J. Hasek, D. Hlavata, K. Huml, Acta Cryst. B, 36, 1782 (1980).
(4) D. Live, S.I. Chan, J. Am. Chem. Soc., 98, 3769 (1976); M. Shamsipur, A.I. Popov, J. Am. Chem. Soc., 101, 4051 (1979).

(continued on page 13)

How to use solid-state NMR to get results in all these applications areas:

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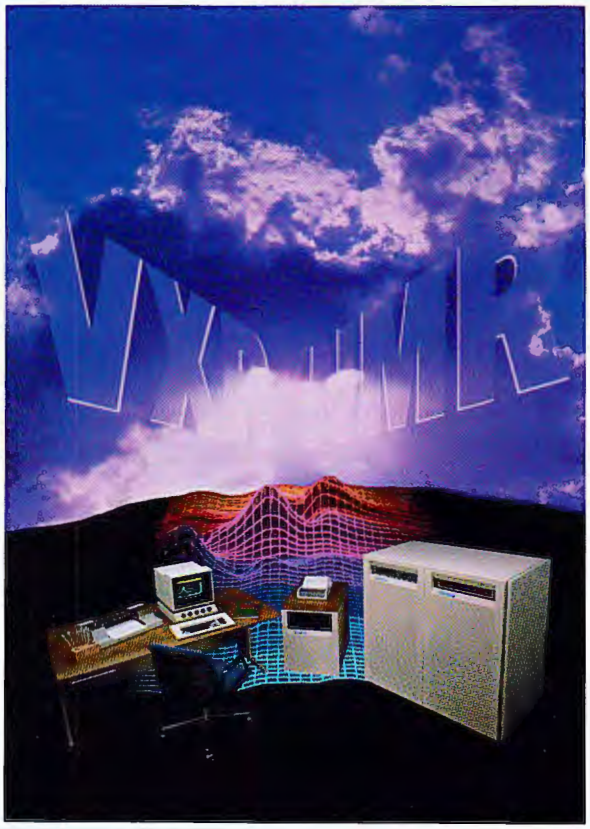

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— *Catalyst Studies*

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Varian wideline solids systems are available now.

^{23}Na NMR powder spectrum of $NaNO_3$ showing detailed crystallite distribution within the sample.

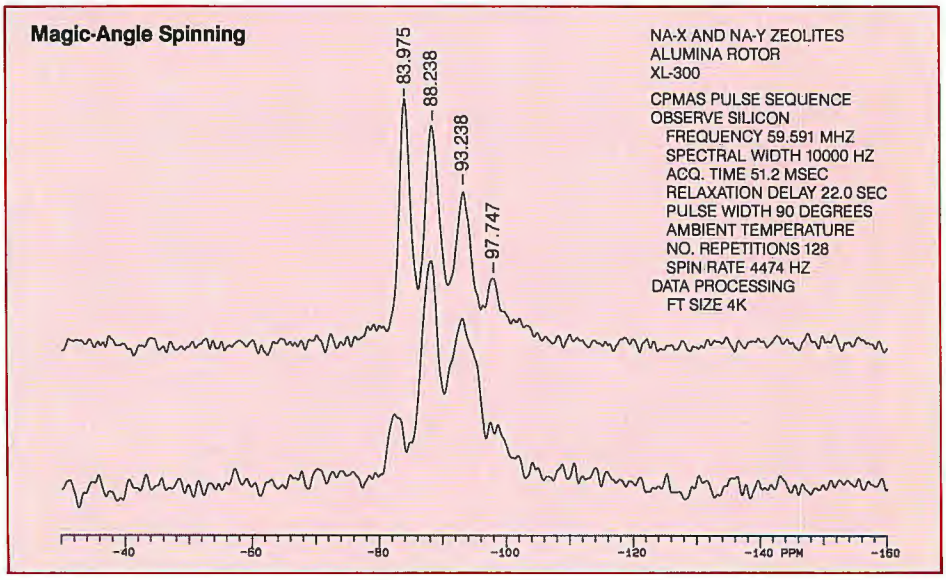
Solid-State Results from Varian NMR

^{29}Si MAS – Zeolites

Silicon is the major nucleus of interest in silicates. MAS reveals information about the types of Si present in a sample. The upper spectrum is of Na-X, which has a lower Si/Al ratio than does Na-Y (lower spectrum).

The resonances correspond to Si[4Al] (lowfield) through to Si[0Al] (highfield). Neither of these Si spectra have been run with cross-polarization, as there are few, if any, framework protons present. However, CP/MAS experiments are used when investigating adsorption of small molecules onto zeolites.

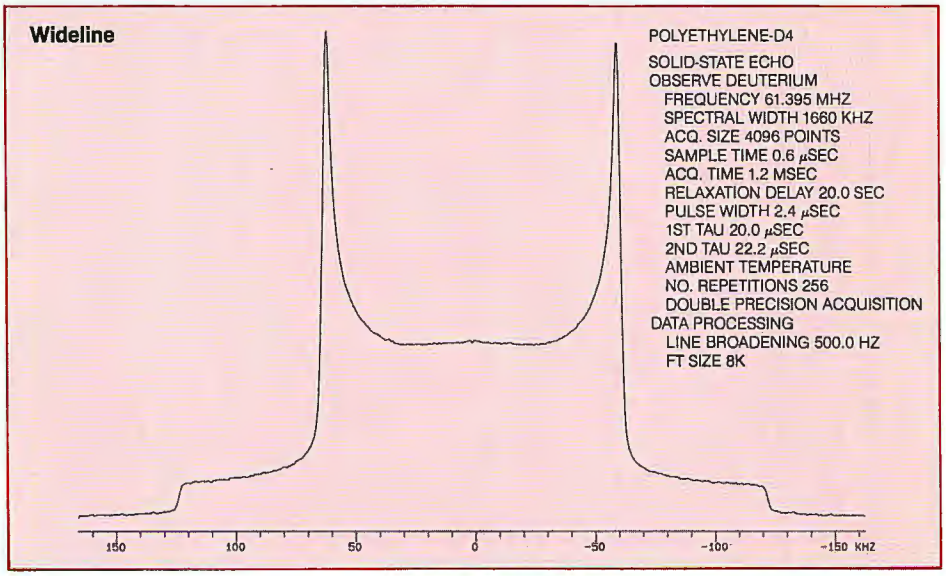
Varian's CP/MAS Accessory allows the user to obtain a wealth of chemical information from many different nuclei at different sample temperatures. Applications range from characterization of polymer dynamics and composition, using ^{13}C CP/MAS, through catalyst investigations (using ^{29}Si, ^{27}Al, ^{195}Pt or ^{23}Na MAS) to organic chemistry problems, e.g., ^{59}Co MAS.



Poly (ethylene-d$_4$)

The sample shown here was mainly crystalline (which gives the doublet spectrum), with some amorphous material (showing as a central hump). The crystalline T_1 relaxation is long, demanding a 10-second wait between acquisitions. Techniques such as this have been used to investigate the chain orientations of stressed or drawn samples. Molecular order may be correlated to sample morphology using spectra such as this.

Varian's Wideline Solids Accessory opens new possibilities for the study of paramagnetic and quadrupolar nuclei. Information can be obtained about molecular dynamics, ordering the morphology of deuterated polymers (^{2}H NMR), microbiological systems (^{2}H, ^{35}Cl, ^{113}Cd, ^{31}P), and solid-state chemical reactions (^{29}Si, ^{27}Al, ^{23}Na ^{51}V, etc.).



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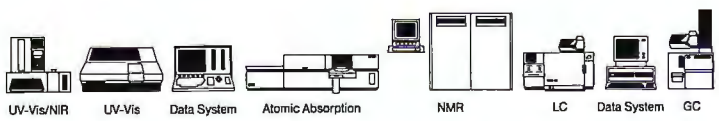

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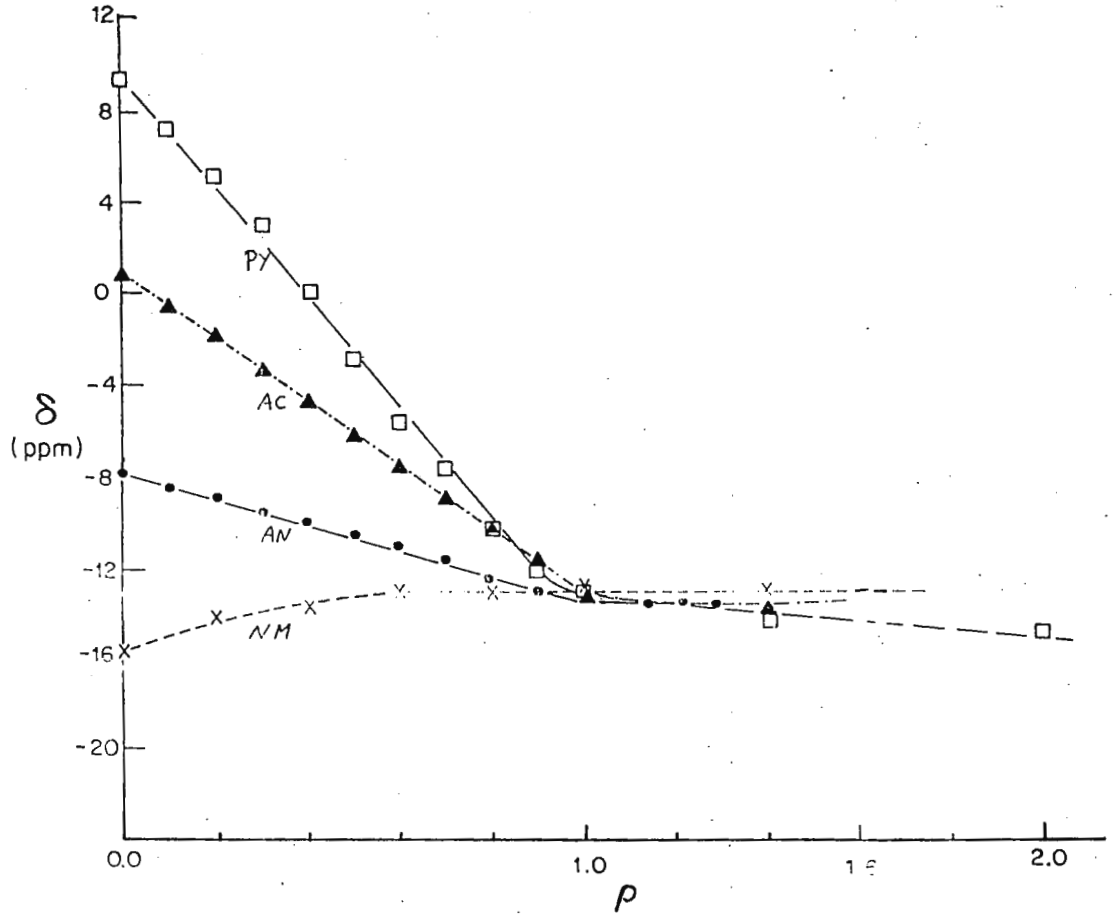

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	2 June 1986	LE	0531/6181-0 Durchwahl 352	952667	24 July 1986

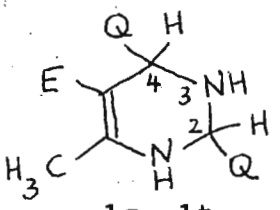
(Received July 30, 1986)

Revised Structures of Tetrahydropyrimidine Nitrosation Products by 2D Short- and Long-Range H,H- and C,H-Shift Correlations

Dear Dr. Shapiro:

thank you for your reminder. I hasten to comply by describing some recent results that I have obtained in collaboration with Prof. Klaus Görlitzer and Christian Heinrici of the Institute of Pharmaceutical Chemistry of the Technical University of Braunschweig.

Formerly[1], the cis- and trans-tetrahydropyrimidines **1c** and **1t** were believed to be transformed, upon nitrosation, into the ring-opened



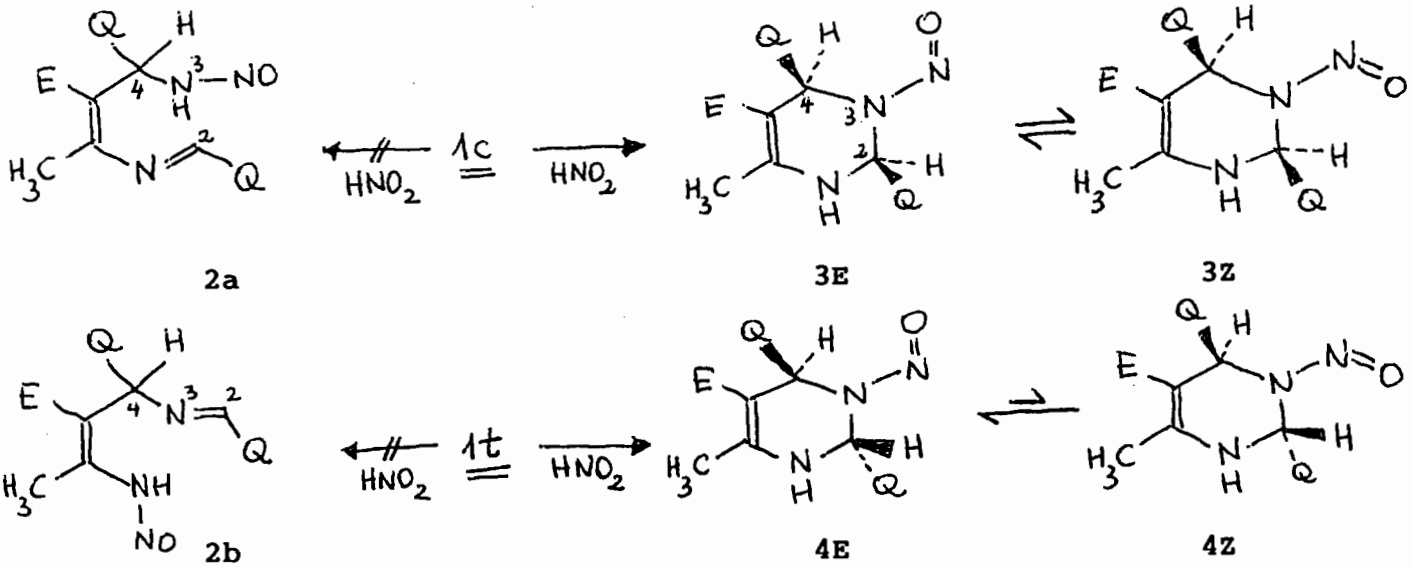
1c, 1t

E = CO_2CH_3
Q = 2-NO_2-C_6H_4

products **2a** and **2b**, respectively. We have now carried out a careful reinvestigation of the products by using 2D-NMR techniques ($^1H,^1H$-COSY and its 'long-range' version as well as $^{13}C,^1H$-COSY and $^{13}C,^1H$-COLOC). Starting with the readily assignable NH-protons we were able to assign all proton and all carbon resonances (including four sets of 2-nitrophenyl signals in each sample) in products **3** (from **1c**) and **4** (from **1t**). Long-range $^1H,^1H$- and $^{13}C,^1H$-correlations across the nitrogen atoms show that the tetrahydropyrimidine rings are not opened under the reaction conditions. Instead simple nitrosation of N-3 takes place furnishing rotameric nitrosamines **3E/3Z** (from **1c**) and **4E/4Z** (from **1t**).

A variable temperature ^1H-NMR study of **3E/3Z** shows reversible

coalescence of the methyl signals at 77 °C (OCH_3) and 63 °C (CCH_3), respectively (300 MHz). This leads to a rotational barrier of ca. 78 kJ/mol (3E→3Z and 3Z→3E) which represents a relatively low value for



2a 3E 3Z

2b 4E 4Z

N-nitrosamines[2]. This low barrier can be rationalized by destabilization of the ground states due to steric interactions of the nitroso and the adjacent aryl groups.

The original[1] misinterpretation of the ^{1}H-NMR spectra was apparently caused by the unusual low-field shifts of H-2 (3E: δ = 7.83, 3Z: δ = 7.55) and of H-4 (3E: δ = 7.29, 3Z: δ = 7.54). ^{13}C,^{1}H-COSY, however, now showed that these protons are bound to sp^3-hybridized carbon atoms.

With kind regards,
sincerely yours,

L. Ernst

(L. Ernst)

References:

1. K. Görlitzer, D. Buß, Arch. Pharm. (Weinheim) 1981, 314, 949.

2. M. Oki, Applications of Dynamic NMR Spectroscopy to Organic Chemistry, p. 73, VCH Verlagsgesellschaft, Weinheim 1985.

Universität Bern

Institut für organische Chemie

CH-3012 Bern, Freiestrasse 3
Telefon 031 65 43 11

Peter Bigler

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

28.7.1986
(Received August 1, 1986)

SELECTIVE SATURATION-DIFFERENCE SPECTROSCOPY

Dear Professor Shapiro

The measurement at higher magnetic fields, the application of special 2D techniques and the use of various difference spectroscopy techniques represent the most common solutions to overcome the problem of multiplet recognition in heavily overlapped spectral regions. Routinely used difference spectroscopy methods as decoupling difference, FT-INDOR or NOE-difference can lead to strong intensity distortions and/or long accumulation times and to unwanted Bloch-Siegert effects in the case of decoupling difference.

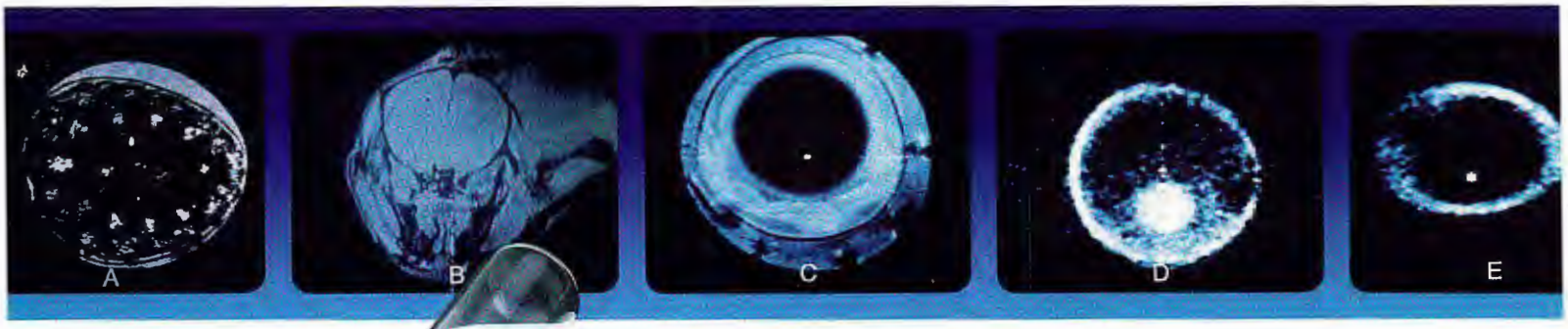
Selective saturation difference spectroscopy (SSD) (Fig. 1) is based on the fact that in most cases at least one line of the multiplet of interest is resolved and can be selectively irradiated with a very weak decoupling power. If the saturation period is long enough the saturation is distributed uniformely over all the transitions of this multiplet due to relaxation processes of the coupled spins. The multiplet can be resolved by subtraction of the data acquired in two successive experiments, where the decoupler is set on resonance and off resonance respectively. A typical result is shown in figure 2b. Spin decoupling during the acquisition for simplification of the resolved multiplet can easily be accomplished by switching the frequency and by increasing the decoupler power to a level adequate for optimal decoupling prior to data accumulation (Fig. 2c).

Sincerely yours

Peter Bigler

(continued on page 19)

The NMR evolution continues:



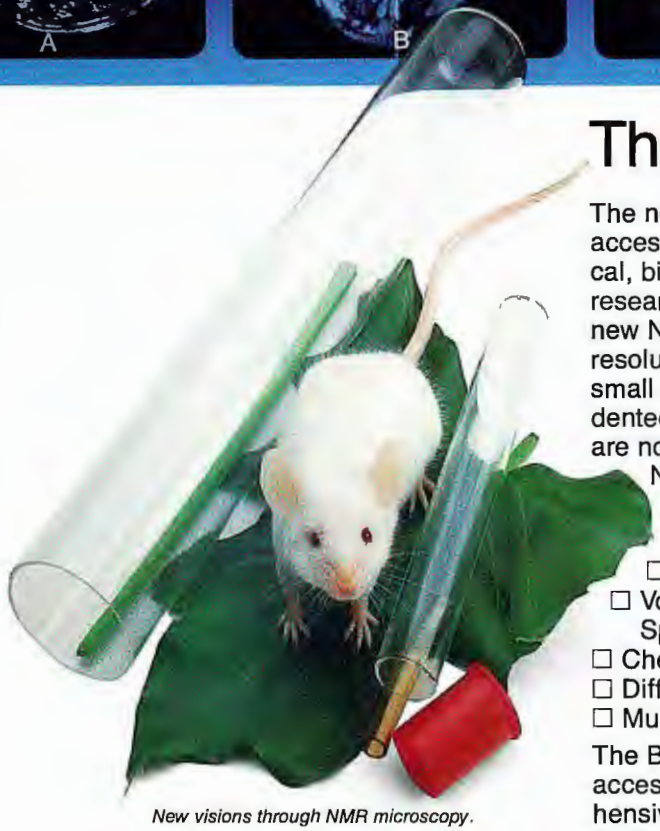


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Fig. B: Cross sectional image of a mouse brain tumor. Resolution 100μ x 100μ x 500μ.
Fig. C: A cross sectional image of a mouse eye, 3 mm in diameter. Resolution 20μ x 20μ x 250μ.
Fig. D: Image of an ovum from laevis (frog egg). Resolution 10μ x 10μ x 250μ.
Fig. E: Diffusion of water through a piece of nylon. Resolution 50μ x 50μ x 1000μ.

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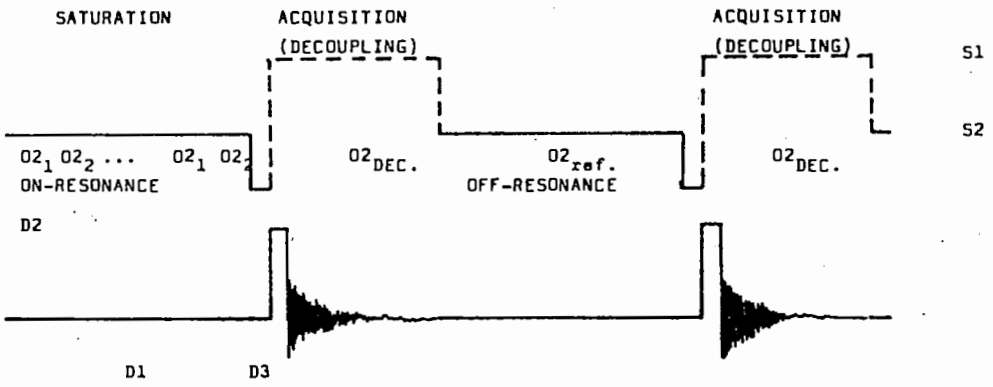
(continued from page 16)

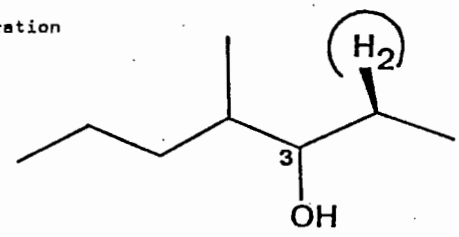


EXPERIMENTAL CONDITIONS : BRUKER AM 400, DUAL-Probehead

D1 = 5s , D2 = 600ms (90°pulse with S2 =54L), if more than one multiplet line can be used for saturation, D3 = 50ms

S1 = 6L for decoupling, S2 = 54L for saturation

Fig. 1 : pulse sequence for the SSD experiment



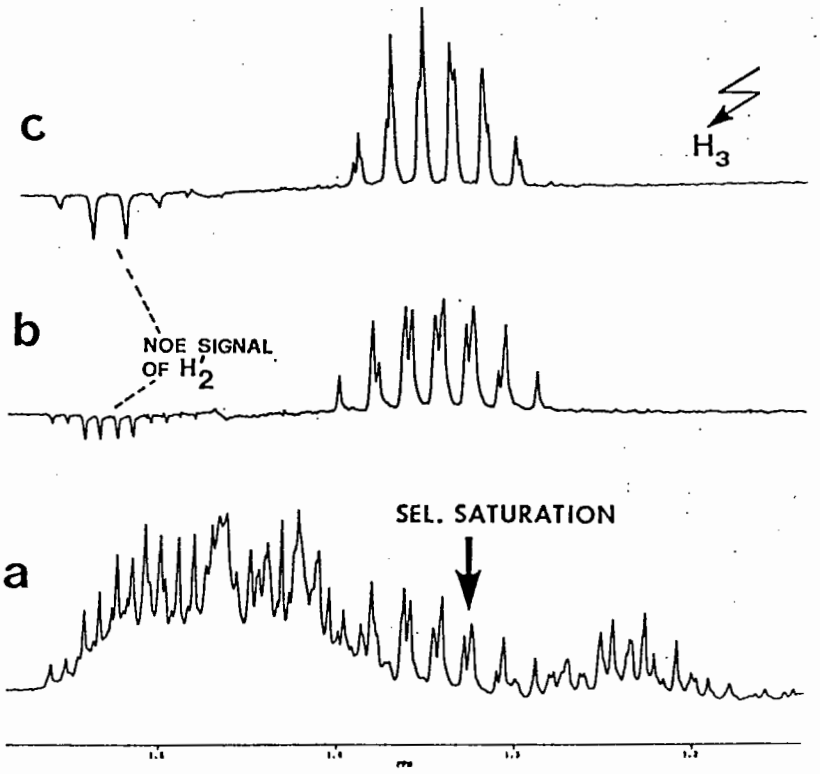


Fig. 2 : SSD spectrum of iso-octanol isomer (5% in $CDCl_3$)
a) part of normal ^1H-spectrum
b) SSD-spectrum (x5) after saturation of one single line (arrow)
c) same as b) but with decoupling of H3

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TRUMAN R. BROWN, Ph.D.
Director, Nuclear Magnetic Resonance
and Medical Spectroscopy
215/728-3049

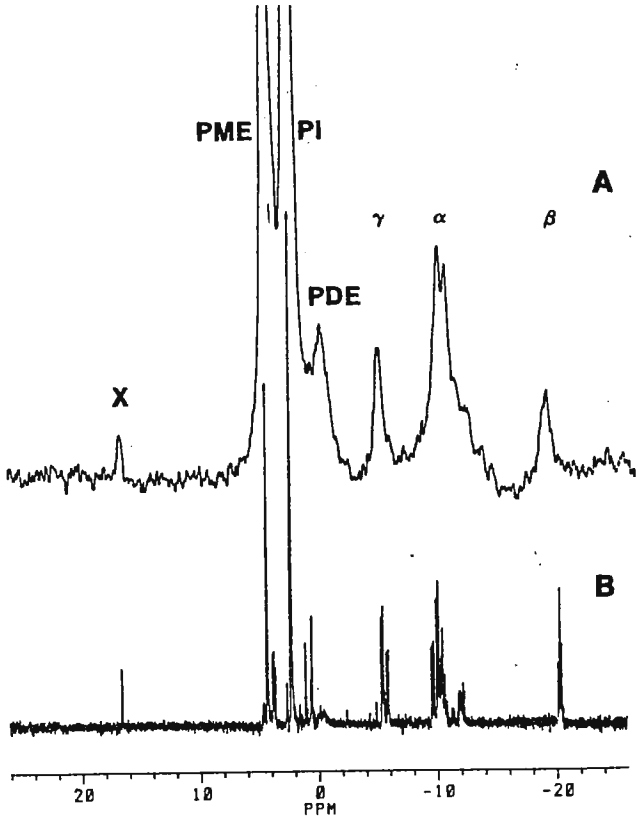
August 6, 1986
(Received August 11, 1986)

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

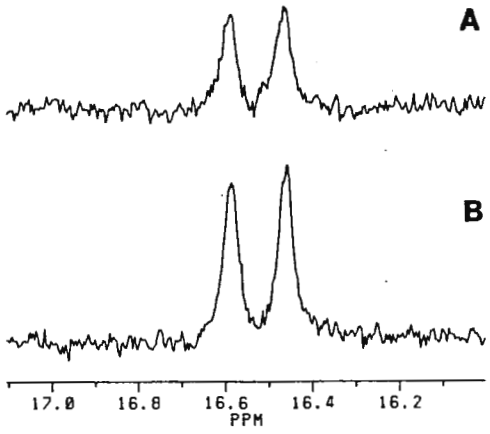
Myo-inositol 1,2 Cyclic Phosphate in a Morris Hepatoma

Dear Dr. Shapiro:

I enclose my first contribution, a recent discovery I and my associates, Bob Graham, Ron Meyer and Ben Szwergold, have made concerning the presence of myo-inositol 1,2 cyclic phosphate at fairly high concentrations in a Morris hepatoma. As can be seen from the spectrum below, there is an unusual resonance at 16.5 ppm which might be thought to be a phosphonate compound. However, its acid lability as well as its sensitivity to enzymatic degradation make this unlikely.



Other phosphate compounds which resonate in this area are the five-membered cyclic phosphate compounds, such as 2',3' AMP. After an investigation of several of these, we determined by direct synthesis of myo-inositol 1,2 cyclic phosphate that this is indeed the unknown at 16.5 by adding the compound to a chloroform/methanol extract of the tumor. The before (a) and after (b) spectra are shown below.



It is generally thought that cyclic inositol phosphate comes from the hydrolysis of phosphatidylinositol by phospholipase C, suggesting a metabolic defect in this tumor involving the turnover of phosphatidylinositides which are thought to be involved in Ca^{++} release and other activities connected with cellular growth control.

As this is our first submission to you, I am uncertain as to whether you require anything further in the way of a contribution, so please let me know. I have also included a small notice indicating that I have a number of positions available here at my laboratory which I would appreciate your inserting in your newsletter as well. Thank you very much.

Sincerely,

Truman R. Brown

Truman R. Brown
Director of NMR and
Medical Spectroscopy

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Two postdoctoral positions are available at the Fox Chase Cancer Center in the area of ultra high resolution NMR imaging and in vivo spectroscopic studies. The imaging research will use an AM400 spectrometer and involve both technical developments in instrumentation as well as its biological applications. The in vivo spectroscopy research involves both animal and human tumor studies on a Biospec 2.3T and a Siemens 2T Magnetom. Those interested should apply to Dr. Truman R. Brown, Director of NMR and Medical Spectroscopy, Fox Chase Cancer Center, 7701 Burholme Ave., Phila., PA 19111.

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DEPARTMENT OF CHEMISTRY

SANTA CRUZ, CALIFORNIA 95064

August 20, 1986
(Received August 25, 1986)

Professor Barry Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843-3255

TITLE: AIR PURGING THE CMD DISK DRIVE

Dear Barry:

With reference to the GN-300 NMR CMD Disk Drive's Absolute Air Filter purging system, I have found, in the past, my confidence very shaky after an Air Filter replacement. Allowing the disk drive to sit and "purge" for an hour and a half still left me wondering if the Read/Write Heads would "crash" when I pushed the Start Button, insofar as the Head Flying Distance is only 30 MICRO IN. The data heads fly on a very thin layer of air that is squeezed between the heads and the disk. The average smoke particle is 250 MICRO IN, dust particles/abrasives average about .00125 IN and the average diameter of a Human hair is .003 IN.

Simply allowing the disk drive to purge statically and then "spinning" the drive to operating speed (3600 RPM) has never felt right to me. I think the most positive method of insuring a contamination free flying distance (Head/Disk Relationship) is to disconnect the carriage assembly's (Voice coil) connector before activating the Start Button. This allows the media to "spin" during air purging, but will not allow the Read/Write and Servo heads to "Load."

I let the disk drive "spin" for about a half hour or so, then I "spin" down the drive, reconnect the "voice coil" connector and re-energize the drive with an ennate confidence that I've removed all contaminates introduced during the Filter change.

Sincerely,

Jim Loo

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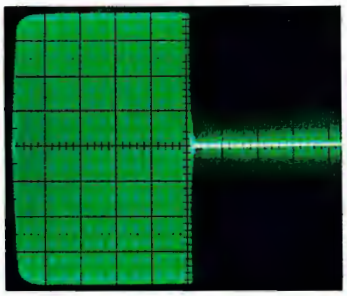
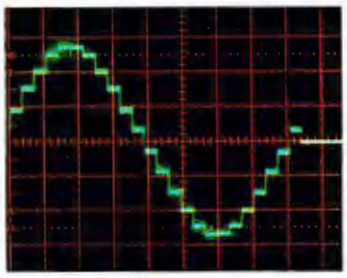
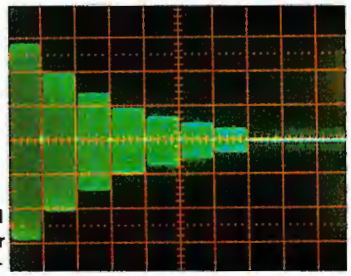




15° phase shift through 360°. ►



Shaped decoupler pulse. ►

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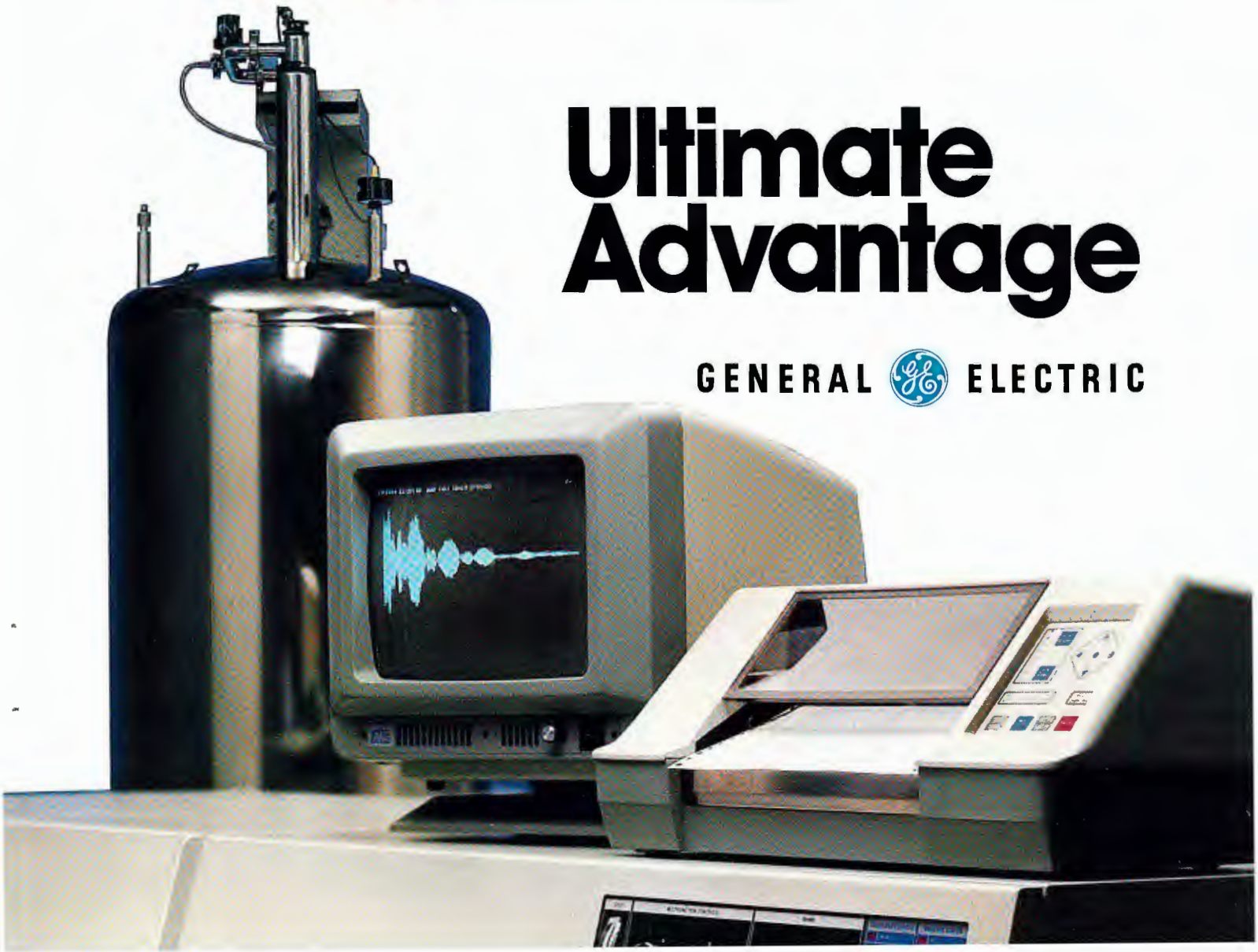

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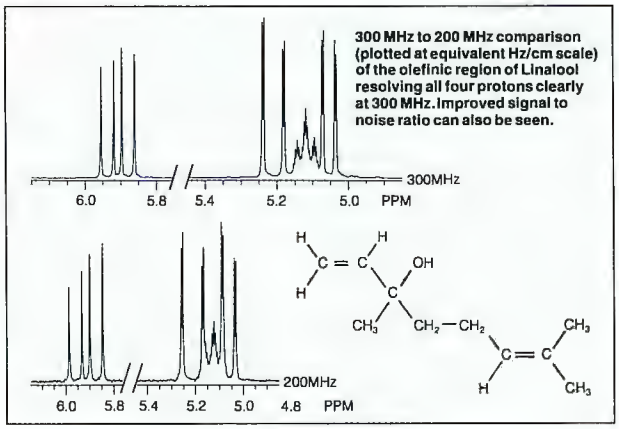

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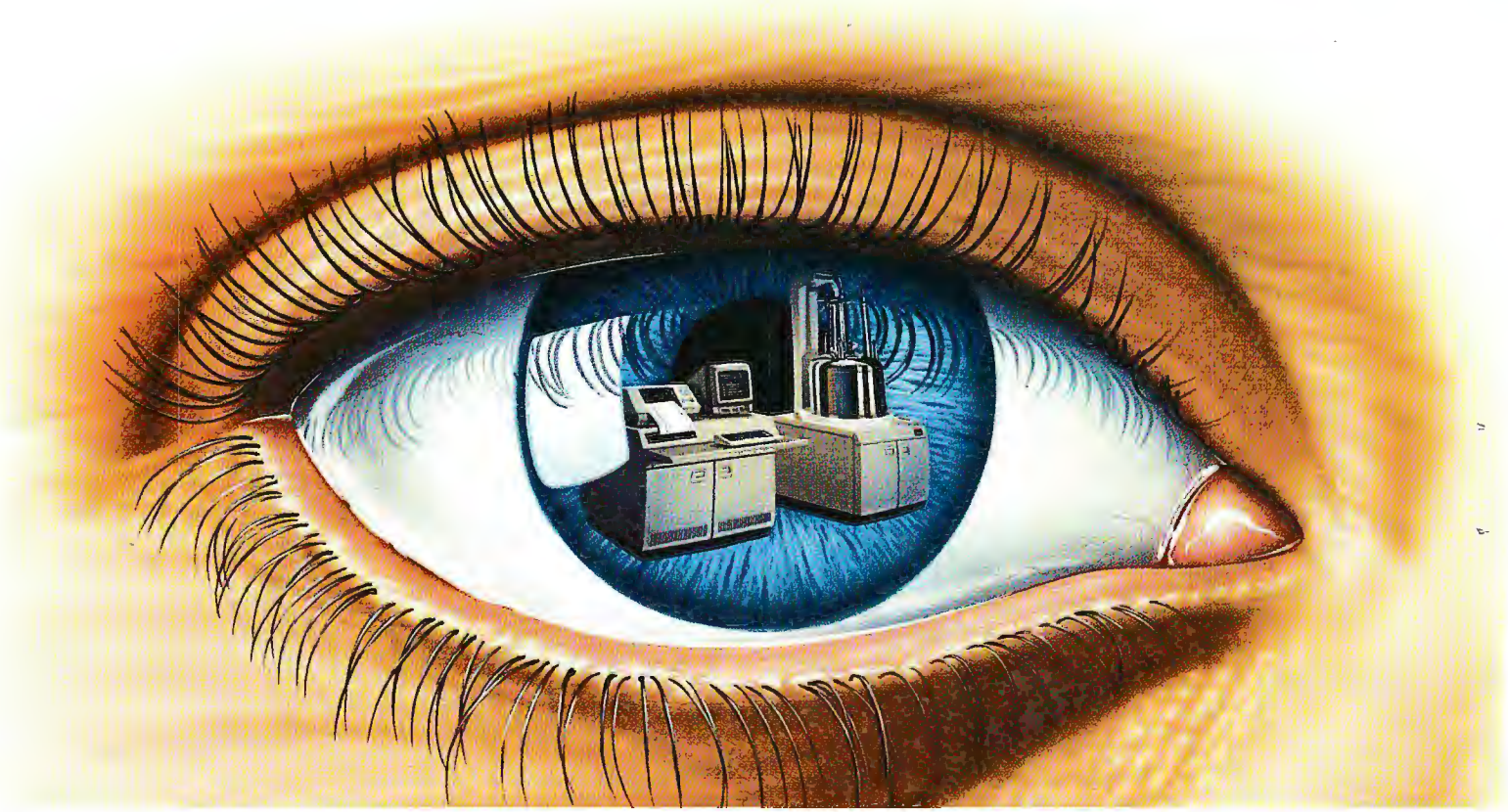

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SCHOOL OF MEDICINE AND DENTISTRY · SCHOOL OF NURSING
STRONG MEMORIAL HOSPITAL
DEPARTMENT OF BIOPHYSICS

August 19, 1986
(Received August 25, 1986)

^{43}Ca CP-MASS NMR

Dear Barry:

The importance of calcium in biochemistry raises the following question: Is there a magnetic resonance experiment that will provide site resolved spectra as in the ^{113}Cd cases? For ^{43}Ca the nuclear quadrupole moment provides a broadening mechanism in liquids that when compared with a small chemical shift range defeats the desired spectral resolution. The solid state experiments that could provide the resolution to do calcium biochemistry include magic angle sample spinning at high magnetic field strengths and nuclear quadrupole resonance. Here we report our first results on ^{43}Ca NMR using MASS methods at 4.7 T.

The problem with the MASS experiment on an I = 7/2 nucleus is that the intensity of the central (+1/2 <--> -1/2) transition is approximately 8 percent of the total signal that is normally available in the liquid state NMR experiment. This loss in S/N may be recovered with a cross polarization experiment where the potential signal gain would more than compensate as suggested by Pines, Gibby and Waugh (J. Chem. Phys. 59: 569-590, 1973).

Figure 1 shows the ^{43}Ca CP-MASS spectrum of a chemically impure calcium acetate obtained at 4.7 T on our home-built solid spectrometer. The relevant experimental parameters are given in the caption. The spectrum shows two important features: (1) CP is possible provided proton or calcium $T_{1\rho}$ does not defeat the polarization transfer; (2) there is a multiple line structure and the line separation and the anisotropy are large, larger than in solution.

The sad part is that the sample picked up water and got heated when we took a static spectrum in the spinning probe. While it did not explode, the heat melted parts of the stator assembly. Thus, we are unable to identify the lines in the spectrum until we find the money to replace the spinner assembly. However, it appears that this approach may provide the needed resolution to attack problems in calcium binding proteins directly.

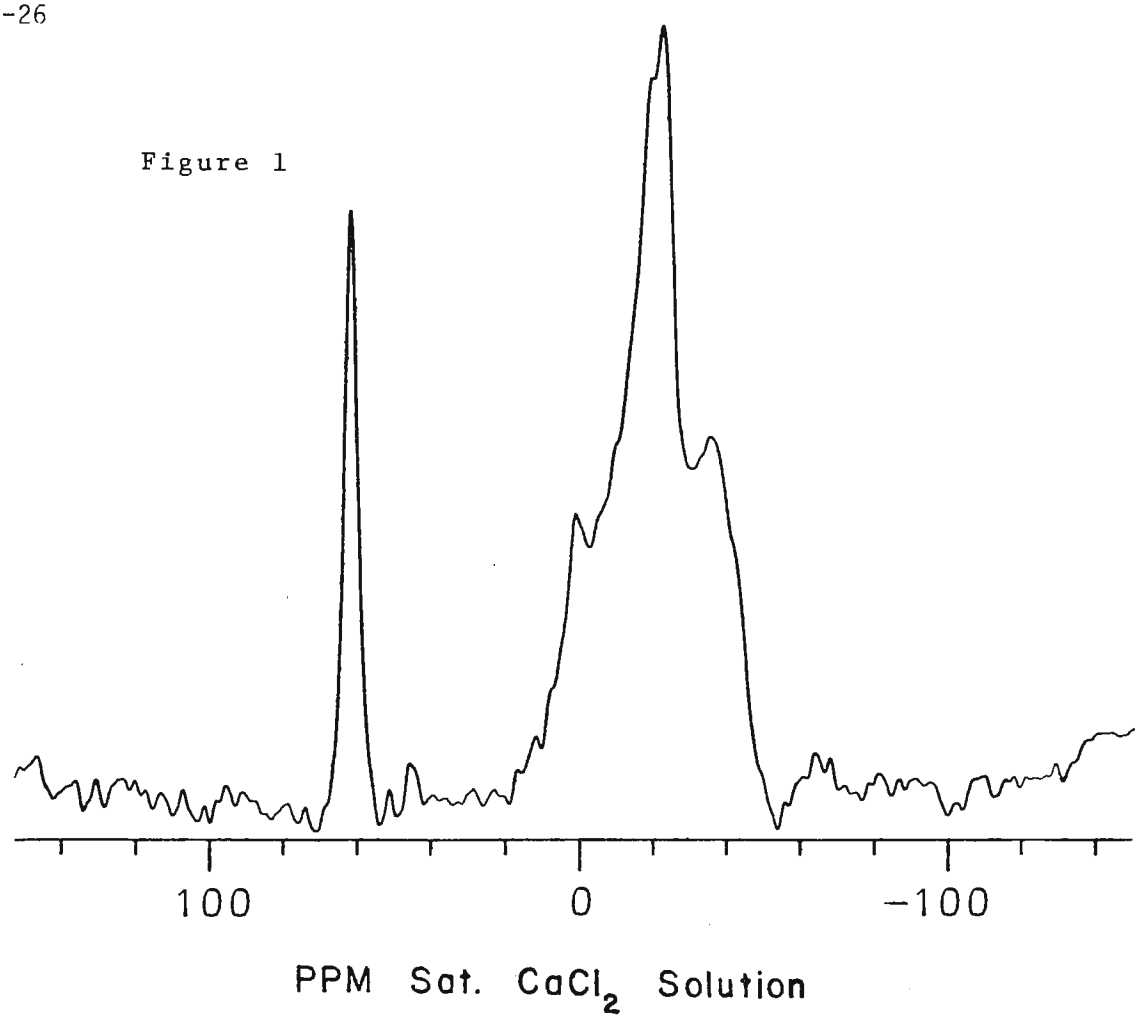
Sincerely,

Robert G. Bryant S. Ganapathy Scott D. Kennedy

/jh

Attachment

Figure 1



Room temperature proton-enhanced ^{43}Ca NMR spectrum, taken with weak dipolar decoupling and magic angle sample spinning at 4.7 T (ν_0 ^{Ca} = 13.4602 MHz), of polycrystalline chemically impure calcium acetate. Mixing time = 30 msec; recycle time = 1 sec; number of scans = 41,000; EM = 10 Hz. The spectrum was obtained on our home-built double resonance spectrometer using a home-built spinning probe employing a Doty Spinner. An almost identical spectrum can be obtained with no decoupling indicating that the strength of the proton-calcium dipolar coupling is less than 3 KHz - the spinning speed.

The University of Texas
Health Science Center at Houston

MEDICAL SCHOOL
Department of Biochemistry
and Molecular Biology

P.O. Box 20708
6431 Fannin Street
Houston, Texas 77225
(713) 792-5600

July 24, 1986
(Received July 31, 1986)

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

RE: Installation of New Equipment and Position Available

Dear Barry:

The University of Texas Health Science Center at Houston has recently installed a GN500 and a broadband QE300. The new equipment from General Electric, along with our wide-bore 270 MHz instrument, are housed in the Analytical Chemistry Center. The installation of both the GN500 and QE300 instruments went reasonably smoothly. In fact, the QE300 was being used for routine organic analysis before installation was completed.

The new facility is currently seeking a NMR specialist to manage the operation and development of the 500, 300 and 270 MHz instruments. The principal responsibilities for the manager include (a) insure smooth day to day operation of the facility, (b) routine instrument maintenance, (c) insure proper training is provided for all scientists utilizing the equipment. In addition, it is anticipated that the manager will participate in the research activities of the facility, by pursuing individual research efforts and by establishing collaborative research programs with the scientists using the facility.

Interested individuals should send a resume and the names, addresses and phone numbers of at least two references as soon as possible to Paul R. Rosevear, Department of Biochemistry, University of Texas Medical School, P.O. Box 20708, Houston, TX 77225.

Sincerely,

Paul R. Rosevear, Ph.D.
Assistant Professor

PRR/tjd

THE PROCTER & GAMBLE COMPANY

IVORYDALE TECHNICAL CENTER CINCINNATI, OHIO 45217

August, 8 1986
(Received August 20, 1986)

Metal Ion/Molecule Interactions
Using NMR

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

Dear Professor Shapiro:

The study of metal ion/molecule interactions using NMR is a well-established, but sometimes forgotten method. We have been investigating the chemical interaction between Mg^{+2} ions and chelating agents with ^{25}Mg NMR ($I = 5/2$, $Q = 0.20 \times 10^{-24}cm$). Under conditions of fast chemical exchange and an excess of free Mg^{+2} ions (the amount of the excess necessary depends on the strength of the binding), the binding constant (K_B)$_{+2}$ can be determined from linewidth changes produced by varying the total Mg^{+2} ion concentration while the concentration of chelating agent is held constant (1,2).

An example of the linewidth changes observed when a simple chelating agent such as citrate (K_B 10^3) is added to a 0.4M solution of Mg^{+2} ions is shown in Figure 1. The K_B value for the Mg/citrate interaction was measured using two different citrate concentrations. The results from the two independent determinations are in excellent agreement with one another and with the known value of K_B when corrected for pH effects.

This type of analysis is very general and can be easily extended to the case of multiple chelating agents and/or other metal ions. In addition, the competitive binding of a chelator for Ca^{+2} in the presence of Mg^{+2} can be determined indirectly from ^{25}Mg NMR experiments. The biggest advantage of the NMR method over other techniques (e.g., ion-selective electrodes) is that the NMR method can be used for measuring binding constants in complex mixtures.

Please credit this contribution to Fouad Ezra's account.

Regards,

T. Michael Rothgeb
Packaged Soap and Detergent
Product Development Division

G. Stephen Caravajal
Packaged Soap and Detergent
Product Development Division

1. Swift, T.J. and Connick, R.E., J.Chem.Phys., 37 (1962), 307-320.

2. Lanir, A. and Navon, G., Biochemistry, 10 (1971), 102-1032.

(continued on page 31)

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(continued from page 28)

FIGURE 1

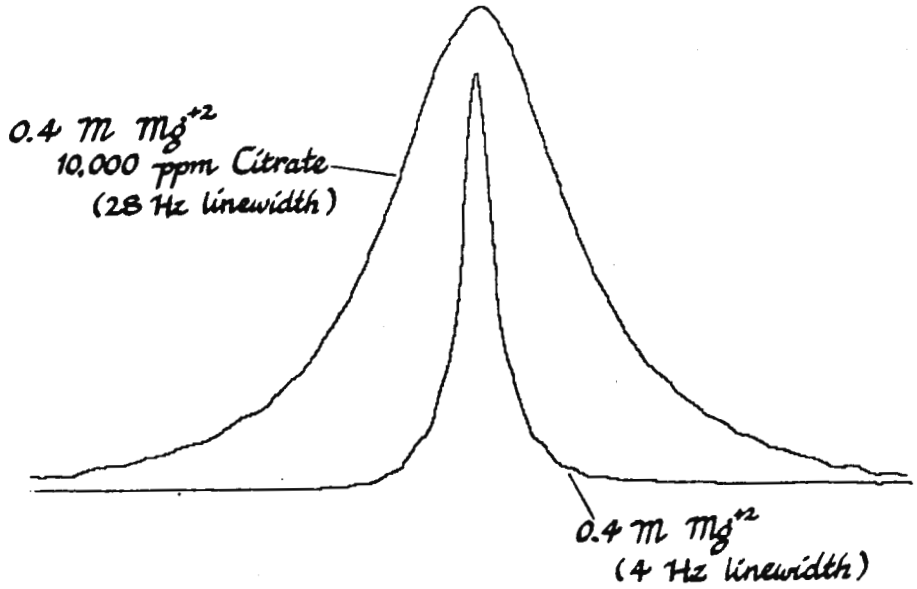
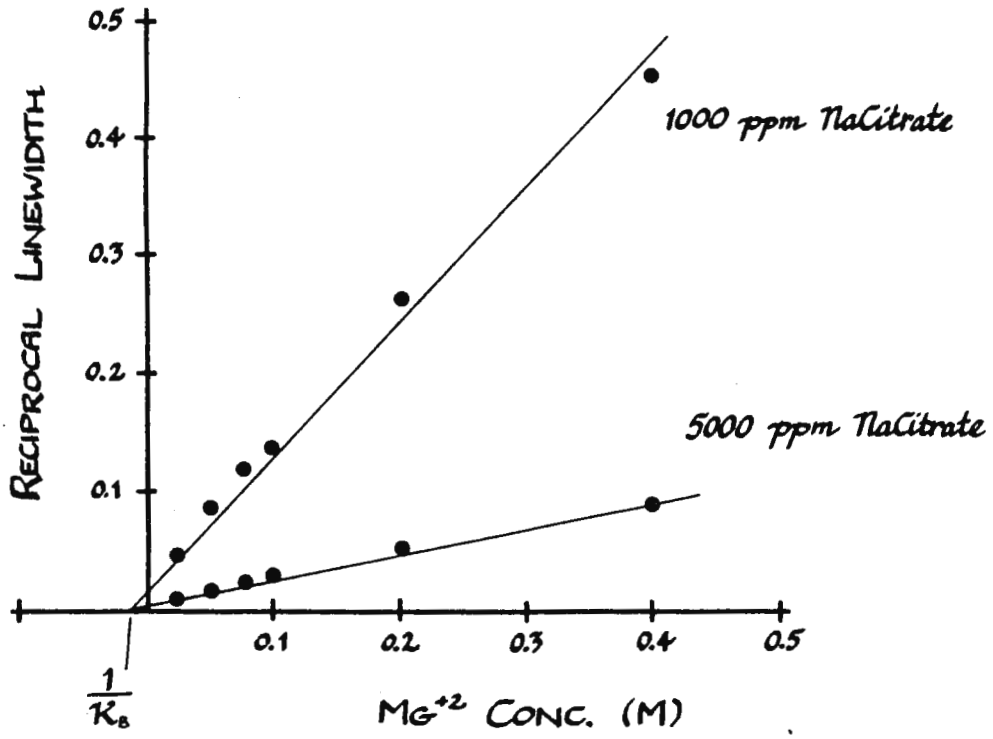


FIGURE 2



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ETH -Hönggerberg
CH-8093 Zürich

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

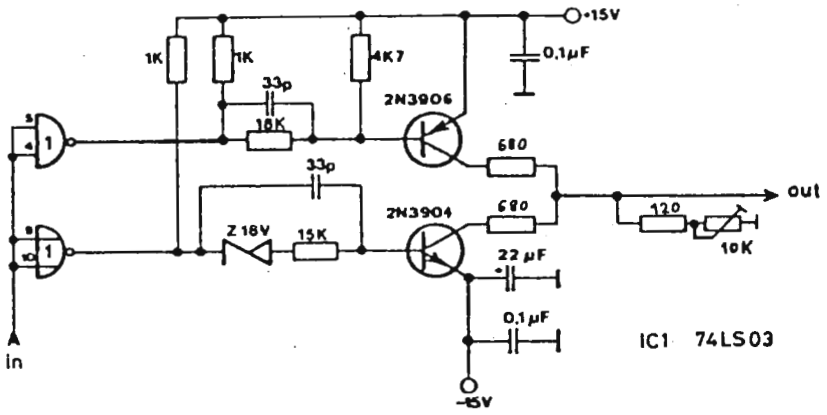
Zürich, August 13,1986
(Received August 20, 1986)

Title: Water Saturation in Decoupler-pulsed Experiments using a fast HF Switch

Dear Barry,

Some pulse sequences used in modern NMR require the decoupler to operate in the high power mode for proton pulses. Examples are proton-detected heteronuclear experiments and homonuclear TOCSY. Since on our instruments the change of the decoupler power from high to low power involves a slow mechanical relay, problems arise with experiments with solvent suppression by selective saturation in H_2O solution. A convenient way around this problem is by feeding the source frequency alternately into the decoupler (operating at high power) and an additional external low power amplifier for water saturation by the use of a fast diode switch (a left-over from the old Bruker HXS-360 console, print No 211ST002, which had been used for feeding the LO frequency into the cascode for ^1H or X nuclei). We now built an interface to drive this switch with the output of the process controller board from the Aspect 3000 (RCP7 to 13), see Figure.

input: TTL pulse from Aspect 3000
out: either + or - 1.7 to 6.8 V
supply voltage: +/- 15 V



Driven by this interface the switch has an insertion loss of < 1 dB, and a channel to channel cross talk of < 54 dB. The switching time is < 4 μs. The bandwidth is > 200 MHz. We routinely use the switch to drive different components (e.g. pulse and CW amplifiers) with the same source frequency. Its short switching time allows to irradiate the water line during delays as short as the initial t_1-period of a 2D experiment.

Sincerely,

A. Eugster G. Otting K. Wüthrich

Albert Eugster Gottfried Otting Kurt Wüthrich

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Entomological Sciences
College of Natural Resources
Berkeley, California 94720

08/07/86
(Received August 14, 1986)

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

Modified Long Range X-H Correlation 2D Experiment:

Dear Prof. Shapiro:

We have been interested in routinely applying long range C-H correlation 2D NMR for structural analysis. Recently, we modified the pulse sequence developed by Freeman et.al. (JMR, 58 (1984) 526) as follows:

1H : RD-45-τ -180-τ -45-t_1/2-180-(T-t_1/2)-90- Δ/2-90-τ -180-τ -90- Δ/2-BB

X : -180- -180- -90- -180- -Acq.

(Phase cycling and delays are as described in the ref.)

Introduction of the 180 X-pulse during evolution achieves X-decoupling in the F1 domain, thereby increasing the overall sensitivity. As in the other long range correlation experiments the polarization transfer efficiency at the end of T depends on the magnitude of $^nJ_{CH}$ and more so on J_{HH}. While any T value between 50-90 msec conveniently covers the most useful $^nJ_{CH}$ range of 2-10 Hz, the choice is mostly dependent upon the J_{HH}. We find that T value of 90 msec is useful for a wide range of $^nJ_{CH}$ and J_{HH} (in some cases a complementary experiment with T=60 msec is needed). The long range correlation (with C-decoupling in the F1 domain) 2D spectrum of the insecticide (1R,cis) phenothrin, obtained in the Bruker WM-300 NMR spectrometer, is illustrated with appropriate experimental conditions.

The correlations in the aromatic region and for multiplet protons are not obvious in this spectrum because the lowest contour level is chosen such that only the correlations of singlet protons are prominent. At lower contour levels the t_1 noise from the intense methyl signals start obscuring other connectivities. Thus, analysis of individual F1/F2 traces at the appropriate

(continued on page 37)

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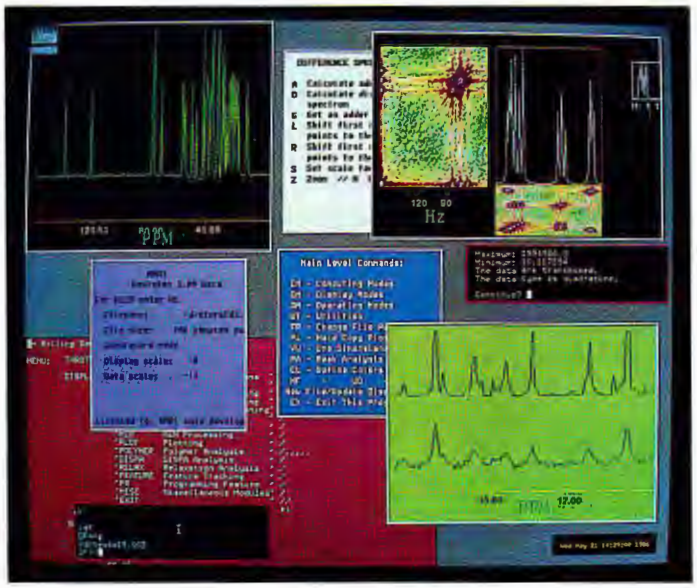

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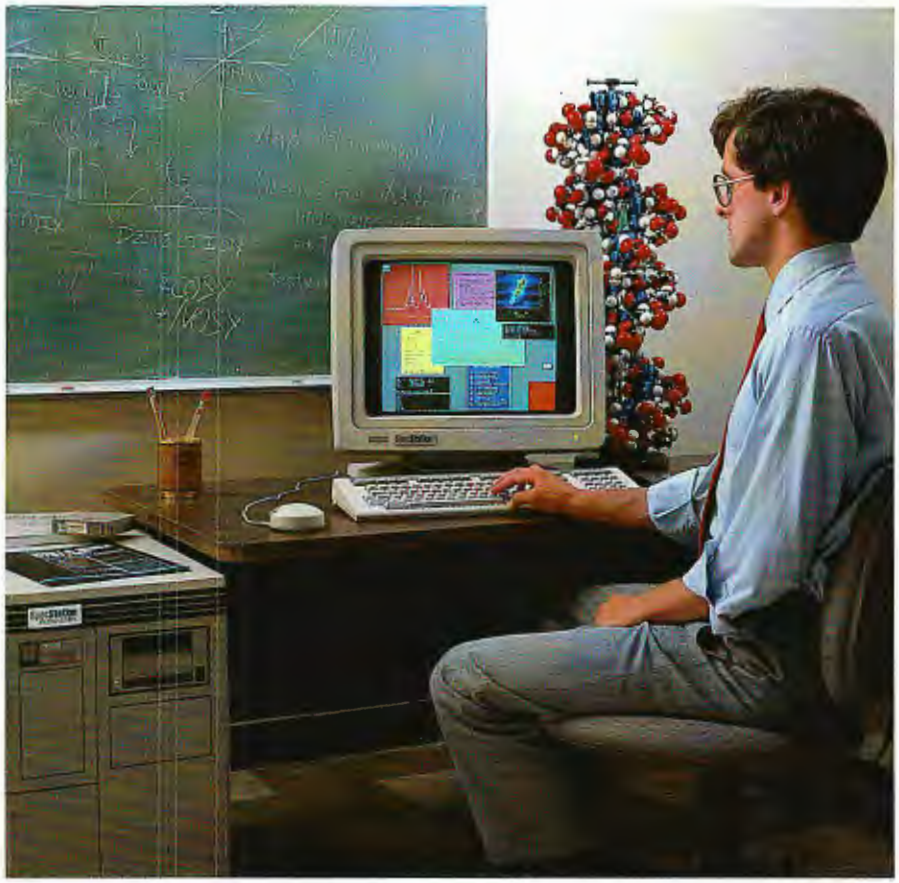

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(continued from page 34)

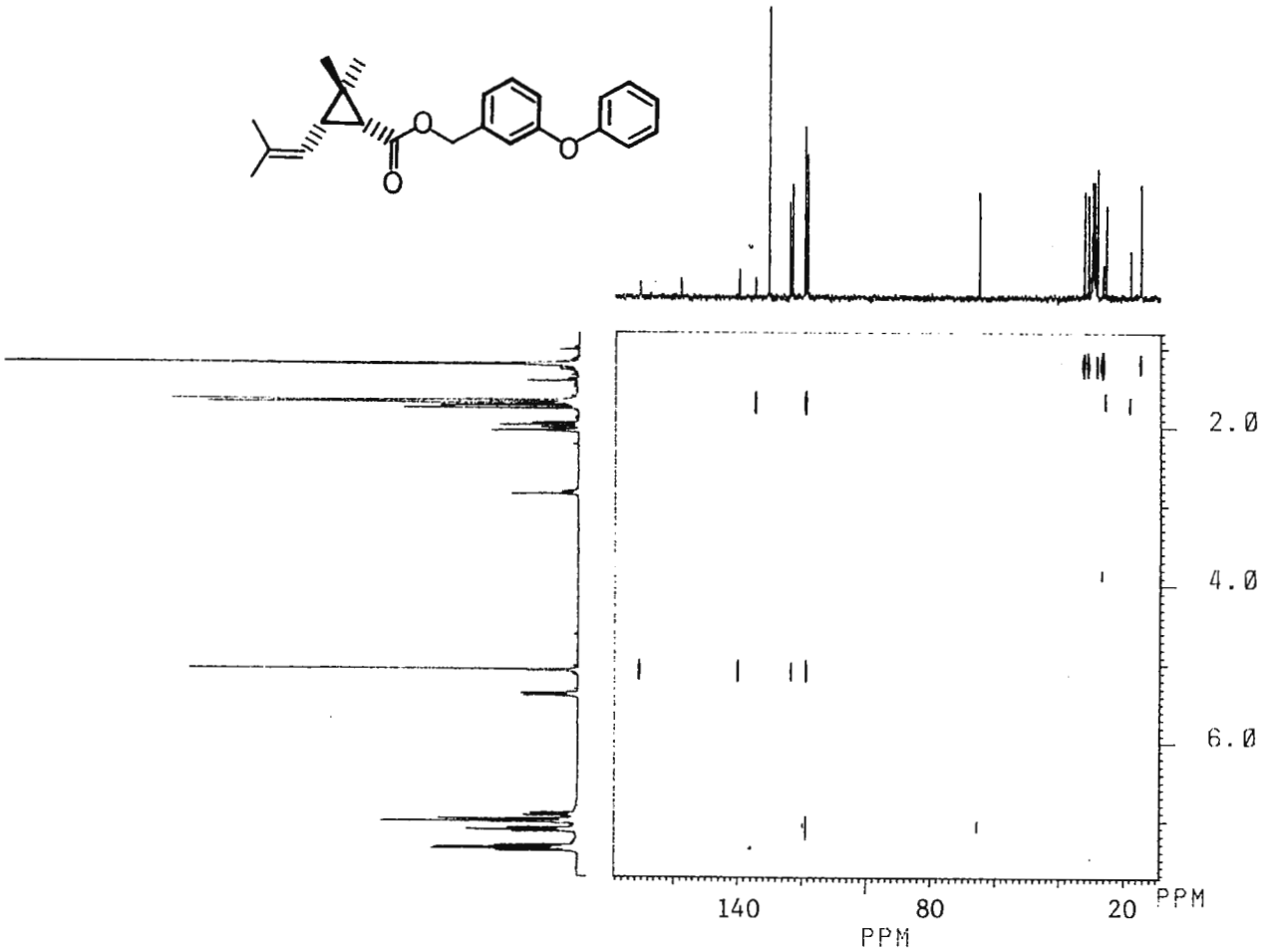
carbon/proton resonances is recommended. Such analysis at each of the carbon/proton resonance frequencies provides almost all geminal and vicinal C-H correlations (and in some cases even ^{4}J and ^{5}J), sufficient to assign all the carbon and proton resonences unequivocally. Complete analysis of the spectrum will be published elsewhere.

Sincerely,

John E. Casida
Professor

V.V. Krishnamurthy
NMR Specialist

P.S. Consider this as a subscription contribution for Dr. V.V. Krishnamurthy.



Long range correlation 2D NMR spectrum of 0.25M (1R,cis)Phenothrin in acetone-d6

(Expt. conditions: RD=1.5 sec; τ =3.3 msec; T=90 msec; Δ =34 msec; 128 scans for each of the 64 different t_1 values; total acq. time: ≃ 4 hr.; transform size: 2048 x 128; initial t_1 value is chosen such that $t_1(max) \leq$ 90 msec.)

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DR. RAY DUPREE

14 August 1986 (Received August 22, 1986)

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

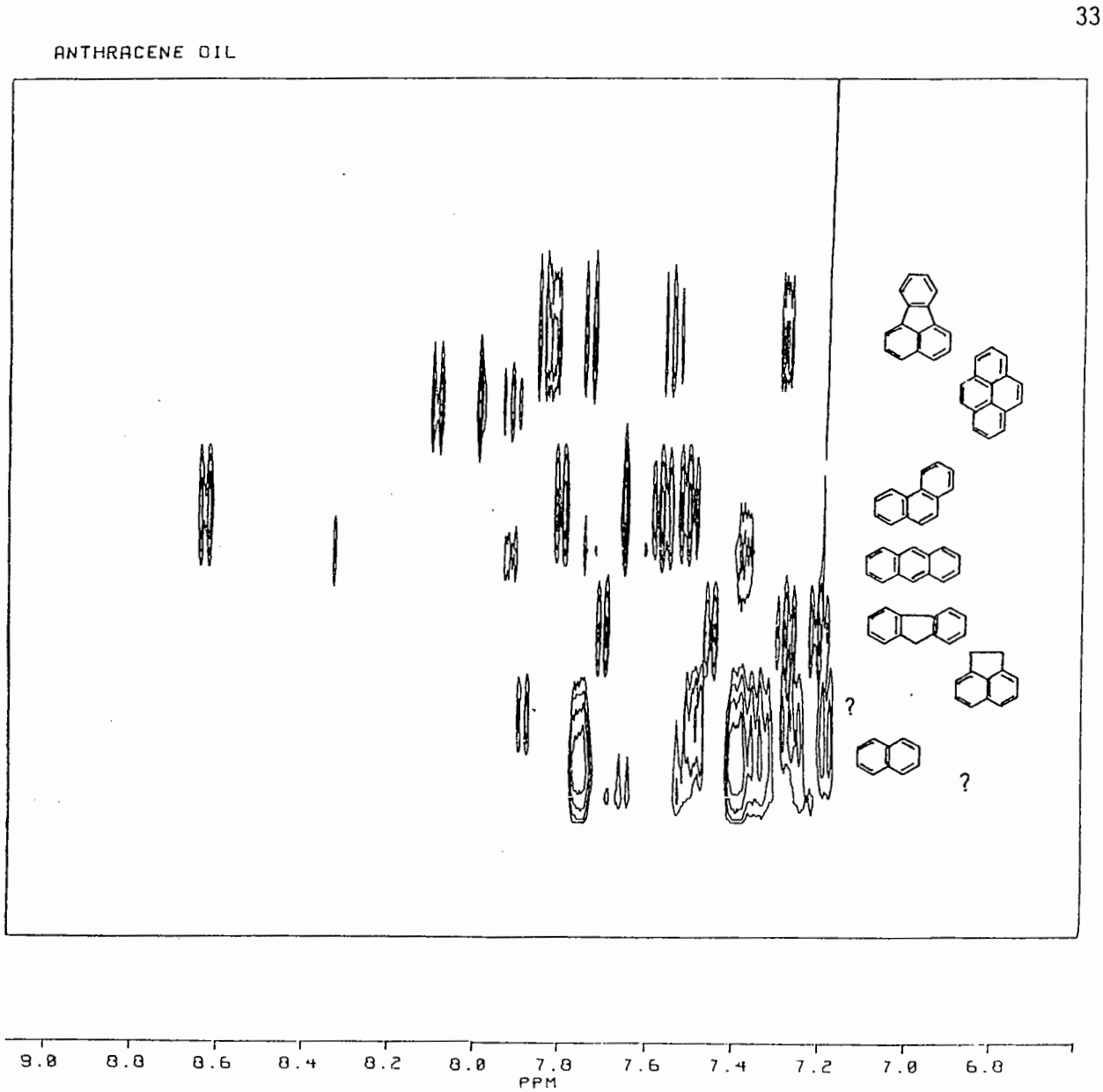
HPLC - NMR

Dear Professor Shapiro

Although it is not an entirely new idea to couple HPLC with ^1H NMR[1], in the past the assumption has been that a special probe is necessary to permit magnetic prepolarisation of the sample. Also the data has often been inconvenient to handle.

As part of a project on coal structure we are finding it necessary to analyse very complex mixtures of hydrocarbons. We separate the coal extracts into the usual broad fractions and then subject a single fraction to HPLC-NMR, such as the aromatic fraction shown in the figure. The 2D presentation uses standard Bruker routines, in their phase-sensitive mode. One can see from the figure that this presentation enables the eye to distinguish most individual species clearly even though their chromatographic separation is incomplete. We normally also run a COSY 2D spectrum of the unfractionated mixture, to confirm the coupling network of each species. Several polycyclic hydrocarbons are identified by this means in the figure. In appropriate cases there is also a confirmatory resonance in the aliphatic region. The unidentified components at the start of the chromatogram, and the bottom of the figure, are probably methylnaphthalenes.

An attractive feature of our method is its simplicity. We use an ordinary static 5 mm NMR tube, and simply lower to the bottom the thin silica tube (S.G.E., 0.1 mm i.d.) leading from the HPLC column. A flow rate of up to 1.0 ml/min is small enough to permit at least 95% prepolarisation, with linewidths of ca. 1.6 Hz. Even at flow rates as low as 0.3 ml/min there is no obvious loss of chromatographic resolution. An injection of 1 micromole can be detected at the level of a single singlet proton resonance, with our Bruker WH400, under these conditions of flow. In the above example 10 mg of a coal fraction high in aromatic hydrocarbons was separated on a nitrile bonded silica column using a 1:3 mixture of purified CCl_4 and $CFCl_2CF_2Cl$. The field was not locked, as is apparent from the slight time-drift of a $CHCl_3$ marker at 7.25 ppm. The



HPLC-NMR chromatogram of anthracene oil, showing only the aromatic region. Time increases vertically.

chromatographic separation is as good as has been obtained previously by more conventional chromatography at this concentration, although the loading is higher than ideal. Our method is now in use for the study of heavier and more complex fractions.

We are grateful to Dr Paul Burchill of British Coal for his assistance and the loan of chromatographic equipment.

Yours sincerely

Oliver Howarth G Ratcliffe

Oliver W Howarth Giles Ratcliffe

1. H.C. Dorn, Anal. Chem. (1984), 56, 747A.

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STATEN ISLAND, NEW YORK 10301

August 11, 1986
(Received August 18, 1986)

DEPT in Model Digestive Mixtures

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

Dear Barry:

We have been interested of late in the molecular biophysics of glyceride digestion; though this bit of physiology is familiar to most scientific conference-goers at the gut level (so to speak), our structural picture of how fats are chewed up and absorbed is quite rudimentary.

To obtain a more detailed view of the mixed lipid aggregates that serve as substrates for digestive enzymes and carriers of hydrolysis products, we conducted a series of parallel studies using dynamic light scattering and ^{13}C NMR. As illustrated below, the DEPT pulse sequence (Pegg, Doddrell, and Bendall, J. Chem. Phys. 77, 2745 (1982)) has proven particularly useful: spectral assignments become straightforward and the signal-to-noise ratio is adequate for both T_1 and paramagnetic broadening (aqueous accessibility) experiments. In CD_3OD, ^{13}C peak intensities provide a reasonably good quantitative measure of the various lipid components. For model digestive mixtures in D_2O, comparison of analogous carbon types reveals signal attenuation at both hydrophobic and hydrophilic bile salt sites (exclusive of the taurine sidechain). Are the "missing" carbons tied up in large aggregates? immobilized in a special structural arrangement? Further speculation and experiments are in progress.

Very truly yours,

Ruth

Ruth E. Stark
Associate Professor of Chemistry

Nasser L. Hadipour
Postdoctoral Research Associate

RES:mg

(continued on page 43)

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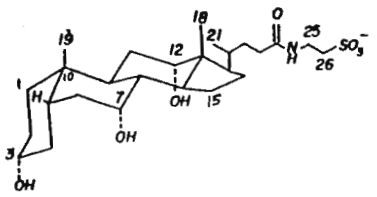
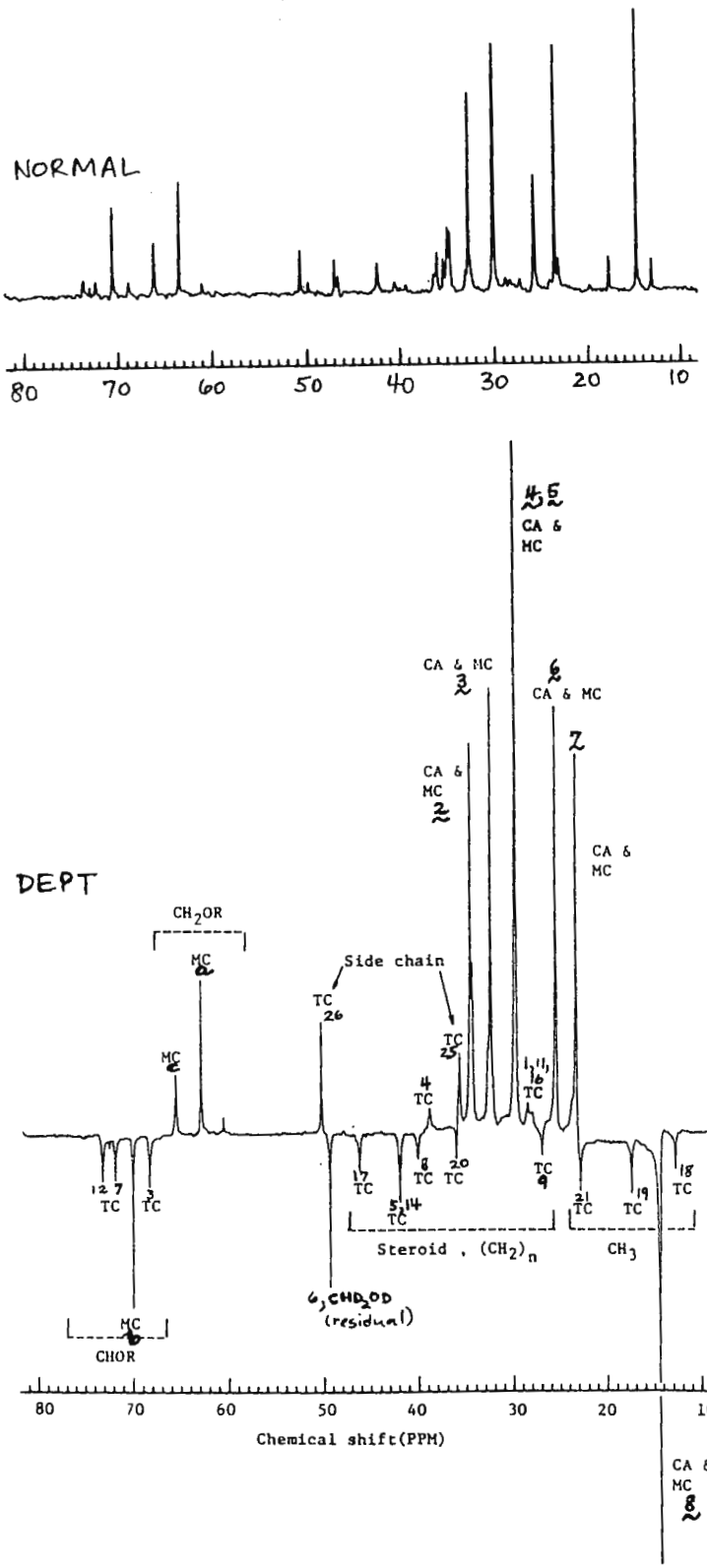
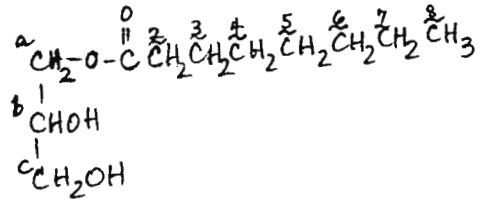
(continued from page 40)

Taurocholate (TC)

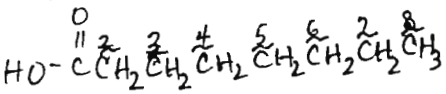




1-Monocaprylyl-rac-glycerol (MC)



Caprylic Acid (CA)



TC	56 mM
MC	66 mM
CA	198 mM

50.3 MHz ^{13}C NMR spectra of a lipid mixture in D_2O with proportions matching those found physiologically after a fatty meal. Top: normal spectrum (carbonyl/carboxyl region omitted); Bottom: DEPT spectrum (turned upside-down).

UNIVERSITY OF WISCONSIN-MADISON

COLLEGE OF AGRICULTURAL AND LIFE SCIENCES

Department of Biochemistry
420 Henry Mall
Madison, Wisconsin 53706-1569 USA
Telephone: 608/262-3026/262-3040
Telex: 26 54 52

(Received August 27, 1986)

National Magnetic Resonance Facility at Madison 608/262-3173

Dear Professor Shapiro:

Over the course of the last year and a half John Markley, Ed Mooberry, and I have been involved in establishing the National Magnetic Resonance Facility at Madison (NMRFAM). The facility is located in the new wing of the Department of Biochemistry of the University of Wisconsin-Madison. The objectives of NMRFAM are to improve and extend NMR and related technologies and to explore new biomedical applications of these technologies. Our primary interests are high-resolution NMR studies of the structure and dynamics of biopolymers, investigations of enzyme mechanisms and noninvasive studies of viruses, bacteria, tissues, and living organisms. The official opening date for the facility will probably be the end of this year after the installation, testing, and acceptance of the new NMR equipment is complete. At that time the facility will provide time, training and assistance on the NMR instruments for users with high-field NMR research needs. When the facility opens, it will contain two Bruker AM-500 spectrometers, a Bruker AM-400 wide bore spectrometer, a General Electric NT-200 spectrometer, and a Bruker WH-270 spectrometer. Also the facility will house a Bruker 1000 off-line data processing station, a Nicolet 1280 data processing station, and a Silicon Graphics IRIS 2400T graphics computer. At the present time all of the equipment is in-house except for the second Bruker AM-500. One AM-500 and the AM-400 WB are at field and undergoing final tests. The General Electric NT-200 and the Bruker WH-270 that were donated to the facility by the Department of Biochemistry were moved into position in April 1986 and are fully operational.

Funding for NMRFAM has come from the NIH Biomedical Research Technology Program, Division of Research Resources; NIH Shared Instrumentation Program; NSF Biological Instrumentation Program; NSF research grant to J. L. Markley and E. L. Ulrich; U. S. Department of Agriculture; University of Wisconsin-Madison Graduate School; University of Wisconsin-Madison College of Agriculture and Life Sciences; and the Department of Biochemistry of the University of Wisconsin-Madison.

Please credit this contribution to the subscription of John Markley.

W. Milo Westler
Operations Director

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August 12, 1986 (Received August 19, 1986)

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

An ^{1}H nmr study of N-carboxyethylindoline

Dear Professor Shapiro:

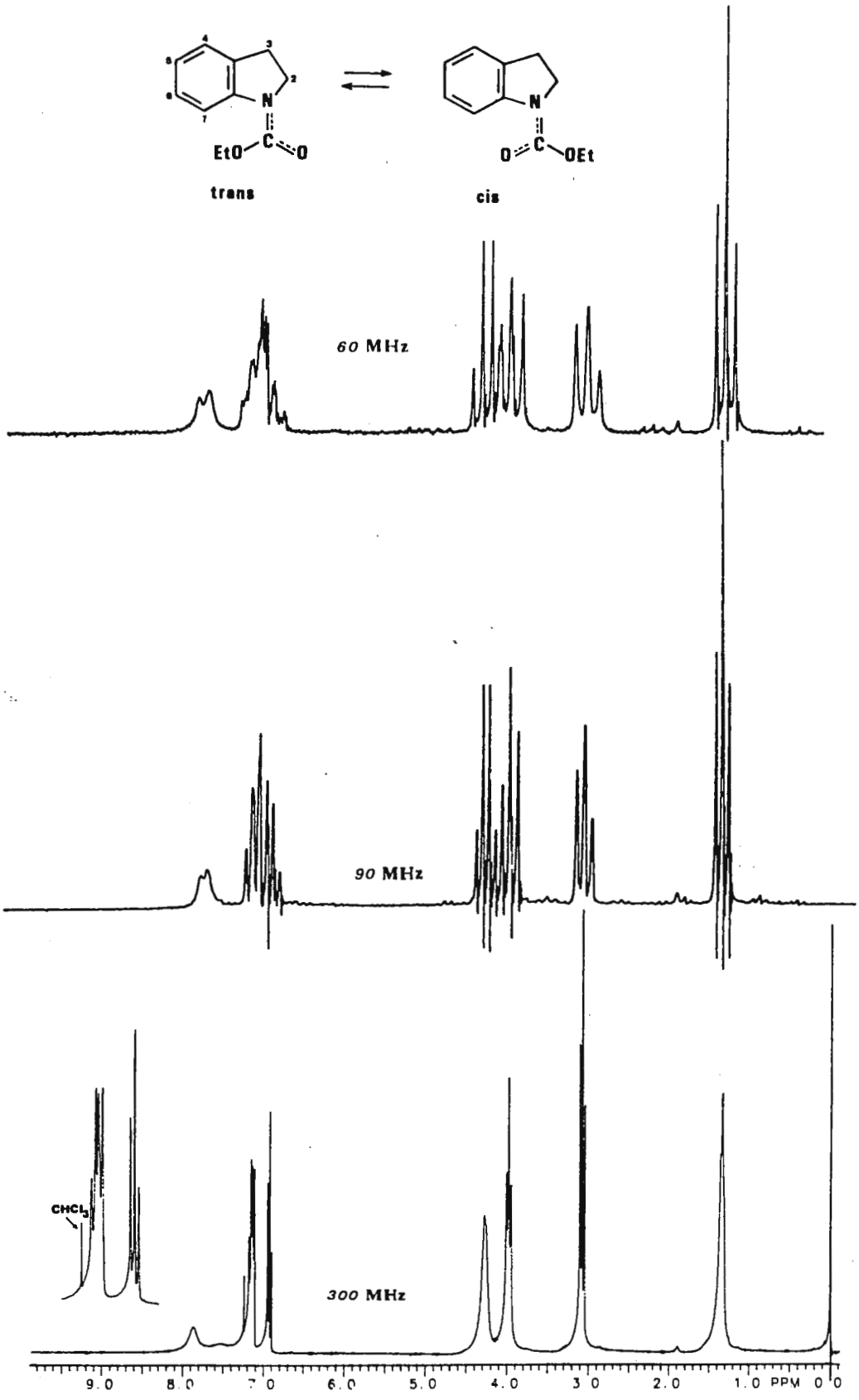
In the course of the total syntheses of a series of highly functionalized indole derivatives we noticed that for some compounds the nmr signal owing to H-7 appears as a very broad peak. In searching what the minimum structural requirements for such a situation might be, we prepared N-carboxyethyl indoline by condensation of indoline with diethyl carbonate in the presence of sodium.
The ^{1}H nmr spectra determined at probe temperatures in three magnetic fields from $CDCl_3$ solutions are depicted in the figure. At 60 MHz the H-7 signal appears as a broad doublet in which the J_{ortho} can be recognized and the remaining three aromatic protons are quite overlaped. At 90 MHz the interpretation of the aromatic protons is amenable being δ 7.17 (H-6), 7.15 (H-4) and 6.94 (H-5). The broadening of the H-7 signal is consequent of an equilibrium between two rotamers, due to restricted rotation about the C-N bond, thus giving rise to two forms as shown by the structures included in the figure. The broad doublet arises from H-7 in the cis rotamer under the deshielding influence of the carbonyl group. In this molecule, it is the preferred conformation of the equilibrium as judged by integration, in contrast with N-formylindoline[1] and N-formylindolinol[2] where the other rotamer is the preferred one. The difference is due to the presence of an ethoxyl residue in the present case, in contrast to an hydrogen atom in the reported[1,2] N-formyl substituted molecules.
That the ethyl proton signals are severly influenced during the equilibrium, becomes evident in the 300 MHz spectrum, where the methylene and methyl signals are so broad that the 7 Hz coupling constant can not be recognized. Furthermore, H-7 owing to both the cis and the trans conformers become evident by the very broad signals at 7.88 and 7.53 ppm, respectively. Thus, on a radiofrequency scale, the 300 MHz spectrum is close to a "coalescence frequency" if such a concept might be extrapolated from the classic coalescence temperature concept.

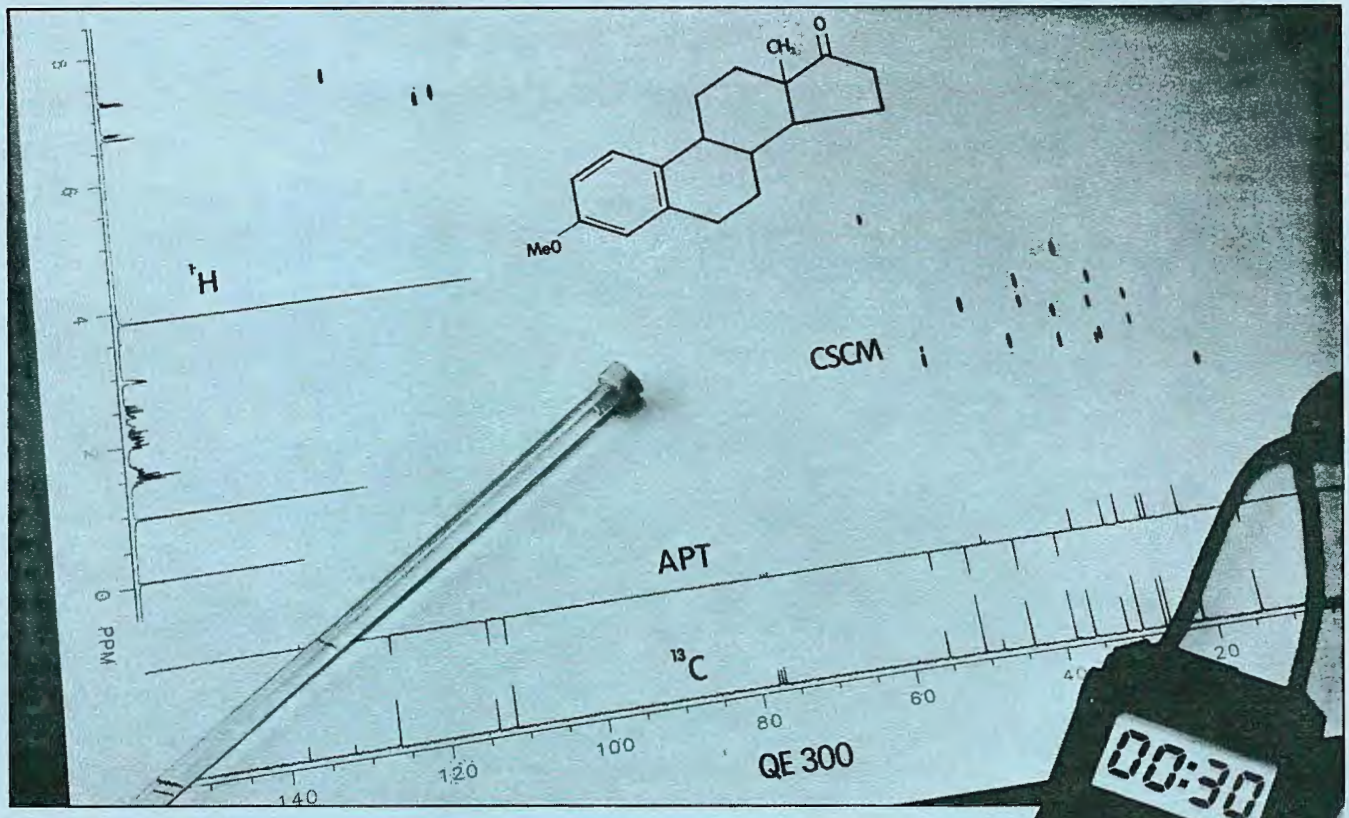
Sincerely yours,

M.S. Morales-Ríos

Pedro Joseph-Nathan

1. K. Nagarajan and M.D. Nair, Tetrahedron, 23, 4493 (1967).
2. O. Buchardt, P.L. Kumler and C. Lohse, Acta Chem. Scan., 23, 115 (1969).


trans
cis
60 MHz
90 MHz
300 MHz
CHCl3
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0 PPM
0.0



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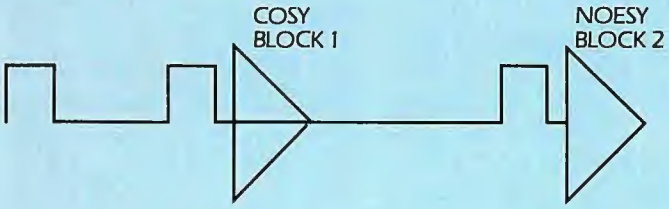

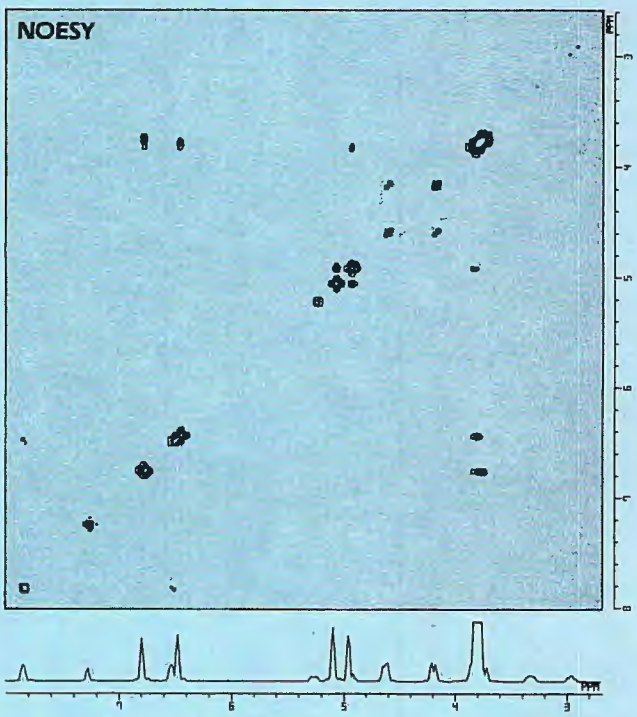

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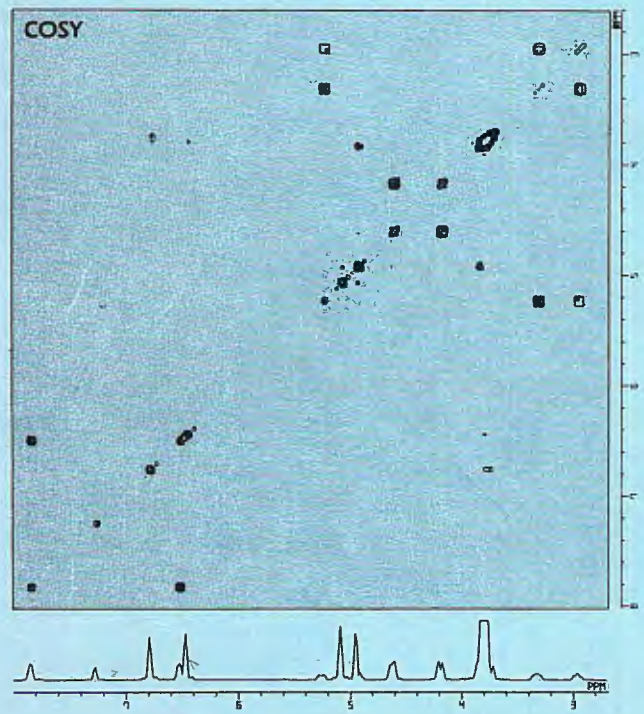

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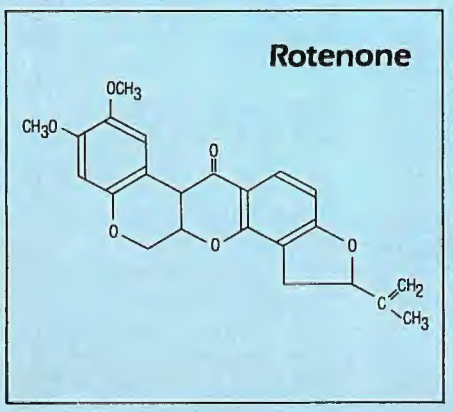

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