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NMR
NEWSLETTER

NO. 338

NOVEMBER 1986

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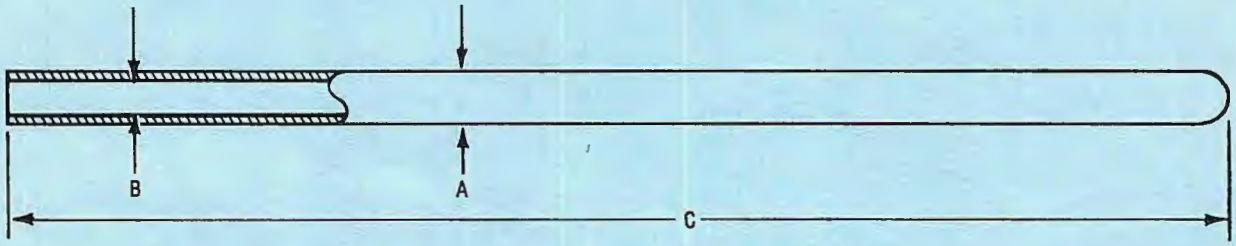

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Cryomagnet Systems, Inc.
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AUTHOR INDEX ----- TAMU NMR NEWSLETTER, NO. 338, NOVEMBER 1986

ADVERTISERS

FORTHCOMING NMR MEETINGS

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. See this Newsletter, p. 55 for information and application.

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. 340 (January) ---- 26 December 1986

No. 341 (February) --- 30 January 1987

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(Received 30 September 1986)

Rome, September 18th, 1986

Telegrammi: ISTISAN - ROMA
Telex 610071 ISTISAN

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

Combined ^{31}P and ^{1}H NMR analysis of phospholipid metabolites in experimental tumors.

Dear Prof. Shapiro,
present expectations are that high resolution NMR spectroscopy may offer powerful approaches to investigate some metabolic alterations associated with either neoplastic growth and/or with effects of antitumoral treatment. In particular experimental evidence is now growing pointing to the interest of investigating alterations in tumors of the pool sizes of phospholipid metabolites, as they may represent well defined biochemical responses of cells to factors regulating their conditions of growth and proliferative capability (1).
It is known that tumor ^{31}P NMR spectra generally exhibit conspicuous resonances arising from phospholipid metabolites, such as phosphorylcholine (PCho) and phosphorylethanolamine (PEtn) in the phosphomonoester region and glycerophosphorylcholine (GroPCho) and glycerophosphorylethanolamine (GroPEtn) in the phosphodiester region. On the other hand, the $N^{+}(CH_3)_3$ peak of choline can also be clearly detected in ^{1}H NMR spectra.
Previous studies in our laboratories, carried out on solid tumors grown in DBA/2 mice after s.c. injection of Friend erythroleukemia cells (FLC), and in vivo treated with murine tumor necrosis factor (TNF) showed that this antitumor agent induces considerable decreases in the pool sizes of intratumoral GroPCho, GroPEtn, PCho and PEtn, and a conspicuous increase in the concentration of α-glycerophosphate.
Combined ^{31}P and ^{1}H NMR spectroscopy recently demonstrated that significant alterations also occur in TNF treated tumors at the level of the intratumoral concentrations of choline and of the ratio [PCho] / [Cho].
Figure 1 (top) shows ^{31}P and ^{1}H NMR spectra obtained at 9.4 T from ethanolic extracts of FLC (clone 3C1-8) tumors, 14 days after implantation, dissected from mice 6 h after intratumoral injection of TNF (4 μg/mouse). The spectra of control tumors (treated with bovine serum albumin, BSA) are shown at the bottom. Tissues were frozen at liquid N_2 temperature immediately after excision and then extracted by $EtOH:H_2O$, 60:40 vol/vol.
Analyses of the ^{1}H NMR peak areas of choline $N^{+}(CH_3)_3$ group (normalized to one gram of tissue wet weight) indicated a 4-fold increase in the concentration of this phospholipid precursor in TNF-treated tumors vs control tumors. The combined analysis of ^{31}P and ^{1}H NMR spectra showed that the [PCho] / [Cho] ratio decreased by a factor of about 18 in TNF-treated tumors.
These results would suggest that the antitumor effects of TNF are associated with substantial alterations of several reactions of the major metabolic pathways for the biosynthesis of phospholipids, both at the level of end-products (GroPCho, α-glycerophosphate) formation as well as at that of precursors metabolic conversions (such as that controlled by choline kinase).

We thank Prof. W. Fiers, the State University of Ghent, Ghent, Belgium, for kindly providing tumor necrosisfactor. This work was partially supported by CNR Special Projects Biomedical and Clinical Engineering n. 85.01516. 57 and Oncology n. 85.02560.44.

F. Podo G. Carpinelli M. Di Vito M. Giannini

E. Proietti F. Belardelli

References

(1) E. Proietti, G. Carpinelli, M. Di Vito, F. Belardelli, I. Gresser, and F. Podo, Cancer Res. 46, 2849-2857 (1986)

(2) F. Podo, G. Carpinelli, M. Di Vito, M. Giannini, I. Gresser, E. Proietti and F. Belardelli, Fifth Annual Meeting Society Magnetic Resonance in Medicine, Montreal, August 18-22, 1986. Book of Abstracts, pp. 37-38.

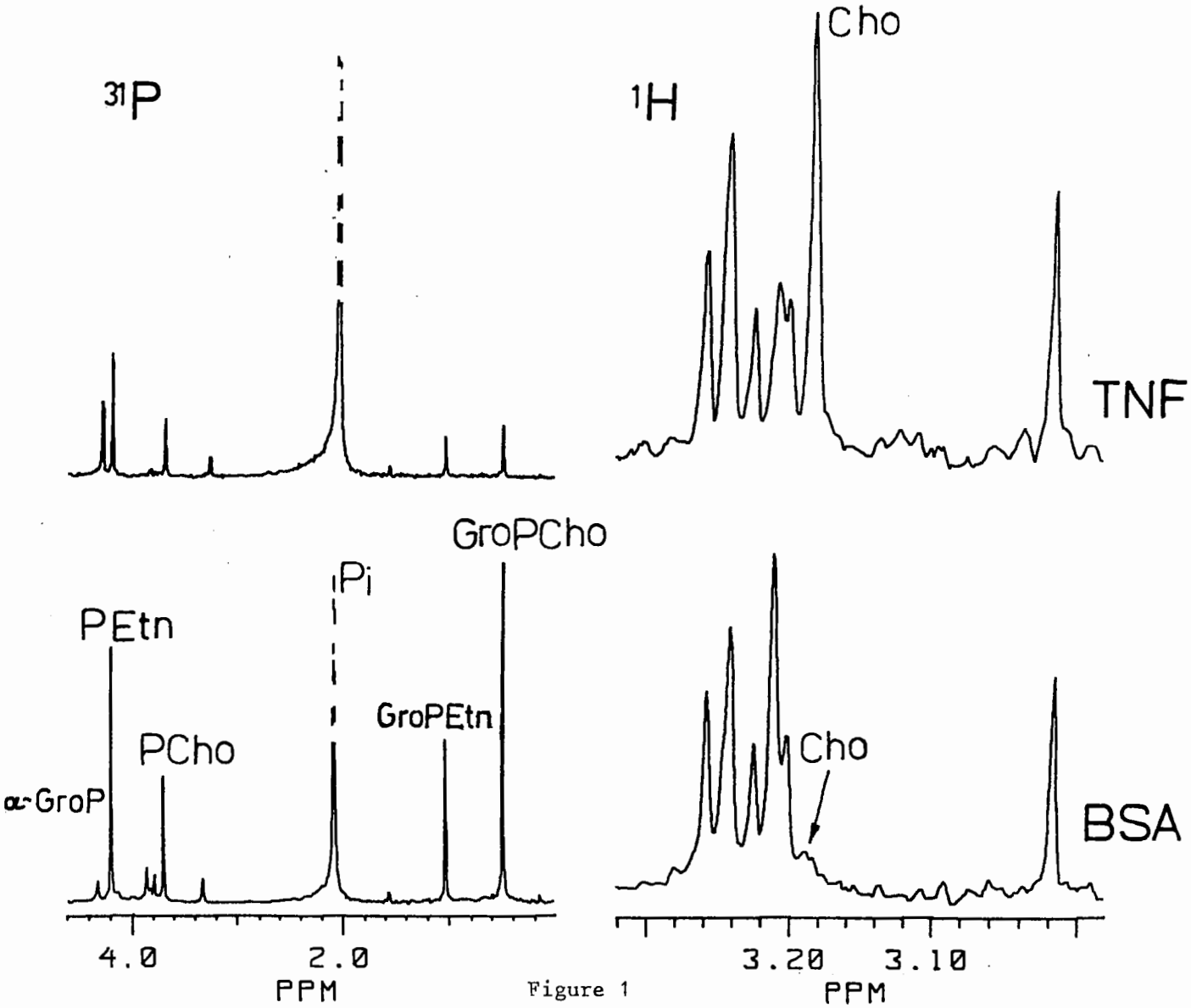

Figure 1

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September 22, 1986
(Received October 2, 1986)

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

HOHAHAing on XL-400

Dear Dr. Shapiro:

We have recently employed 2D Homonuclear Hartmann-Hahn (HOHAHA) experiments to aid in the assignment of the 1-H spectrum of the 33 amino acid antimicrobial protein NP-5. These experiments were performed on our Varian XL-400 spectrometer. The observe and decoupler channels on the spectrometer are phase locked which allowed us to use different power levels for the 90° pulse and the spin lock pulse. The 90° pulse was generated by the observe channel using the high power pulse amplifier. A 7.8k Hz Rf field spin lock pulse was generated on the decoupler channel by adjusting the output of the broadband 1-H decoupling amplifier on the spectrometer. Our initial 2D experiments employed simple phase alteration of the spin lock pulse along the ±X axis (1). This method proved unsatisfactory since it gave no better coherence transfer than a RELAYED-COSY experiment. We next employed a MLEV-17 pulse sequence (2) to reduce the decay of magnetization from $T_{1\rho}$ during the spin lock period. The standard XL-400 spectrometer cannot perform multipulse experiments, but Varian provided us with the necessary information to modify the output board so that it can execute "hardware looping". With this modification and Version 6.1 software the XL400 is able to perform the MLEV-17 pulse sequence. Figure 1 shows a contour plot of a portion of the phase sensitive 2D HOHAHA experiment on NP-5. A 72 ms spin lock pulse was used to transfer coherence through a number of protons on the amino acid side chains in NP-5. The connectivities on two amino acids, Leu-29 and Val-25, are illustrated in the figure. Coherence was transferred from the C^{α} protons through the C^{β} protons to the C^{γ} and C^{δ} protons on these two residues. We were unable to observe any significant transfer of magnetization from C^{α} to C^{δ} protons in a DOUBLE RELAYED-COSY experiment and thus conclude that the MLEV-17 based HOHAHA experiment is superior to multiple-relay experiments for spin system assignments in proteins. A detailed discussion of the complete resonance assignment of NP-5 will appear elsewhere.

1. Davis, D.G. & Bax, A. [1985] J. Am. Chem. Soc. 107, 2820-2821.

2. Bax, A. & Davis, D.G. [1985] J. Magn. Res. 65, 355-360.

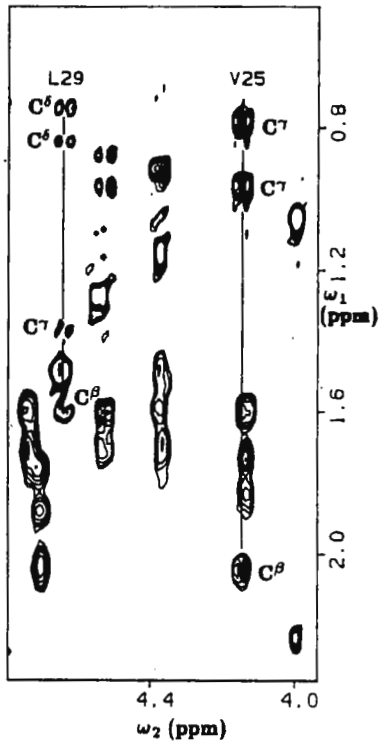


Figure 1. Contour plot of a phase sensitive ^1H 2D HOHAHA spectrum of 7mM NP5 in D_2O at 20°C. Quadrative detection was used in both the t_1 and t_2 time domains. The spectrum was acquired with 512 complex points in t_2, 256 complex FIDs in t_1 and 64 transients for each FID. The t_1 and t_2 data sets were zerofilled to 1K complex points before Fourier transformation. The $C^{\alpha}H$ chemical shifts appear along the ω_2 axis while the C^{β}, C^{γ} and C^{δ} chemical shifts appear along the ω_1 axis. Connectivities from the C^{α} proton to the C^{β} and C methyl protons are shown for Val-25. Similarly, connectivities from the C^{α} proton to all the side chain protons are shown on Leu29.

Sincerely yours,

Arthur Pardi

Alvin C. Bach, II

Telephone 554455

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
LEICESTER LE1 7RH
ENGLAND

(Received October 27, 1986)

PLOTTING PHASE-SENSITIVE 2D SPECTRA

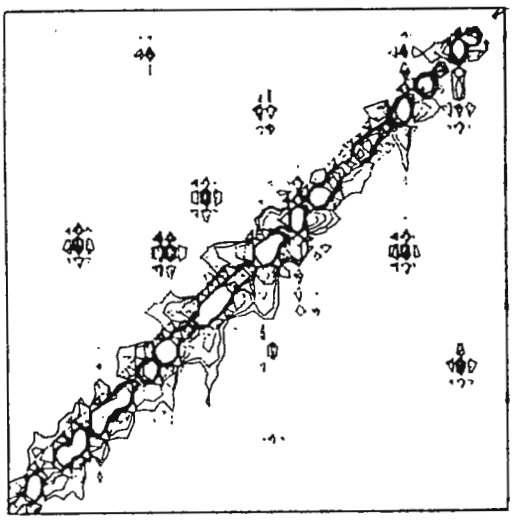
Dear Barry,

Now that the popularity of phase sensitive COSY spectra [D.Marion and K.Wüthrich, BBRC **113** 967 '83] is spreading, I'd like to draw attention to the potential advantages of the *double dispersion* mode [for a picture see Prog. NMR Spectrosc. **17** p341 '85]. There is little difference in the S/N ratio as compared with the double absorption for lines which are not well digitised [J.Magn.Reson. **61** p48 '85]. However, if spin coupled multiplets are poorly resolved, the pure absorption lineshapes interfere destructively [cf. J.Magn.Reson. **53** p269 '83] whereas the pure dispersion builds up intensity at the centre of the multiplet and therefore gives better sensitivity [Prog. NMR Spectrosc. **17** p350 '85]. The biggest advantage may be that while the cross peaks are double dispersions, the diagonal peaks are double absorptions [W.P.Aue, E.Bartholdi and R.R.Ernst, J.Chem.Phys. **64** 2229 '76] and the tails are therefore much less obtrusive. As a result, the spectra look a little like the double-quantum filtered COSY, but the sensitivity is much higher. The example below is taken from the aromatic region of a 10kD protein and shows both positive and negative levels. In closing, I should stress that this information can be pieced together from the literature and that it does not apply to experiments with net magnetisation transfer such as NOESY.

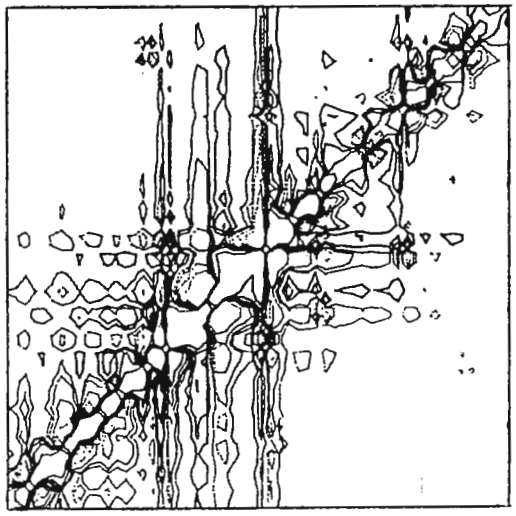
With best wishes,

David Turner

Double dispersion plot.



Double absorption plot.



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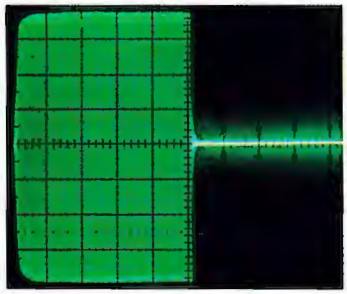
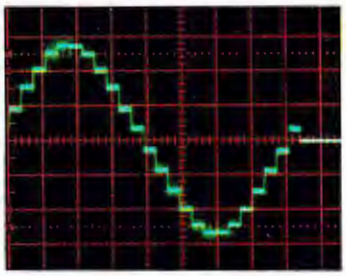
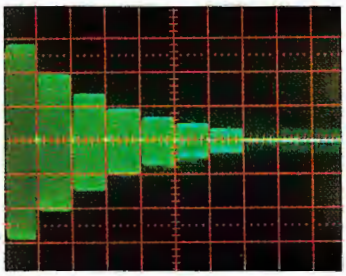




15° phase shift through 360°. ►



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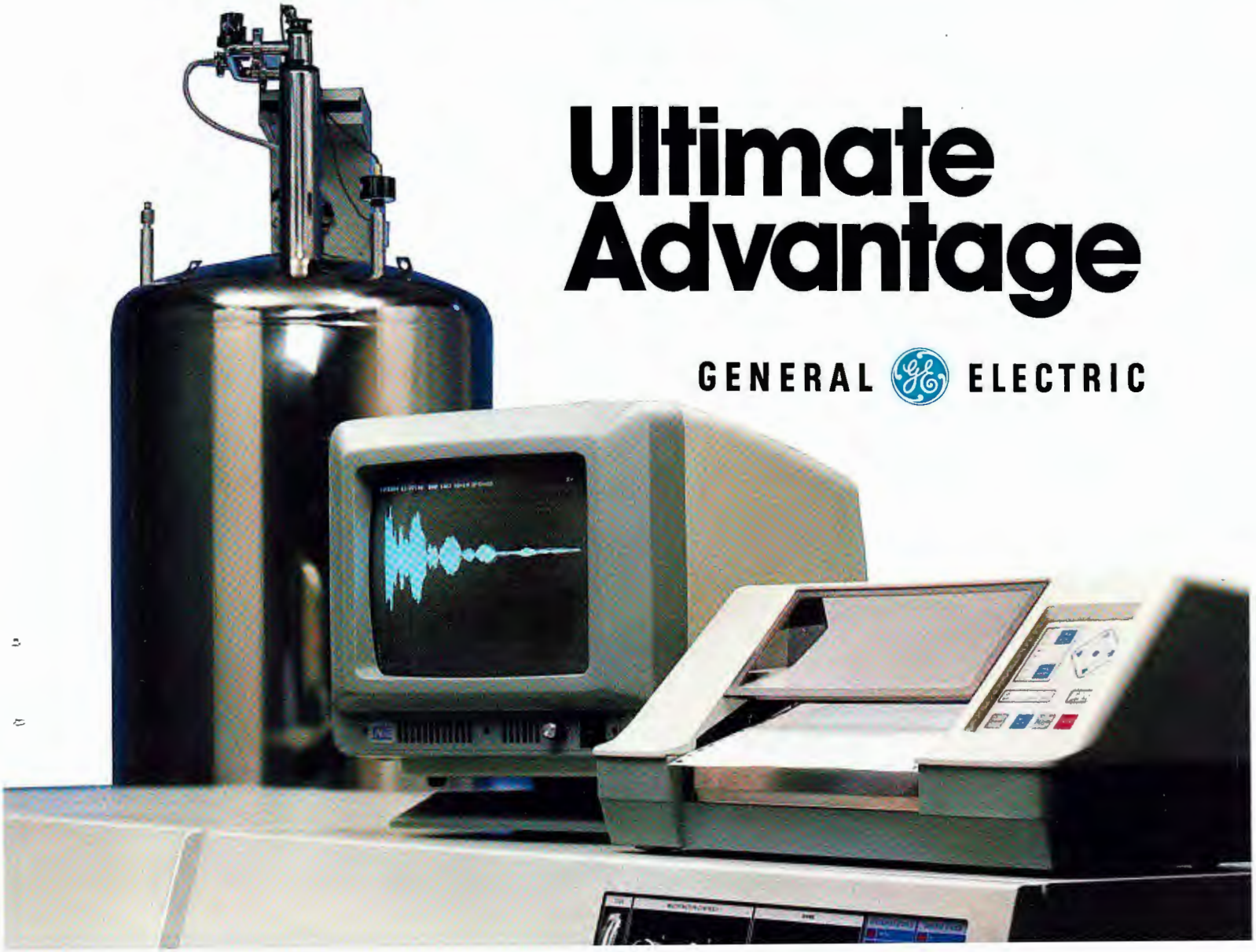

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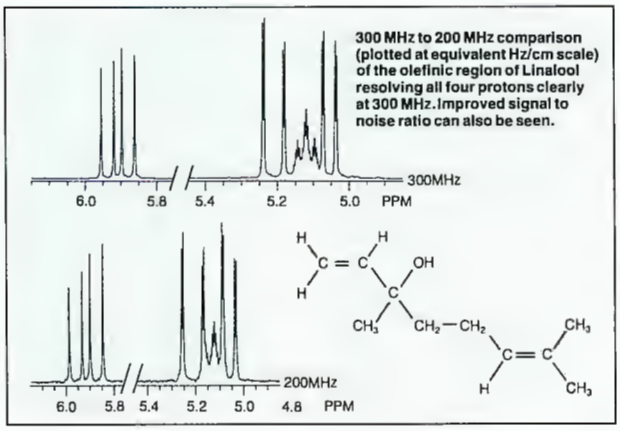

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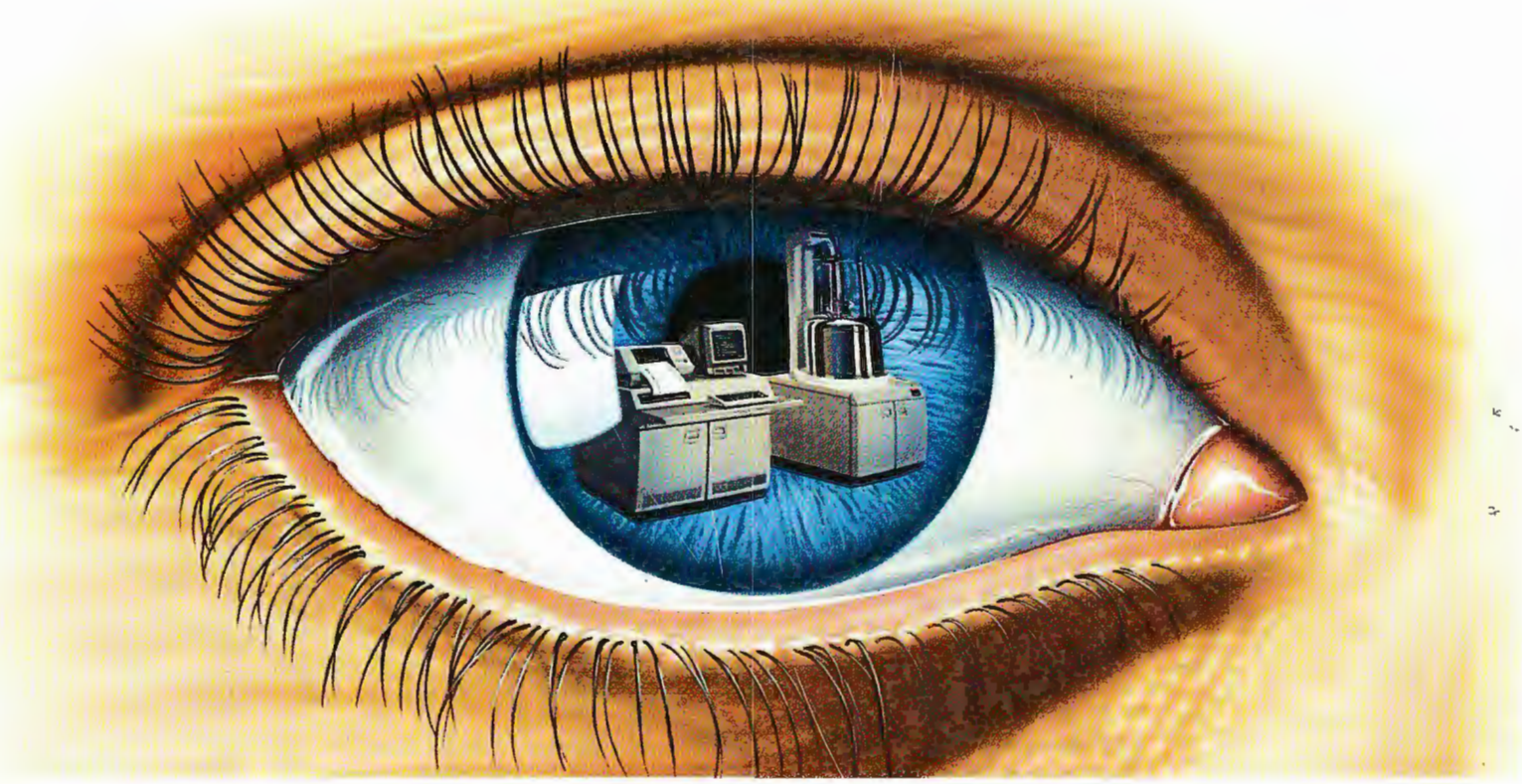

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October 7, 1986
(Received October 13, 1986)

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

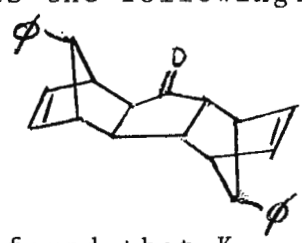
"A Novel Equilibrium"

Dear Barry:

As you well know, one of my hobbies is the examination of complex equilbria by NMR methods. The most practical application of this in my work is the examination of the fast-exchange equilbria encountered with LSR's.

LSR's complex via a simple two-step mechanism, L + S = LS and LS + S = LS_2. Most studies carried out in analyzing this equilibrium system are routine and straight-forward and, as would be expected, K_1 is greater than K_2. That is, one would expect the second ligand to be less well-bound than the first. Exceptions to this rule are quite rare.

In some work I am doing in collaboration with Alan Marchand at North Texas State University, we have found an exception to this rule. In this case the LSR was $Eu(fod)_3$ and the substrate was the following:



In this case it was found that K_1 = 4 and K_2 = 30. Statistical analyses of these data shown these numbers to be well within experimental error. Thus, a rather novel equilibrium system has been uncovered. We are currently working on explanations of this phenomenon.

Sincerely yours,

Milt

Milton D. Johnston, Jr.

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Veterans Administration Medical Center
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San Francisco, California 94121

September 26, 1986 (Received October 13, 1986)

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

NMR and MRI Program at the Veterans Administration Medical Center, University of California, San Francisco; Position Available

Dear Dr. Shapiro:

In our first letter to your newsletter, we will describe our magnetic resonance spectroscopy and imaging program at the Veterans Administration Medical Center, University of California, San Francisco.

I am a physician interested in developing and using NMR spectroscopy techniques for investigating the regulation of metabolism in animals and human subjects; specifically, to determine the metabolic alterations which occur in disease and to develop NMR techniques for clinical investigation and diagnosis.

We have been fortunate to acquire excellent instrumentation which is well suited for this purpose. We have a Philips Medical Systems 1 meter bore 2.0 Tesla NMR imaging/spectroscopy system which is broad-banded and capable of obtaining high resolution NMR spectra from localized volumes within the human body. We also have a General Electric CSI 2 Tesla animal system.

Dr. Gerald Matson, Ph.D., recently recruited from the University of California, Davis, is directing an effort to develop further spectroscopic localization techniques. These studies are being performed in close collaboration with Dr. Jan den Hollander at Philips Medical Systems in Eindhoven, Holland, who is working on pulsed gradient localization techniques such as SPARS and ISIS. These techniques have been implemented in our laboratory. Furthermore, Dr. Robin Bendall of Griffiths University in Australia will be spending three months in our laboratory this winter and will be working with Dr. Matson to implement a variety of B_1 localization techniques such as the rotating frame experiment and depth pulsing. Other scientists in our laboratory are working on computer simulations of these various localization techniques, and development of specialized coils for spectroscopy on human subjects. This year we have several scientists joining us on sabbatical leave including Dr. Klaus Roth from the Free University of Berlin and Dr. Yasuo Nagai from Takeda Pharmaceuticals in Osaka, Japan. The program is supported by the National Institutes of Health, the Veterans Administration Research Service, and Philips Medical Systems.

We are interested in recruiting postdoctoral fellows and junior faculty who have a background in NMR spectroscopy and who wish to

become involved in various aspects of in vivo spectroscopy and imaging. I am collaborating with a number of cardiologists, neurologists, neurosurgeons and radiologists to apply these techniques to a wide variety of human diseases and animal models. We also have a particular need for physicists or engineers with an emphasis in instrumentation, especially rf coil design.

The acquisition of the equipment described above, and a team of physicians and spectroscopists, provides us with an interesting opportunity to explore the many possibilities of NMR to the investigation of human metabolism, and ultimately for clinical diagnosis.

In future letters we will provide progress reports on our work.

With kindest personal regards.

Sincerely yours,

MICHAEL W. WEINER, M.D.
Associate Professor of Medicine and Radiology

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California 91125

Division of Chemistry and Chemical Engineering
Gates and Crellin Laboratories of Chemistry

John D. Roberts
Institute Professor of Chemistry

October 6, 1987
(Received October 10, 1986)

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

Succinic Acid Conformations as a Function of pH

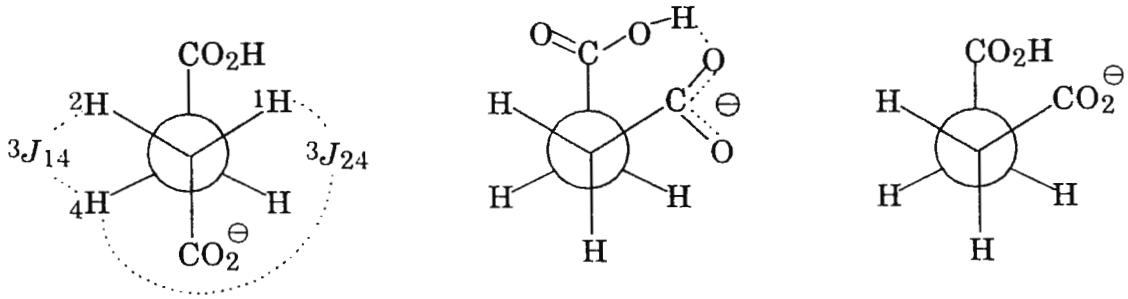
Dear Barry,

Your strident call for the mandatory contributions to TAMU NMR came during continuing magnet and computer problems with the GE 4.7-T CSI unit installed at the Huntington Medical Research Institutes, which we had hoped to employ for some stirring research this summer. It has not been possible to stir anything, so this will be a report on a minor NMR project.

For some years, I have been interested in conformational changes which occur in acid-base ionizations and, lately, I decided I needed to know what happens in the case of succinic acid. V. Gil and coworkers, *Tetrahedron*, **37**, 611-614 (1981), did a nice job of measuring the proton-proton couplings in the ^{13}C satellites as a function of pH, but in the analysis of their results, did not determine the couplings which are characteristic of the monoanion. Indeed, their analysis of the % of the various conformations as a function of pH shows rather large error bars in the region where the monoanion is expected to predominate.

Gil reports that one of the proton-proton couplings changes by 6 Hz over the pH range and the other by only about 1.3 Hz. This coupling with the larger pH change, designated by Gil as $^3J_{14}$, could be readily analyzed by the procedure we used earlier for the ionization of urocanic acid, J. *Am. Chem. Soc.*, **104**, 3945-3949 (1981), where the only inputs are the respective couplings at each pH and the couplings at the extremes, which correspond to un-ionized and fully ionized acid. The computer takes this input and thrashes around trying for the best possible fit to the data for the first and second ionizations and the couplings of the monoanion. Ten data points yielded $pK_1 = 4.1$ and $pK_2 = 5.3$, and $^3J_{14}$ for the monoanion as 6.1 Hz. The fit was excellent, with a correlation coefficient of 0.997. The literature pK_A values are 4.1 and 5.5, respectively. Forcing the literature pK_A values onto the fit, made $^3J_{14} = 6.6$ Hz and the correlation coefficient 0.995. The change of $^3J_{24}$ with pH is too small to treat very accurately in the same way, but assuming $pK_1 = 4.1$ and $pK_2 = 5.3$, then $^3J_{24}$ comes out as 7.7 Hz, with a correlation coefficient of 0.973.

The increase in $^3J_{14}$ sugests that monoionization of succinic acid leads to an *increase* in preference for conformation **1** with carboxyls *trans*, which is somewhat surprising because of the possibility of hydrogen bonding between un-ionized CO_2H and $-CO_2^{\ominus}$, **2**.



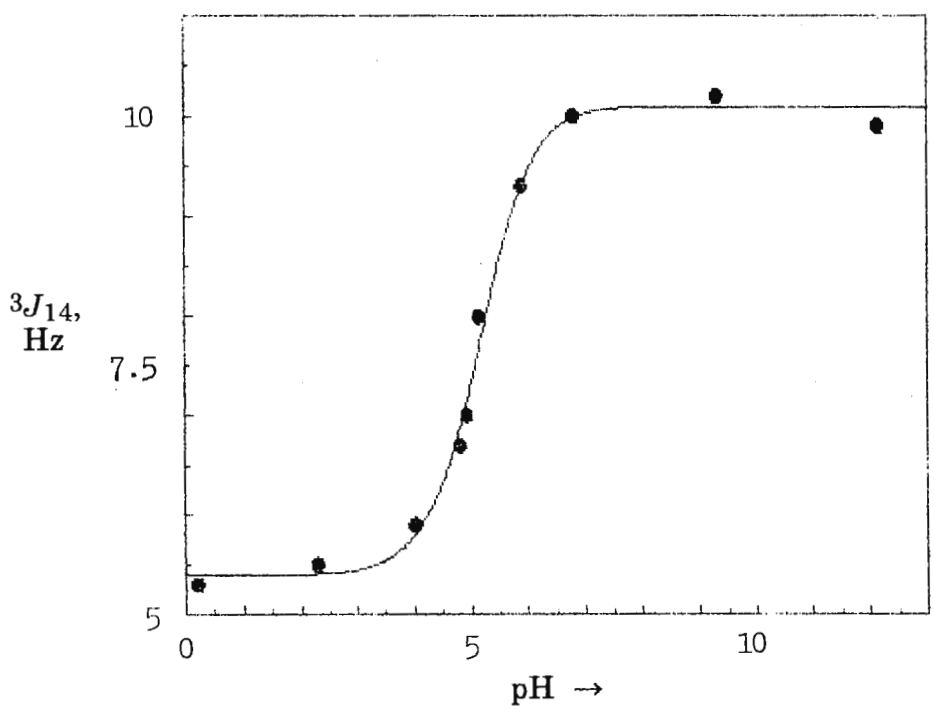
1 **2** **3**

The Gil analysis of the conformational equilibria has some further difficulties in that it assumes that the coupling constants of **1** and **3** are independent of whether the carboxyls are un-ionized, monoionized or diionized. Certainly, **3** could well have an expanded $CO_2^{\ominus}$--$CO_2^{\ominus}$ distance when ionized, as compared to monoionized or un-ionized **3**. There are also some possible additional ambiguities about the assignments of the couplings, and it would seem desirable to have a look at the couplings in *meso*-1,2-dideuteriosuccinic acid as a function of pH, which I hope we can do.

With all good wishes,

Very truly yours,

Jack



Fit of experimental points for change of $^3J_{14}$ for succinic acid with pH.

September 25, 1986 (Received October 13, 1986)

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

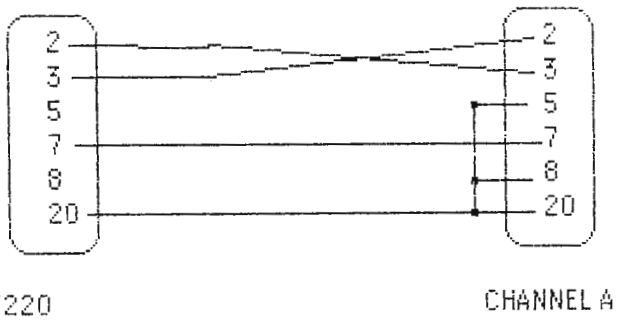
Dear Professor Shapiro:

SUBJECT: Early experiences on a new AM500

We have recently completed the installation of a Bruker AM500 at the Kodak Research laboratories. Here are a few notes from our early days.

We have received VAXCOM from ABACUS (c/o Syd Brownstein and Jack Bornais) to allow communications between our microvax II and the AM500. Vaxcom is written for the Silent 700 terminal; whereas we have the LCD terminal. To overcome this problem, we operate the console off port B and attached a VT200 to channel A. Channel A is converted to a baud rate of 300 on the I/O board. The cable connections are shown below.

For most operations we run on channel B from the keyboard, but for vax communications we switch port B to the vax and use the VT220 as a vax terminal running the program VAXCOM. I admit this is somewhat of a band aid but it got us going.



Although veteran AM users know this the new user will fall into this one! On the new console, the alpha lock key is easily hit while adjusting the A,B,C, and D knobs. This causes approximately 1/2 of DISNMRP to fail to respond most notably in EP mode. For the uninitiated this takes a day to solve! As a note, IBM tells me they hard-wire the alphalock key.

Finally, a note on probes. Dennis Hare had mentioned to me that different style proton probes at 500 MHz had shown different abilities to handle presaturation of 90% H O solutions. Bruker kindly lent us one of their older probes and I'm pleased to say our new probe was significantly better at producing a good suppression of the water peak without humping on the low field side. This is not a statistical survey but for those thinking of handling high water containing samples it may be worth noting.

Sincerely,

Richard.

Richard N. Moore
Corporate Research Laboratories

Department of Physical & Inorganic Chemistry
THE UNIVERSITY OF ADELAIDE
GPO Box 498, Adelaide
SOUTH AUSTRALIA 5001

Telephone (08) 228-5333
Telex UNIVAD AA 89141

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

6 October, 1986

(Received October 16, 1986)

TITLE : SOLID STATE NMR STUDY OF BISMUTH(III) XANTHATES

Dear Prof. Shapiro,

As a part of an ongoing study of the coordination of the xanthate ion ($^{-}S_2COR$) with the main group elements, the xanthates of bismuth(III) have been prepared and their properties investigated.

In the solid state $Bi(S_2COiPr)_3$ exists as a polymer, as evinced by an X-ray study; the polymer arising as a result of substantial intermolecular Bi-S interactions. Further, two of the $^{-}S_2COiPr$ anions (which do not participate in the generation of the polymer) are related to each other across a crystallographic mirror plane and therefore in the solid state there are only two unique $^{-}S_2COiPr$ moieties. If the methyl analogue, $Bi(S_2COMe)_3$, is isomorphous with the polymeric $Bi(S_2COiPr)_3$ derivative then, the solid state ^{13}C nmr spectrum would be expected to show two resonances due to the methyl carbon atoms, and similarly only two thiocarbonyl resonances should be present.

The proton enhanced solid state ^{13}C spectra were run on a Bruker CXP300 spectrometer with magic angle spinning, in macor rotors with delrin caps.

The spectrum (Fig. 1) of $Bi(S_2COMe)_3$ shows three methyl resonances (δ 62.6, 63.7, 64.8 PPM) and two thiocarbonyl resonances (δ 224.1, 225.7 PPM); an observation inconsistent with the presence of a crystallographic mirror plane. A subsequent X-ray analysis has revealed that $Bi(S_2COMe)_3$ does possess a *pseudo* mirror plane but is not polymeric. The two xanthate moieties related across this plane coordinate the bismuth centre in a similar manner; and together are different from the third xanthate. We suggest that the thiocarbonyl carbons of the former two are insufficiently different to be resolved in the nmr experiment whereas the methyls (crystallographically inequivalent) give rise to three separate signals. It's nice to know that X-ray crystallographers and nmr spectroscopists can agree sometimes!

Please credit this contribution to the account of the NMR Centre, University of Adelaide.

Regards,

A. Hounslow

Ms A.M. Hounslow

E. Tiekink

Dr E.R.T. Tiekink

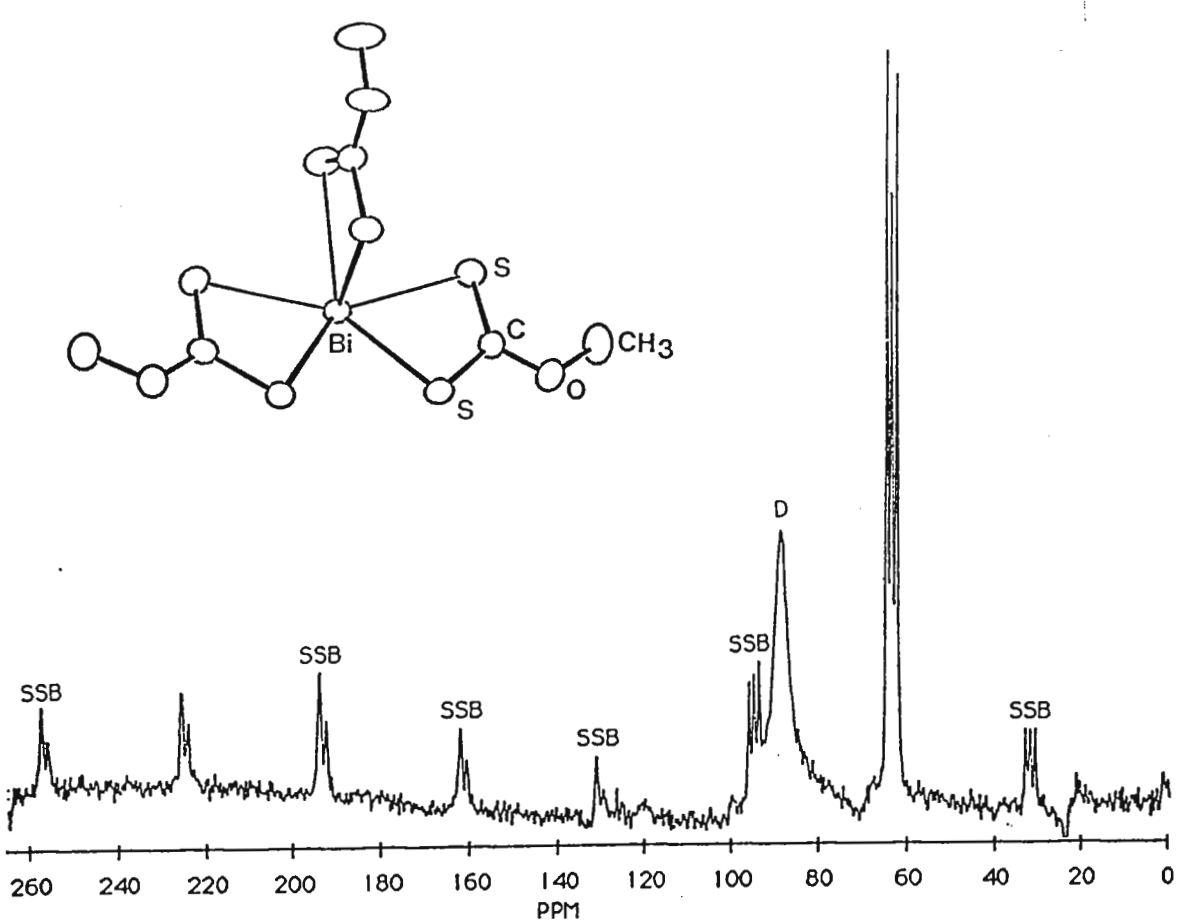


Fig 1. (SSB = spinning side band; D = delrin)

The NMR evolution continues:

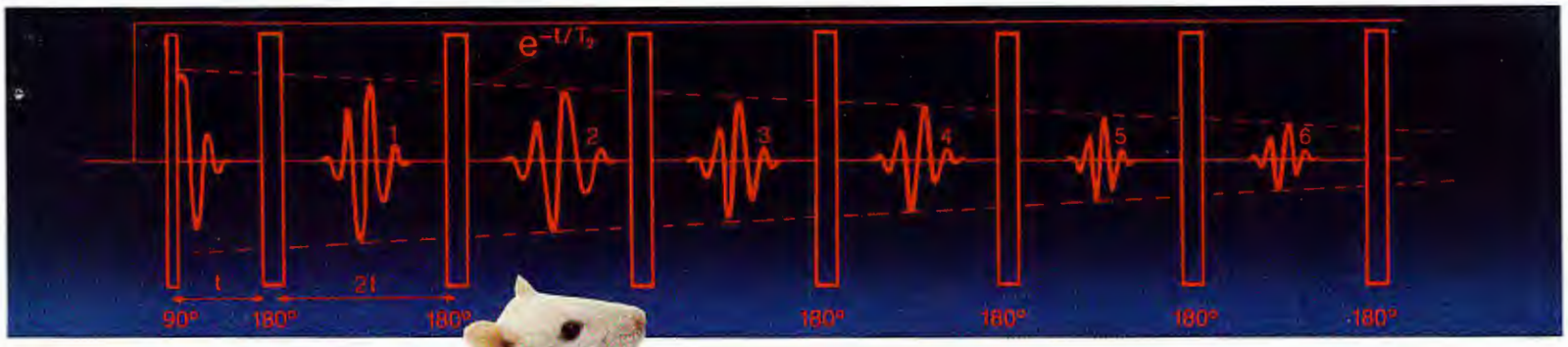


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Fig. 2—Comprehensive MR imaging, including two-dimensional multi-slice/multi-echo and rapid imaging techniques.

Fig. 3—Combined imaging and spatially resolved spectroscopy techniques, such as I.S.I.S.

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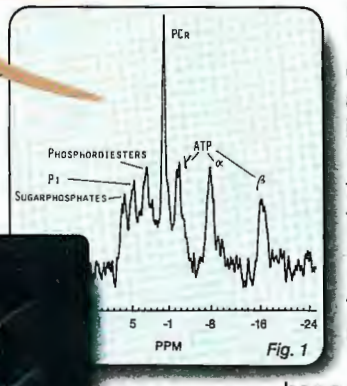

Fig. 1

Fig. 2

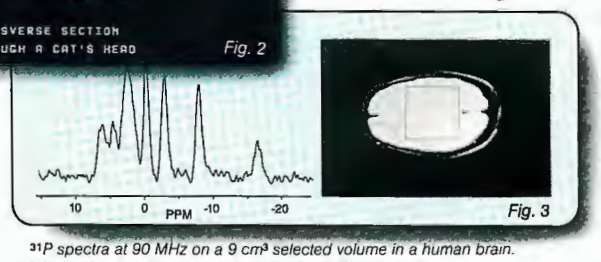

Fig. 3

^{31}P spectra at 90 MHz on a 9 cm³ selected volume in a human brain.

Acknowledgement: Obtained in cooperation with the Department of Molecular Biophysics and Biochemistry, Yale University.

*Biospec II is not a clinical system. Its use with humans is for investigative purposes only.

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Chemistry

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Telex: 777759 STUNIV G

Professor B. Shapiro,
TAMU NMR Newsletter,
Department of Chemistry,
Texas A&M University
College Station, TEXAS 77843
USA

02 - 10 - 86
(Received October 7, 1986)

Dear Barry,

BULK SUSCEPTIBILTY EFFECTS AGAIN IN SHIFT REAGENTS

Charlie Springer's recent letter to you concerning the importance of bulk magnetic susceptibility effects in determining the efficacity of shift reagents is borne out by some results we have recently obtained.

As an organic chemist it irks me (FGR) that the best aqueous shift reagents for the alkali metals are inorganic, with tripolyphosphate being the best of all. The three main essentials for the design of a good shift reagent are now known: there must be a ligand containing a large number of anionic sites that are relatively close together, the ligand must coordinate well with a triply charged lanthanide ion but less well with the singly charged alkali metal species, finally the complexes must be fairly water soluble. Further considerations are that the molecular weight of the complex should not be so big as to lead to too large a correlation time and the EFG it creates at the metal ion should not be too large. These factors lead to rapid quadrupolar relaxation and broad lines. We have one case where ^{23}Na has a 3000Hz linewidth! Finally, the reagent should not be too expensive, a factor which precludes extensive synthetic work. We have been looking at some further possible organic contenders.

Butane 1,2,3,4-tetracarboxylic acid (BTCA) should be interesting as it fulfills the conditions laid down above. We perform our experiments in a slightly different way to Springer in that we add our lanthanide to the solution of the alkali metal salt of the shift reagent. When we added Dysprosium to the sodium salt of BTCA we observed small shifts to high frequency. We thought that we possibly had a new but poor shift reagent. However, checking back on the bulk magnetic susceptibility of the corresponding concentration of sodium chloride showed that what we were observing was totally accounted for by the bulk susceptibility.

Like Springer we have also looked at diethylenetriaminepentaacetate (DTPA) and find that it gives up to 4ppm shifts to high frequency at a molar ratio of just over 1:1 Dy^{3+}:DTPA (300K). For triethylenetetraminehexaacetate we observe a maximum shift of ca 3.5ppm to low frequency again at a molar ratio of just over 1:1. These shifts are small in comparison with what is available with tripolyphosphate (ca 40 ppm) which makes it unlikely that they will replace the tripolyphosphate shift reagents.

We haven't yet given up hope of finding suitable organic ligands and are still searching for suitable simple candidates. We still have one or two tricks up our sleeves!

Best wishes,

Frank

(Frank G. Riddell)

(S. Arumugam)

CALIFORNIA INSTITUTE OF TECHNOLOGY

SOUTHERN CALIFORNIA REGIONAL NMR FACILITY

Mail Code 164-30, Pasadena, CA 91125

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

October 13, 1986
(Received October 17, 1986)

A DUTY-CYCLE LIMITER FOR HIGH-POWER NMR

Dear Barry:

A recent letter (TAMU **331**, p. 32) described a circuit designed to protect high-power amplifiers and probes from rf pulses which have been inadvertently set too long. We had need for similar protection for our home-built solid state spectrometer in the Regional Facility. However, simply limiting an individual pulse length was not a suitable approach, since in the cross-polarization experiment (and others) long pulses are acceptable, as long as the duty cycle is not too great. Therefore, we (JMY) designed a circuit (see Figure) which limits the total length of all pulses in a given interval (set to ca. 4s) to a preset value (ca. 100ms). When this duty cycle is exceeded, the pulses are disabled and a panel light comes on until manually reset.

This was most conveniently accomplished by utilizing the 5v signals which are used to blank our two high-power AR amplifiers, which go to zero when the amplifier is turned on. The circuit integrates these two blanking pulses and converts them to a DC level, which is fed to a comparator which in turn drives a TTL latch. The output from the latch is used to create a forced blanking condition.

The integrator A1 samples two TTL signals through R1,R2, which together with C1 determine the time constant of the circuit (in our case, approximately 4s, which is a typical recycle delay). P1 and P2 provide an adjustment to bias the ramp starting point and comparator A2 has a threshhold level adjustment; all three are used to adjust the maximum total pulse length permitted (ca. 100ms in our case). A Zener diode is used to clamp the comparator to positive values of less than 5v, protecting the input of U1C. U1D is used as a power on reset and allows resetting of the latch by switch S1B.

In operation the TTL blanking levels are at +5v, causing the integrator output to remain near zero. During "unblanking" the output begins ramping towards -8v. If the unblanking continues beyond the preset comparator threshhold value, the latch will trigger. Once the latch is triggered it remains on until the reset switch S1 is depressed.

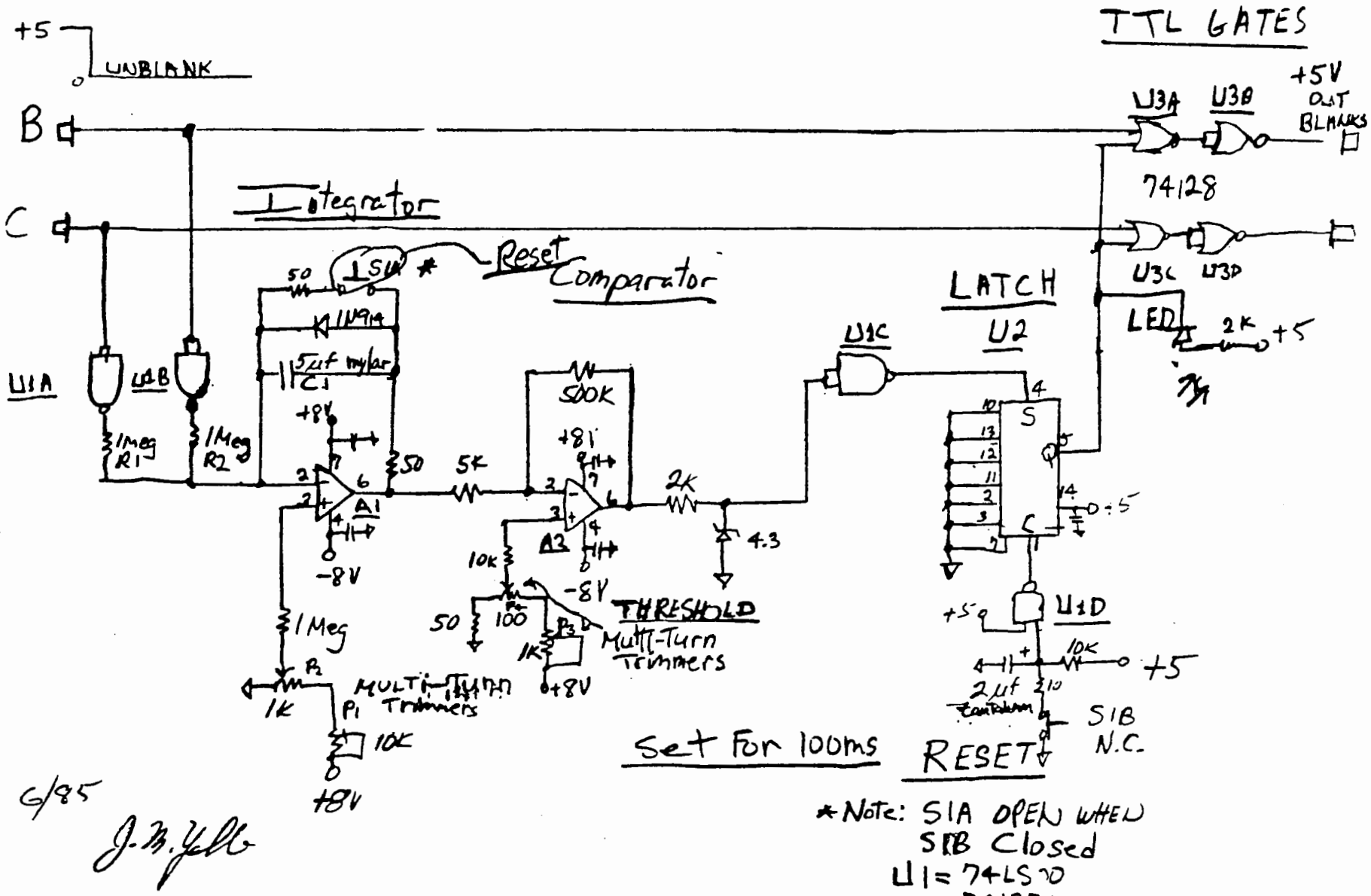
Any questions about this device should be addressed to John Yehle at (818) 356-6069.

I hope that this communication will prevent our excommunication.

Sincerely yours,

James Yesinowski John Yehle

James P. Yesinowski, Manager
John Yehle, Electronics Engineer
Southern California Regional NMR Facility



*Note: S1A OPEN WHEN S1B Closed

U1 = 74LS00
U2 = 74LS74
U3 = 74128
A1 & A2 = OP-27

UNIVERSITY OF WISCONSIN MADISON

DEPARTMENT OF CHEMISTRY

1101 UNIVERSITY AVENUE
MADISON, WISCONSIN 53706

6 October 1986
(Received October 10, 1986)

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

Dear Barry,

Carbon-13 Differential Line Broadening and the
Absolute Sign of Carbon-Hydrogen Spin Coupling Constants

Recent literature reports of "strange asymmetries" in NMR spectra (and your pink reminder) prompt this letter. These asymmetries are sometimes the result of multiple relaxation processes which can constructively or destructively interfere with one another. In Figure 1 we have shown the proton-coupled ^{13}C NMR spectra for the acetylene carbon in phenyl acetylene at 25°, -18° and -28° C. The integrated intensities of the two lines are equal for all temperatures, but the peak heights and line widths become increasingly different as the temperature decreases. As the temperature becomes lower, the molecular correlation time becomes longer and the differential line broadening (DLB) for the two lines of the doublet increases. This DLB has been observed with increasing frequency in the chemical literature (especially at magnetic fields of 9.5 tesla and higher). It arises from interference effects between dipolar and chemical shift anisotropy (CSA) relaxation. In the present case the broad line (at the higher frequency) has a much shorter T_2 value, and hence a greater width, than the narrow line.

These DLB effects occur under the following conditions:

1) High magnetic fields ($B_o \geqslant 4.7$ tesla)

2) Long correlation times ($10^{-8} \geqslant \omega\tau_c \geqslant 10^{-11}$) such as occur in polymers, at low temperature, or absorbed molecules (with restricted motion).

3) For nuclei with large CSA (e.g. ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P, etc.), and in situations where the magnitude of the dipolar and CSA interactions are comparable and have the same correlation time.

(continued on page 25)

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(continued from page 22)

If the sign of the carbon CSA is known, as it is for the acetylene carbon in phenylacetylene, then the absolute sign of the carbon-hydrogen spin coupling constant can be determined; it is positive, J_{C-H} = + 252.1 Hz. The details of such observations and the theory of DLB will be published in 4 or 5 months in J. Am. Chem. Soc. Preprints will be available in a few weeks for anyone interested.

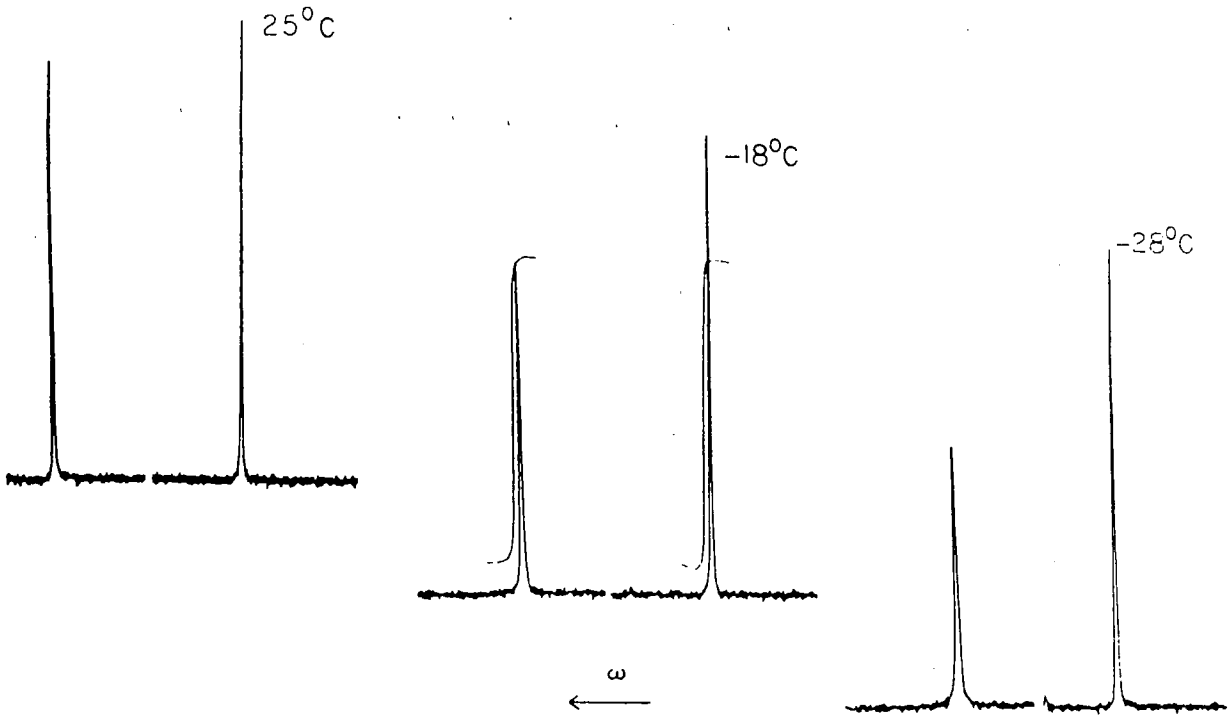
Best regards,

Tom.

TCF/mm

Thomas C. Farrar
Professor of Chemistry

fig 1



DEPARTMENT OF THE NAVY
NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20375—5000

IN REPLY REFER TO:

6120-712:ANG:mbr
7 October 1986

(Received October 15, 1986)

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

Postdoctoral and Visiting Scientist Programs at NRL

Dear Barry:

The Naval Research Laboratory has programs for both postdoctoral research fellows and visiting scientists.

There are two postdoctoral programs at NRL: the National Research Council (NRC) associateship and the Office of Naval Technology (ONT) fellowship, administered through the American Society for Engineering Education (ASEE). Each program selects applicants on a competitive basis. Relocation and professional travel allowances are provided. An immutable requirement is that the applicant be a U.S. citizen.

The NRC appointment is for two years; the stipend is expected to be $26.35K. A third year of contractual support from the Office of Naval Research may be available for NRC associates who continue research at an academic institution. There are two selection cycles yearly with deadlines of 15 January and 15 April 1987. Applications are available from:

Associateship Office, JH 608
National Research Council
2101 Constitution Avenue, N.W.
Washington, D.C. 20418
(202) 334-2760

The ONT program is newer and smaller than the NRC program. The ONT research projects are somewhat more applied than those of the NRC. ONT appointment is for one year, renewable for a second and possibly third year. The ONT stipends start at $31K. There are four award cycles with deadlines of 1 January, 1 April, 1 July and 1 October 1987. For applicant's packages, contact:

ASEE
Projects Office
11 Dupont Circle, Suite 200
Washington, DC 20036
(202) 293-7080

The Laboratory has a program for visiting faculty members on sabbatical or leave, under the provisions of the Intergovernmental Personnel Act (IPA). Depending on the circumstances, supplemental or full support may be available. An IPA agreement may cover any period from a few months to two years. Allowances are provided for moving expenses and travel to scientific meetings. There is also an ASEE summer fellow program which brings university faculty to NRL for a 10 week period.

Within the Polymer Diagnostics Section we address a wide range of problems through magnetic resonance. Present efforts and interests include: adsorbed molecules; NMR imaging in solids; mechanical properties of polymers; hydrodynamics of polymers in solution; NMR and ESR in phospholipids. We have a new joint program involving NMR on archaebacteria with the NRL Molecular Bioengineering Branch: someone with a more biological bent would be very helpful.

Please encourage anyone interested to contact me or Henry Resing directly and informally.

A. N. Garroway (202) 767-2323
H. A. Resing -2025

The January NRC deadline approaches rapidly.

Your assistance in publicizing these postdoctoral and visiting scientist programs is greatly appreciated.

Sincerely,

AG

A. N. Garroway, Head
Polymer Diagnostics Section
Code 6122
Polymeric Materials Branch
Chemistry Division

The University of Alabama at Birmingham
Comprehensive Cancer Center
NMR Core Facility / CHSB B-31
205/934-5696

October 8, 1986
(Received October 15, 1986)

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

In Vivo Surface Coil NMR Probe for Studies on Rats

Dear Dr. Shapiro:

We have recently designed an *in vivo* surface coil NMR probe (1) with a simple and efficient support system (Figure 1) for studies on rats. This probe was used (on our 4.7T Bruker CXP-200 system) for cardiac allograft rejection studies by ^{31}P NMR (2,3) and the neurology pilot studies on the effect of total cerebral ischemia on water proton relaxation times (4).

The system consists of a single-sided, glass-epoxy printed circuit board (PCB) and a copper tube (hard-drawn 1/4 inch copper pipe). A small electronics shelf is soldered to the copper tube and the PCB to provide rigidity and a place for the various matching and tuning capacitors. The copper foil on the upper portion of the PCB may be etched away. The remaining copper foil provides a convenient ground for the coil and also shields the electronics of the probe from the animal's body.

If double-sided glass epoxy board is used, the side toward the animal may be used as a shield (if properly grounded) and the circuit running to the coil may be etched on the reverse side. Alternatively, a coaxial cable may be used for this circuit.

The method we used for etching away the copper foil uses plastic tape and a saturated solution of $FeCl_3$. The plastic tape masks the area of copper not to be removed. The PCB is agitated in a small beaker with the iron chloride solution until the etching is complete. After cleaning, the tape is removed and the board is ready for use.

The subject rat is placed against the coil which is attached to the flat side of the PCB. A small piece of nylon string or suture is then placed behind the two upper front incisors of the rat's mouth and passed through a small hole in the copper tube. A few pieces of masking tape are then placed around the rat's body. Alternatively, small holes may be drilled along the periphery of the PCB. Small pieces of nylon line may be placed through the holes and then around the animal's body. This provides maximum rigidity and produces very little trauma to the animal. The rigid support system improved the reproducibility of the NMR measurements.

The support system uses very little of the precious room in the probe, is easy to construct from commonly available materials, and requires very little machine work.

Sincerely,

Mike E. Brown

N. Rama Krishna

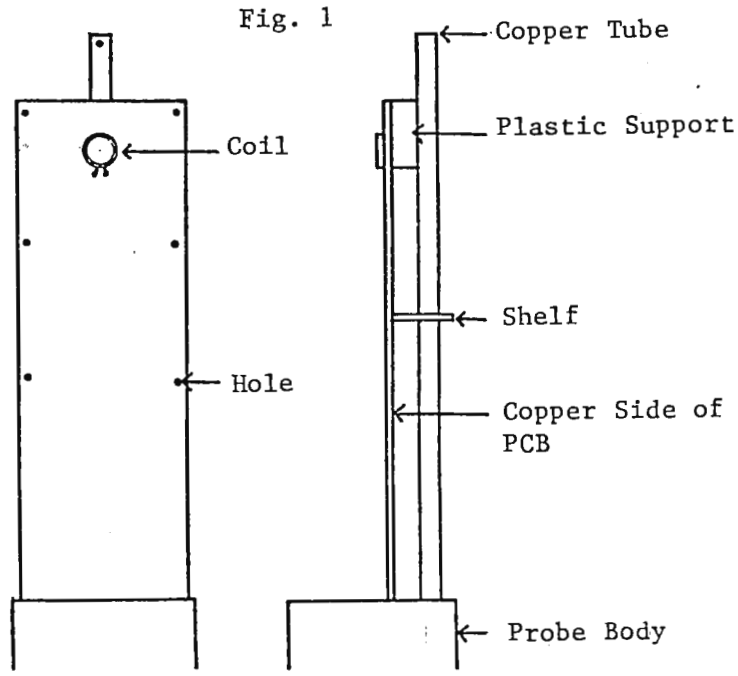
(1) J.J.H. Ackerman, T.H. Grove, G.G. Wong, D.G. Gadian, and G.K. Radda, Nature (London) 283 167 (1980).

(2) W.T. Evanochko, R.C. Canby, J.K. Kirklin, D.C. McGiffin, L.V. Barrett, R.C. Reeves, R.E. Foster, and G.M. Pohost, Vol. 3, p. 616, Book of Abstracts Society of Magnetic Resonance in Medicine 5th Annual Meeting, August 19-22, 1986, Montreal, Canada.

(3) R.C. Canby, W.T. Evanochko, L.V. Barrett, R.E. Foster, G.M. Pohost, R.C. Reeves, J. Am. Coll. Cardiol., 7:230A, 1986.

(4) M.E. Brown, N.R. Krishna, and J. Halsey, unpublished studies, 1985.

Fig. 1



MINISTERE DE L'EDUCATION NATIONALE
ET DE LA CULTURE FRANÇAISE

UNIVERSITE DE L'ETAT A MONS
FACULTE DE MEDECINE
Avenue du Champ de Mars, 24
7000 MONS (Belgique)
Tél. 065/37.31.11.

Mons, 09/30/1986.
(Received October 14, 1986)

NMR Dispersion Curves of Gels

Dear Professor SHAPIRO,

Agar and agarose gels eventually doped with paramagnetic substances are often used as "standard" tests objects for Magnetic Resonance Imaging. Since these standard samples are supposed to be used to test imagers working in a range of magnetic fields extending between 0.02 T and 1.5 T, we measured the Nuclear Magnetic Relaxation Dispersion of water protons in agarose gels containing paramagnetic ions over almost four decades of proton Larmor frequencies. The measurements have been done on a field cycling relaxometer builded by S.H. KOENIG et al. at the IBM T.J. Watson Research Center. (We take this opportunity to mention that, thanks to Drs S.H. KOENIG and R.D. BROWN, further work will take advantage of the fact that our lab is now equipped with one "clone" of their relaxometer). The figures 1 and 2 represent the NMR dispersion curves at 20° C of gels containing 3% af agarose and 0.0005 M/l of $MnCl_2$ and $GdCl_3$ respectively.

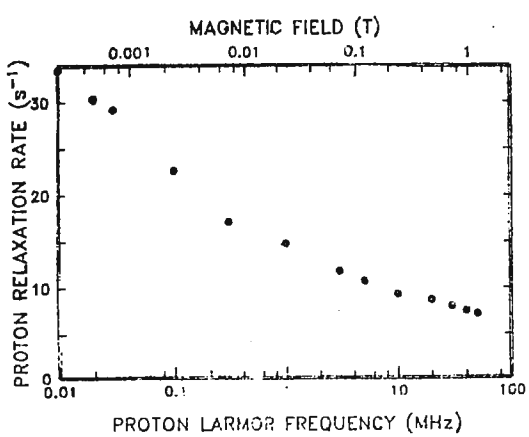


Figure 1

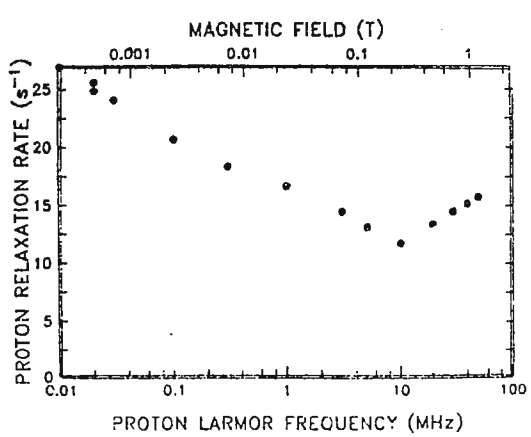


Figure 2

(continued on page 33)

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Integrated solutions for the laboratory

IBM Instruments Inc.

(continued from page 30)

The T1 dispersions are clearly different for both solutions. The analysis of the results shows that the Mn^{2+} aquoion reorientates nearly at the same rate in the gel than in the aqueous solution whereas the tumbling of the Gd^{3+} ion is much slower in the gel than in the aqueous solution. This observation is related to the bigger size of the Gd^{3+} aquoion as compared to the Mn^{2+} one.

Profiles recorded on agar gels doped with Gd^{3+} exhibit between 1 and 50 MHz larger variations than those observed for agarose gels. These different behaviors of gels do not preclude their use as standard materials but suggest the necessity to record their NMRD profiles in the range of magnetic fieds in which they are supposed to be used.

We also want to point out the importance of the choice of the glassware of the NMR tube used for this kind of studies.

In a normal glass tube, the T_1 at 20 MHz of a 5.3 10^{-4} M $GdCl_3$ aqueous solution initially at pH 3.5 varies from 0.22 s to 0.56 s after 71 hours. In a pyrex tube, the T_1 remains constant. This is explained by the pH variation of the solution contained in the glass tube due to the Na^+/H^+ exchange. The Na^+ ions go from the glass to the solution while the protons from the solution enter the glass. The resulting pH increase induced the precipitation of gadolinium hydroxyde and a concomittant increase of the T_1 values.

Sincerely,

Prof. Y. VAN HAVERBEKE.

Dr. R.N. MULLER.

Dr. L. VANDER ELST.

M. CORSELLE-DUHAMEL.

UNIVERSITY OF CALIFORNIA, BERKELEY

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DEPARTMENT OF CHEMISTRY BERKELEY, CALIFORNIA 94720

Oct. 9, 1986
(Received October 16, 1986)

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

PC-TALK III to Aspect 3000 and Nicolet 1180/1280

Dear Barry,

Recently we needed to extract data from a Nicolet 1180 for analysis using a PC. The DTL routine in GENT[1] can be used to dump signed decimal numbers in ASCII (select BO, even parity). The PC is running PC-TALK III[2] (version 830909; use shift-tab to check). Using the Receive File command (Alt-R) the dump is captured to disk.

PC-TALK III is written in BASIC and easily modified. To speed things up we patched PC-TALK to run at 19200 and 38400 Baud. The 8250 UART chips can be programmed for these rates but MS-DOS or PC-DOS (and most application programs) do not use rates higher than 9600 Baud.

We have been successful in dumping at 19200 Baud. At 38400 Baud we experience transmission errors. We are not yet certain as to where these occur. Due to recent pink mail we were not able to find out more at this time. An XON/XOFF modification to GENT is being worked on.

To receive ASCII files from a Bruker Aspect 3000, the RS-232 channel B is used ("ON B"). Only pins 1, 2, 3, and 7 are wired between the Aspect and the PC. To capture a file, e.g. DEPT.AU, use the Alt-R command in PC-TALK and then issue the ADAKOS command "LIS DEPT.AU" from the PC. The file can now be edited on the PC using a text editor, e.g. EDIX (word processors are not recommended).

To send edited (or new) files back to the Aspect we activate TECO from the PC (e.g. TECO<cr>, EWDEPT1.AU<esc><esc>, I<cr>). "I" enters the insert mode. Then using the Transmit File (Alt-T) command in PC-TALK send DEPT1.AU in ASCII format. Close the TECO generated file by sending "EX<esc><esc>, H<esc><esc>". This permits several versions of an experiment to be prepared off line without tying up the instrument, and without having to learn more than four TECO commands. The changes (lines 4045-4405) cause PC-TALK to wait for the character to be echoed; this avoids overflow of the buffer in TECO, which was a problem with this method. We are working on a patch to interface to SPECNET to further simplify transfers.

The listing included below can be typed in on top of PC-TALK III or put into a separate merge file. Lines 5300-5380 are the subroutine which resets the UART to the higher Baud rate after the serial port is opened for 9600 Baud[3]. Lines 427, 5027-5283, and 5672-5673 support the entry of the two higher Baud rates, which must be entered as 19K (upper case K) and 38K.

Sincerely,

Rudi Nunlist Richard Mazzarisi

Changes to PC-TALK III:

```
427 IF BAU1$="19K" OR BAU1$="38K" THEN GOSUB 5300
4045 FOR I=1 TO 128:PRINT INPUT$(1,#1);:NEXT
4240 PRINT#1,Z$;:IF TR$="P" THEN IF Z$=CR$ THEN PRINT INPUT$(1,#1);
     :GOSUB 4425:GOTO 4210
4250 PRINT INPUT$(1,#1);:GOTO 4210
4405 FOR I=1 TO LEN(Y$):Z$=MID$(Y$,I,1):IF Z$=LF$ THEN 4415 ELSE IF
     Z$<>CR$ THEN PRINT#1,Z$;:PRINT INPUT$(1,#1);:GOTO 4415 ELSE
     PRINT#1," "+CR$; :PRINT CR$;:B$="":GOSUB 4420
5027 PRINT"   5 -  19K,N,7,1  (Bruker)    6 -  19K,E,7,1  (Nicolet)
5060 Q=VAL(Q$):IF Q<1 OR Q>6 THEN BEEP:GOTO 5045 ELSE PRINT Q
5081 IF Q=5 THEN BAU$="9600":PAR$="N":BAU1$="19K
5082 IF Q=6 THEN BAU$="9600":BAU1$="19K"
5088 IF Q>4 THEN GOSUB 5300
5283 IF BAU1$="38K" OR BAU1$="19K" THEN GOSUB 5300
5300 ' set high Baud rate
5305 COMBASE=&H3F8  ' for COM1
5310 IF COMMPORT$="COM2:" THEN COMBASE=&H2F8
5320 IF BAU1$="19K" THEN LOW=6
5325 IF BAU1$="38K" THEN LOW=3
5340 HIGH=0
5345 DIVLSB=COMBASE
5350 DIVMSB=COMBASE+1
5355 LINECTRL=COMBASE+3
5360 OUT LINECTRL,INP(LINECTRL) OR &H80  ' set DLAB
5365 OUT DIVLSB,LOW: OUT DIVMSB,HIGH
5370 OUT LINECTRL,INP(LINECTRL) AND &H7F  ' clear DLAB
5375 COMM$=COMMPORT$+BAU1$+","+PAR$+","+DTA$+","+STP$+COMMINIT$
5380 RETURN
5672 BAU1$=BAU$
5673 IF BAU$="19K" OR BAU$="38K" THEN BAU$="9600"
```

1. General Electric Co., Medical Systems Group, GENT Program Manual, 1985.
2. A. Fluegelman, The Headlands Press, Inc., P.O. Box 862, Tiburon, CA 94920.
3. Allen E. Tract, American Laboratory, March 1986, pp.127-137.

Pharmaceuticals Division
CIBA-GEIGY Corporation
Summit, New Jersey 07901

CIBA–GEIGY

October 14, 1986

(Received October 16, 1986)

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

Preliminary Studies of Vascular Smooth Muscle Physiology and Metabolism by ^{31}P NMR.

Dear Professor Shapiro:

In preliminary studies of vascular smooth muscle physiology and metabolism by ^{31}P NMR, we have compared a variety of hog carotid artery preparations. Under all conditions studied, comparisons of metabolite concentrations have yielded a phosphocreatine (PCr) to ATP ratio of less than one. This is true whether the tissue is relaxed or contracted, whether the tissue strips are mounted isometrically or isotonically, whether the superfusate is bubbled with room air or 100% oxygen and at superfusate flow rates varying from 5.0 to 15.0 ml/min. per gram of tissue. Furthermore, we have found that oxygenation of the sample with 100% O_2 prior to and during perfusion is critical to obtaining high PCr concentration. The spectra shown in figure 1 illustrate this fact. The low phosphocreatine concentration in spectrum A is obtained from tissue oxygenated only with room air, whereas in spectrum B the tissue is oxygenated with 100% O_2 and shows a larger PCr concentration. As indicated, the PCr/ATP ratio is always less than one with the magnitude dependent on the conditions during perfusion.

The overall low PCr/ATP ratio is in agreement with other studies of vascular smooth muscle but contrasts with results obtained from smooth muscle from other organs. This result could be explained by the fact that distribution of smooth muscle in the body is more heterogeneous than skeletal and cardiac muscle. Therefore, the relative concentrations of intracellular phosphagens may be more varied as well.

Sincerely,

Nina C. Gonnella

Nina C. Gonnella, Ph.D.
CIBA-GEIGY Corp.

Thomas Grieder

Thomas Grieder
University of Medicine and
Dentistry of New Jersey

/dp

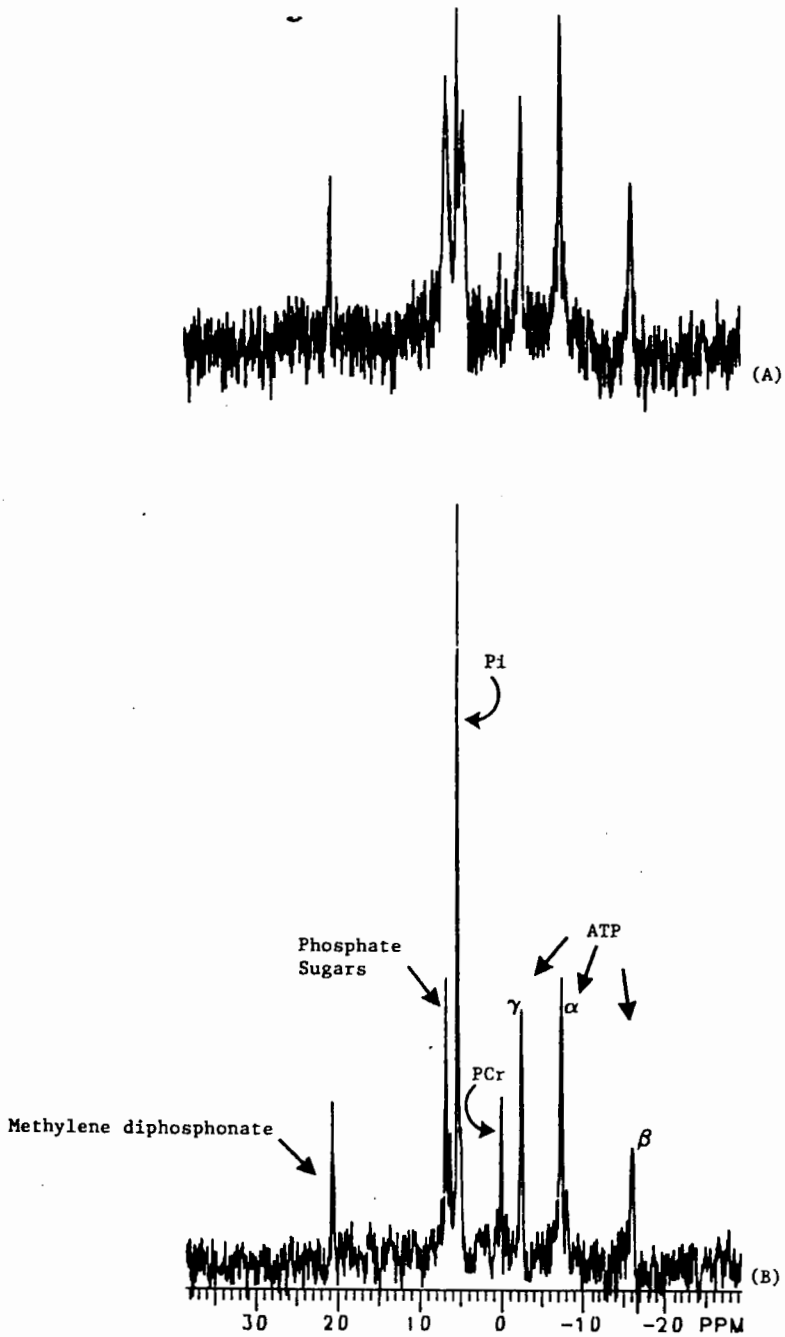


Figure 1. Spectrum A: Hog carotid artery oxygenated with room air.
Spectrum B: Hog carotid artery oxygenated with 100% O_2.

UNIVERSITY OF MISSOURI-COLUMBIA

College of Arts and Science

Department of Chemistry

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

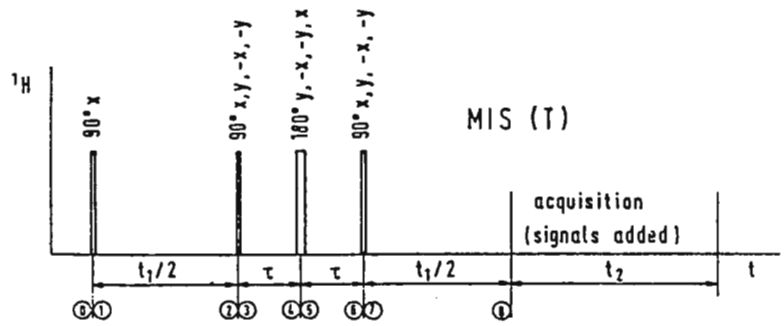
October 24, 1986 (Received 31 October 1986)

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

Selective Suppression of Particular Signals in homonuclear 2-D NMR

Dear Dr. Shapiro:

We have been experimenting with incorporating the homo-nuclear bilinear rotation pulse into COSY-type experiments to effect selective observation of certain signals. The results are not as clear as in the heteronuclear case. However, the following pulse sequence was found to be useful for certain types of molecules (e.g. oligosaccharides, polyaromatics).



In these types of molecules, the spin system (or a part of the spin system) follows the condition

$$J \sim J(I_1,I_2) \sim J(I_2,I_3)\cdots\sim J(I_n-1,\ I_n) \qquad [1]$$

and all other coupling constants being substantially smaller.

The results from this pulse sequence with τ set equal to 1/2J will give a homonuclear CSCM map in which the signals of

(1) single spins are eliminated (the solvent peak is also suppressed);
(2) inner spins (I_2, I_3 $\cdots$ I_{n-1} in [1]) are eliminated from the diagonal;
(3) terminal spins (I_1 and I_n) show up prominently in the diagonal. The patterns for spin-pairs (n = 2) and for terminal spins in a chain (n>2) are different and can be easily distinguished.
(4) The off diagonal peaks, which are "spurious" in this experiment provide J-connectivity information (even between signals which are absent from the diagonal).

These results (illustrated in Fig. 1) should be useful in providing a valuable starting point for the assignment of COSY maps for very congested spectral regions by eliminating selected signals.

(continued on page 41)

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(continued from page 38)

Reversing the phase of the last 90° pulse will reverse the signals preserved and the signals suppressed.

Sincerely yours,

Venceslav Rutar Wei Guo Tuck C. Wong

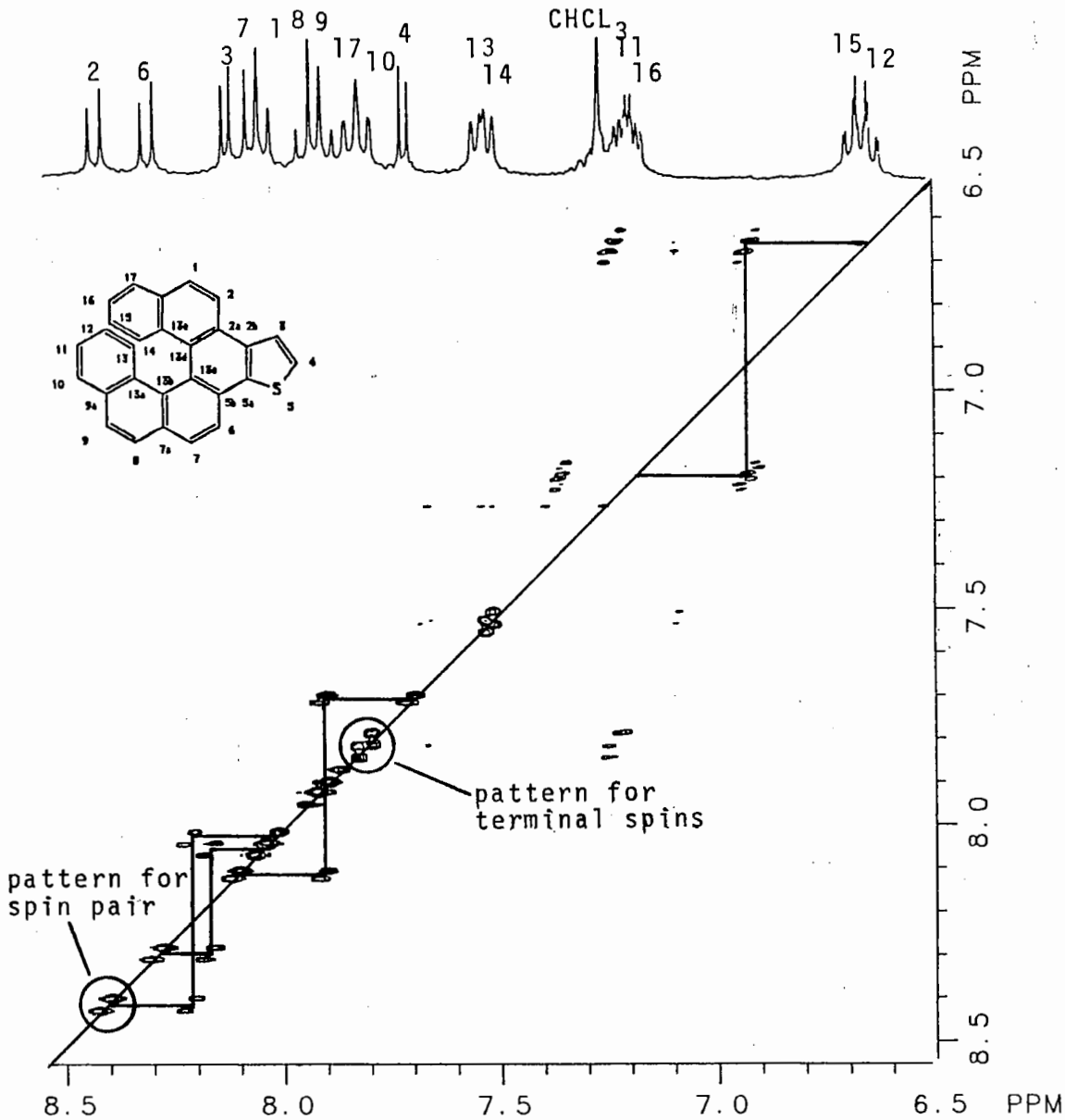

Fig.1 The contour map resulted from the pulse sequence shown in the previous page. Only part of the correlations has been illustrated.

Los Alamos

Los Alamos National Laboratory
Los Alamos,New Mexico 87545

DATE: 15-October-1986
MAIL STOP: MS C345

(Received October 20, 1986)

Prof. Barry Shapiro, Editor
Texas A&M University NMR Newsletter
Texas A&M University
Department of Chemistry
College Station, Texas 77843-3255

Dear Barry,

Subject: Multiquantum NMR of solids on a CXP

We have been working on some multiple quantum NMR experiments in solids[1] using time reversal[2] and "phase domain"[3] data acquisition. To do this it was necessary to install a variable phase shifter on our CXP-200. We used a Merrimac 8-bit digital phase shifter model PSDW-84-50.33 which operates at 50.33 MHz (*i.e.* ^{13}C at 4.7 T) with a phase shift resolution of 1.4 degrees. It is rather difficult to give a detailed description of the entire installation and operation of this phase shifter within the limits of a letter so we will give only a functional description here. Any CXP users interested in details can contact us for a more complete description.

The rf installation is straightforward, with the phase shifter being installed between the "rf modulator" and the "preamplifier" with BNC cables. We found it necessary to insert a small, broadband amplifier to make up for the $\approx$ 3 dB loss in the phase shifter. Although the phase shifter only gives a linear 1.4° phase shift per control bit when operated at 50.33 MHz, we have performed proton experiments at 200.13 MHz by mixing the CXP's 60 MHz intermediate frequency down to 50 MHz, phase shifting and then mixing back to 60 MHz. This corresponds to using two IF's for proton operation.

It was difficult to get flexible and fast communication between the spectrometer and the phase shifter to set the 8 control bits. We wanted to be able to switch phase quickly during a pulse program and to be able to switch back and forth between a manually preset phase and a pulse programmer controlled stepped phase for the phase domain data acquisition. This means that the phase shifter must be controlled by the pulse programmer, Z17c, rather than the Aspect computer. Basically, we use the levels of the first 8 bits of counter 4 in the pulse programmer (which are available at a 25 pin connector labelled "counter out" at the rear of the Z17c) for rapid advancing of the phase. We have built an interface with 8 switches providing TTL levels for preset, manual switching of the phase shifter. To switch rapidly between the "preset" phase and the phase set by counter 4 we use the receiver blanking pulse (which is on the Burndy connector at the rear of the pulse programmer) to switch between the two phases. The receiver in our CXP is sufficiently well protected by the duplexer and preamp protection circuits that giving up the receiver blanking function doesn't affect our data.

The interface with the pulse programmer was relatively easy to build and in operation the system is very simple. The biggest problem was sorting out the errors in our schematic for our Z17c pulse programmer. We have been quite successful in getting multiple quantum spectra with magic angle sample spinning as can be seen in the paper coming out this month. It would be nice to have more steps in our pulse programs because even with looping and phase lists, we have an insufficient number of steps for a few sequences that we would like to try.

We have documented the details of this system for our own future use so anyone needing a detailed description can contact us.

REFERENCES

1. B.H. Meier and W.L. Earl, "Excitation of Multiple Quantum Transitions Under Magic Angle Spinning Conditions: Adamantane" to be published in *J. Chem. Phys.* 1 November 1986.

2. Y.S. Yen and A. Pines, *J. Chem. Phys.* **78**, 3579 (1983) and J. Baum, M. Munowitz, A.N. Garroway, and A. Pines, *J. Chem. Phys.* **83**, 2015 (1985).

3. S. Emid, *Physica* **128B**, 79 (1985).

Sincerely,

ON VACATION
IN MEXICO

Bill

Bill

Beat H. Meier William E. Wageman and William L. Earl.

Los Alamos

Los Alamos National Laboratory
Los Alamos,New Mexico 87545
Group INC-4, Mail Stop C345

Position Available:

I would like to point out that we have a labwide, competitive, postdoctoral program at Los Alamos with many nice features including salaries near 30 k per year. I would be interested in hearing from any potential applicants. Our present interests are primarily in solid state NMR especially in molecular dynamics and solid state chemical reactions and in some curious and difficult inorganic compounds. The detailed projects would depend on the interest and background of the applicants. Applications and final acceptance are made through a labwide competition so there is a delay of several months in the application process. Interested applicants can contact me at the address above or by telephone at (505) 667-0773. They should include a *curriculum vita*, transcripts of undergraduate and graduate grades (not necessarily an official transcript), a simple, informal description of interests, a list of publications (including those submitted but not yet published), and the names of at least 3 references. Applicants should know NMR but not necessarily solid state NMR.

Bill

William L. Earl.

CHEMICAL INSTITUTE
UNIVERSITY OF AARHUS

NMR Laboratory
Department of Organic Chemistry
HANS JØRGEN JAKOBSEN

8000 Aarhus C, Denmark
Telephone 45-6-12 46 33
Telex 64767 AAUSCI DK

October 16, 1986
HJJ/ATL

(Received October 29, 1986)

Professor BERNARD L. SHAPIRO
Department of Chemistry
Texas A & M University
COLLEGE STATION, Texas 77843-3255
USA

An Efficient Probe for High Field Multinuclear CP/MAS NMR of Solids

Dear Barry:

We wish to inform the readers of the Newsletters on some important improvements of our CP/MAS probe reported earlier (TAMU NMR 322-61) and developed for the Varian XL-300 spectrometer. The improvements concern both the spinning speed and electronic performances of the probe and are illustrated in the accompanying spectra of figures 1 and 2. With our modifications we now have the following features for the probe:

(1) The spinning speed of the 7 mm o.d. rotors can routinely and accurately be set at any value up to at least 10 kHz with a stability of a few hertz. To obtain spectra at high spinning frequencies we use rotors machined from PSZ and Si_3N_4 ceramics, e.g. Si_3N_4 rotors for 10 kHz spectra. Air drive pressures of 1 and 4 bar are required for 4.5 and 9.0 kHz spinning, respectively.

(2) The double-tuned X/^{1}H probe circuit has a broadband observation channel. So far we have observed nuclei in the frequency range from ^{27}Al (78.16 MHz) to ^{2}H (46.04 MHz) using switchable chip capacitors.

(3) The isolation of the observation (e.g. ^{13}C) channel from the ^{1}H decoupling channel is about 45 db.

(4) With the high Q for the decoupling channel (Q ~ 350) we generate a ^{1}H decoupling field $\gamma_H B_{1H}/2\pi$ = 80 kHz (B_{1H} = 19 gauss) using only about 25 watts of power. For the observation channel we generate a 90° ^{13}C pulse in 6.1 μsec (B_{1C} = 38 gauss) using 100 watts of power.

(5) The sensitivity (S/N) for the observation channel of the probe is illustrated in Figs. 1 and 2. For example for ^{13}C we obtain a S/N ratio of 200-230/1 for 160 mg of hexamethylbenzene based on the CH_3 resonance from a CP/MAS experiment using 4 scans.

Sincerely,

Preben Daugaard Vagn Langer Hans J. Jakobsen

Preben Daugaard Vagn Langer Hans J. Jakobsen

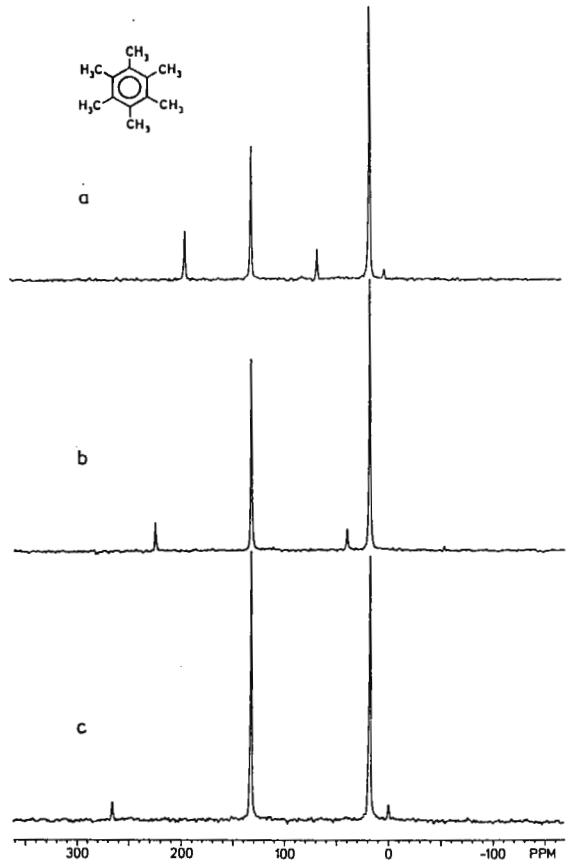

Fig. 1. ^{13}C (75.43 NHz) CP/MAS NMR spectra of hexamethylbenzene (160 mg) recorded on a Varian XL-300 spectrometer at 7.05 Tesla using different spinning rates, ν_R, and rotor materials. (a) Macor rotor, ν_R = 4860 Hz; (b) Al_2O_3 rotor, ν_R = 7000 Hz; (c) Si_3N_4 rotor, ν_R = 10080 Hz. The spectra were obtained using 4 scans and a linebroadening of 50 Hz has been applied.

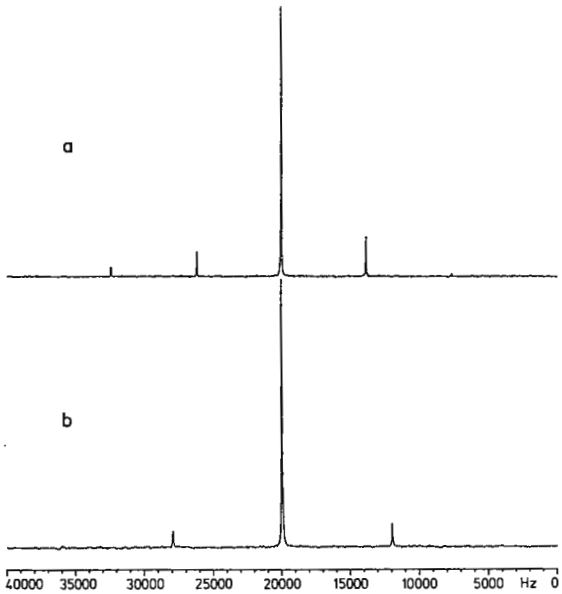

Fig. 2. ^{113}Cd (66.54 MHz) CP/MAS NMR spectra of $Cd(NO_3)_3 \cdot 4\ H_2O$ (390 mg) obtained in 4 scans using (a) Al_2O_3 rotor, ν_R = 6200 Hz; (b) Si_3N_4 rotor, ν_R = 8000 Hz. A linebroadening of 25 Hz has been employed for both spectra.

PHYSICAL CHEMISTRY LABORATORY

OXFORD UNIVERSITY

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OXFORD
OX1 3QZ

RF/SL

17th October, 1986.

(Received October 24, 1986)

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

Dear Barry,

"Computer Optimized Solvent Suppression"

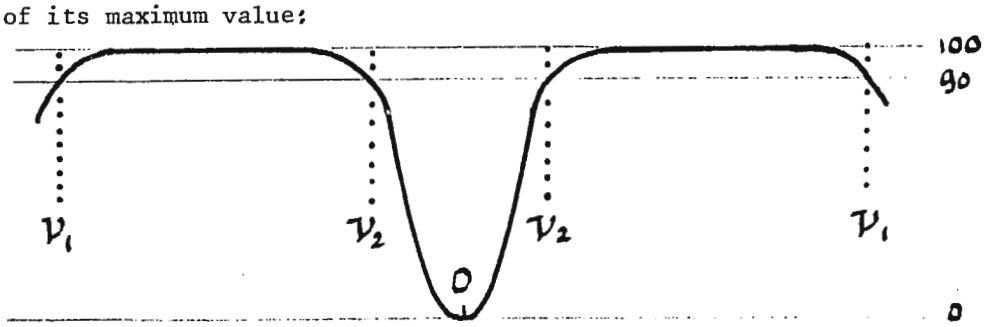
I am so terrified of being disenfranchised after so many years as a subscriber to TAMUNMR that I have borrowed this story from my colleague Peter Hore who has an independent NMR group in this laboratory.

You will remember that some time ago Peter Hore proposed the $1\bar{3}3\bar{1}$ sequence for solvent peak suppression (1), and showed that the null condition at the carrier frequency is relatively broad and insensitive to B_0 and B_1 inhomogeneity. It also tolerates a missetting of the 1:3 ratio of pulsewidths.

The difficulty with this and the related solvent suppression sequences is that the spectral region where there is appreciable excitation is relatively narrow, leading to severe intensity distortions for the observed spectrum. The idea is to make this excitation region broader and flatter by modifying the pulse sequence using A.J. Shaka's method of non-linear computer optimization (2). Peter defines a figure of merit ψ such that

$$\psi = \frac{|\nu_1 - \nu_2|}{|\nu_1 + \nu_2|} \qquad 0 < \psi < 1$$

where ν_1 and ν_2 are the offsets defining the region where the excitation is 90% of its maximum value;



We want ψ to be as large as possible, to give a flat excitation region not too distant from the carrier.

(continued on page 49)

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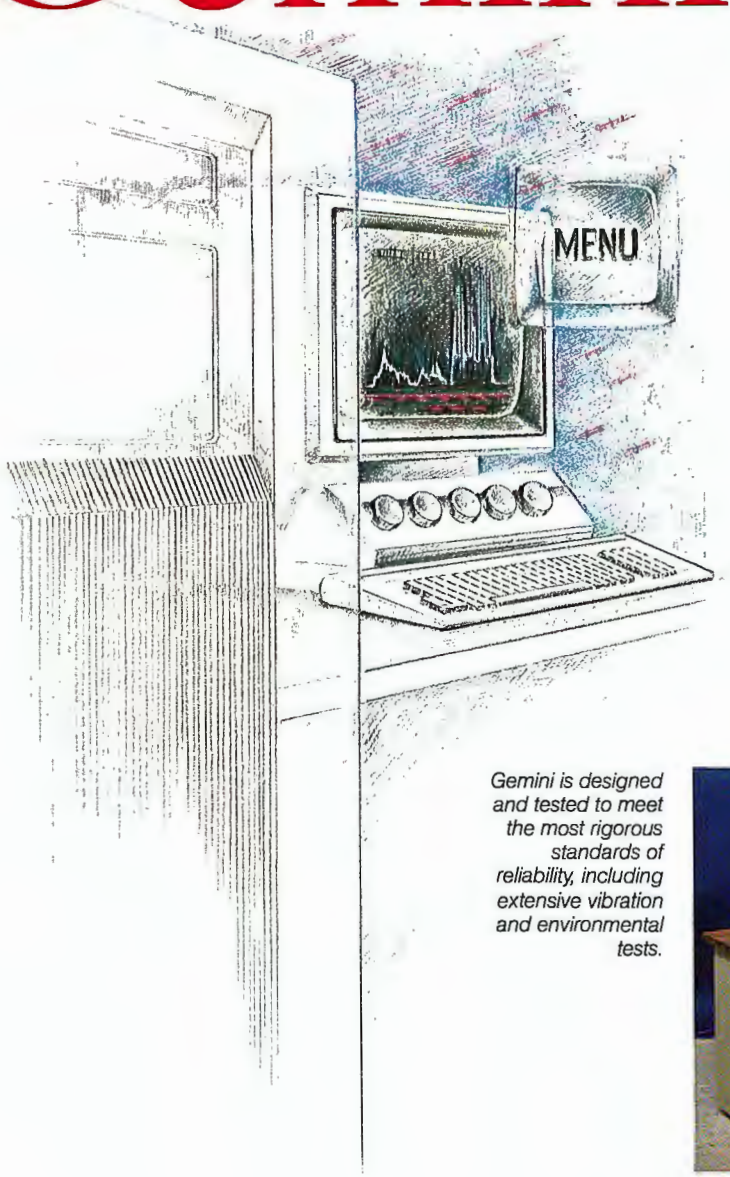

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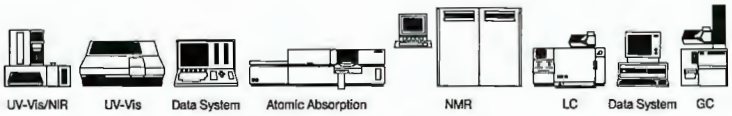

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(continued from page 46)

To cut a long story short, I will simply say that the search yielded two new pulse sequences A and B that have figures of merit markedly better than that of the $1\overline{3}3\overline{1}$ sequence ($\psi = 0.28$).

The A sequence is:

$$7.1 - 4\tau - \overline{10.9} - \tau - \overline{55.1} - \tau - 55.1 - \tau - 10.9 - 4\tau - \overline{7.1}$$

where the flip angles are in degrees and overbars indicate phase inversion. This has $\psi = 0.76$.

The other sequence B is:

$$6.8 - \tau - 4.5 - \tau - \overline{7.4} - \tau - \overline{53.3} - \tau - 53.3 - \tau - 7.4 - \tau - \overline{4.5} - \tau - \overline{6.8}$$

This has $\psi = 0.66$ but a smaller phase gradient across the spectrum.

Note that these sequences are antisymmetrical about their centres; the second half is the same as the first half but reversed in time and inverted in phase. Such sequences behave symmetrically with respect to resonance offset and have a null at the transmitter frequency. Note, however, that unlike the binomial sequences, the pulse phases do not alternate along the sequence.

Interestingly, the computer search also identified two sequences previously proposed by Starčuk and Sklenář (3) for the same purpose.

When the pulse sequences A and B were tested experimentally on our Varian XL-400 there was good agreement with the theory, confirming that they do indeed have a wide excitation bandwidth. Suppression ratios for the solvent peak were in the range 200-400, comparable with that obtained with the $1\overline{3}3\overline{1}$ sequence.

Yours sincerely,

Ray

Ray Freeman

(1) P.J. Hore, J. Magn. Reson. 55, 283 (1983).
(2) A.J. Shaka, Chem. Phys. Lett. 120, 201 (1985).
(3) Z. Starčuk and V. Sklenář, J. Magn. Reson. 66, 391 (1986).

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMISTRY
CAMBRIDGE, MASSACHUSETTS 02139

October 27, 1986

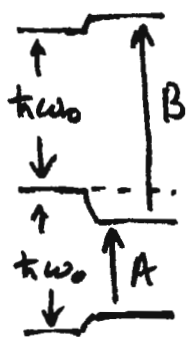
(Received 31 October 1986)

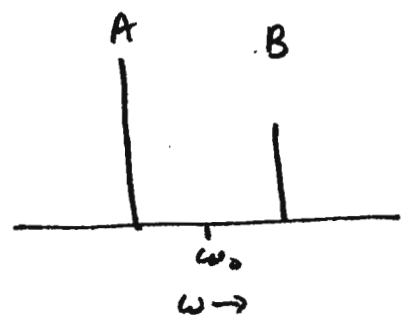
Professor B. L. Shapiro, Editor
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, Texas 77843

NMR Line Shape Thermometry

Dear Barry:

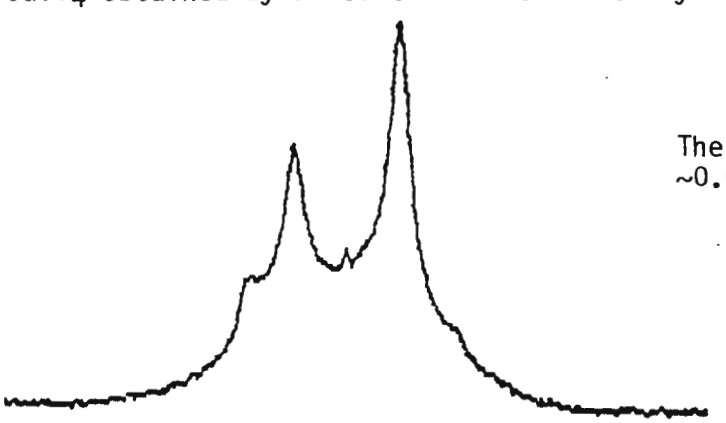
In our work on NMR at very low temperatures it became important to verify that the temperatures of our samples were actually the same as measured by conventional means (i.e., by a carbon resistance thermometer mounted a few cm from the sample, calibrated at "high" temperatures against the vapor pressure of helium). The NMR spectrum of a multi-level system offers an attractive possibility: Consider the classic Pake doublet arising from a 2-spin system





In the high temperature approximation $\hbar\omega_0/kT \ll 1$ the lines are equally intense, but at low temperatures the intensity ratio $B/A = e^{-\hbar\omega_0/kT}$ departs from unity.

Here is a proton powder pattern from the H_2O molecular slightly hydrated $CaSO_4$ obtained by FT of the FID elicited by an 8° pulse.



The temperature comes out to ~0.010 ± .001K.

The following points will be amplified later:

1. A small-angle tipping pulse must be used.
2. Such experiments can determine "absolute signs" of spin-coupling constants.
3. Slightly hydrated $CaSO_4$ is not the thermodynamically expected mixture of $CaSO_4$ and $CaSO_4 \cdot \frac{1}{2}H_2O$.
4. There are "anomalies" in the spin-lattice relaxation of this and related samples.

Yours,

Philip Kuhns John Waugh Oded Gonen

IBM Instruments Inc.

Orchard Park
PO Box 332 Danbury CT 06810

Telephone: 203 796 2500

September 29, 1986
(Received October 2, 1986)

Professor Bernard L. Shapiro
TAMUNMR
Texas A&M University
Department of Chemistry
College Station, TX 77843-3255

"FT NMR Techniques for Organic Chemists"

Dear Barry:

Bob Johnson and I have just completed a short article covering the fundamentals of FT NMR from the organic chemists' standpoint. It covers how NMR works, and takes the chemist through the assignment of the proton and carbon lines in the spectrum of a tripeptide using DEPT, COSY, and proton-carbon correlated 2D techniques. While it will not contain any "news" to any of TAMUNMR's readers, it might be helpful in educating graduate students or more synthetically oriented colleagues.

With the advent of PC-based "desk top publishing," we were able to get from idea to camera ready copy in just a couple of weeks and we will have copies to distribute on request by the time this appears in print.

Sincerely,

Jim Bob

James W. Cooper Robert D. Johnson

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D-8046 GARCHING , 22.10.1986
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Telex: 17898174
Teletex: 898174
(Received 31 October 1986)

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

Title: ^{185}Re and ^{187}Re solid state NMR

Dear Professor Shapiro,

our ^{127}I solid state NMR studies of metaperiodates with alkyl- or aryl-substituted cations of main group V revealed second order quadrupole effects with quadrupole coupling constants in the range of 2 - 7 MHz [1]. In the special cases of the samples $(CH_3)_4PIO_4$ and $(C_2H_5)_4NIO_4$ the ^{127}I solid state NMR spectra showed no visible quadrupole effects of first or second order [2].

From these results we calculated maximum values of the ^{185}Re and ^{187}Re quadrupole coupling constants of the analogous metaperrhenates. We expected them in an accessible range of our Bruker CXP 200 FT-NMR spectrometer. Despite the very large ^{185}Re and ^{187}Re nuclear moments we succeeded in measuring solid state NMR spectra of $(CH_3)_4PReO_4$ and $(C_2H_5)_4NReO_4$. For the first time, it was possible to record ^{185}Re and ^{187}Re NMR powder spectra of rhenium compounds apart from a Knight shift investigation of cubic ReO_3 at T = 1 - 4 K [3].

For polycrystalline $(CH_3)_4PReO_4$ we measured a complete ^{185}Re and ^{187}Re solid state NMR spectrum with second order quadrupole splittings. The quadrupole coupling constants of this metaperrhenate are calculated:

$e^2qQ(^{185}Re)/h = 18.2 \pm 0.2$ MHz for T = 307 K, $\eta \rightarrow 0$ and

$e^2qQ(^{187}Re)/h = 16.9 \pm 0.2$ MHz for T = 307 K, $\eta \rightarrow 0$.

The measured temperature coefficient $\bar{\alpha} = -1.2 \cdot 10^{-2}\ K^{-1}$ indicates the presence of strong volume effects in the sense of the Kushida-Benedek-Bloembergen theory [4]. The temperature dependent quadrupole splitted NMR signals of polycrystalline $(CH_3)_4PReO_4$ do not give any indication of a change of the asymmetry parameter η.

For $(C_2H_5)_4NReO_4$ we also found ^{185}Re-, ^{187}Re-solid state NMR spectra. In this case the electric field gradient at the Re-nuclei is so small that no quadrupole effects of first or second order are resolvable. Detailed results will be published soon.

Yours sincerely

P. Burkert

(Dr. P.K. Burkert)

D. Klobasa

(Dr. D.G. Klobasa)

Please credit this contribution to Prof. F.H. Köhler.

References:

[1] D.G.Klobasa, P.K.Burkert and G.Müller, Z.Naturforsch.41a, 330 (1986).

[2] D.G.Klobasa, Thesis, TU München 1986.

[3] A.Narath and D.C.Barham, Phys.Rev.176, 176 (1968).

[4] T.Kushida, G.B.Benedek and N.Bloembergen, Phys.Rev.104, 1364 (1956).

IBM Instruments Inc.

Orchard Park
P.O. Box 332, Danbury, CT 06810

Telephone: 203-796-2500

October 8, 1986
(Received October 10, 1986)

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

TITLE: F1 Quadrature Detection for Rotating Frame 2DNMR

Dear Barry:

We have found that the phase programs which we developed for chemical exchange in the rotating frame (1) can also be applied, with the appropriate phase alternation where needed, to CAMELSPIN (2), to ROESY (3), to TOCSY (4), and to HOHAHA (5). We noticed that the diagonal after 2DFT goes from upper left to lower right corner no matter how we modified the basic phase programs. This is due to the fact that spin locking occurs whether spins and rf field are parallel or antiparallel. However, the REV command in the DISNMR software allows for reversal of the F1 dimension and therefore the use of symmetrization through the SYM command.

Sincerily,

Hermann E. Bleich

Hermann E. Bleich

(1) Bleich and Wilde, J.Magn.Reson. 56,149-150(1984)
(2) Bothner-By et al. J.Amer.Chem.Soc. 106, 811-813 (1984)
(3) Bax and Davis, J.Magn.Reson. 63, 207-213 (1985)
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(5) Davis and Bax, J.Amer.Chem.Soc. 107, 2820-2821 (1985)

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NMR SPECTROSCOPY

Main Speakers

N Boden	*Leeds, UK*
G Bodenhausen	*Lausanne, Switzerland*
R G Griffin	*MIT, USA*
H Günther	*Siegen, FRG*
L Jelinski	*Bell Labs, USA*
R Kaptein	*Groningen, The Netherlands*
W Klemperer	*Illinois, USA*
A E Merbach	*Lausanne, Switzerland*
D Neuhaus	*Parke-Davies, Cambridge, UK*
D J Patel	*Columbia, USA*
J Seelig	*Basel, Switzerland*
C P Slichter	*Illinois, USA*
I C P Smith	*Ottawa, Canada*
J A S Smith	*KQC, London, UK*
J Staunton	*Cambridge, UK*
R L Vold	*California, USA*
C S Yannoni	*IBM, San Jose, USA*

UNIVERSITY OF KENT AT CANTERBURY
6–10 JULY 1987

Eighth International Meeting on NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY
University of Kent at Canterbury
6–10 July 1987

Introduction

The eighth international meeting on NMR Spectroscopy will take place at the University of Kent at Canterbury from Monday 6 July to Friday 12 July 1987, with participants foregathering on the afternoon and evening of Sunday 5 July 1987.

The meeting is being organised jointly by the Royal Society of Chemistry, and the Society's NMR Discussion Group.

The meeting is the eighth in the series (now biennial), previous meetings having taken place as follows:

1969 Birmingham	1972 Guildford	1975 St Andrews	1978 York
1981 Exeter	1983 Edinburgh	1985 Cambridge	

Important Note

Numbers for the meeting may exceed the capacity of the lecture theatre, and as a consequence, arrangements may have to be made for a closed circuit TV link, or even to limit the number of persons registering. Details regarding any such arrangements will be notified in Circular 2.

Scientific Programme

The meeting will deal with selected topics in NMR Spectroscopy and will comprise the following eight symposia:

1. **NMR in Organic Chemistry**
   Chairman: I H Sadler
   Invited speakers: Dr J Staunton
   Professor H Günther

2. **NMR in Solids**
   Chairman: K J Packer
   Invited speakers: Professor C P Slichter
   Dr C S Yannoni
   Professor J A S Smith

3. **NMR in Industry**
   Chairman: G R Bedford
   Invited speakers: Dr D Neuhaus
   Dr L Jelinski

4. **NMR in Inorganic Chemistry**
   Chairman: J W Akitt
   Invited speakers: Professor W Klemperer
   Professor A E Merbach

5. **Biomedical NMR**
   Chairman: P J Sadler
   Invited speakers: Professor I C P Smith
   Professor J Seelig

6. **Large Molecule NMR**
   Chairman: G C K Roberts
   Invited speakers: Professor R G Griffin
   Professor D J Patel

7. **Experimental Techniques in NMR**
   Chairman: R Freeman
   Invited speakers: Dr G Bodenhausen
   Professor R Kaptein

8. **NMR in Physical Chemistry**
   Chairman: J Emsley
   Invited speakers: Professor R L Vold
   Dr N Boden

Poster Sessions and Contributed Papers

Two poster sessions are planned for the programme. There will also be an opportunity for a limited number of short contributions to be presented orally in the symposia. Anyone wishing to contribute a paper to one of the poster sessions, or to one of the symposia, should submit, **NOT LATER THAN 26 JANUARY 1987** a title and synopsis (up to 250 words) to Dr John F Gibson, The Royal Society of Chemistry, Burlington House, London W1V 0BN, indicating the appropriate symposium topic.

Synopses will **NOT** be published.

Social Programme

A full programme of evening social events is planned, to include:

Receptions (Sunday and Monday)
Concert in Canterbury Cathedral (Tuesday)
Conference Dinner (Thursday)

As has been the practice with all previous NMR meetings, the scientific sessions on Wednesday will terminate at lunchtime, so as to enable persons to participate in organised excursions on Wednesday afternoon and evening. Excursions proposed include: Leeds Castle, Hever Castle and other places of historic interest and scenic beauty in the area.

In addition, an accompanying persons programme will be arranged.

Fees

The fees for attendance at the meeting have not been finalised, but it seems likely that the conference fee will be around £80 (students £35), and the accommodation for the full five day period will be around £100.

TO: Dr John F Gibson
Secretary (Scientific)
The Royal Society of Chemistry
Burlington House
London W1V 0BN

Please send me further details of the eighth international meeting on **NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY**, to be held at the University of Kent at Canterbury, 6–10 July 1987. (Available in February/early March 1987).

PLEASE WRITE NAME AND ADDRESS CLEARLY ON THIS LABEL

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If undelivered, please return to:

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Burlington House, London W1V 0BN, UK.

Please insert an 'X' in the appropriate box(es):

☐ I am interested in attending the 8th NMR meeting and would like to receive the Second Circular.

☐ I intend to offer a paper, for POSTER/ORAL presentation in Symposium

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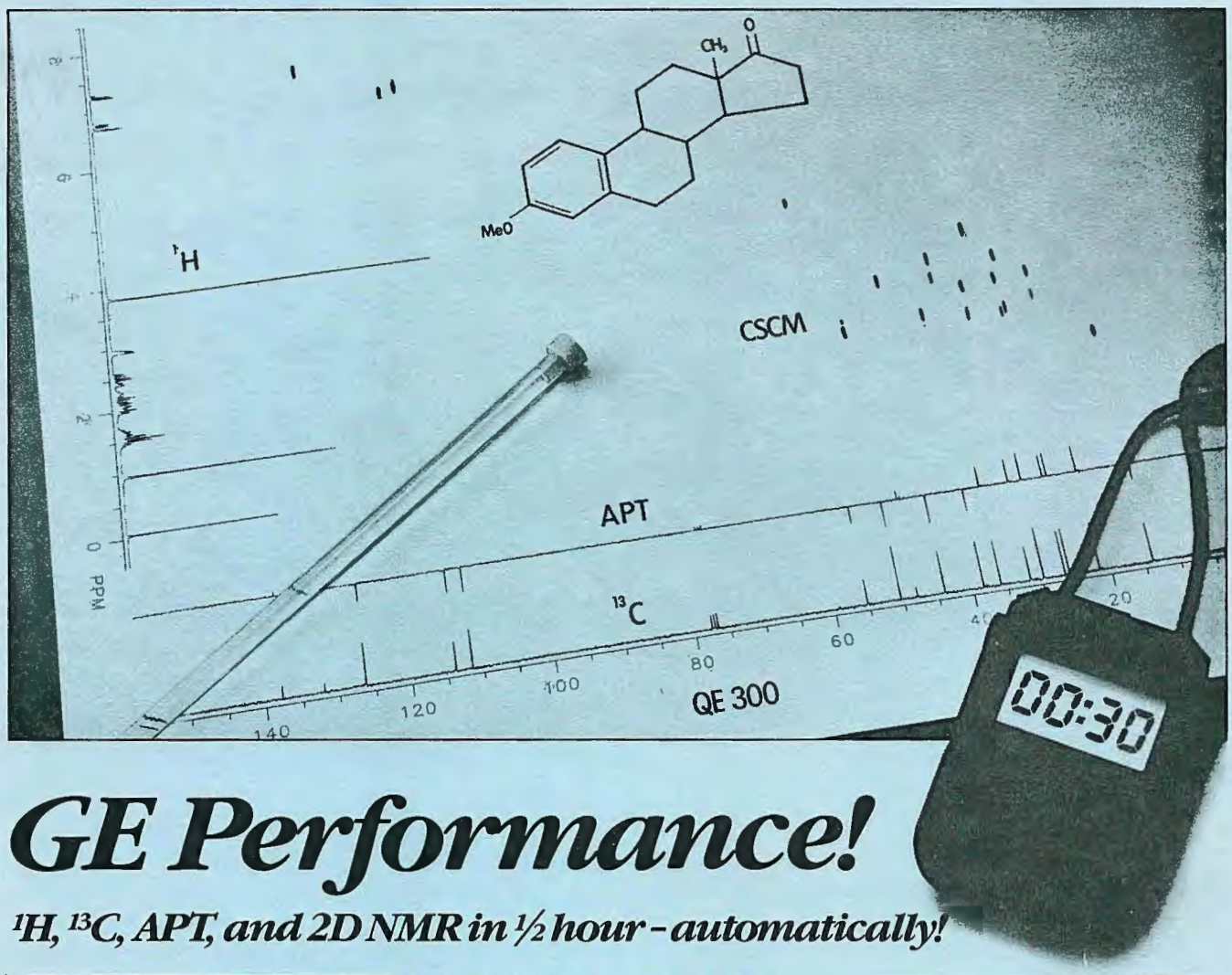
Please indicate whether POSTER or ORAL contribution preferred, and also the particular symposium



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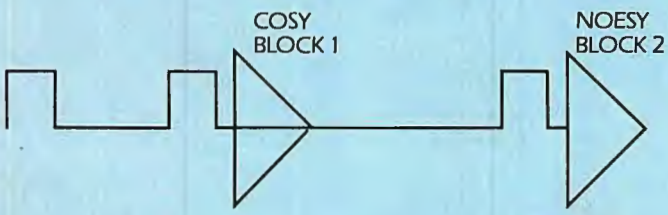

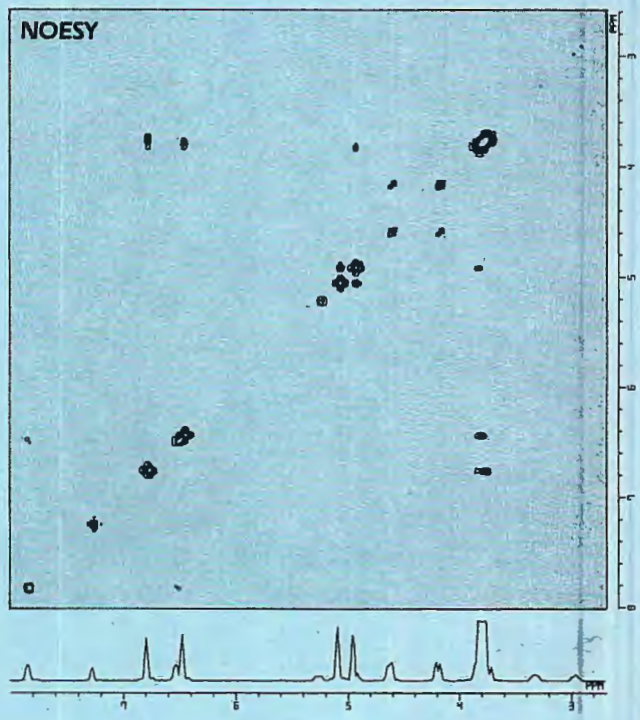

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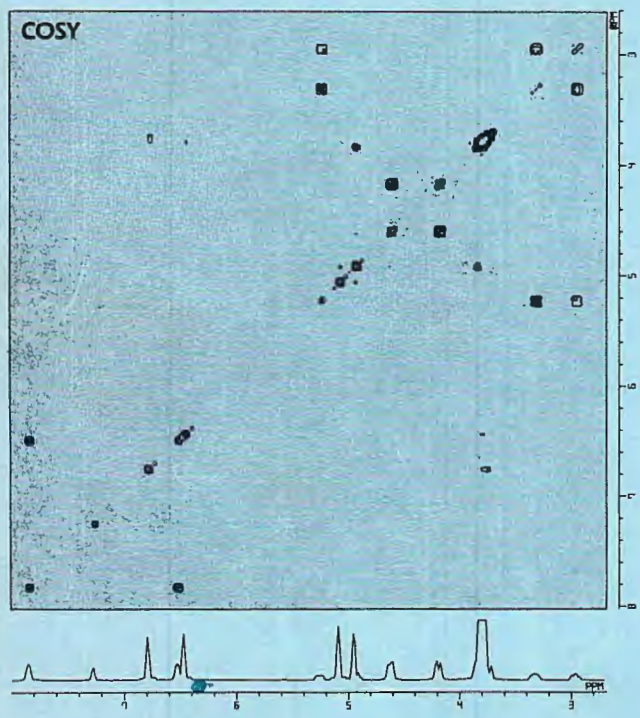

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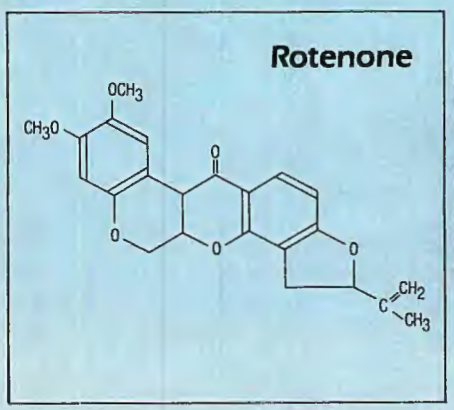

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