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# NMR

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**Forthcoming NMR Meetings** (Additional listings are solicited)

**Seventh International Meeting on NMR Spectroscopy** - July 8-12, 1985, University of Cambridge; Chairman: Dr. Derek Shaw; Details from Dr. John F. Gibson, Secretary (Scientific), The Royal Society of Chemistry, Burlington House, London W1V 0BN England.

**12th FACSS Meeting** - Sept. 30-Oct. 4, 1985, Philadelphia, PA; NMR Program Chairman: Rodney D. Farlee, E.I. du Pont de Nemours & Co., Inc., Experimental Station, Building 328, Wilmington, Delaware 19898; see page 9.

**27th ENC** - April 13-17, 1986, Baltimore Hilton; Chairman: R.G. Bryant, Department of Radiology, University of Rochester Medical Center, 601 Elmwood Avenue, Rochester, New York 14642.

Suggestions for other types of articles, news items, etc., to appear in the Newsletter would be welcomed - please make your wishes known.

*Have you returned the readership survey card which was inserted into issue No. 317 (February)? If not, please let us know promptly how many people routinely read, inspect, or have the opportunity to use your copy of the Newsletter. Your cooperation will be appreciated.*

Newsletter readers will note that this issue contains more advertising than usual. We are, of course, happy that more advertisers are finding the Newsletter a useful means of communication. We also are very gratified at the continuing support of our several long-standing, regular advertisers. For both new and older companies who have helped support the Newsletter for so long, it would be useful and appreciated if the readership would take what opportunities present themselves to make their appreciation known to the advertisers, and to mention the appearance of useful advertising copy in the Newsletter. It will be helpful for our advertisers to learn that their Newsletter advertisements are in fact being read and considered. With the continuing increase in costs, primarily those for printing and postage, the Newsletter certainly could use a few additional advertisements, as well as increased Sponsorship and Contributorship participation by those companies, etc., able to help. Your efforts along these lines will be greatly appreciated, and we will be happy to provide suitable details to anyone interested.

Please note revised dates.

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. 321 ----- 29 May 1985

No. 322 ----- 26 June 1985



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Dr. Bernard SHAPIRO  
Department of Chemistry  
Texas A & M University  
COLLEGE STATION  
Texas 77843  
USA

V/Réf.

N/Réf. LH/ri/mtt 2.1

Lausanne, le

February 21, 1985

Concerns : Exchange rates at variable pressure as obtained by NMR measurements without high pressure NMR facilities.

Dear Professor Shapiro,

In our laboratory we have studied the exchange on water molecules on hexa-aqua ruthenium(III) as a function of temperature using  $^{17}\text{O}$  labelled  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ . The complex was mixed with acidified ordinary water and the exchange process monitored by recording  $^{17}\text{O}$  spectra at fixed time intervals (Fig. 1). The observed exchange rates  $k_{\text{obs}}$  are very slow, leading to half-lives between 10 min and 120 h depending on temperature and acidity. Because we were very interested in the assignment of a reaction mechanism for this exchange, we had to measure exchange rates at variable pressure to obtain the volume of activation.<sup>2</sup>

Using the isotopic labelling technique, we have to follow the reaction 3 half-lives to obtain reliable results blocking our spectrometer for weeks. We chose to prepare a series of solutions of various acidities by mixing the enriched complex with water into teflon cells (Fig. 2) and pressurized them in stainless steel vessels immersed into a thermostated bath. We used 4 bombs each of them containing 3 cells and set to 1, 700, 1400, and 2100 bars, respectively. NMR spectra were recorded in the following way : the bomb was slowly brought to ambient pressure, the teflon cells transferred into ordinary 10 mm o.d. NMR tubes, FID's were accumulated, and finally the samples were brought back into the bomb and the pressure reset. The overall operation took about 15 min and thus the errors in  $k_{\text{obs}}$  due to pressure changes are less than 5 %. Caution was taken to lower and raise the pressure slowly to avoid cooling or heating of the samples. The pressure was controlled during the whole experiment by piezoelectric gauges interfaced to a Commodore 64 micro-computer.

The exchange rates for water substitution on ruthenium(III) obtained by this method are shown in Fig. 3. The volumes of activation are  $-8.3 \pm 2.1 \text{ cm}^3 \text{ mol}^{-1}$  for exchange on  $\text{Ru}(\text{H}_2\text{O})_6^{3+}$  and  $-2.1 \pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$  for water exchange on the  $\text{Ru}(\text{H}_2\text{O})_5\text{OH}^{2+}$  species.

- (1) P. Bernhard, Ph.D. Thesis, University of Bern, 1984.  
 (2) A.E. Merbach, Pure and Appl. Chem, 54, 1479 (1982).

With my best regards

Yours sincerely

*L. Helm*

Dr. Lothar Helm

P.S. Please credit this contribution to the account of A.E. Merbach

Fig. 1.  $^{17}\text{O}$ -NMR spectra, recorded at 27.11 MHz; bound water signal (a) about 35ppm downfield from free water (b) ( $T = 314.3 \text{ K}$ )

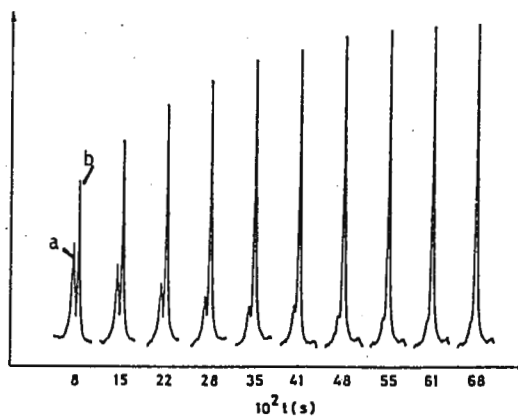


Fig. 2. home built teflon cell, fitting into ordinary NMR tubes (10 mm o.d.); sample volume about  $0.9 \text{ cm}^3$

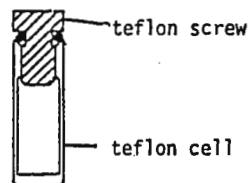
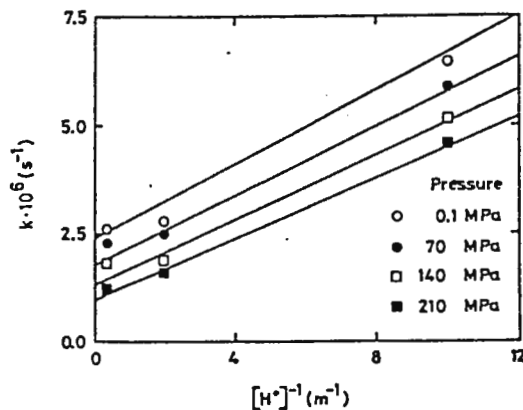


Fig. 3 pressure and acid dependence of the observed exchange rate ( $T = 288 \text{ K}$ )



Princeton University

DEPARTMENT OF CHEMISTRY

PRINCETON, NEW JERSEY 08544

February 28, 1985

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

"Fluorine-Carbon Coupling in Rigid Polycyclic Systems"

Dear Professor Shapiro,

We report here the results of C-13 chemical shifts and C-13/F-19 coupling constants for a series of related norbornadiene derivatives. Compounds 1-3 were all formed via difluorocarbene reaction with norbornadiene. Their C-13 nmr spectra all show unequal coupling between the fluorine atoms and each carbon atom, with one exception. This difference is most remarkable at C-1, with a difference of 44.2 Hz for the exo-substituted derivative 1. We also see substantial 4-bond coupling in these systems, of as much as 14.5 Hz (again in derivative 1).

Sign determinations of the coupling constants were not made. Couplings not reported were less than 0.5 Hz.

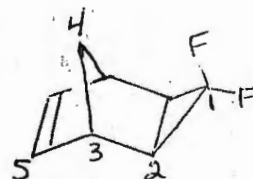
Please credit this contribution to the account of Mary W. Baum.

Sincerely,

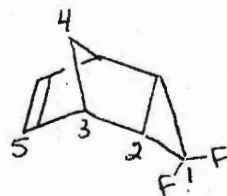
*Maitland Jones, Jr.*  
 Maitland Jones, Jr.

*Ulf Misslitz Mary W. Baum*  
 Ulf Misslitz Mary W. Baum

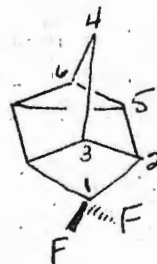
Carbon	$\delta$	$n_J$		$n_F$
1	126.66	318.7	274.5	1
2	34.60	2.7	-	2
3	42.40	15.5	9.5	3
4	40.89	14.5	-	4
5	140.73	3.5	2.0	4



Carbon	$\delta$	$n_J$		$n_F$
1	116.00	268.9	247.9	1
2	31.91	14.5	10.8	2
3	43.99	-	-	3
4	66.15	11.7	8.7	4
5	136.10	3.3	-	4



Carbon	$\delta$	$n_J$		$n_F$
1	128.23	300.4	271.2	1
2	49.29	20.1	20.1	2
3	33.91	13.8	2.3	3
4	31.80	6.4	-	4
5	12.92	5.6	-	3
6	25.64	4.7	-	4





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## STATION DE RECHERCHES SUR LA VIANDE



Professor SHAPIRO  
Department of Chemistry  
College of Science  
Texas University  
College Station TX 77843  
U.S.A.

Références à rappeler :

NMR MEASUREMENTS ON MEAT  
OF VARIOUS QUALITIES\*

THEIX, March 4, 1985

Dear Doctor SHAPIRO,

One of the most important meat quality characteristics is water holding capacity (WHC), which depends on the binding of water to meat proteins. NMR is a technique for studying the motility of water in relation to the surrounding structures in biological samples and could be useful in the study of water binding mechanisms in muscle.

The  $^1\text{H}$  spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation times of water protons were recorded at 20 MHz. The observed  $T_1$  was single-exponential but a two-component  $T_2$  relaxation behaviour (components referred to as  $T_{2a}$  and  $T_{2b}$ ) was observed at 24 h post mortem. Highly significant relationships were found between  $T_1$  and all the meat characteristics studied.  $T_{2a}$  was related only to ultimate pH, whereas  $T_{2b}$  was more closely related to the rate of post mortem pH fall and protein denaturation criteria.

Sincerely yours,

A handwritten signature in dark ink, appearing to read "G. Monin", with a stylized flourish at the end.

G. MONIN

A handwritten signature in dark ink, appearing to read "J.P. Renou", with a stylized flourish at the end.

J.P. RENOU

\* RENOU J.P., MONIN G., SELLIER P. submitted for publication "Meat Science"



Montana State University  
Bozeman, Montana 59717

Department of Chemistry  
College of Letters and Science

Telephone (406) 994-4801

February 26, 1985

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

Title: Natural Abundance Carbon-13 Spectra of Yeasts

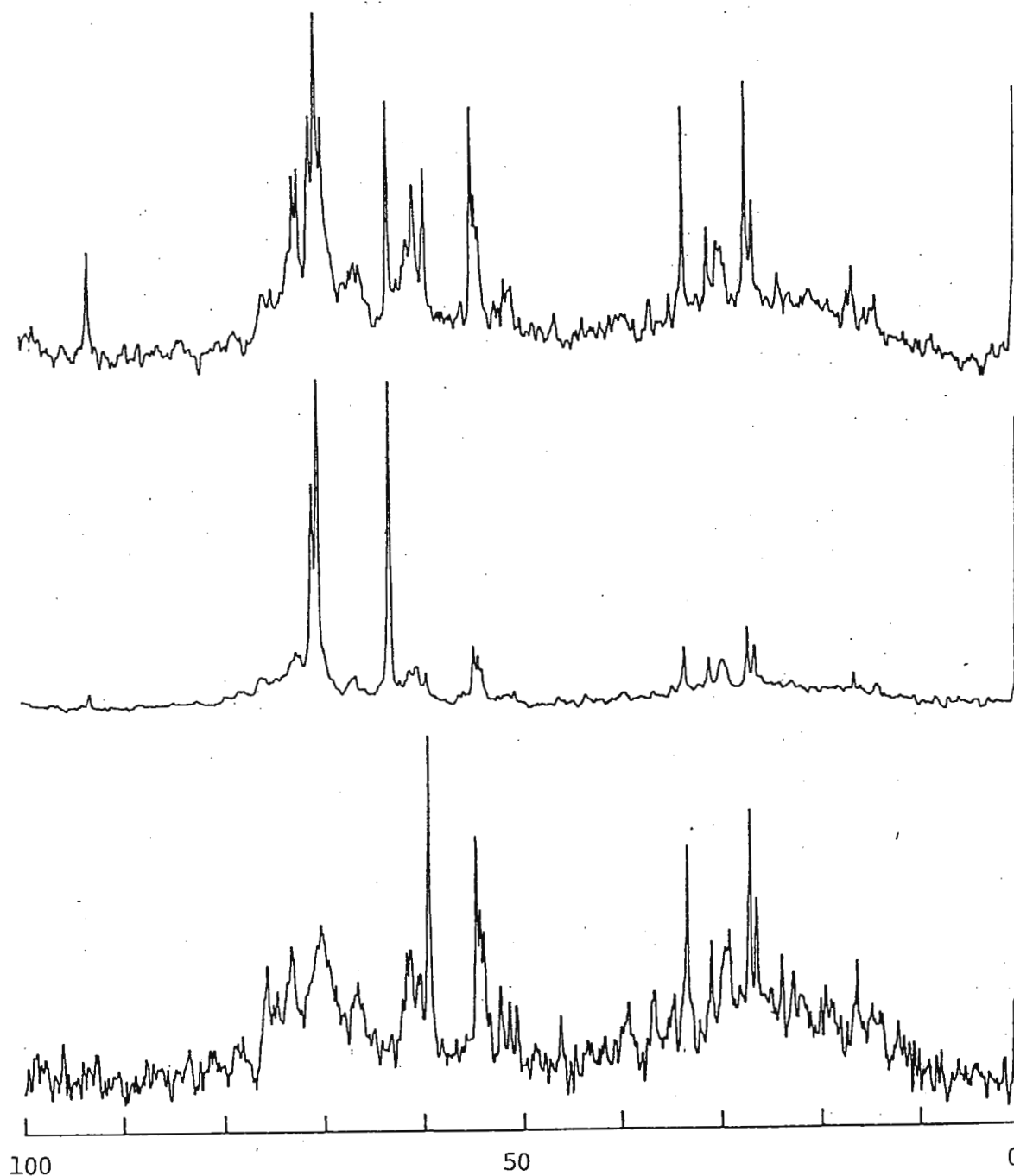
Dear Barry:

In recent years there have been many elegant uses made of high resolution carbon-13 NMR of living systems. These studies usually have entailed enriching at least one site of a metabolic precursor molecule with carbon-13 and observing the sequence of chemical reactions for the enriched site. High resolution natural abundance carbon-13 signals have been observed in living systems and a few studies have been reported on them. Studies have been carried out on mammalian tissue, plant tissue, single cell organisms, and several other life forms.

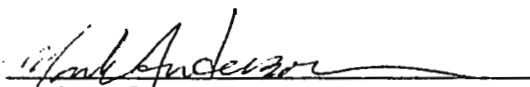
In the course of studying a problem in yeast metabolism via enriched carbon-13 NMR spectroscopy, we noticed that natural abundance spectra are well resolved, complex, and can be quite intense in this organism. There are many strains of yeast and many are virulent and widespread pathogens. Because of its simplicity and its noninvasive nature, carbon-13 spectroscopy seemed to present a reasonable tool for studying the differentiation of the strains of this organism and their biochemistry. Elsewhere we will soon report a detailed study of the spectra which are observed and some of the experimental conditions which influence these spectra.

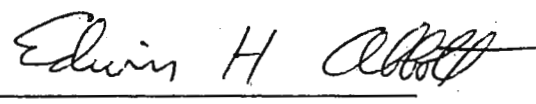
We have studied twenty-five different strains of the yeast Candida albicans under carefully controlled conditions of temperature, media and growth phase. The carbon-13 spectra of these strains fall into three general categories illustrated below.





These spectra are easily obtained. Six hundred pulses on a WM-250 are adequate. It is important to stress that the spectra are profoundly affected by virtually any change in the conditions under which the yeast are grown. If conditions are carefully controlled, NMR affords a convenient, rapid means of distinguishing among different species of yeast and among certain strains.

  
Mark Anderson

  
Edwin H. Abbott

## University of Durham

Department of Chemistry

Science Laboratories, South Road, DURHAM,  
GREAT BRITAIN, DH1 3LE  
Telephone: Durham (0385) 64971

Professor of Chemistry:  
Robin K. Harris

18th February, 1985.

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

Dear Barry,

## SOLID-STATE NMR OF DIPHOSPHINE DISULPHIDES

Your dunning letters have at last forced me to respond, though there is no chance that this will reach you before your 4th February deadline. I shall assume a cross-Atlantic delay of up to a month is acceptable.

This is, of course, my first contribution from a new address. I am now at England's third-oldest university, sited in the historic city of Durham. Our Bruker CXP200 was moved here from Norwich without any disasters, though it took longer to smooth out all the difficulties than I had hoped. It is now working well, and is devoted exclusively to solid-state NMR, mostly of nuclei other than  $^{13}\text{C}$ . Recently, we have been looking at high-resolution  $^{31}\text{P}$  spectra of solid diphosphine disulphides, in collaboration with Professor G. Hägele of Düsseldorf University, and Figures 1-3 show three examples. There are extensive spinning sideband patterns because the  $^{31}\text{P}$  shielding anisotropy is large. However, this letter is only about the centreband structure.

For  $\text{MeEtP(S)-P(S)EtMe}$  (pure meso form) only a single peak is seen. Therefore we assume there is only one type of crystallographic site for the molecule and that symmetry relates the two halves of each molecule. In the case of  $\text{Me}_2\text{P(S)-P(S)Me}_2$  two centrebands are seen, with a 2:1 intensity ratio when integrated. The high-frequency line is, however, substantially broader than the other peak. This is understandable. X-ray diffraction studies show there are two crystallographic sites in 2:1 occupation. The less populated site has a symmetry relationship between phosphorus atoms whereas the other site does not. It may be concluded that the broad intense NMR peak is a superposition from two crystallographically inequivalent phosphorus sites, with a small (P,P) coupling.



The third compound,  $\text{Pr}^i\text{Bu}^t\text{P}(\text{S})-\text{P}(\text{S})\text{Bu}^t\text{Pr}^i$ , again gives two bands, one of which is appreciably broader than the other. In this case the sample consists of a mixture of the meso and racemic forms, so the appearance of two bands does not have the same origin as for Figure 1. We do not have separated samples of the two diastereoisomers at present so we cannot be certain of the assignment of the peaks to the two forms, though an informed guess could be made.

The spectra illustrate the sort of chemical and crystallographic information that can be obtained. We are proceeding to look at a greater range of compounds of the above type, and to link the results to the crystal structure as determined by X-ray diffraction.

Best wishes

*Robin*

*L. Merwin*

R.K. HARRIS

L.H. MERWIN

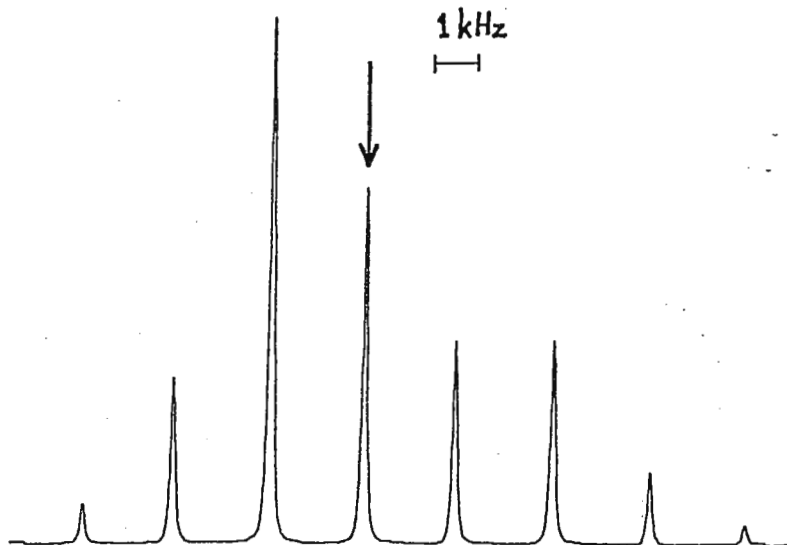


Figure 1: 80 MHz CP/MAR/ $^{31}\text{P}$  spectrum of meso  $[\text{MeEtP}(\text{S})]_2$ , obtained using a contact time of 1 ms, a recycle delay of 20 s, and 32 transients. The centreband is marked by an arrow, and occurs at  $\delta = 45.1$  ppm.

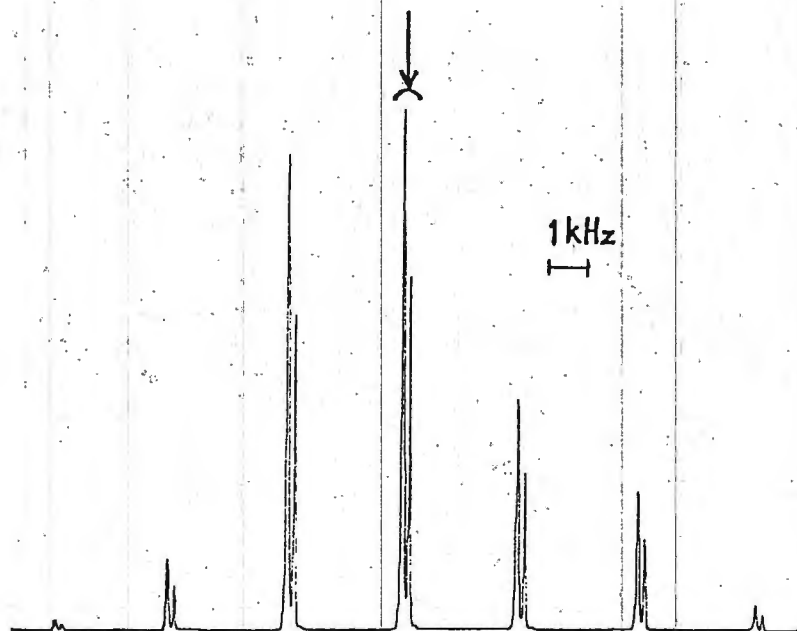


Figure 2: 80 MHz CP/MAR  $^{31}\text{P}$  spectrum of  $[\text{Me}_2\text{P}(\text{S})]_2$ , obtained using a contact time of 1 ms, a recycle delay of 10 s, and 16 transients. The centrebands, marked by an arrow, are at  $\delta = 34.3$  and  $37.0$  ppm.

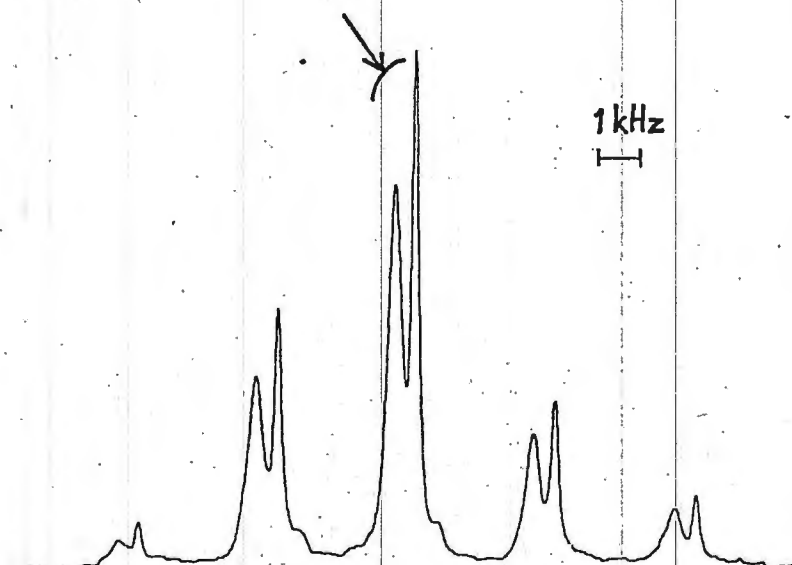
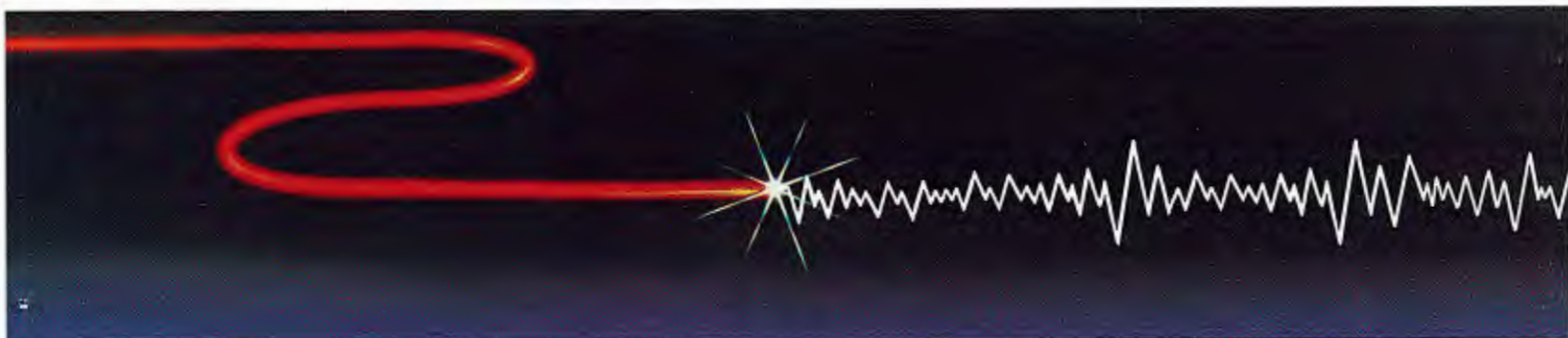


Figure 3: 80 MHz MAR  $^{31}\text{P}$  spectrum (without CP) of a mixture of the meso and racemic forms of  $[\text{PriButP}(\text{S})]_2$ , obtained using a  $90^\circ$   $^{31}\text{P}$  pulse, a recycle delay of 30 s, and 12 transients. The centrebands, indicated by an arrow, are at  $\delta = 68.5$  and  $74.2$  ppm.

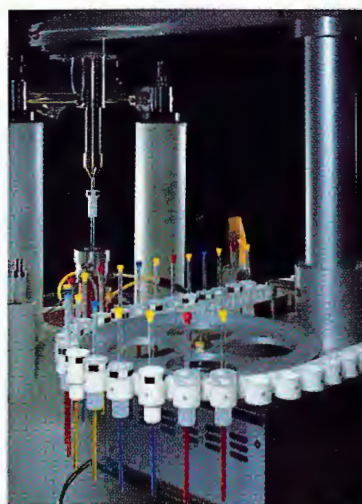


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215/728-6900

February 21, 1985

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

 RE: Electrostatic Shields

Dear Professor Shapiro:

We have now built several NMR probes for studies of living systems. In our first probe (1) we employed solenoid coils. A 10 mm surface coil has been added to that probe. More recent radiofrequency coils include a 100 mm surface coil (15 MHz) for studies of a selected area of whole body imaging, and a 20 mm saddle shaped coil (162 MHz). Except for the solenoid coils, we have found it advantageous to incorporate an electrostatic shield between the radiofrequency coil and the sample.

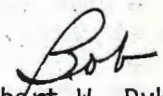
The electrostatic shield consists of a screen of parallel wires connected together at one end and connected to ground. The shield serves to minimize dielectric losses and, hence, to maintain the "Q" of the coil. Results of loading radiofrequency coils with a solution of 100 mM NaCl is given below.

	Q	
	<u>Unloaded</u>	<u>Loaded</u>
100 mm surface coil (15 MHz)	435	400
20 mm saddle shaped (162 MHz)	231	191
Commercial 20 mm probe (162 MHz)	187	107

The distributed capacitance of the shield for the 20 mm saddle shaped coil had to be reduced in order to tune the probe at 162 MHz. This was accomplished by inserting a small capacitance (1.5 pF) in the ground lead of the shield.

Please credit this contribution to the subscription of Dr. Mildred Cohn.

Cordially yours,

  
 Robert W. Dykstra

RKD/m

(1) R.W. Dykstra, TAMU Newsletter No. 308, 19 (May, 1984)



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Department of Medicinal Chemistry

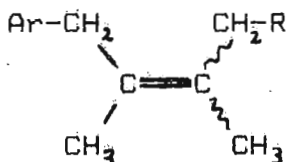
February 27, 1985

## **Why you really should use incremented mixing for 2D NOE measurements!**

Dear Barry:

I am happy to make a contribution to the newsletter, having, in your words, "decoupled myself from JEOL."

Early on in my new position, I was called upon to determine whether one of our compounds (I) was cis or trans (I will allow the reader to fill in the structure of groups Ar and R). The structure had previously been identified internally as cis, but there was a great deal of nervousness with this assignment. It looked like one of those tailor made situations for impressing one's new superiors with an application of a sophisticated NMR technique which would fairly spit out the answer. "Duck soup for 2D NOE", I said to myself, smugly.



I

Needless to say, I was somewhat distressed to discover that my XL-300 had no resident sequence for accomplishing an incremented mixing 2D NOE measurement. This had been one of my favorite sequences that I had used successfully at JEOL. Fortunately (the good news) there was a listing in the Varian manual of a sequence for accomplishing this. Unfortunately (the bad news), even though I was able to enter and compile the sequence, I was unable to get the sequence to run. No one at Varian has yet been able to explain why this is, but I'm sure that will be resolved in time. In the meantime, the nature of bosses being what it is, the only local interest that I could detect was in the answer - cis or trans? The details could go into the report.

Hence, I was forced to use the basic 2D NOE sequence, which works quite well. An example of one of the runs is shown in Figure 1. Because of my extreme fear of possible errors caused by J cross peaks contributing to the NOE peaks, I performed an extreme number of measurements, 18 in all for mixing times varying from 0.1 - 5 sec. A plot of the variation in cross peak intensity as a function of mixing time is shown for a number of the peaks (Figure 2), the particular

interaction being indicated on each plot. Note the oscillation which appears on many of the cross peaks due to J modulation of the intensities. As luck would have it, there is a complicating long range coupling between the two peaks of greatest interest, the vinyl methyls.

Of course, the compound is clearly shown by this careful work to be trans. The reason for the previous error was the aforementioned J coupling between the two methyls. Because of the reversal of assignment, the sample was submitted for XRAY crystallographic analysis. Of course, my work was vindicated.

For those friends of mine who are interested, I enjoy my new job very much. I must admit, however, that I was somewhat chagrined to discover that there is an entire body of people out here who have been having to work for a living while I've been just having fun working for the instrument companies. But now that I'm one of them, it ain't so bad.

See you at ENC!!

Sincerely,

*Andy*

C. Anderson Evans

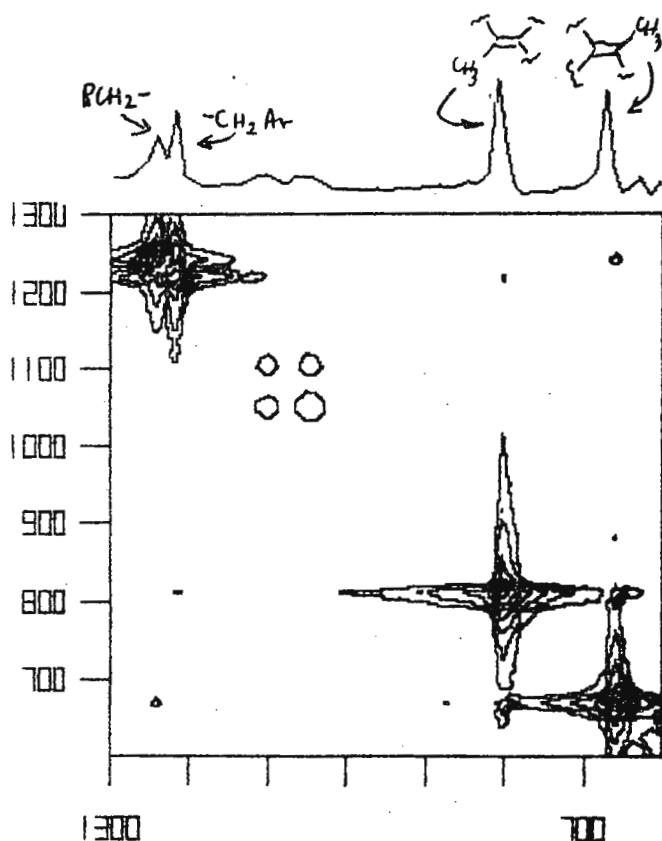


Figure 1

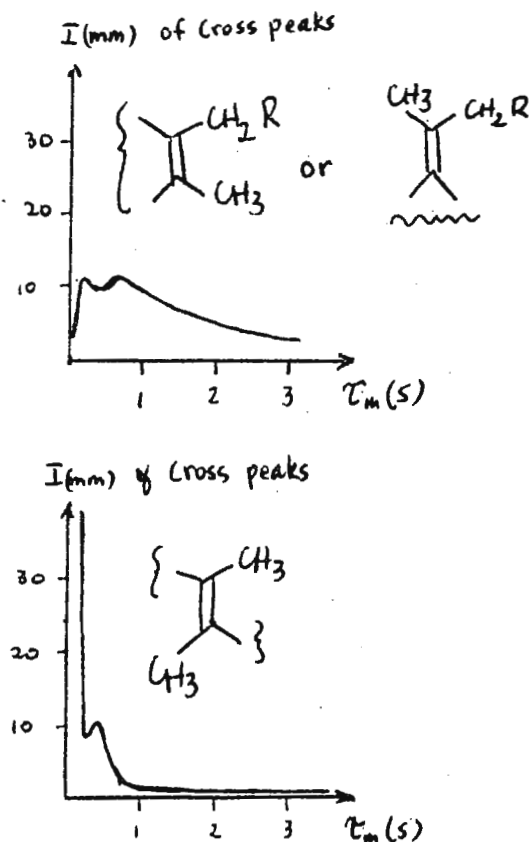


Figure 2



Hercules Incorporated  
Research Center  
Wilmington, DE 19894  
(302) 995-~~3030~~ -3505  
Telex: 83-5479

March 1, 1985

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

Dear Dr. Shapiro:

$^{13}\text{C}$  NMR Analysis of Vinyl Copolymers

In the NMR analysis of polymers, the conventional approach is to take the polymer sample, run the  $^{13}\text{C}$  NMR spectrum, assign the resonances, devise computational schemes, and obtain the sequence distribution and the comonomer reactivity ratios:

Spectrum  $\rightarrow$  Assignments  $\rightarrow$  Sequences  $\rightarrow$  Reactivity Ratios.

For convenience, we shall call this the "analytical" approach.

An alternative method is to reverse the process. Thus, one starts by simulating the copolymerization with a reaction probability model and then determine the sequence distribution of a typical polymer chain. Empirical equations can then be used for the prediction of  $^{13}\text{C}$  shifts, and the  $^{13}\text{C}$  NMR spectrum can be simulated. A comparison of the observed versus the simulated spectra provides a measure of how accurate the reaction probability model is.

Reaction Probability	$\rightarrow$	Polymer	$\rightarrow$	Shift	$\rightarrow$	Simulated
Model		Chain		Prediction		Spectrum

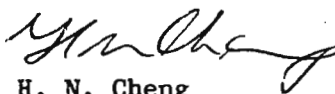
This is called the "synthetic" or the spectral simulation approach. Owing to the large amount of calculations involved, this method invariably requires the use of computers. The first attempt was reported on binary and ternary copolymers of olefins (Ref. 1). An advantage of this method is that it is readily applicable to the analysis of copolymers and terpolymers (or even 4- or 5-component copolymers), which are difficult to do by the "analytical" approach. It may also be noted that this is a predictive approach and depends on the availability of neither the actual polymer samples nor NMR instruments. Thus all copolymer types (random, blocky, or alternating) can be simulated, including those polymers which do not exist as yet.



Mark Bennett and I have recently generalized the earlier effort and developed a computer program (Ref. 2) that can produce the simulated spectra of homopolymers, and binary and ternary copolymers of common vinyl and vinylidene groups. A key requirement in the use of the "synthetic" approach is the existence of shift prediction equations. These have been given for 21 common vinyl groups (Ref. 2). For example, the observed and the simulated spectra of ethylene-vinyl alcohol copolymers are given below.

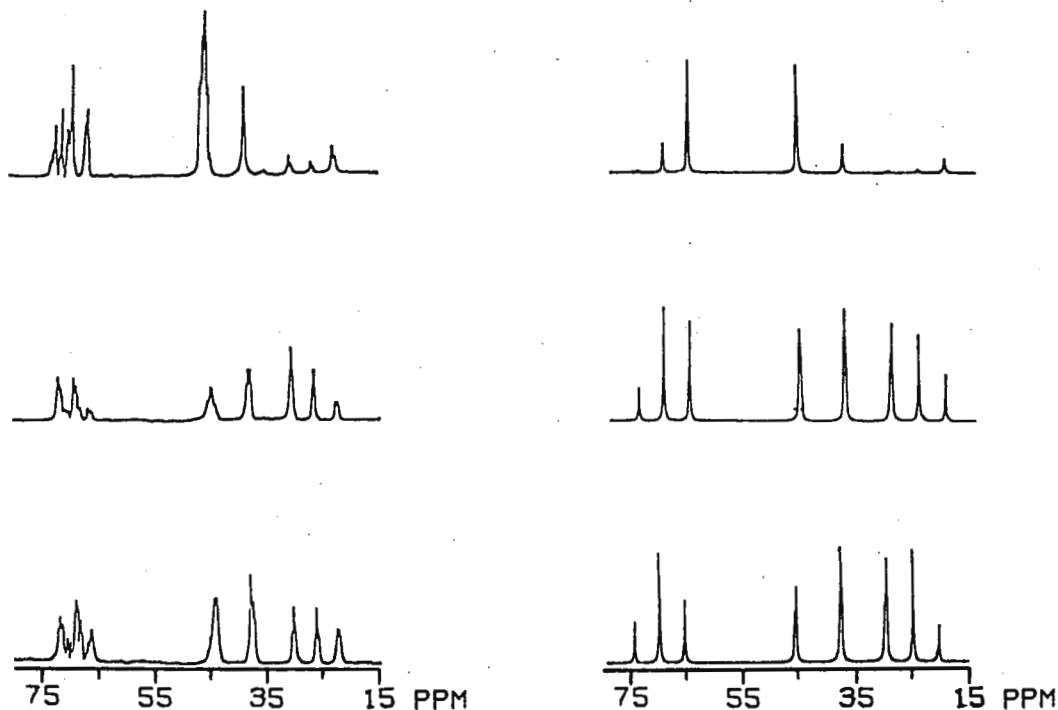
The resulting computer program (called PSPEC) is user-friendly and can be implemented on the Nicolet 1280 computers. An alternate version is available on the Prime 9950 (thanks to Mr. R. J. Gambogi). In addition an Apple II version also exists, albeit in an abbreviated form. Interested readers may write to me for a program listing of any version.

Yours very truly,

  
H. N. Cheng  
Analytical Division

#### References:

1. H. N. Cheng, in "Transition Metal Catalyzed Polymerizations, Alkenes and Dienes", R. P. Quirk, Ed., Harwood Academic Publishers, New York, 1983, pp. 617-628.
2. H. N. Cheng and M. A. Bennett, *Anal. Chem.*, **56**, 2320 (1984).



Observed (left) and Predicted (right) Spectra of  
Ethylene-Vinyl Alcohol Copolymers. The Ethylene  
Content is 13.28, 45.16, and 60.20 mole %



The College of Liberal Arts and Sciences  
 Department of Chemistry  
 Box U-60  
 Room 151  
 34 Glenbrook Road  
 Storrs, CT 06268

March 14, 1985

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

Dynamic  $^{13}\text{C}$  NMR of Electrochemically Formed  
 Dehydrodimers of 1,2,3,4-Tetrahydrocarbazole

Dear Professor Shapiro:

The electrochemical oxidation of tetrahydrocarbazole in strong base ( $\text{KOCH}_3$  in  $\text{CH}_3\text{OH}$ ) at a potential of +.15 V (vs. SCE) and using a graphite felt anode led to the formation of a series of compounds having interesting stereochemical and  $^{13}\text{C}$  nmr properties. The compounds can be depicted as having structures I and II.

Structure I refers to a mixture of four isomers which was obtained in a yield of 9.2%, but which was not separated. It consisted of two pairs of enantiomers which exist only because of completely hindered rotation around the 4a-N bond. The  $^{13}\text{C}$  nmr spectrum showed a complete set of pairs of peaks (Fig. 1), each pair corresponding to one carbon of the structure. This is a clear case of atropisomerism involving a bond between nitrogen and an  $\text{sp}^3$  carbon. Only one other such example has been reported.<sup>1)</sup>

Structure II is more complex and represents a unique case of stereochemistry as shown by dynamic  $^{13}\text{C}$  nmr. Two diastereomers were isolated, a meso compound and a dl mixture. These have been separated and isolated in yields of 9.4% and 20%, respectively. When the dl mixture in  $\text{CDCl}_3$  was cooled to about  $-31^\circ\text{C}$ , each peak separated into two unequal peaks (Fig. 2). When the meso isomer in deuterated THF and  $\text{CS}_2$  was cooled to  $-113^\circ\text{C}$ , each peak separated into two equal peaks (Fig. 3).

The peak separation is obviously due to restricted rotation around the 4a-4a' bond. However, the reason for the splitting is different in each case, and both are dependent upon the fact that the anti conformation around the C-C,  $\text{sp}^3$  bond is prevented by steric effects. While this phenomenon is difficult to see for II, it can easily be seen for the analogous case of 2,3-dibromobutane, III, as shown in Fig. 4.

In the dl form of III, if rotation is restricted and, if the anti conformation is forbidden, the two gauche forms are diastereomers and would exist in different amounts. The result would be a series of pairs of peaks of unequal size. This is

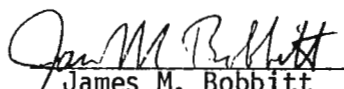


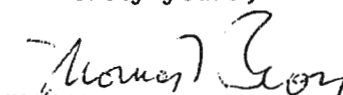
what one sees for the dl form of II (Fig. 2). In the meso form of III, under the same restrictions, the two gauche forms would be enantiomers. However, within a single enantiomer, all of the carbons are stereochemically and magnetically different and would show sets of equal peaks. This is what one sees in the spectrum of meso II at low temperature.

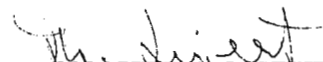
The reason that the anti form of II is unlikely is that the molecule looks like two unsymmetrical flat bars joined at the middle of the flat portion. In either the eclipsed conformation or the anti conformation, the bars must themselves be eclipsed, which is difficult.

To our knowledge, this is the first time that such a phenomenon has been described for an acyclic system involving two  $sp^3$  carbons. In cyclic systems, of course, an anti conformation is forbidden by the ring structure. Thus, in cis-1,2-dimethylcyclohexane, the  $^{13}C$  nmr peaks of the methyl groups are split into two equal peaks at low temperature.<sup>2)</sup>

Sincerely yours,

  
James M. Bobbitt

  
Thomas T. Chou

  
Thomas Leipert

- 1) D. Dave, J. B. Stothers, E. W. Wahnhoff, Tetrahedron Lett., 4229 (1973).
- 2) D. K. Dalling, D. M. Grant, LeRoy F. Johnson, J. Am. Chem. Soc., 93, 3678 (1971).

P.S. Please credit this paper to Professor Edward Samulski's account.

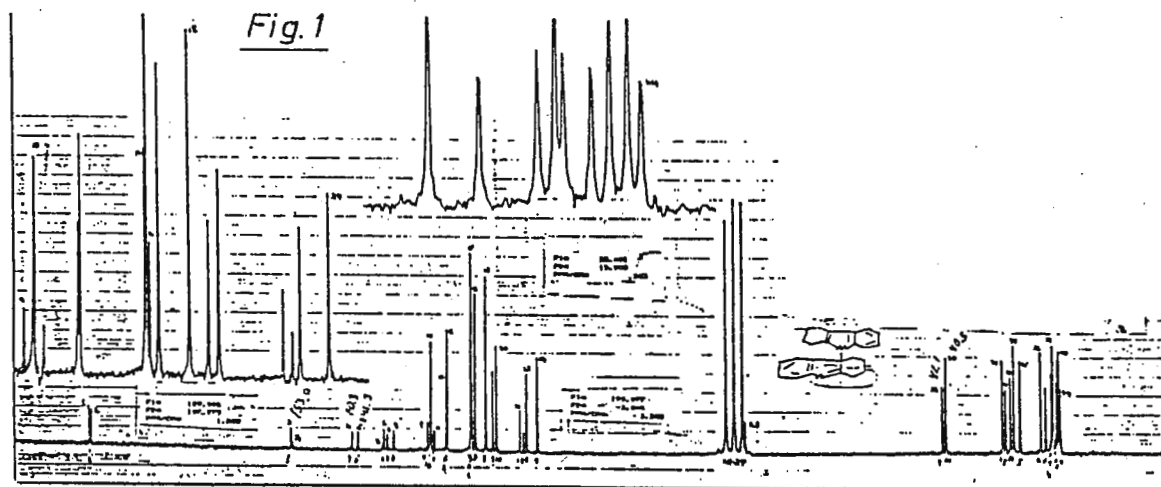
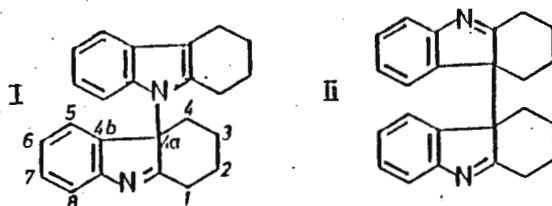




Fig. 2

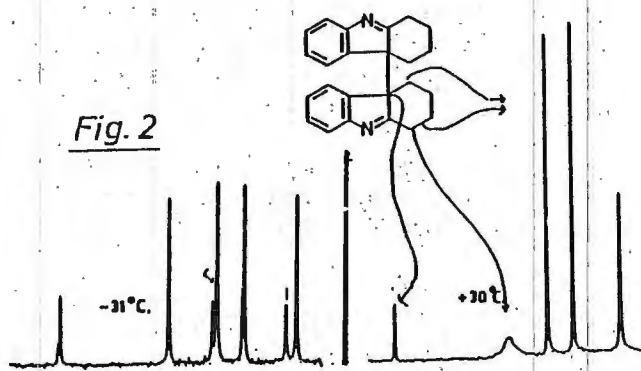
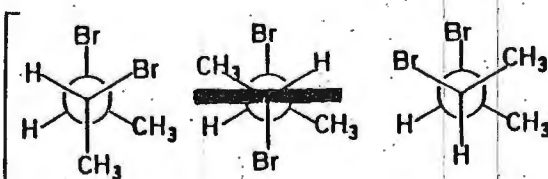
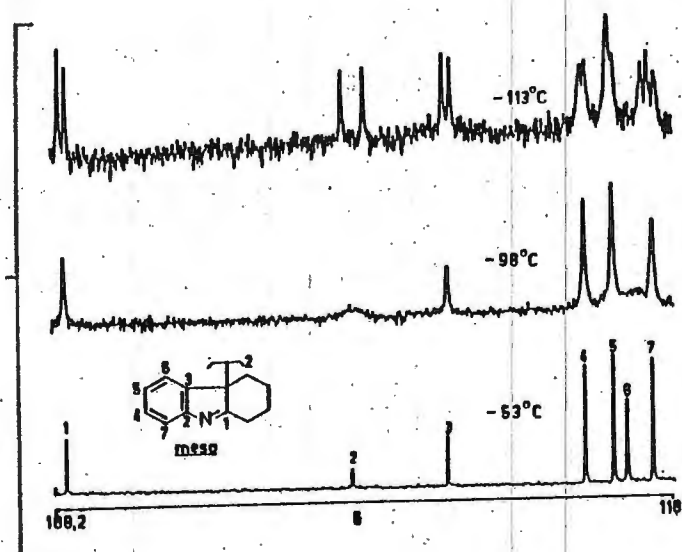
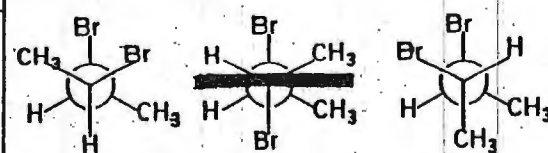


Fig. 3



pair of enantiomers—all atoms different

Fig. 4



diastereomers—two different compounds  
two pair of enantiomers





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Frank D. Blum  
(215)-895-2650

Re: Instructor-Postdoctoral Position Available

Dear Barry:

I would like to inform your readers that I expect to have an Instructor-Postdoctoral position available starting in September 1985. The position involves half time teaching (6 credit hours, normally in general chemistry) and half time research in my group during the academic year. The summer involves full time research. Support for up to three years is normally possible. The research currently being performed in our group involves using NMR to study i) polymer reorientation via deuterium relaxation times, ii) solvent transport in polymer systems using pulsed-field gradient spin-echo studies and iii) dynamics in micelles, liquid crystals, and microemulsions. Interested parties should have their resume and two letters of reference forwarded to me.

Sincerely,

Frank D. Blum  
Assistant Professor  
of Chemistry

---

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March 14, 1985

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

## Temperature Dependence of Relative LIS

Dear Barry:

During an extensive multinuclear investigation of the lanthanide induced shifts of adamantanone we looked at the temperature dependence of the shifts. Contact and pseudocontact shifts have long been known to respond differently to temperature variation, although the precise mathematical form of the temperature dependence has been argued. Since geometry calculations with LIS are limited to pseudocontact shifts, it is important to identify significant contact contributions to the experimental LIS. We have found that the temperature dependence of relative LIS provides a convenient technique for recognition of those nuclei in a particular substrate having significant contact shifts. The key to the method is normalizing the LIS to those of a nucleus that should have little or no contact shift (i.e., which is separated from the coordination site by several saturated carbons).

The following Table summarizes the temperature dependence of the ytterbium induced shifts of adamantanone (relative to  $H_\delta$ ). Inspection of the Table shows that the relative LIS are constant for  $^1H$  signals except for  $H_\alpha$ . Similarly, the contact contribution to  $^{13}C$  LIS appear to decrease with the number of bonds separating the observed nucleus from the coordination site.

# Temperature Dependence of Yb(fod)<sub>3</sub> Induced Shifts of Adamantanone<sup>a</sup>


Nucleus	-113°C <sup>b</sup>	-25°C	20°C	45°C
C <sub>α</sub>	-	4.90	-	5.55
C <sub>β</sub>	-	2.38	-	2.48
C <sub>γ</sub>	-	1.81	-	1.84
C <sub>δ</sub>	-	1.33	-	1.36
H <sub>α</sub>	3.88	4.12	4.15	4.19
H <sub>βsyn</sub>	2.19	2.18	2.17	2.18
H <sub>βanti</sub>	1.35	1.38	1.38	1.39
H <sub>γ</sub>	1.14	1.12	1.12	1.12
H <sub>δ</sub>	1.00	1.00	1.00	1.00

<sup>a</sup> Normalized to the LIS for H<sub>δ</sub>.

<sup>b</sup> In CFCl<sub>3</sub> (slow exchange); other data is for CDCl<sub>3</sub>.

The results of this procedure are in good agreement with other, more elaborate methods for separation of contact and pseudocontact shifts. Its simplicity recommends it as a useful check when observed LIS are being fitted to the pseudocontact equation.

Sincerely,

  
Douglas J. Raber  
University of  
South Florida

  
Joop A. Peters  
Delft University  
of Technology

P.S. Please credit this to the account of DJR (with the expectation that said account will be reinstated). Those colored messages really do have some significance after all.



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

IN REPLY REFER TO:

6120-161:ANG:log  
5 March 1985

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

Phase Enhancement for Precise Determination of  
Small Rf Phase Angles

Dear Barry,

I recently had the privilege of a year's sabbatical in Professor Alex Pines' lab at U.C. Berkeley. With colleagues Jean Baum and Mike Munowitz, I concentrated on multiple-quantum NMR in strongly coupled solids. Creation and detection of very high order coherences (60 quanta and above) put a severe burden on the rf digital phase shifter as well as on ones credulity. Though the required phase increments are small (ca  $1.4^\circ$  for an 8-bit phase shifter), these increments must also be set to great precision since, compared to a single-quantum coherence, an n-quantum coherence is n-times more sensitive to any phase error. Precise measurement of small phase shifts is rather difficult; one approach is following.

To measure small deviations from the nominal value of the phase increment, in principle one can increase the effective phase shift by multiplying the frequency of the digitally phase shifted 30 MHz carrier by  $2^m$  and then phase detecting against an unmodulated carrier at  $2^m \times 30$  MHz. This is some what analogous to the actual multiple-quantum NMR experiment as well as the broadcasting method which increases the phase modulation index by frequency multiplication. In practice, I mixed the 30 MHz IF down to 1.25 MHz and then multiplied up, to avoid phase detecting at inconveniently high frequencies. By stepping the digitally selected phase linearly in time, a sinusoid results and can be Fourier transformed to show the power spectrum of the phase deviation, as in the figure. Details will appear in J. Mag. Reson.

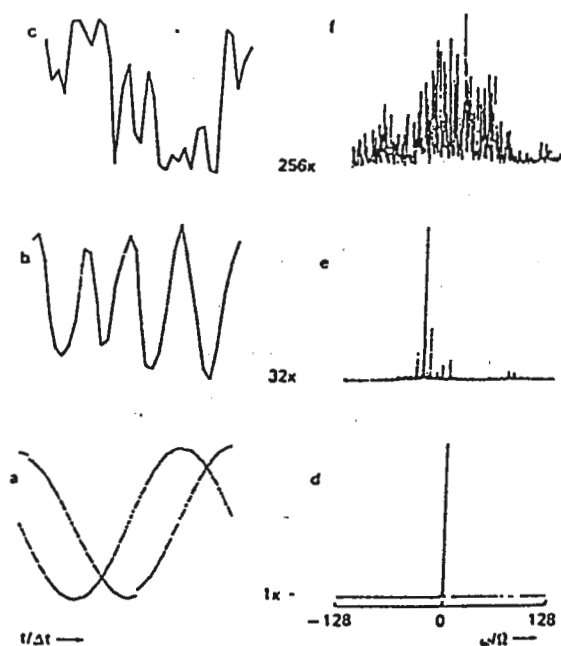
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Best regards,

AK  
Allen N. Garroway, Head  
Polymer Diagnostics Section  
Polymeric Materials Branch  
Chemistry Division  
Code 6120



# Phase Enhancement for Precise Determination of Small RF Phase Angles



An eight-bit digitally phase shifted signal and associated magnitude transforms for phase enhancements of 1x, 32x, and 256x. Sidebands indicate unequal step sizes in the digital phase shifter and these errors are most clearly seen under high magnification.

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Dr. B. L. Shapiro  
Texas A&M Nmr Newsletter  
Department of Chemistry  
College Station, TX 77843-3255

Dear Barry:

NMR2D Software-- and Pascal vs C

As you know, I've been concerned with the problem of off-line processing of 2D nmr data on the System-9000 Nmr workstation, which resulted in the release of the NMR2D software package at the end of last year. We are always glad to hear from users about their ideas for enhancements for such products.

On another note, I have been spending some of my "spare" time looking at the C language for use by scientists, since as you know, I have been a Pascal partisan (bigot?) for some time. In case any of your readers might be interested in my opinions so far, I am summarizing them below.

Pascal is friendlier, but wordier. Pascal compilers are more likely to catch mistakes that C lets go by. C assumes that you know what you are doing at the word-byte-bit level of your machine, while Pascal is considerably more of an abstraction. Many versions of Pascal do not allow double precision real arithmetic (although ours does), while C generally works in double precision.

Other than portability, C is supposed to generate faster running code. In general, I have not found this to be true, since this represents a combination of measurements of the skill of the compiler writer and the user. However, if you need to perform frequent multiplications or divisions by 2 by shifting a computer word right or left, C has a definite advantage, since these functions are not present in many other languages. This could be of great value in writing graphics display routines without resorting to assembly language code.

For the scientist who does occasional programming, Pascal is usually more friendly, but for the dedicated processor of data in unusual ways, C may be advantageous. Needless to say, these comments may not be universally agreed to by your readership, but they should give those who are starting out some pointers on what to look for.

Let me pose the following in reply to your scrawled note: Why can't Eskimos build fires while icefishing? I'll tell you at the ENC.

Best regards,

James W. Cooper

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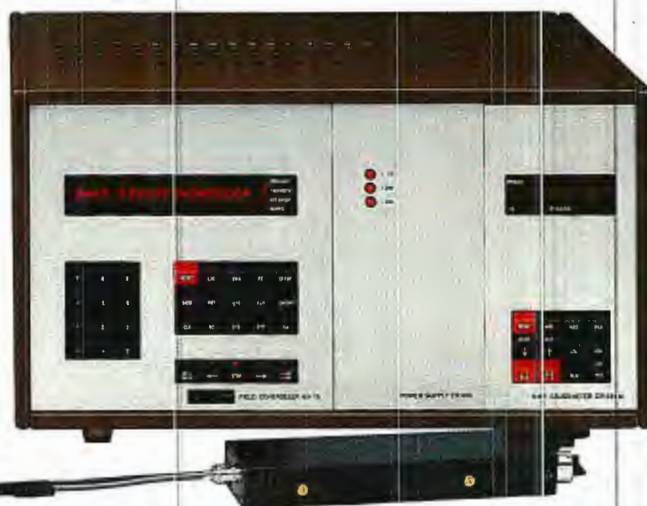
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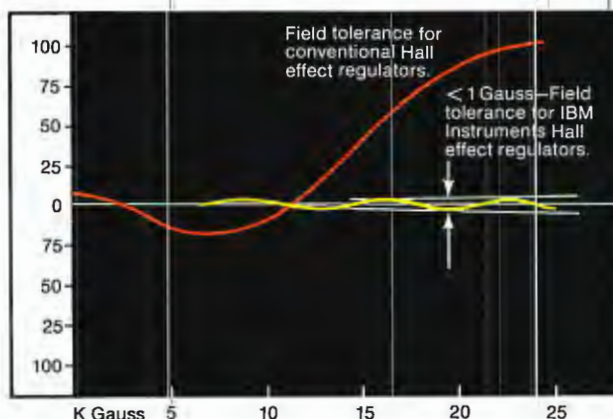
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March 1, 1985

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

**Modification of the Frequency Control Board of Earlier PTS-160 Synthesizers for  
 Compatibility with the Bruker SY Interface**


Dear Barry:

Recently, we upgraded our Bruker CXP 90 MHz spectrometer to 200 MHz with the addition of a Cryomagnet Systems, Inc widebore magnet. In order to generate the proton or fluorine frequency needed for solution homodecoupling experiments, we have adopted a technique similar to that described by Mooberry (TAMU 314-33). The standard Bruker 90 MHz output, controlled by the "O2" software command, is mixed with a fixed 110 MHz (98 MHz for fluorine) to generate 200 (188) MHz. The 110 MHz is derived from the CXP console PTS-160 synthesizer, which would otherwise be unused. The frequency is controlled via the "SY" command using an interface/cable supplied by Bruker. One problem we encountered was that our earlier vintage PTS-160 (with program board #PR1014) does not provide jumper options to configure the strobing sequence of the BCD codes to be compatible with this cable. Whereas the CXP interface strobes in the entire synthesizer word in parallel (and hence functions properly independent of the PTS interface strobing configuration), the SY interface/cable strobes in the BCD digits serially in a specific sequence.

This problem can be rectified with the following 3 changes on the PTS-160 frequency control interface board, which is mounted on the rear panel. (1) Connect edge connector pin 46 to pin 47. (2) Cut the connection between U6(pin 4) and U7(pin 13). (3) Connect U6(pin 13) to U5(pin 4). With these modifications, both the CXP interface ("SF" command) and the interface/cable ("SY" command) will correctly load the synthesizer word. The table below shows the original and modified edge connector pins for the BCD strobe lines.

Digit	<u>Latch Enable Edge Connector Pin</u>	
	<u>Original</u>	<u>Modified</u>
10 MHz	23	23
1 MHz	24	24
100 KHz	24	24
10 KHz	25	25
1 KHz	25	25
100 Hz	46	25
10 Hz	46	46, 47
1 Hz	47	46, 47
0.1 Hz	47	46, 47

Sincerely,

  
 Samuel Kaplan



University of Alberta  
Edmonton

Department of Chemistry  
Faculty of Science

Canada T6G 2G2

E3-43 Chemistry Building East, Telephone (403) 432-3254

March 5, 1985

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

Dear Barry:

Re: More Solvent Suppression

While running some Multiple Solvent Peak Suppression spectra on our Bruker WH400 and WH200, (rapidly switching the decoupler frequency for several seconds to presaturate the solvent peaks), we noted that the effectiveness of the technique depended strongly on the length of the short interval spent at each frequency and less so on the total saturation time. Investigation indicated that for any number of solvent peaks the best suppression occurs when each peak is repeatedly excited by a soft  $180^\circ$  pulse. The following microprogram accomplishes this:

1 ZE	;DP=30L dB
2 O2	;P1=53000 us
3 (P1 PH1) : D	;C=T <sub>TOTAL</sub> /P1 (85-189)
4 LO TO 2; TIMES C	;PW=90°
5 GO=2	

PH1=B0 B2

By making C an integer multiple of the number of peaks +1, the last nucleus irradiated before acquisition will be cycled.

Attempting to document this phenomenon proved the basic truth of the hypothesis but also showed a complication. Fig. I is a plot of the average integral of the two solvent peaks relative to 0.5%  $H_2O$  of a solution of cholesterol ( $10^{-3}M$ ) in a 40/60 mixture of  $C_6H_6$  and  $(CH_3)_2CO$  vs decoupler pulse angle. The number of pulses is adjusted to give a total saturation time of 10 sec. in each case. There is the expected minimum at  $180^\circ$  (~2%); however, near  $0^\circ$  the amplitude oscillates between about 35% and 100%; similarly, near  $360^\circ$  an oscillation between 20%-50% occurs. We suspect that the amplitude and frequency of the oscillation is a function of the  $H_1$  inhomogeneity (which, for this particular probe, is rather bad) and of the offset, respectively.

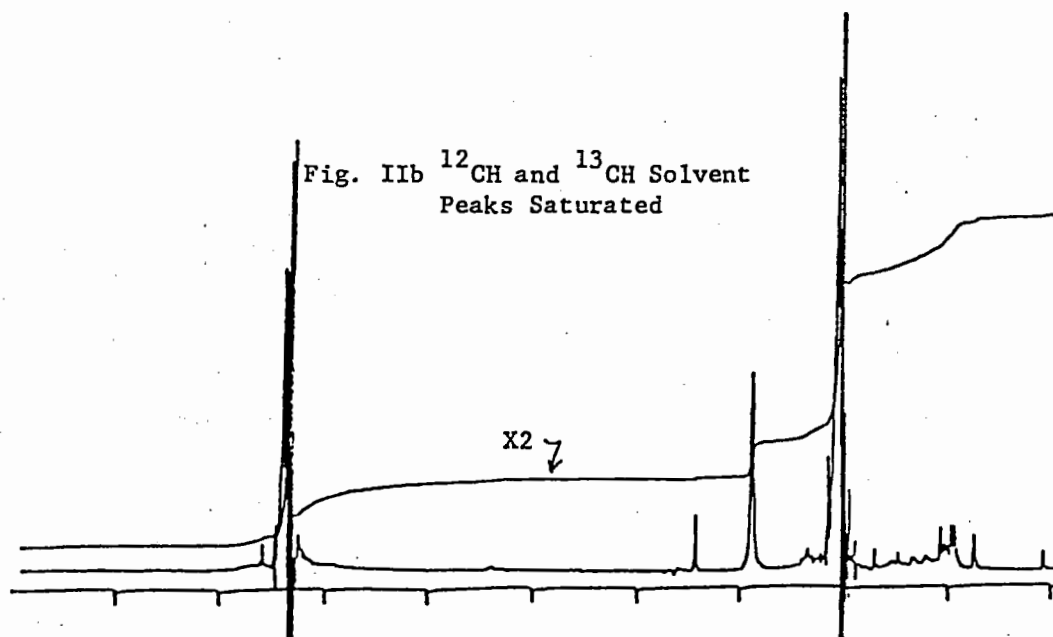
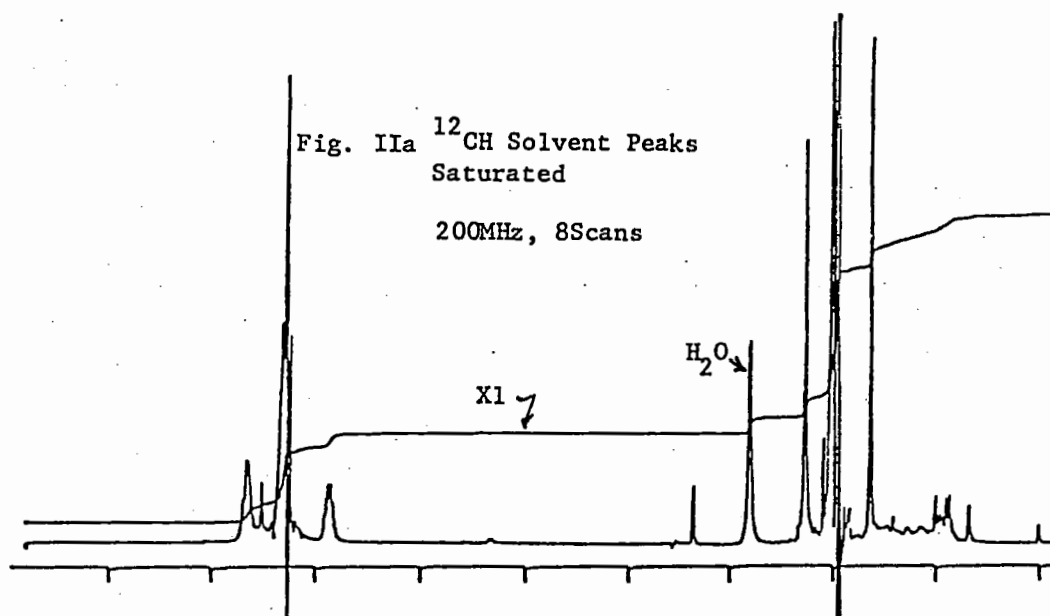
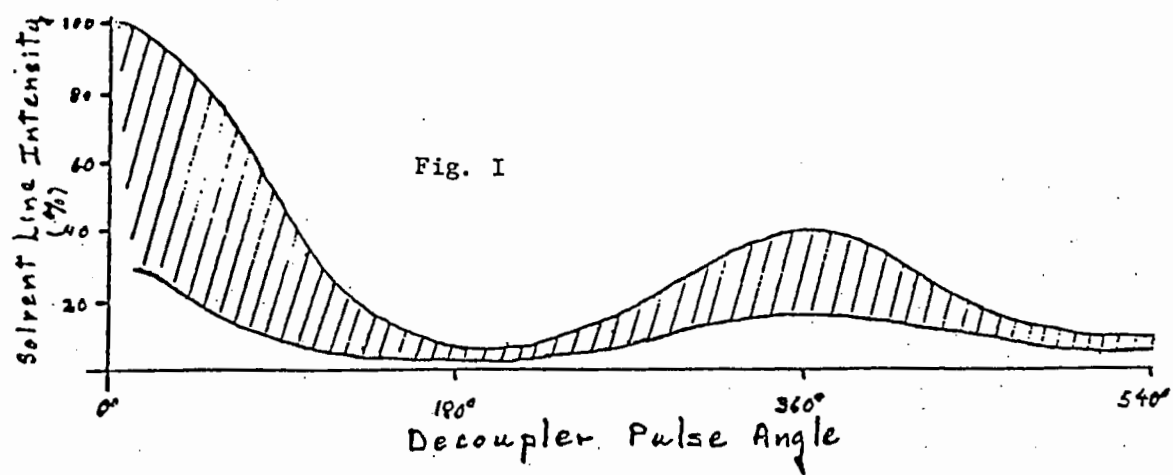
This technique allows one to reduce any number of solvent peaks to <3% (Cf. Fig. IIB. Six peaks, the  $^{12}CH$  and  $^{13}CH$  peaks of two solvents, are suppressed just as well as the two  $^{12}CH$  peaks in Fig. IIA). It can be as selective as desired--the excitation bandwidth is  $2/P1$ . If anyone can think of a reason for doing an NOE experiment with multiple saturations, this is the way to do it.

Please credit this contribution to Tom Nakashima's subscription.

Yours sincerely,

Glen Bigam

GB/lf





WASHINGTON UNIVERSITY



ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY

March 5, 1985

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

Dear Barry,

SATURATED WITH SATURATION

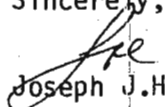
Cullis and coworkers in 1980 demonstrated that single frequency irradiation within the broad, membrane derived  $^{31}\text{P}$  hump resulted in complete and relatively rapid saturation of this broad resonance with perfused liver in vitro. (1,2) Building on this soft-tissue result, we demonstrated the success of such an approach in vivo with a primarily hard-tissue derived  $^{31}\text{P}$  hump (bone/membrane) observed in surface-coil studies of brain. (3) These in vivo brain results have been confirmed (4) as have Cullis's perfused liver results (5).

I for one am now satisfied that the laws of physics are independent of observer position. However, it is worth reemphasizing that, as in Cullis's original work, the use of DANTE type hard-pulse sequences (6) is an extremely convenient way to carry out such effective CW saturation. Although this eliminates the need for a second  $^{31}\text{P}$  irradiation channel, such hard-pulse sequences do not appear to be in vogue with hump suppressionists.

The accompanying figure illustrates the efficacy of hard-pulse saturation. The right hand spectra are of perfused rat liver in vitro taken under identical conditions in the absence (top) and presence (bottom) of a DANTE saturating sequence applied at a frequency position indicated by the arrow. Efficient suppression of the baseline hump is obtained. The left hand spectra are of rat kidney in vivo taken with a surface-coil in the absence (top, 4616 scans-5 min) and presence (bottom, 200 scans-3.3 min) of a DANTE saturating sequence applied at a frequency position indicated by the arrow. Again, efficient suppression of the baseline hump is obtained, although it is clear that one needs to be cautious with respect to placement of the saturating frequency and alert for modulated peak intensities.

Spectra in the accompanying figure were obtained by Dr. Mike Crowley, Dr. Joe Schuh, Dr. Robert Shalwitz, Miss Coleen Ewy, and Mr. Bruce Berkowitz. This work will not be the subject of a forthcoming paper.

Sincerely,

  
Joseph J.H. Ackerman

JJHA/kk  
enclosures

1. B. DeKruijj, G.A. Morris, and P.R. Cullis, Biochim. Biophys. Acta, **598**, 206 (1980).
2. B. DeKruijj, A. Reitveld, and P.R. Cullis, Biochim. Biophys. Acta, **600**, 343 (1980).
3. J.J.H. Ackerman, J.L. Evelhoch, B.A. Berkowitz, G.M. Kichura, R.K. Deuel, and K.S. Lown, J. Magn. Reson., **56**, 318 (1984).
4. R. Gonzales-Mendez, L. Litt, A.P. Koretsky, J. Von Colditz, M.W. Weiner and T.L. James, J. Magn. Reson., **57**, 526 (1984).
5. W.J. Thoma, L.M. Henderson, and K. Ugurbil, J. Magn. Reson., **61**, 141 (1985).
6. G.A. Morris and R. Freeman, J. Magn. Reson., **29**, 433 (1978).

(continued on page 39)



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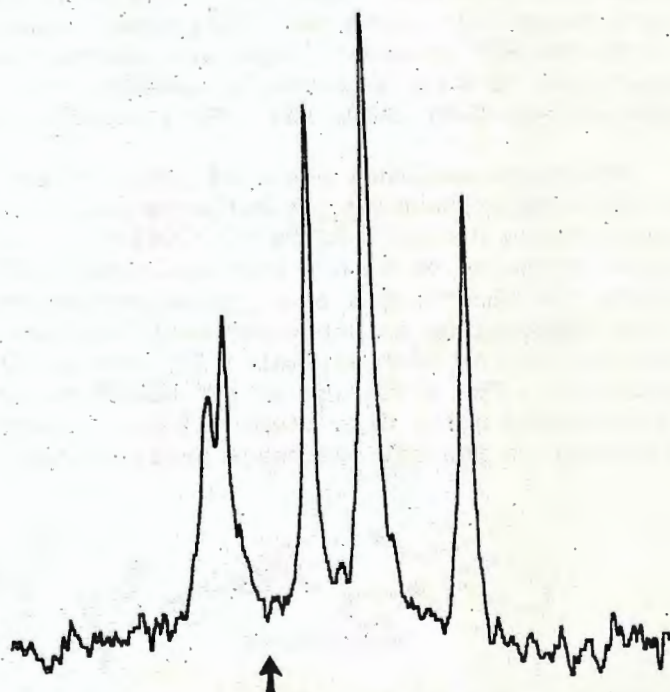
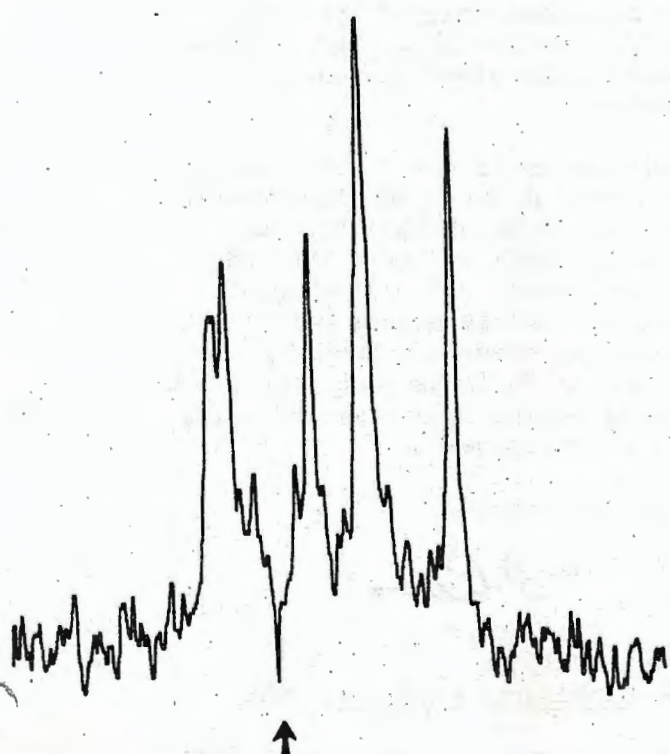
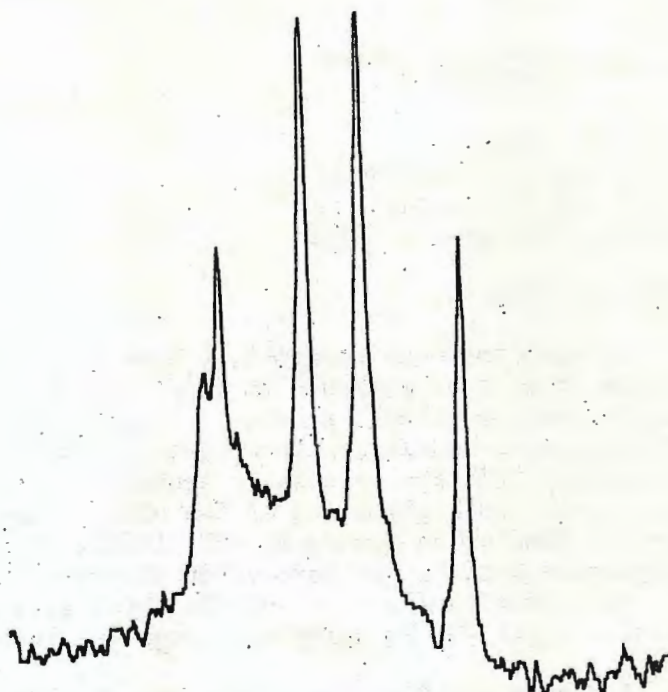
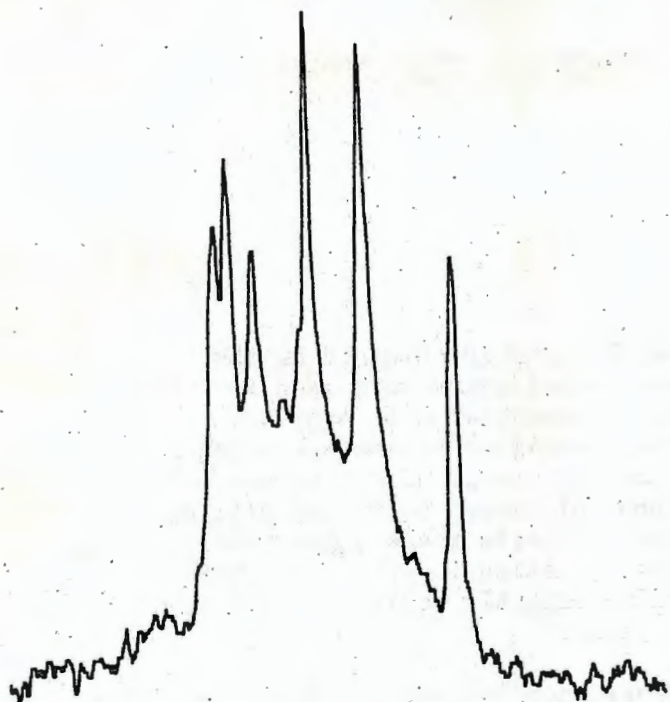
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# Kidney

# Liver



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DIVISION OF NATURAL SCIENCES  
THIMANN LABORATORIESSANTA CRUZ, CALIFORNIA 95064  
March 6, 1985

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

Dear Dr. Shapiro,

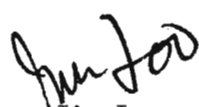
On more than one occasion we have experienced difficulty in determining the number of protons attached to a  $^{13}\text{C}$  during structural elucidation work upon a complex marine natural product. A major complication associated with many one-dimensional J-modulation techniques is that non-ideal peak intensities are often observed.  $\text{CH}$ 's are especially troublesome because a large range of  $J_{\text{CH}}$  values can exist, and application of the DEPT technique does not always solve the problem. Another limitation occurs in APT, INEPT, or DEPT when opposite phase degenerate resonances cancel. We have often observed the first situation in APT experiments for carbons with  $J_{\text{CH}} = 180\text{--}200$  Hz which give nulled or slightly negative peaks and for  $J_{\text{CH}} > 200$  Hz which give negative intensity peaks.<sup>1</sup>

A simple modification of the Patt/Shoolery APT sequence has allowed us to circumvent most of the above problems. Our procedure involves obtaining Residually Coupled APT (termed RECAPT)<sup>2</sup> spectra by single frequency off-resonance proton decoupling during an APT experiment. This leads to expected variations in  $^{13}\text{C}$  signal phases, but each resonance also exhibits residually coupled narrowed multiplets. An example of RECAPT results is shown in Figure 1 for a marine sponge metabolite heteronemin (1). Note that C-24 would be assigned as a quaternary C type from the normal APT spectrum (Fig. 1a), whereas the RECAPT spectrum (Fig. 1b) clearly shows C-24 to be a doublet. In addition the location of all other quaternary C's such as C-4, C-8, C-10, and C-13 is easily established.

The pulse sequence employed (Fig. 1) may be implemented in new or old spectrometers with no hardware or software modifications. Many older FT/NMR instruments employ Noise Bandwidth knobs (including our JEOL FX-100) in which the computer turns the noise on or off and the Noise Bandwidth knob itself controls the width. During  $^{13}\text{C}$  observation in a typical off-resonance experiment, reduced coherent proton decoupling is performed away from the resonances (off-resonance point) because the computer automatically reduces the decoupling power and turns the noise off. The advantage of our RECAPT method is that an "off resonance" spectrum is generated using high power which is accomplished by moving the noise decoupler frequency to the off resonance position and disabling the bandwidth.

Sincerely,

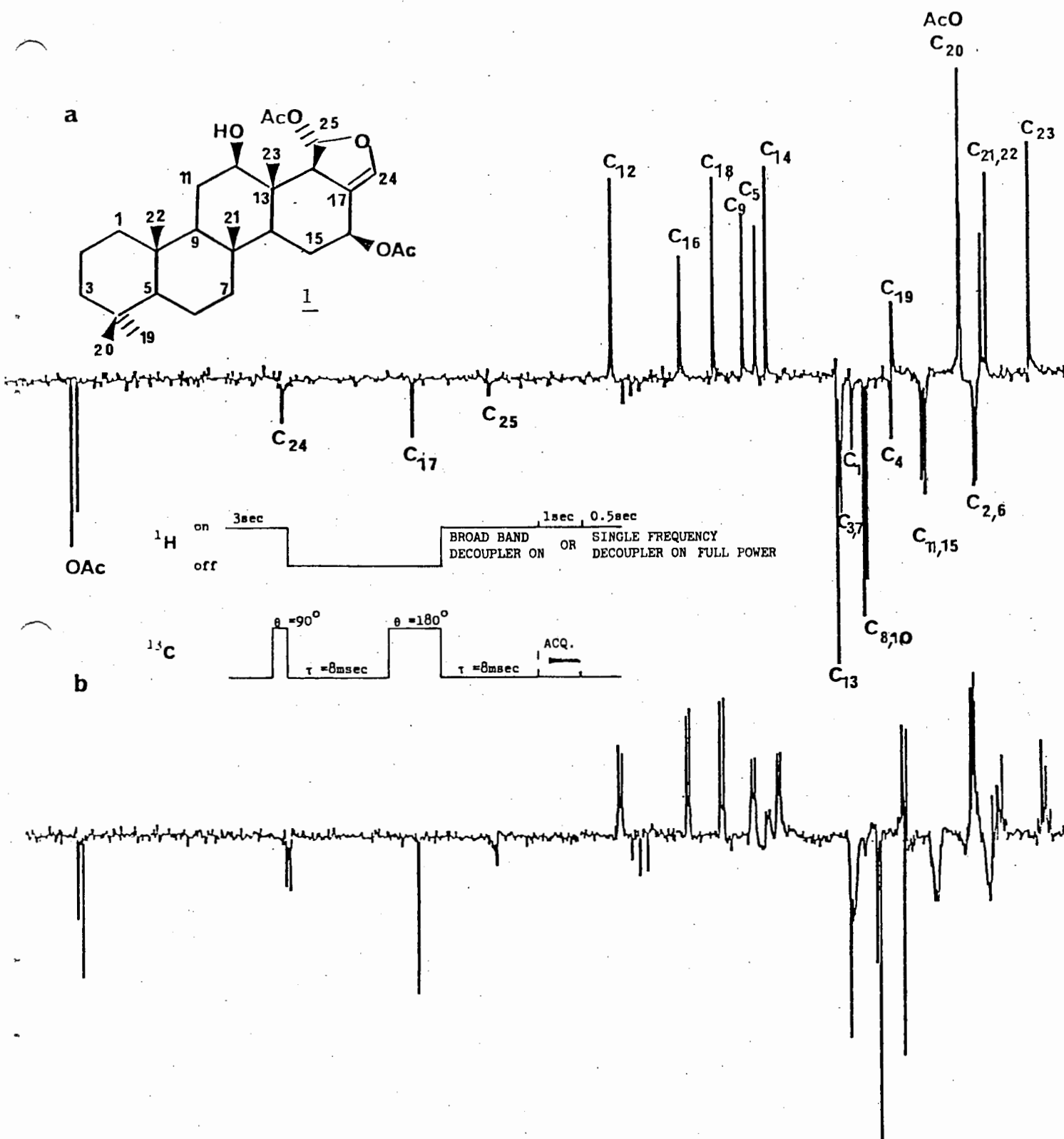
  
Larry Manes

  
Jim Loo

  
Phil Crews

<sup>1</sup>Crews, P.; Myers, B.L.; Loo, J.; Ball, D.; Ide, C. J. Natural Products, 1985, submitted.

<sup>2</sup>Crews, P.; Naylor, S.; Myers, B.L.; Loo, J.; Manes, L.V. Magn. Reson. Chem. 1985, in press.





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SANTA BARBARA • SANTA CRUZ

SCHOOL OF PHARMACY  
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

March 6, 1985

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

Dear Professor Shapiro:

We are having fun on our new GE-500 MHz NMR spectrometer that arrived last fall. One of our long term projects is to understand the basis for the sequence specific damage of DNA caused by the anticancer drug, bleomycin. To this end we have designed and synthesized a nonpalindromic DNA hexamer,  $5'CCACGG/3'GGTGCC$ , that contains a "high affinity cleavage site" at the  $5'GT$  pair. The behavior of our hexamer under assay conditions has fully lived up to our expectations.

We are a little disturbed, however, by the results of  $^1H$  NMR studies of the binding of bleomycin, or Zn:bleomycin to the hexamer. As shown in Figure 1, Zn:bleomycin is in fast exchange with the oligomer and only the resonances of the bithiazole moiety are significantly perturbed upon binding. We do not observe major shifts of resonances of the nucleotide bases or the metal binding portion of bleomycin, a result consistent with the absence of bithiazole intercalation. Furthermore the  $t_m$  decreases from  $42^\circ C$  for the oligomer to  $37^\circ C$  for the 1:1 mixture with Zn:bleomycin. These results lead us to ask whether sequence specific damage is more of a kinetic effect rather than reflecting a thermodynamically stable complex? In any case we are exploring the binding properties of other metal complexes to see if the nature of the metal will influence the binding affinity or kinetics of the complex with DNA oligomers.

Please credit this letter to the account of Tack Kuntz.

Sincerely yours,

A handwritten signature in cursive script, reading "Norman J. Oppenheimer".

Norman J. Oppenheimer

Associate Professor of  
Pharmaceutical Chemistry

P.S. I expect to have a postdoc position available this coming fall to continue work on bleomycin:DNA interactions and related work. Anyone interested should please contact me.



UNIVERSITÄT TüBINGEN  
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Prof. Dr. O. Lutz

D-7400 TüBINGEN 1, den 19.03.1985  
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Professor B.B. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station  
Texas 77843

L USA

Ihr Zeichen

Unser Zeichen

Ihre Nachricht vom

Lu/Sc

$^{23}\text{Na } T_1$  in Pig Tissue

Dear Barry

Recently we have been interested in relaxation times of  $^{23}\text{Na}$  in tissue since a 1.5 T whole body NMR imaging system from Siemens is now in operation at the University of Tübingen.

As a demonstration for the signal-to-noise ratio a typical example of a  $T_1$  FT inversion recovery measurement using our 2.1 T Bruker SXP 4-100 Fourierspectrometer is given in fig. 1 together with some experimental parameters.

In fig. 2 results for different pig tissues are presented, indicating that  $T_1$  is rather short for rapid pulsing and different by a factor of two for the various pig tissues favouring the contrast in imaging.

Some further results have been published in Z. Naturforschung 39a, 616 (1984)

(by U. Brändle, E. Kammerer, D. Köhnlein and O. Lutz).

Sincerely yours



(Otto)

(continued on page 47)





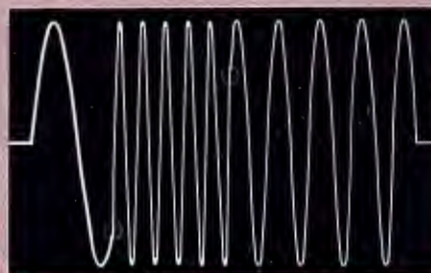
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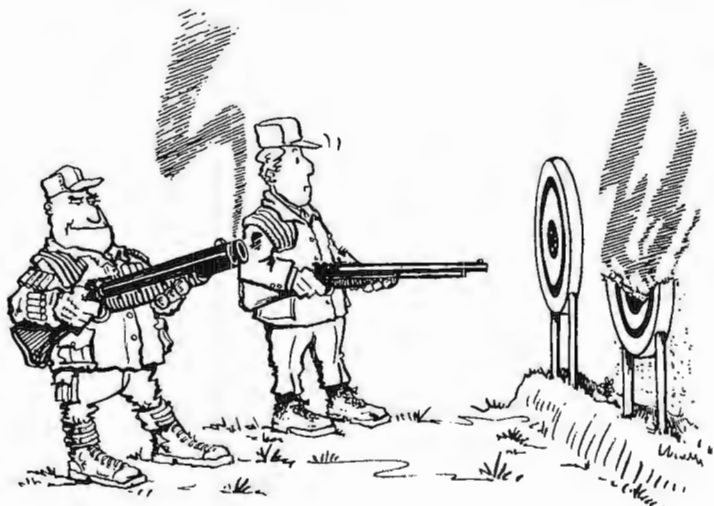
Phase-continuous switching

### SPECIFICATIONS

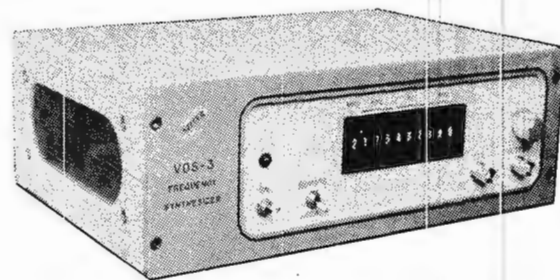
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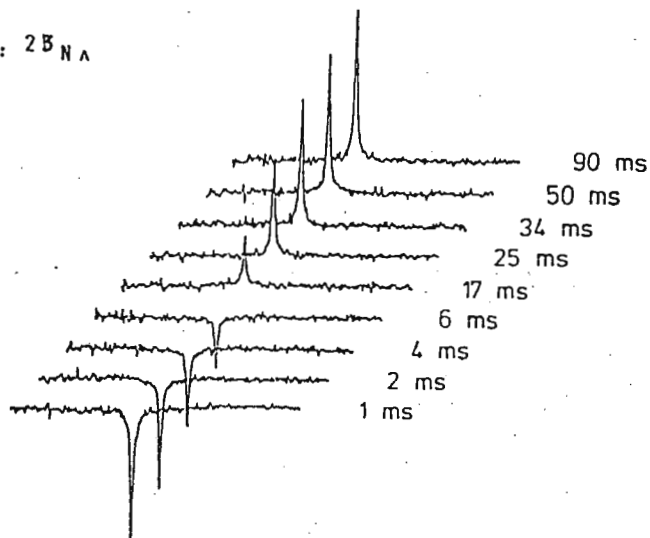
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D-7400 TüBINGEN 1, den  
Morgenstelle  
Telefon (070 71) 29 67 14

NUCLEUS:  $^{23}\text{Na}$



FREQUENCY: 23.808 MHz, 2.11 T

SAMPLE: PIG SPLEEN, 0.7 cm<sup>3</sup>

EXP. SPECTRUM WIDTH: 5200 Hz

NUMBER OF PULSES: 1000

REPETITION TIME: 100 ms

MEASURING TIME: 18.8 min

RELAXATION TIME  $T_1$ : 15.3 ms

Fig. 1.

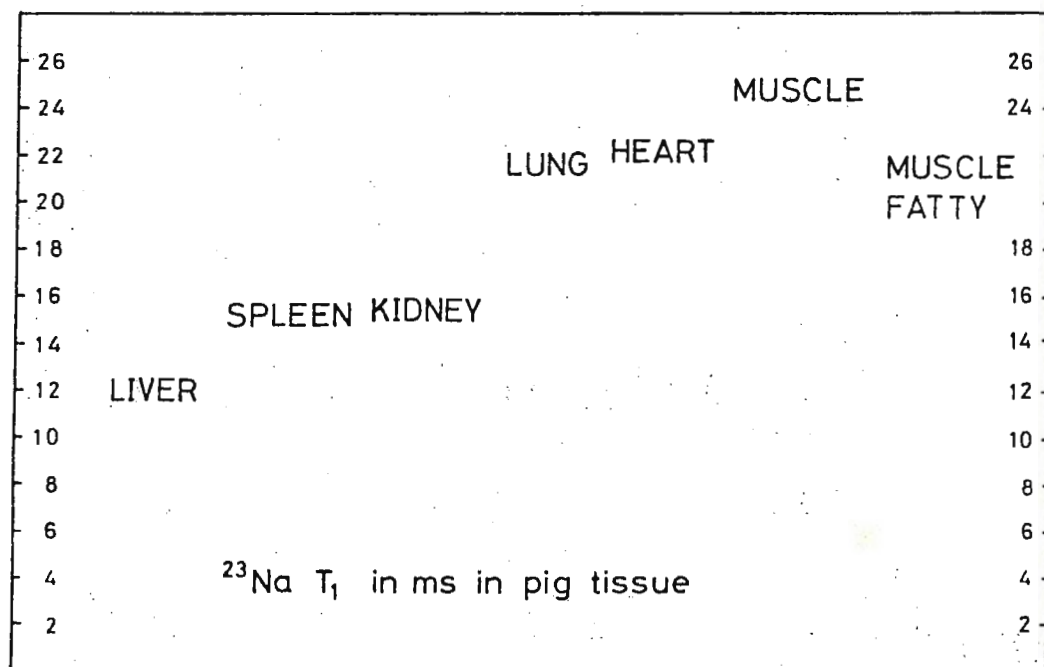


Fig. 2.



Prof. Dr. D. Leibfritz  
Universität Bremen  
Fachbereich Chemie/Biologie

NW 2 Leobenerstraße  
2800 Bremen 33  
Telefon (0421) 218-2818/17/41

Prof. B.L. Shapiro  
Dept. of Chemistry  
Texas A & M University

March 21, 1985/hg

College Station, TX 77843

Title

"P-31-in-vivo-spectroscopy of the gaster"

Dear Dr. Shapiro,

A theoretician who has lost his key in the dark is said not to seek it at the very locus of the loss but under a lamp post because there is light to see. So do in vivo spectroscopists, including us, whose pet is the Lengendorff heart just because the spectra are obtained so easily. Spectra of the gaster, another interesting organ, are more like a search in the dark, as the muscle is thin and decays fast when superfused.

The upper spectrum overleaf was recorded immediately after excision. The inorganic phosphate is already immense, and in the course of the experiment, still increases and shifts towards more acidic pH, while phosphocreatine and later ATP vanish rapidly. The superfused gaster is so short-lived that meaningful experiments with physiological stimuli are nearly impossible.

Therefore, we decided for in situ experiments. A surface coil directly attached to the gaster (this technique works well with, e.g. the heart) delivered a poor signal only when damping was carefully minimized and the organ was stimulated with acetylcholine. A solenoid coil wound around gaster and duodenum gave sort of a spectrum. Finally, an implanted solenoid coil granted the familiar  $^{31}\text{P}$  spectrum depicted as lower trace. The organ seems to be rather intact and will, hopefully, remain so for a time sufficient for further extended studies.

Yours sincerely

*D. Leibfritz*

*Wolfgang J. Schaefer*

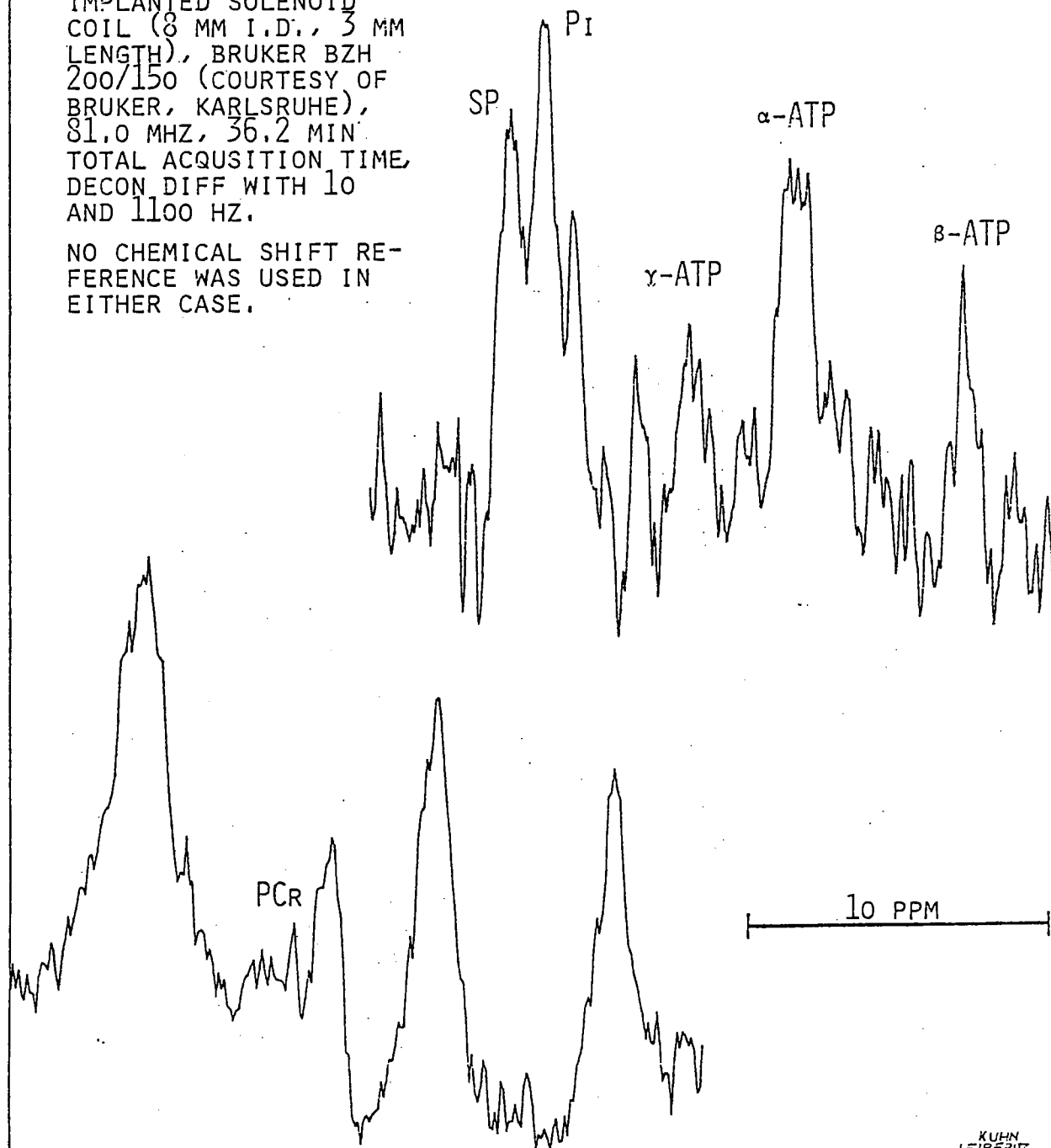
## RAT GASTER

200 G MALE WISTAR.

UPPER TRACE: SUPERFUSED, IMMEDIATELY AFTER  
EXCISION, BRUKER WH 360 NARROW BORE, 145.8  
MHZ, 1.7 MIN TOTAL ACQUISITION TIME, DECON-  
VOLUTION DIFFERENCE WITH LINE BROADENINGS  
OF 30 AND 680 HZ.

LOWER TRACE: IN SITU,  
IMPLANTED SOLENOID  
COIL (8 MM I.D., 3 MM  
LENGTH), BRUKER BZH  
200/150 (COURTESY OF  
BRUKER, KARLSRUHE),  
81.0 MHZ, 36.2 MIN  
TOTAL ACQUISITION TIME,  
DECON DIFF WITH 10  
AND 1100 HZ.

NO CHEMICAL SHIFT RE-  
REFERENCE WAS USED IN  
EITHER CASE.



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# THE UNIVERSITY OF NEW ENGLAND

ARMIDALE, N.S.W.

Department of Chemistry

March 22, 1985

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

Dear Barry,

## BARRIERS TO INTERNAL ROTATION ABOUT N-N SINGLE BONDS

Strongly hindered rotation about N-N single bonds was first reported in 1965 as a result of n.m.r. studies on an  $N,N'$ -diacylated cyclic hydrazine derivative (a tetrahydropyrazine), where it leads to a barrier to ring inversion of 79 kJ/mol (1), and in 1966 from n.m.r. studies on tetra-acylated open-chain hydrazine derivatives, barriers to rotation being estimated as 75-88 kJ/mol (2).

The barrier in hydrazine itself is only ca 10 kJ/mol ("best" *ab initio* estimates; the experimental value of 16 kJ/mol is based on an incorrect assumption), but direct comparison is somewhat misleading: in hydrazine (and alkyl derivatives), the N atoms are pyramidal in both ground state and transition state for rotation whereas, in the acylated derivatives, these centers are planar.

*Ab initio* estimates of the barrier for internal rotation of  $D_{2d}$  hydrazine via the  $D_{2h}$  "transition structure" lie in the range 85-95 kJ/mol, so acyl substituents may actually lower the barrier. As an approach towards simulating some of the molecules studied experimentally, Dr Leo Radom and I have made *ab initio* calculations on hydrazines constrained to planarity at the N atoms and with cyano groups as model  $\pi$ -electron acceptors. In 1,1-dicyanohydrazine, the barrier is lowered to 25 kJ/mol, a result attributed to delocalization of the lone-pair electrons on the substituted N atom and consequent reduction of the mutual repulsion of the lone pairs on the adjacent N atoms. In this molecule, however, the lone-pair electrons on the  $NH_2$  group are more localized in the perpendicular ground state than in the planar transition state; introducing two more cyano substituents benefits the ground state more than it does the transition state, and the barrier for tetracyanohydrazine rises to 49 kJ/mol.

More strikingly, incorporating one N atom of hydrazine into a 1-aza-2,3-diboririne ring results in such great delocalization of its lone pair that, whether the other N atom is allowed to adopt its preferred pyramidal structure or is constrained to planarity, the form with coplanar



lone-pair orbital axes becomes the ground state (which we believe is the first time such a result has been predicted); the calculated barrier to rotation of the fully planar form is 17-18 kJ/mol. Consistently, incorporating the second N atom into another such ring benefits the the perpendicular form more than the planar form, and the calculated barrier is lowered to 8-9 kJ/mol.

Since we made the above calculations, synthesis of a substituted 1-aza-2,3-diboririne has been reported (3) for the first time, and extension to the synthesis of (substituted) 1-amino derivatives would appear to be feasible. We await confirmation of the prediction above, although the barrier to rotation in accessible compounds may be too low to allow this by n.m.r. methods.

Appropriate parts of the above are being submitted for publication.

Yours sincerely,

  
N. V. Riggs

Professor of Organic Chemistry

References:

- (1) J. C. Brelière and J. M. Lehn, J. C. S., Chem. Commun., 1965, 426.
- (2) B. H. Korsch and N. V. Riggs, Tetrahedron Letts., 1966, 5897.
- (3) F. Dirsch, H. Nöth, and W. Wagner, J. C. S., Chem. Commun., 1984, 1533.

# PURDUE UNIVERSITY

BIOCHEMICAL MAGNETIC RESONANCE LABORATORY

February 28, 1985

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

## A POOR MAN'S PHASE SHIFTER OR WHAT CAN I DO WITH HOMOSPOIL?

Dear Barry,

We recently upgraded the pulse programmer on our NT-470 spectrometer, and now we finally have more than 16 steps of pulse programming allowing longer pulse sequences and more sophisticated phase cycling routines. However, in the days prior to this implementation we had to resort to any means available in order to perform experiments that required more capabilities than the old 293a' pulse programmer could provide.

We tried one approach using a homospoil unit (designed, built, and implemented on the NT-470 by Dr. Robert Santini and G. Carlton Schlicher) to select coherence transfer echos in two-dimensional experiments. Following the method of Bax et al. (*Chem. Phys. Lett.* **69**, 567-570, 1980) if a pulsed field gradient is placed immediately before the mixing period of a one- or two-dimensional experiment, the p-quantum coherences of the evolution time are dephased by a factor

$$-\gamma_i \Delta B_0(r, \tau)$$

where  $\gamma_i$  is the magnetogyric ratio of the nucleus,  $\Delta B_0$  is the order of the coherence, and  $B_0(r, \tau)$  is the time-dependent field gradient. Following the mixing period, a second pulsed field gradient of the same sign is applied to select the coherence transfer echo which is then detected as a single quantum coherence. The length of the second field gradient pulse is set equal to  $p$  times the length of the dephasing gradient, where  $p$  is the order of the homonuclear coherence dephased by the first field gradient. One advantage of selecting the coherence transfer echo is that the sign of the frequency during the evolution period is determined; therefore, the spectrometer frequency can be placed in the center of the frequency range.

Figure 1 is the pulse sequence used to collect the two dimensional COSY spectrum (Figure 2) of a tripeptide, glycyl-leucyl-tyrosine, in DMSO- $d_6$ . On our instrument, the strength of the field gradient was about 0.14 gauss corresponding to a proton line width of 600 Hz. The dephasing and the rephasing pulse field gradient lengths were 4 ms. The spectrometer carrier frequency was at the center of the spectrum, and the spectral width in both dimensions was  $\pm 2136.75$  Hz. The COSY spectrum shown in Figure 2 was left unsymmetrized in order to demonstrate the good cancellation of p-type peaks which, if present, lead to an anti-diagonal spectrum perpendicular to the normal spectrum. Residual artifacts at the carrier frequency are due to



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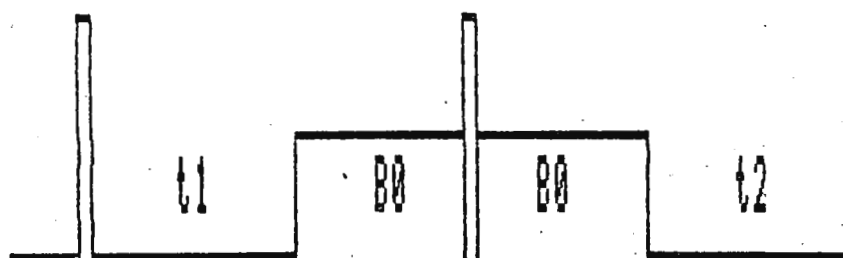
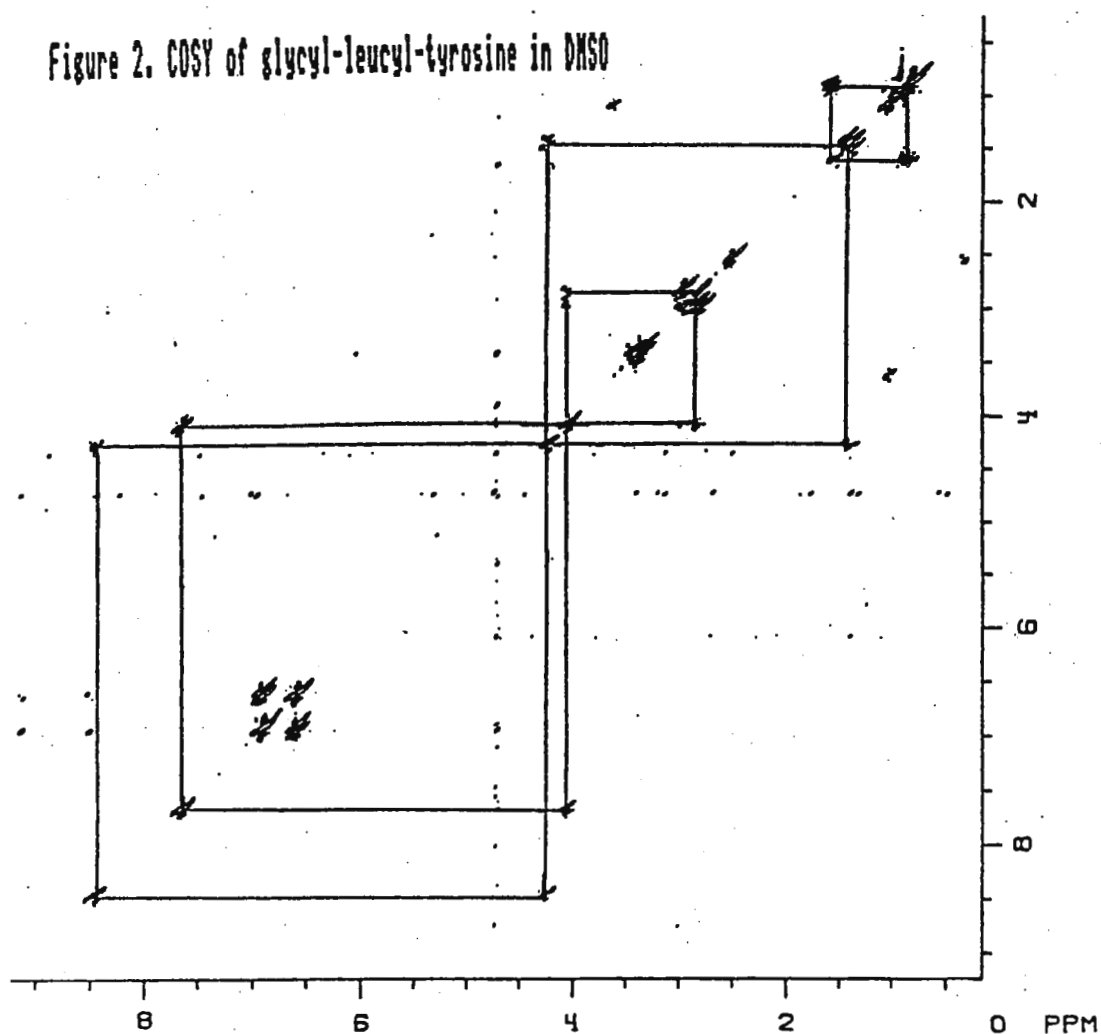


Figure 1. COSY with pulsed  $B_0$  field gradients

Figure 2. COSY of glycyl-leucyl-tyrosine in DMSO



February 27, 1985  
Professor B.L. Shapiro

incompletely suppressed axial peaks. These probably could be reduced by the use of stronger field gradients. We also have had success in using the pulsed field gradient method to obtain quadrature double-relayed COSY and double-quantum spectra. One obvious disadvantage of the use of field gradients is the disturbance of the lock signal; in these experiments the lock signal was perturbed, but the spectrometer was able to retain lock for the entire collection time. We are now investigating the use of B1 field gradients for the selection of specific orders of coherence.

Sincerely,

*Milo*

*M. Albert Thomas*

*JL*

William M. Westler    M. Albert Thomas    John L. Markley

---

Re: NMR Spectroscopists

Dear Dr. Shapiro:

Two research associate positions are available immediately in the Division of Radiology. Currently, we have Technicare 1.5T, 0.6T, and 0.15T whole-body imagers. A Varian high-resolution XL-200 and a 4.7T animal unit will arrive shortly. These individuals will have the opportunity to participate in research and development of multi-nuclei imaging and spectroscopy, ranging from animal to human scale. Research on human subjects is done in collaboration with physicians of various disciplines. Salary is commensurate with qualifications and experience. For further information, please write or call me at the address or number listed above.

Sincerely,

*Thian C. Ng, Ph.D.*

Thian C. Ng, Ph.D.

jed



KEMIAN JA BIOKEMIAN LAITOS  
**TURUN YLIOPISTO**  
 20500 TURKU 50

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

**UNIVERSITY OF TURKU**

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Turku.

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

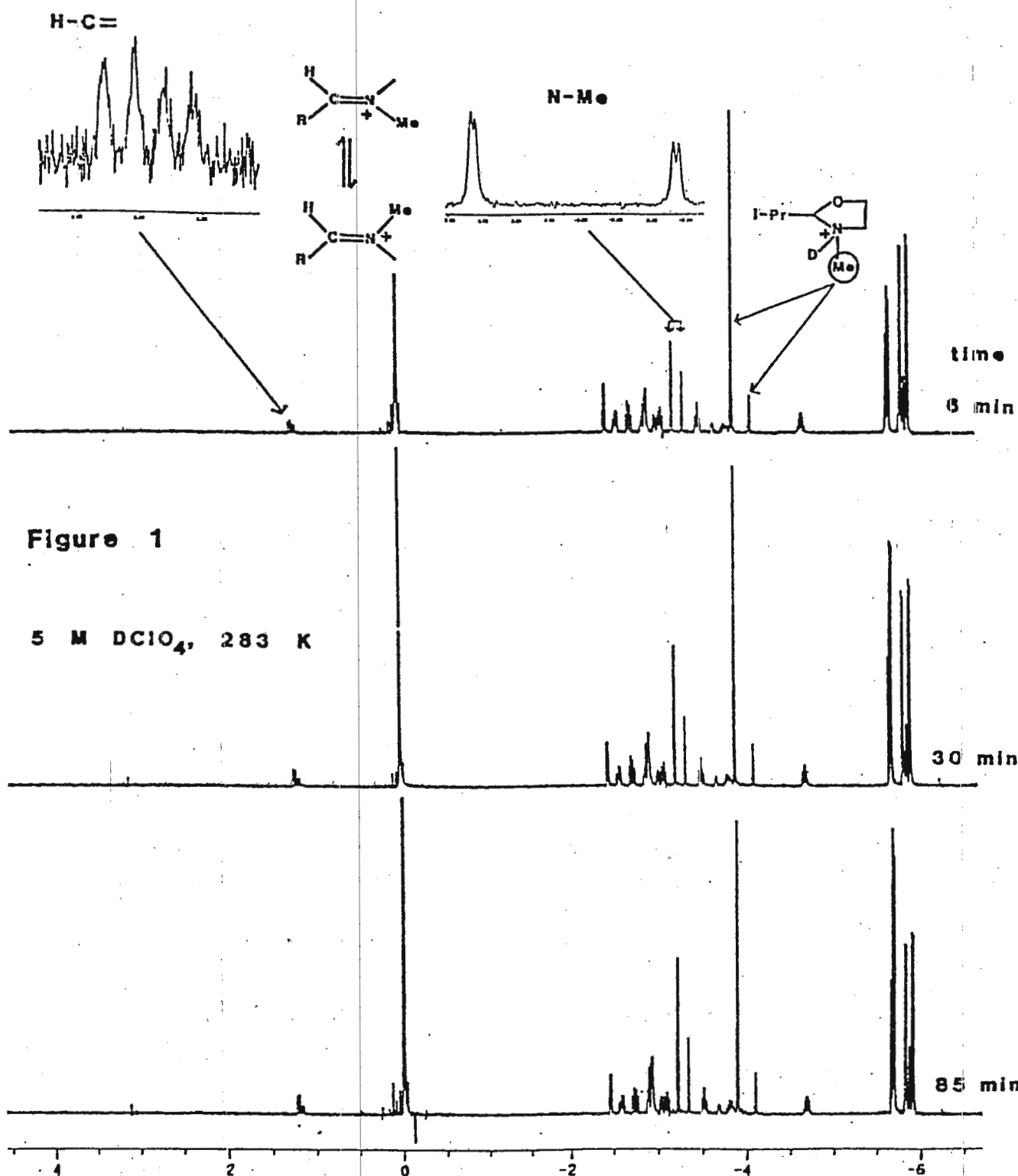
400 MHz  $^1\text{H}$  NMR Spectroscopy - A Powerful Tool in the Study  
 of Organic Reaction Mechanisms

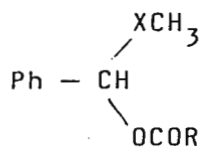
Dear Professor Shapiro,

In context with our studies on the role of Schiff's base intermediates in the hydrolytic decomposition of some N-alkyl-substituted 1,3-oxazolidines and tetrahydro-1,3-oxazines<sup>1</sup> we found out that because of its high sensitivity and resolution 400 MHz  $^1\text{H}$  NMR spectroscopy<sup>2</sup> offers a valuable insight into the reaction.

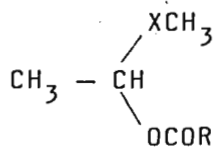
For instance the formation of the Schiff's base intermediate (SBI) at 283 K in 5 mol dm<sup>-3</sup> DC10<sub>4</sub> solution from 2-isopropyl-3-methyl-1,3-oxazolidine can be seen in the figure. Two isomeric ring forms (due to the protonation) as well as SBI's can be easily pointed out. The ring opening has a finite rate in these conditions whereas SBI's decompose further very slowly. The ratio [SBI]/[ring forms] changes from 0.48 (6 min) to 0.75 (30 min) and to 0.91 (85 min). At 323 K [SBI]<sub>tot</sub> reaches its maximum value within a few minutes in accordance with kinetic data for 2-alkyl-3-methyl-1,3-oxazolidines.<sup>1</sup> Many other observations related to the real course of these reactions can also be made.

Other cases of interest which we intend to (or already did) tackle with are the hydrolytic reactions of alkoxyalkylesters (1, 2)<sup>3</sup>, 2-alkyl-1,3-dioxanes and -1,3-oxathianes (3, 4) and thiomethylalkylesters (5, 6).

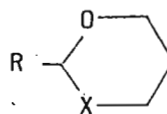




X  
O 1<sup>3</sup>  
S 5



X  
O 2  
S 6



X R  
O CH<sub>3</sub>  
S CH<sub>3</sub>

At any rate our preliminary results together with some attempts made in literature lend support to the significance of superconducting <sup>1</sup>H NMR techniques in increasing of a proper understanding of organic reactions and their mechanisms.

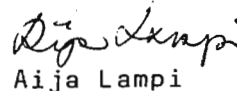
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1. K. Pihlaja; A. Parkkinen; H. Lönnberg J. Chem. Soc. Perkin 2, 1983, 1223 and references therein.
2. K. Pihlaja; A. Parkkinen; H. Lönnberg Abstracts, 7th IUPAC Conference of Physical Organic Chemistry, Auckland, New Zealand, 20-24.8.1984.
3. B. Capon; K. Nimmo; G. Reid J. Chem. Soc. Chem. Comm. 1976, 871.

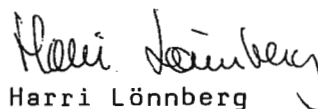
Sincerely yours,

  
Kalevi Pihlaja

  
Aija Parkkinen

  
Aija Lampi

  
Jorma Mattinen

  
Harri Lönnberg



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

IN REPLY REFER TO:

6120-148:CFP:ANG:log  
28 February 1985

Professor Barry Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 72843

Dear Barry,


JEOL PS-100 Components Available

This spring we will be decommissioning our PS-100 magnet system. The magnet, power supply/electronic console, probe assortment and water conditioner are available for transfer to any other government agency or to a university. The magnet and power supply were recently in use as part of a home-built spectrometer; by itself, this PS-100 is not a working spectrometer and would be useful only as a magnet system or a source of parts. Anyone who is interested in acquiring this system should contract one of use as soon as possible. (Chester F. Poranski 202-767-2488; Allen N. Garroway 202-767-2323)

We are removing this equipment to make room for a Bruker MSL-300 spectrometer system due to arrive this summer. This system will be a welcome addition to our present FX60Q, SXP with CP/MAS, solid state imaging and two Bruker/IBM 200D esr spectrometers.

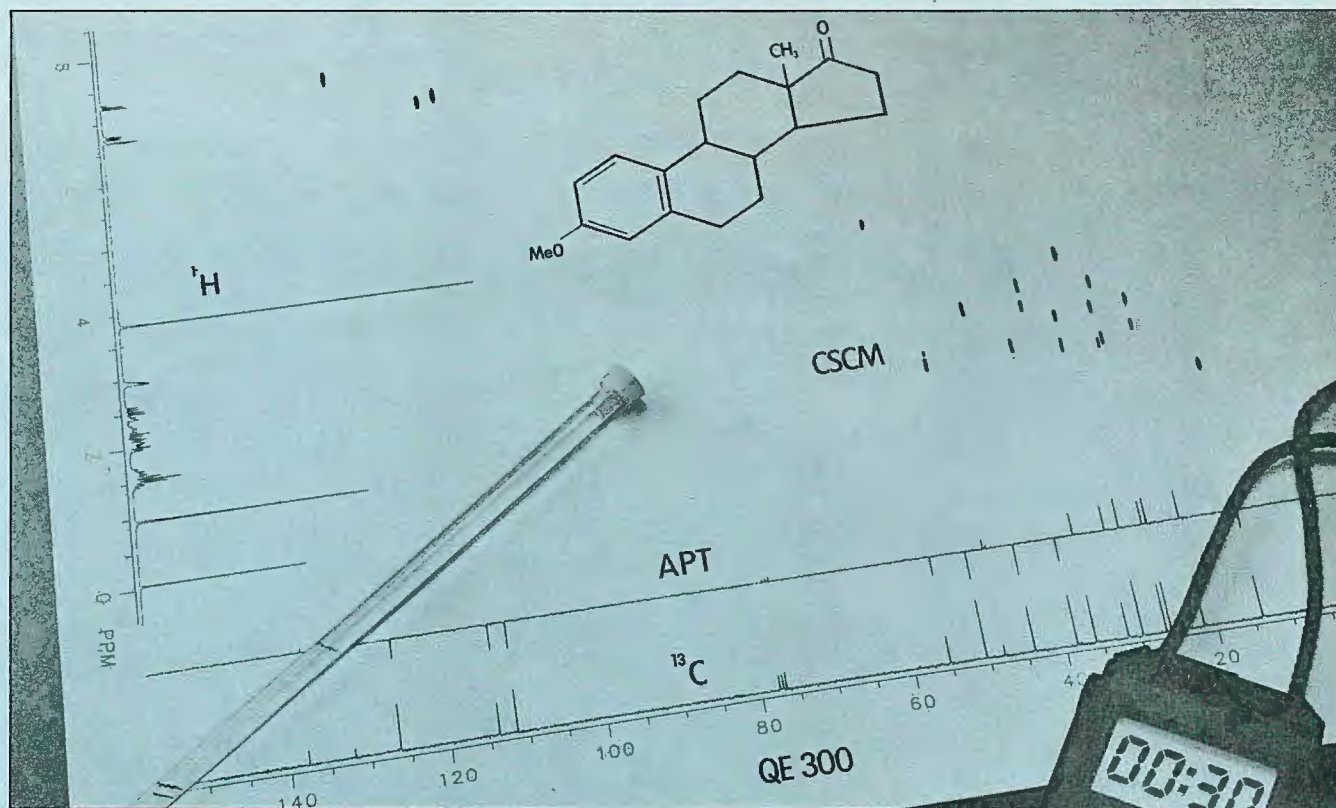
Our work in solid-state imaging and NMR structural studies of solids continues. A new Chemistry Division program in Bio-molecular Engineering may provide opportunities in new areas of research for us.

Sincerely,

  
Chester F. Poranski  
Polymeric Materials Branch  
Chemistry Division

41  
Allen N. Garroway  
Head, Polymer Diagnostics  
Section  
Polymeric Materials Branch  
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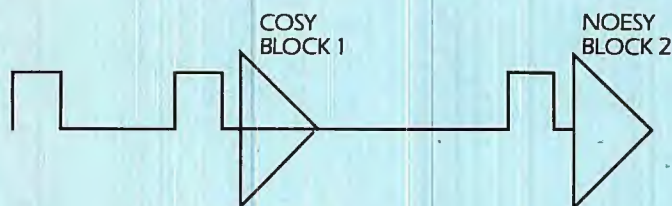
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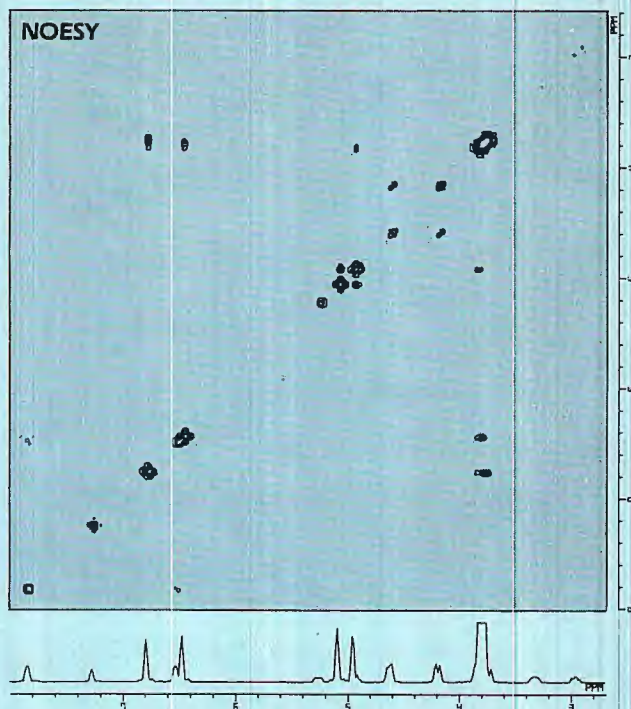
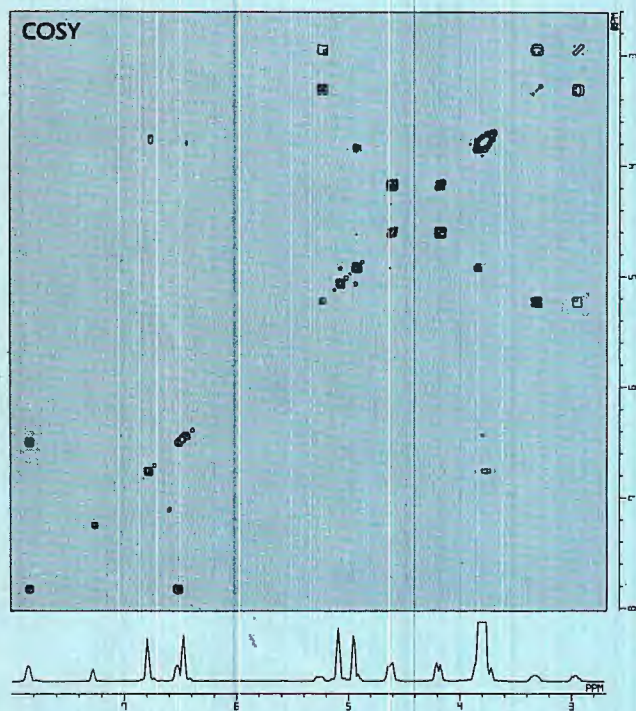


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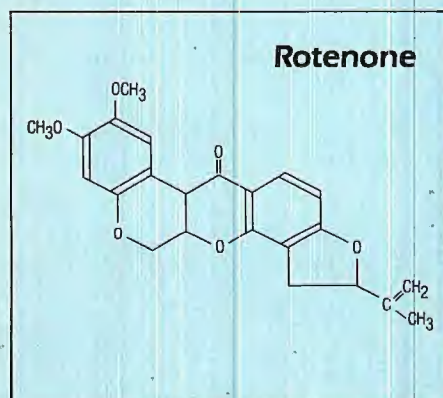


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