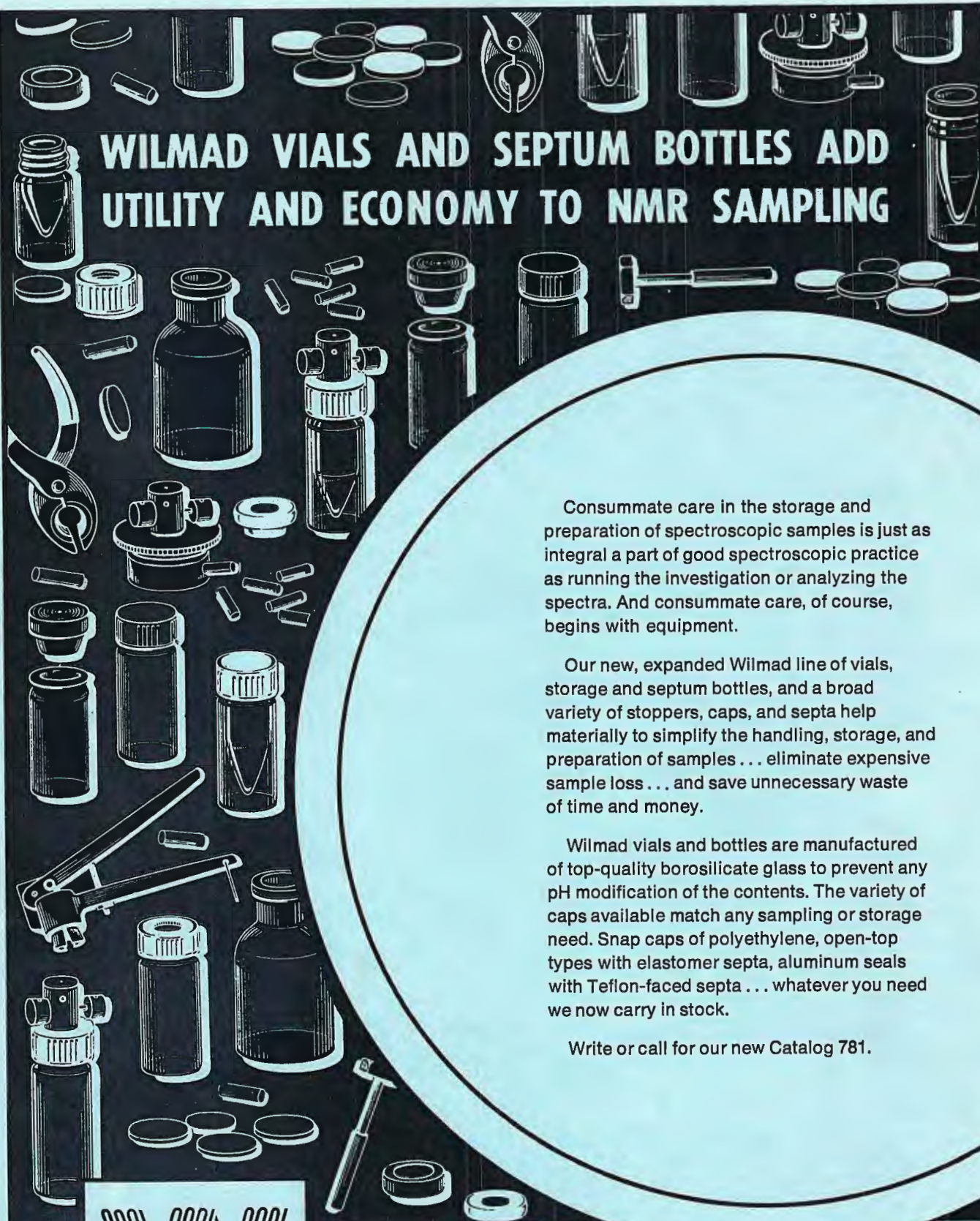


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DEADLINE DATES: No. 280 4 January 1982  
 No. 281 1 February 1982

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

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

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Carleton University  
Ottawa, Canada K1S 5B6

October 28, 1981.

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

Dear Barry:

<sup>15</sup>N NMR OF DIAMAGNETIC METAL ION: NUCLEOSIDE  
INTERACTIONS

We have begun a program to investigate heavy metal :  
nucleotide component interactions by Nitrogen NMR. As an  
example of our findings to date, I enclose a plot of the <sup>15</sup>N  
Chemical shift changes for guanosine, examined as a 0.5 M  
solution in DMSO-d<sub>6</sub>, as a function of added Hg<sup>2+</sup> ion.

It appears that N-7, which experiences an upfield shift  
of ca 20 ppm on addition of one equivalent HgCl<sub>2</sub>, is the preferred  
metallation site. This finding is consistent with results of  
M.O. calculations which suggest that N-7 is involved in the  
primary binding sites of nucleoside to "soft" metals.

Metallation site selectivity has also been noted for  
the nucleosides adenosine and cytidine, again <sup>in</sup> DMSO-d<sub>6</sub> solution.

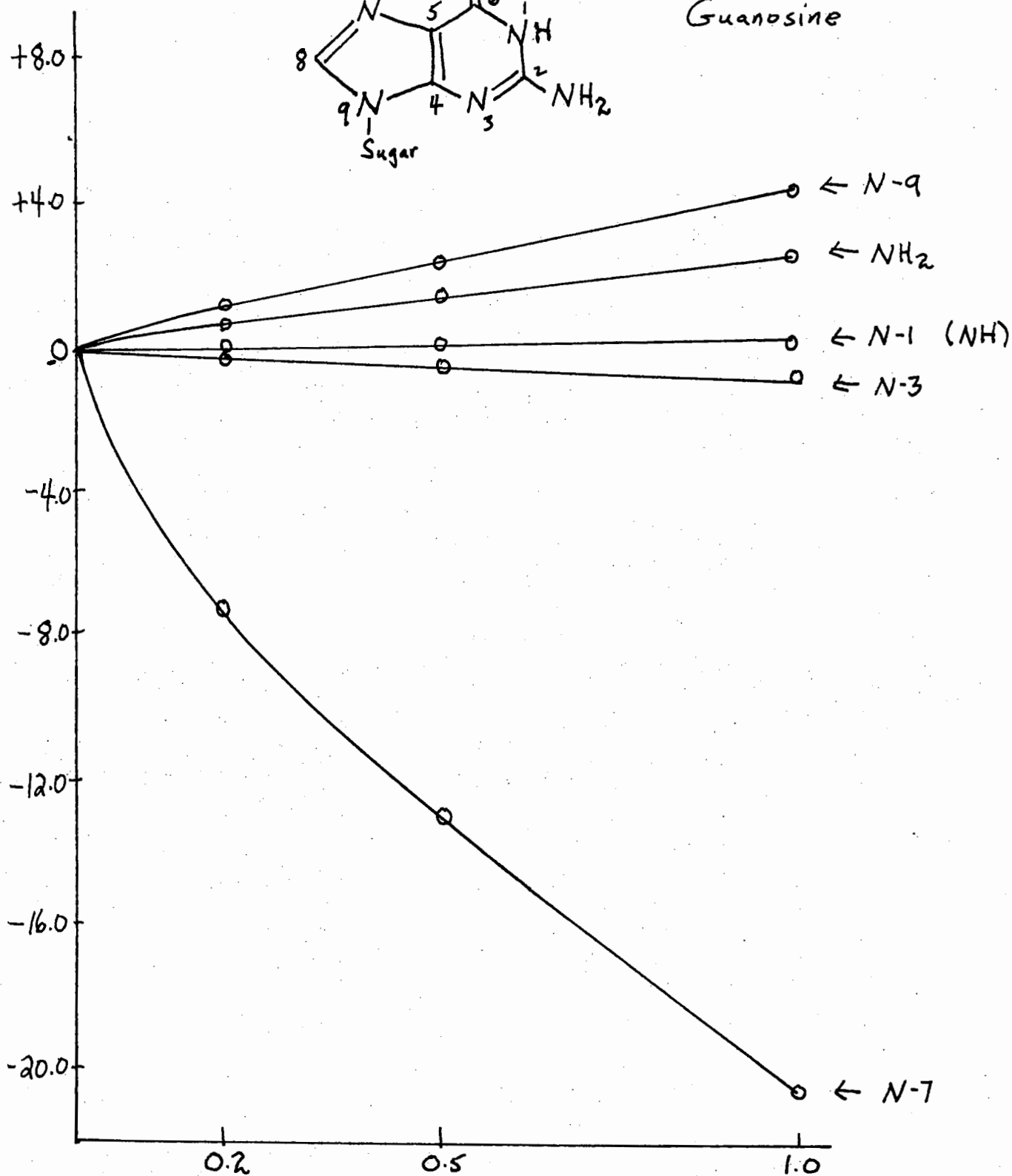
We are extending this work to aqueous solutions, and to  
base-paired dinucleotides which form mini-helices in water.

Sincerely,

G.W. Buchanan,  
Associate Professor.

MCS



$\Delta\delta_N$  (ppm)Equivalents  $\text{HgCl}_2$



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November 5, 1981

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

Re: Observation of P-P NOE

Dear Dr. Shapiro:

Recently we have become deeply involved in 2-D techniques and would like to present our preliminary results of phosphorus NOESY experiment (S. Makura & R. R. Ernst, Mol. Physics 41(1), 95 (1980)), which, as far as we know, was not yet performed. Fig. 1a is the 2-D spectrum of 220 mM ATP. Off-diagonal peaks represent transient NOEs between different phosphates while the "normal" ATP spectrum appears on the diagonal. Vanishingly small  $P_{\alpha}-P_{\beta}$  interactions comparing to  $P_{\beta}-P_{\gamma}$  interactions are obvious. It is instructive to compare this spectrum to the one of dilute (46 mM) ATP (Fig. 1b). While still less pronounced than  $P_{\beta}-P_{\gamma}$  interactions,  $P_{\alpha}-P_{\beta}$  interactions are now clearly visible. Allowing for the S/N of these spectra, the ratios of  $P_{\alpha}-P_{\beta}$  to  $P_{\beta}-P_{\gamma}$  cross-peaks integrated intensities is  $<0.05$  for the concentrated ATP and  $0.6$  for the dilute ATP.

While we are still working on this case trying to get a better understanding of NOE's buildups, our feeling is that these results reflect a "soft" structure ATP molecules assume in concentrated solutions.

These experiments were initiated by us as the first step towards elucidation of net phosphate fluxes in the PEP/ATP/ADP/AMP/ $P_i$  system in living mammalian cells by 2-D NOE spectroscopy, which was shown (S. Makura, et al., J. Mag. Res. 43, 259 (1981)) to be a powerful and promising tool for the elucidation of chemical exchange processes (B. H. Meier & R. R. Ernst, JACS 101, 6441 (1979)).

Please credit this contribution to the account of Dr. R. Highet.

Sincerely,

Lev Jacobson

James A. Ferretti  
Physical Sciences Laboratory  
Division of Computer Research  
& Technology

Encl.

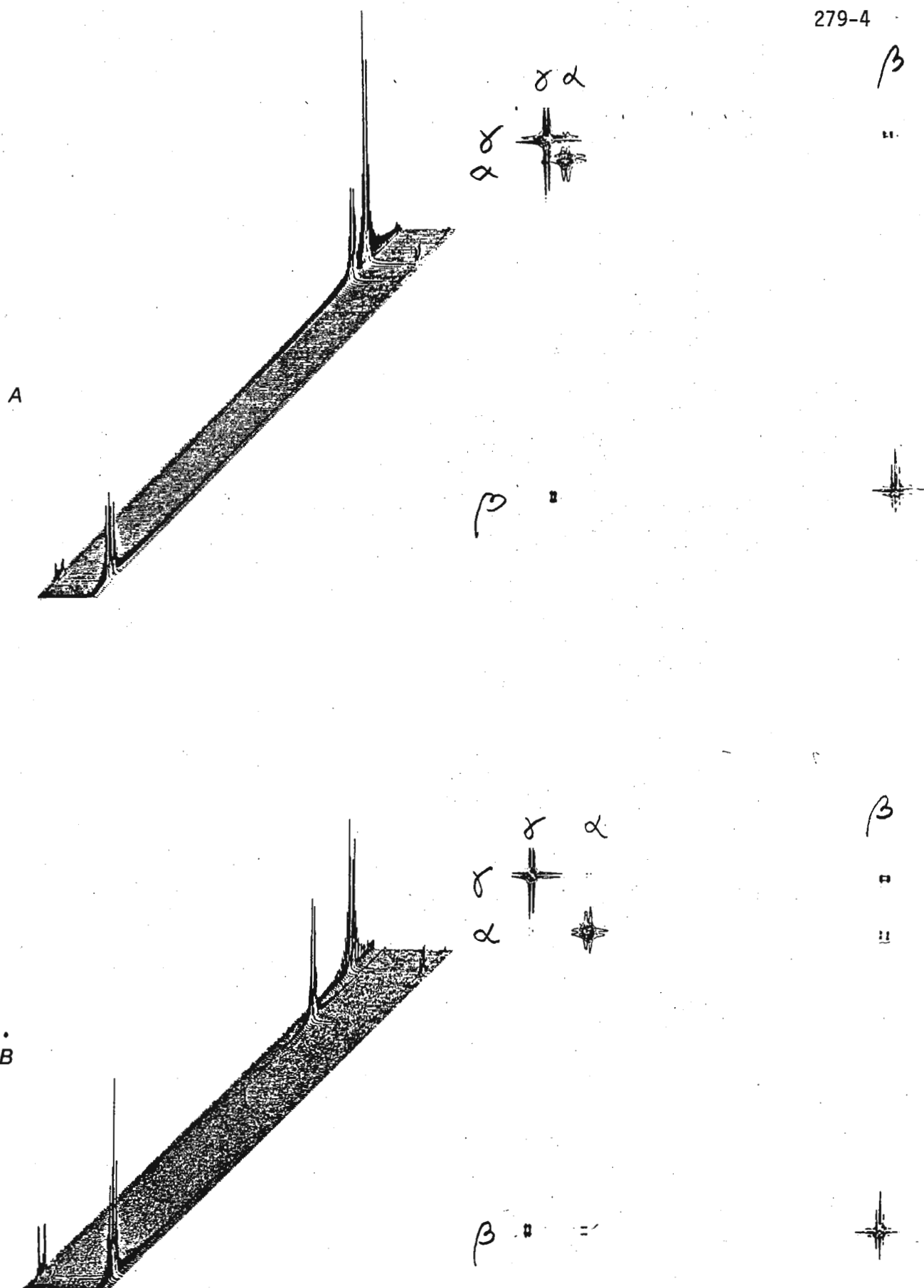


Fig. 1.  $^{31}\text{P}$  two-dimensional NOE spectra and corresponding contour maps of 226 mM (A) and 46 mM (B) ATP in H<sub>2</sub>O, pH 8.



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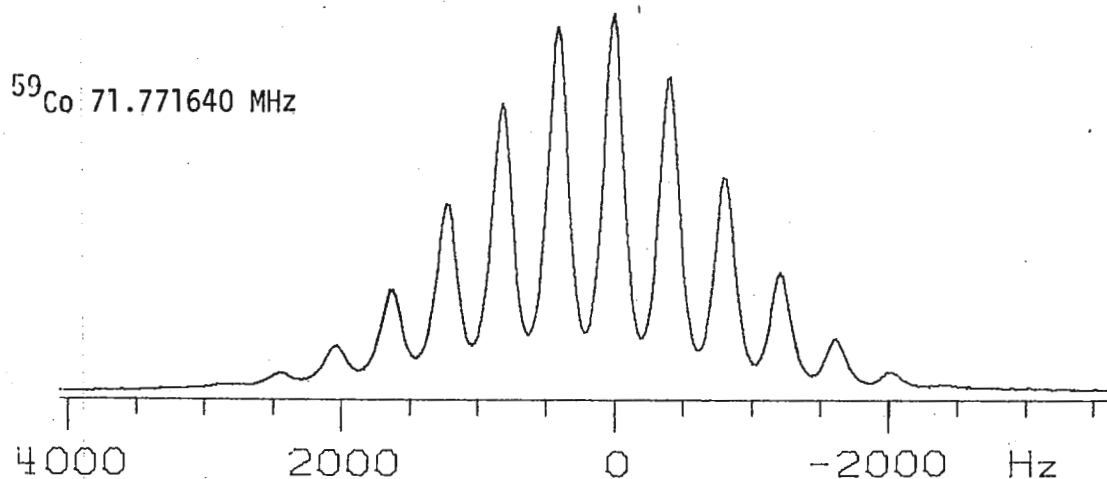
November 5, 1981

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

Dear Barry,

The spectrum below is, I think, a particularly clear example of the sensitivity of  $^{59}\text{Co}$  shifts to subtle environmental effects. With a chemical shift range that spans parts per thousand, it is possible to detect very minor differences in structure. The spectrum below, taken on a 300 MHz Nicolet spectrometer, is from a sample of hexamminecobalt(III) chloride that had equilibrated for some time in a 1:1 mixture of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The resulting pattern arises from the D-H distribution among the nitrogen atoms. Of the total possible peaks of 19, we have here resolved only 14; however, clearly a shift in the solvent composition will shift the spectrum towards the ends of the pattern.

While this spectrum is perhaps of remote interest by itself, it clearly shows the possibility of studying the proton exchange from coordinate nitrogen atoms in more detail than may be even useful. It also points out a potential problem when one routinely uses deuterium oxide as a lock solvent in cobalt-59 spectroscopy. Depending on pH any of the coordinated amines will also exchange protons and give rise to additional isotope shifted resonances that may be thought of as impurities initially.



Best regards,

*Bob Bryant*  
Robert E. Bryant

*Stephen B. Philson*  
Stephen Philson



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Professor B L Shapiro  
Department of Chemistry  
Texas A & M University  
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Texas 77843  
USA

19 November 1981

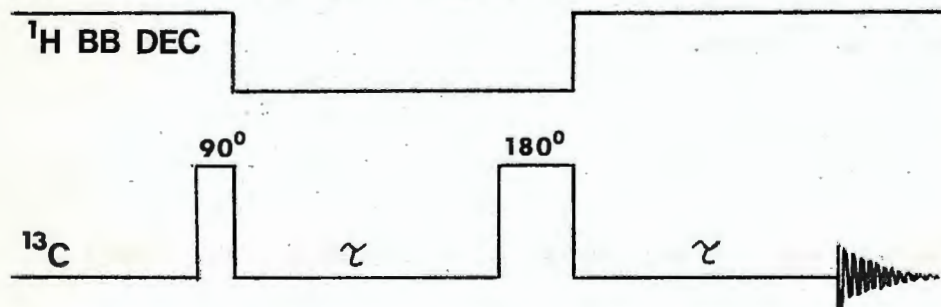
Dear Barry,

A MOVE INTO THE 20th CENTURY; J MODULATED SPIN ECHO SPECTRA ON A  
BRUKER WP 80 SY

This year we have begun the updating of this department's FT NMR instrumentation. In June we replaced our original iron magnet FT instrument with a Bruker WP 80 SY including multinuclear and dedicated proton probe. Next spring we look forward to the delivery of a Bruker 360 MHz instrument. Meanwhile we are enjoying the increased versatility of our new low field instrument.

On the one hand this increases our work load since we can now run routine spectra on a wider range of nuclei. However, we also now have the capability of using up to date techniques as an aid to our regular problems. One of these is the common problem of distinguishing between  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$  and  $\text{C}$  groups in  $^{13}\text{C}$  spectra of complex molecules such as steroids. Previously we only had available the single frequency off resonance proton decoupling technique with the usual problems of second order effects and overlapped lines. On our new instrument we are able to use the J-modulated spin echo technique as a further aid to assignment.

We have been testing a pulse sequence (shown below), easily usable on our WP 80 SY and made available by Bruker, which is based on the sequence published by Le Cocq and Lallemand<sup>1</sup>.



The first delay  $\tau$  allows the J modulation to evolve according to the magnitude of  $J_{\text{CH}}$  and multiplicity of the protons on the carbon atoms<sup>1</sup>, during the second  $\tau$  delay with BB decoupler on, the chemical shifts refocus prior to acquisition of the echo signal. When  $\tau = \frac{1}{J}$  the  $\text{CH}$  and  $\text{CH}_3$  carbons yield negative signals while  $\text{CH}_2$  and  $\text{C}$  yield positive signals.

The spectra shown here are for the steroid androstanolone (210mgs/cc of  $\text{CDCl}_3$ ). The JMODSE middle spectrum is drawn with  $\text{CH}_3$ , CH positive and  $\text{CH}_2$ , C negative and was obtained with  $\tau=8$  m sec corresponding to  $J=125 \text{ MHz}$ . The bottom spectrum is the broad band decoupled spectrum and the top is the single frequency off resonance decoupled spectrum recorded with the proton decoupler set about 700 Hz upfield of TMS. The spectra were run under conditions such that the JMODSE spectrum took about the same time as the BBD spectrum (around 20 minutes) whereas the SFORD spectrum was accumulated for about 4.5 times as long.

The SFORD spectrum enables the quaternary carbons, C3, C13, C10 to be identified immediately. Also, the CH groups C17, C9 and to a lesser extent C14 can be picked out as doublets. The two  $\text{CH}_3$  groups C18, C19 are clearly distinguished. In the intervening regions from 20 to 50 PPM the JMODSE spectrum enables the  $\text{CH}_2$  and CH groups to be identified without the ambiguity of the SFORD spectrum. The quaternary carbon C10 and the methine C8 are seen to be very nicely separated by the JMODSE technique.

We aim to test this technique on everyday samples. Whether it proves to be such a useful adjunct to SFORD in practice, for samples of limited quantity, as it is here, remains to be seen.

I must apologise for being so late with this first contribution and I should like to thank Dr J Hanson for the sample of adrostanolone and help with the chemical shift assignments shown below:

C1	38.4	C5	46.6	C9	53.8	C13	42.8	C17	81.4
C2	37.8	C6	28.6	C10	35.5	C14	50.6	C18	11.00
C3	211.6	C7	31.1	C11	20.8	C15	23.2	C19	11.20
C4	44.4	C8	35.3	C12	36.5	C16	30.2.		

Best regards,

*Michael D. Rowe.*

Michael D Rowe

*Reference:*

1. C. LeCocq and J.-Y Lallemand, J.C.S.Chem.Soc. 150, (1981).





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October 29, 1981 Ref. No. 56

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

MAS of quadrupoles

Dear Prof. Shapiro,

Please excuse our long silence. We are too busy working on various solid-state high resolution NMR projects, spinning all possible nuclei at or near the magic angle. In this letter we want to show that magic angle spinning (MAS) can provide useful information about the isotropic chemical shifts and quadrupole coupling parameters of nuclei with spin  $I = 3/2, 5/2, 7/2 \dots$  in powder samples. MAS not only averages out the chemical shift anisotropy and dipolar interactions, but also reduces fourfold the linewidth of the central transition. For easy interpretation, the condition

$$v_{\text{rot}} \geq \frac{3(e^2qQ/h)^2}{16 v_{\text{Larmor}}} \cdot \frac{I(I+1) - 3/4}{I^2(2I-1)^2}$$

must be satisfied. In this case the spinning sidebands will be clearly separated from the centerband. The calculation of lineshape is an easy task for the Bruker Aspect-2000 computer and a library with various asymmetry parameters  $\eta$  can be memorized for handy reference.

Other interaction parameters change only the scaling of line along frequency axis. The isotropic chemical shift practically coincides with the bottom of the left slope of the composite lineshape, while the other features provide information about the principal values of the quadrupole interaction tensor. A more detailed analysis is in press in Chem. Phys. Letters. We have studied various compounds containing  $^{23}\text{Na}$ ,  $^{27}\text{Al}$ ,  $^{11}\text{B}$  and other quadrupole nuclei. In the accompanying Figure, the  $^{23}\text{Na}$  spectra of  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  are shown.

We seem to have found a crystalline modification of it, where  $\eta$  is 0.25 rather than 0.47 as reported by Holuj and Petch [Can. J. Phys. 34, 1169 (1956)].

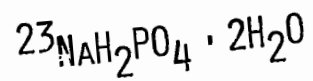
Sincerely yours

A. Samoson

*A. Samoson*

E. Lippmaa

*E. Lippmaa*



CXP - 200

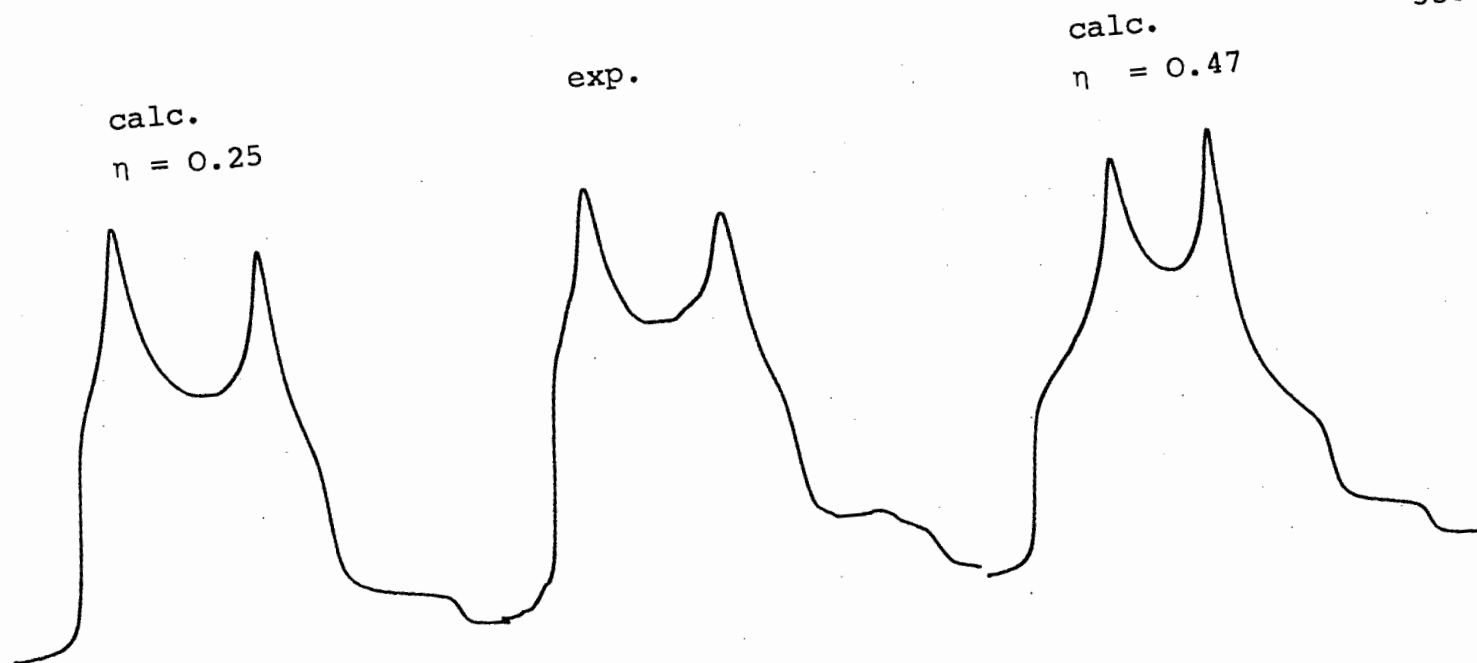
$^{23}\text{Na}$  MAS

$\nu_L = 53 \text{ MHz}$

$\nu_Q = 1.18 \text{ MHz}$

$\nu_{\text{rot}} = 3.5 \text{ kHz}$

330 Hz/cm



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THE UNIVERSITY OF ALBERTA  
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October 21, 1981

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

Dear Barry:

Re: Summer Symposium on Analytical Applications  
of NMR Spectroscopy

Each year, the Analytical Division of the American Chemical Society sponsors a "Summer Symposium on Analytical Chemistry". This coming summer, the symposium will be held on June 28-30 at Michigan State University. The subject of the symposium is "Analytical Applications of NMR Spectroscopy".

The symposium program is not yet complete, but the plans are to have a comprehensive coverage of state-of-the-art NMR techniques and applications including recent advances in instrumentation and software, carbon-13 NMR, multi-nuclear NMR, methods for resolution and sensitivity enhancement, new NMR techniques, 2D FT NMR, analytical applications of NMR in industrial laboratories, in environmental laboratories, in energy-related problems, etc., NMR of solid samples, and NMR measurements on biological samples. We also are planning poster sessions. Anyone wishing to participate in the poster session should contact the program chairman.

Further information may be obtained from either the General chairman or the program chairman.

Sincerely yours,

Alexander I. Popov  
General Chairman  
Department of Chemistry  
Michigan State University  
East Lansing, Michigan

Dallas L. Rabenstein  
(Program Chairman)  
Department of Chemistry  
University of Alberta  
Edmonton, Alberta, Canada  
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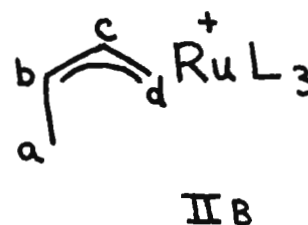
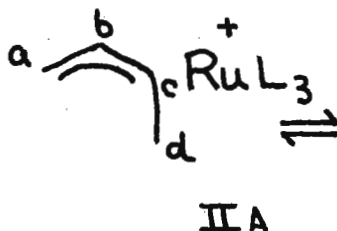
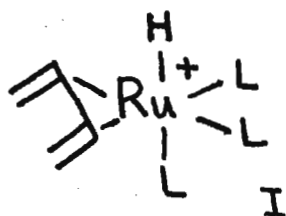
Your file

Professor B.L. Shapiro  
 Texas A & M University  
 COLLEGE STATION  
 Texas 77843  
 United States of America

Dear Professor Shapiro

AN INTERMEDIATE EXCHANGE RATE TRAP

Recently, we fell into the trap set by an organometallic complex which had been characterised by X-ray crystallography as the 18-electron butadiene metal hydride structure I,  $L = \text{PMe}_2\text{Ph}$ .



The  $^{13}\text{C}$  spectrum ( $30^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ ) failed to show, however, any lines for the butadiene portion so we rashly suggested to the chemist responsible (Dr T.V.Ashworth) some fault in the sample preparation. After several more attempts with the same outcome we cooled the solution to  $-60^\circ\text{C}$  and lo and behold four lines appeared at 41.2, 94.9, 67.2, and 2.8 ppm. Respectively T,D,D and Q in the s.f.o.r.d.

Clearly, at  $30^\circ\text{C}$  the molecule is in the intermediate exchange region, the slow exchange structure being not I but the formally 16-electron allyl species II, although I may be the intermediate in the exchange  $\text{IIA} \rightleftharpoons \text{IIB}$  as suggested by Ittel *et al.* (*J. Amer. Chem. Soc.*, 101, 6905 (1979)) for an analogous Fe complex. The Fe complex is at slow exchange at  $30^\circ\text{C}$  but both complexes show pronounced shielding of the methyl group carbon and proton resonances putting the latter in a region which the unwary might assign to a metal hydride.

Yours sincerely

A.A. Chalmers  
CHIEF RESEARCH OFFICER

# CONCORDIA UNIVERSITY

DEPARTMENT OF CHEMISTRY



November 6, 1981

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

Dear Barry:

## STERIC INFLUENCES ON METHYL GROUP $^1\text{H}$ RELAXATION

In the course of  $^1\text{H}$  spin-lattice relaxation studies of methyl groups in a series of substituted toluenes, a substantial differential in the methyl group  $R_1$  values for ortho- and meta-toluidines was observed. This difference is attributed to steric hindrance of methyl rotation by the amino function in the ortho-isomer. This results in a slower rate of methyl group rotation, which affects the  $R_1$  value by reducing the spin-rotation contribution<sup>1</sup> and increasing the dipolar relaxation efficiency, relative to a freely rotating methyl group. Evidently the dipolar contribution dominates. To allow for a direct measurement of this effect in a single experiment, the  $R_1$  values of 2,4- and 2,5-dimethylaniline were measured, with similar results (see Table).

We needed to find out if the ortho methyl group was picking up any relaxation from an adjacent amino proton. Calculations based on a static spatial relationship between amino and methyl functions showed that this was a possibility. To check, N,N-dideutero-2,4-dimethylaniline was prepared and the  $R_1$  values were measured. The normalized  $R_1$  values and hindered-to-free methyl  $R_1$  ratios were essentially unchanged (see Table). Also, if there were any relaxation contributions from an amino proton, an NOE enhancement, rarely seen for a methyl group<sup>2</sup>, would be evident upon saturation of the amino function. We measured the NOE difference spectrum<sup>3</sup> for 2,4-dimethylaniline and found no measureable enhancement of the methyl signal intensity. From these experiments we concluded that the  $R_1$  differential does, in fact, arise from the steric hindrance to methyl rotation.

.....

Dr. B.L. Shapiro

November 6, 1981

This example of the sensitivity of methyl  $^1\text{H}$   $R_1$  values to the steric environment demonstrates the potential of these values for the determination of structure and stereochemistry.

Best regards,

Yours sincerely,

*Walter*

W.J. Chazin

*Lauril*

L.D. Colebrook

/ac

<sup>1</sup> Rowan, et al.<sup>2</sup> measured a spin-rotation contribution to  $^1\text{H}$  relaxation of about 25% for the freely rotating methyl group in 3,5-dichlorotoluene.

<sup>2</sup> R. Rowan, P. Mazzocchi, C. Kanagy, and M. Regan, J. Magn. Res., 39, 27 (1980).

<sup>3</sup> L.D. Hall and J.K.M. Sanders, J. Am. Chem. Soc., 102, 5703 (1980).

Table

Compound	Normalized $R_1$ values*		Ratio H:F
	Free	Hindered	
m-Toluidine	1.33	-	-
o-Toluidine	-	1.63	1.22
2,4-Dimethylaniline	1.43	1.66	1.16
N,N-Dideutero-2,4-dimethylaniline	1.44	1.64	1.14
2,5-Dimethylaniline	1.42	1.69	1.18

\* Normalized to the  $R_1$  value of a remote aromatic proton. 400 MHz spectra.



**Diamond Shamrock**

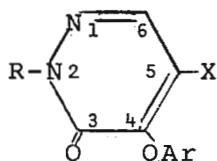
T. R. Evans Research Center

November 9, 1981

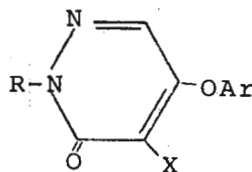
Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, TX 77845

APPLICATION OF C-H COUPLING CONSTANTS FOR DETERMINATION  
OF REGIOSELECTIVITY WITH THE AID OF A SOLVENT INDUCED SHIFT

Discrimination of products from OAr substitution of a  
dihalopyridazinone,



I



II

X = halogen

is possible by measurement of the two and three bond C-H coupling constants bearing between proton H-6 and carbons C-5 and C-4. Larger coupling is anticipated over the three bond path than over the two bond route<sup>1,2,3</sup>. Therefore, if OAr is at C-4, then the C-H coupling there should be larger than at C-5. In three derivatives studied thus far, OAr preferentially appears at C-4. The following pertinent parameters have been measured:

Derivative	<sup>2</sup> J (H-6,C-5)	<sup>3</sup> J (H-6,C-4)	δ (C-4)	δ (C-5)
1	4.3 Hz	7.3 Hz	150.4 ppm	116.8 ppm
2	4.9	6.7	146.7	128.1
3	3.7	5.9	149.0	126.6

Because of interfering peak overlap using CDCl<sub>3</sub>, these measurements had to be made in DMSO-d<sub>6</sub> solvent where a small induced shift provided the requisite peak resolution. "High resolution" <sup>13</sup>C NMR spectra were obtained on our WH-90 using gated <sup>1</sup>H decoupling.



November 9, 1981

Sincerely,

*George E. Babbitt*

George E. Babbitt

jsb

P.S. Please credit Diamond Shamrock's account with this contribution.

<sup>1</sup>Wherli, F. W. and L. Wirthlin, Interpretation of Carbon-13 NMR Spectra, Heyden, New York, (1976).

<sup>2</sup>Levy, G. C., R. L. Lichter and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance Spectroscopy, 2nd edition, John Wiley & Sons, New York (1980).

<sup>3</sup>Organic Magnetic Resonance, 15, 18 (1981).

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Telex 78841



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

## TWO-DIMENSIONAL NMR:

### THE FIRST TEN YEARS.

Dear Professor Shapiro,

It is exactly ten years ago that J. Jeener first pointed out the general principle and potential usefulness of two-dimensional Fourier-Transform NMR, in that memorable lecture at the 2nd Ampere Summer School in Yugoslavia. And ever since, chemists and NMR spectroscopists have been intrigued by the concept and its power and at the same time put off by ill-conceived statements like "2D NMR is orders of magnitude less sensitive" or "it only works at very high magnetic fields" or "the processing of the data takes ages" or "the spectra look nice but you never get the information you really want" or "commercial instruments will never meet the experimental requirements".

True: the spectra do look nice indeed. But as far as all those other statements are concerned....

We are now regularly using the new standard software ("rev.G") on our XL-200, and we are realizing that, with the powerful 2D capabilities it provides, we can solve all kinds of real-life analytical problems much more rapidly and elegantly than with the old-fashioned double resonance methods. There are some key requirements, however, which must be met by the spectrometer's datasystem before one can even start to think about using 2D NMR in a routine fashion:

- Mass storage media must allow simultaneous storage of original F.I.D.'s, first domain, and second domain data. Very often, repeated Fourier transformations are required to achieve optimum presentation of data. The ideal combination of exponential weighting, convolution-difference, and pseudo-echo is often not found at first shot.
- Fourier-transform times (and this includes all overheads that account for data storage on and retrieval from the mass media, weighting, phasing, and display) must be short. But since even a pretty fast program has to chew for some 30 minutes on a 1000 by 1000 spectrum, you MUST have the capability of processing your 2D data while you are acquiring other data. Otherwise the other guys who want to do their normal accumulations on the machine will never let you do the fancy 2D stuff.

- Very flexible spectrum presentation on video display and in hard copy: full and partial spectra; stacked and contour display; rotations, cross-sections, projections; phased and absolute-value in first and second domain must be available to achieve optimum presentation of all types of 2D spectra and retrieval of full spectral detail. As an example, you can never measure real, precise splittings in a J-resolved spectrum if you are looking at absolute-value data.
- Pulse sequence programming capabilities must allow for generation of ALL types of 2D experiments (homo- and heteronuclear J-resolved, shift-correlated, NOE-correlated, multiple-quantum coherence-correlated...), for quadrature detection in both frequency domains (for optimum use of data space), for extensive and complex phase-cycling (to minimize spectral artifacts), and for very precise timing (to avoid phase jitter and t1 noise).

With the two enclosed spectra, we'd like to illustrate some of the points discussed above, and to document what one might call "The State Of The Two-Dimensional Art At 4.7 Tesla"!

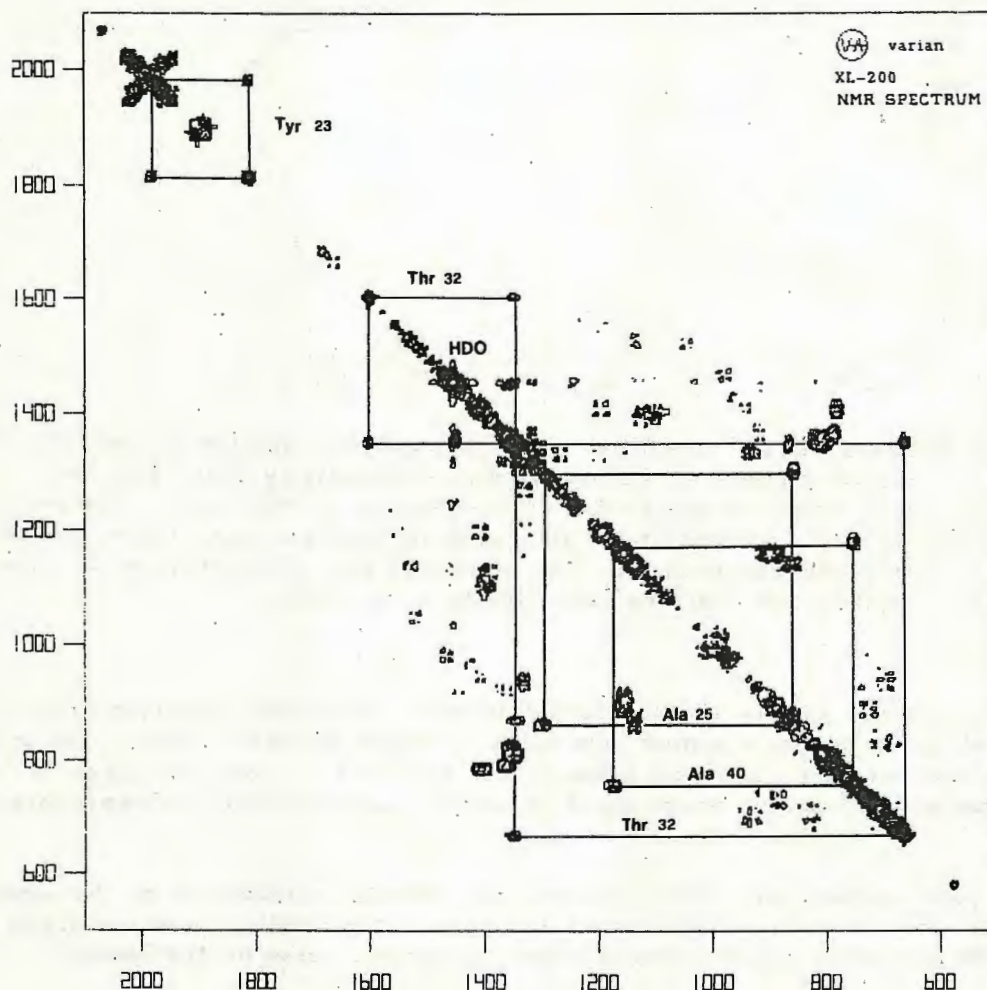


Figure 1 shows the 2D-correlated Proton NMR spectrum of the Bovine Pancreatic Trypsin Inhibitor at 200 MHz and 60 Deg.C, in D<sub>2</sub>O. The 1000 X 1000 data matrix was recorded overnight. High precision timing and quadrature phase detection in both time/frequency domains, "pseudo echo" treatment, and symmetrisation yields a spectrum which is free of artifacts and sufficiently well resolved to allow assignment of most of the aliphatic amino acid residues (we have marked a few of them).

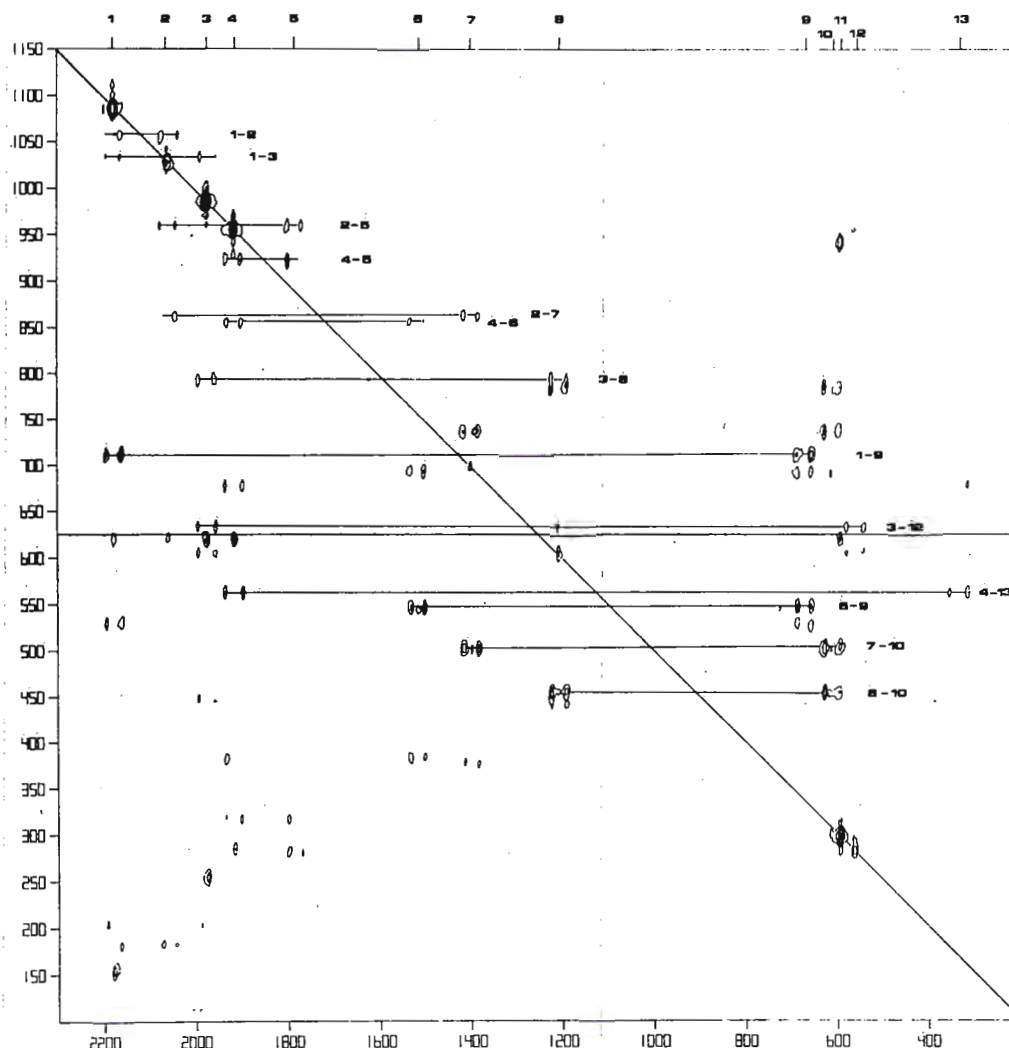


Figure 2 shows a "CCCCP" spectrum: a two-dimensional version of the "INADEQUATE" experiment yielding directly a "Carbon-Carbon Connectivity Plot" and hence the full structure of an unknown molecule. The structure of this novel diterpene follows immediately from the connectivities indicated in the spectrum. The spectrum is the result of a weekend accumulation. The compound was obtained from Dr. Reinaecker, Max Planck Institute for Coal Research, Muelheim, Germany.

All text and one of the figures shown in this letter were obtained from a PAPER TIGER dot matrix graphics printer and using standard XL-200 hardware and software. By the way; wouldn't that be a great idea for some of your contributors: an NMR spectrometer that can be programmed to answer all your colorful reminders all by itself!

Any of your readers who wish to obtain more detailed information on the experiments described above (or on a text system for generating TAMUNN contributions...) are invited to drop us a line for preprints and application notes on the subject.

Yours sincerely,

*Rene Richarz*

*Tom W. J. de Leeuw*

The Varian Team, Europe

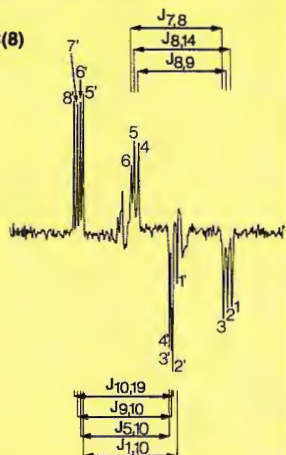
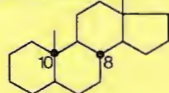


# We produced these spectra—

## <sup>13</sup>C-Satellite Excitation Using "INADEQUATE"

C(10) and C(8)

5 $\alpha$ -Androstane

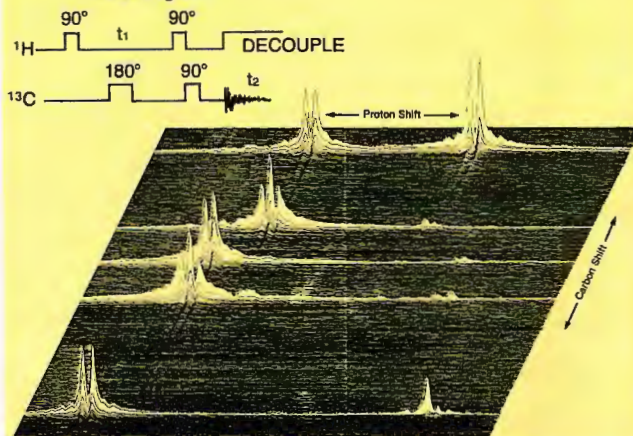


Expansion of the partial INADEQUATE spectrum of 5 $\alpha$ -androstane, showing overlapping <sup>13</sup>C satellites of carbon 8 and 10. Note the efficiency of center-band cancellation resulting from the hardware stability and the software flexibility of the XL-200 pulse programmer. Assignments shown are the result of the "COSMIC" automatic analysis program on the XL-200.

\*A. Bax, R. Freeman and S.P. Kempell, JACS, 102, 4849 (1980).

## Heteronuclear Correlated 2-D Coumarin

Pulse Diagram:



Heteronuclear Correlated 2-D NMR on coumarin. Presence of a resonance indicates presence of a C-H bond. The sub-splittings along the proton direction are the homonuclear <sup>1</sup>H-<sup>1</sup>H splittings, even though the experiment is <sup>13</sup>C observe. The phase cycling employed in the pulse sequence allows quadrature operation in both frequency domains.

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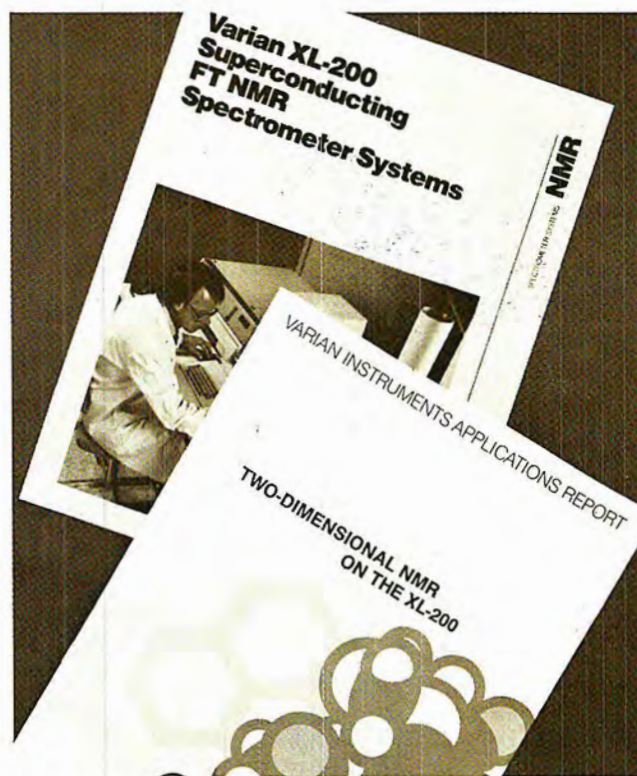
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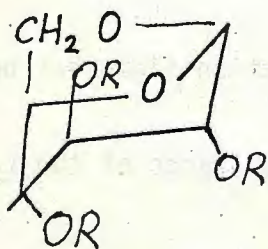
November 17, 1981

Assignment of  $^{29}\text{Si}$  chemical shifts from Hammett-type correlations  
in sugar derivatives

Dear Barry,

Some time ago, despite the opposition of a referee, we published<sup>1</sup> unassigned  $^{29}\text{Si}$  chemical shifts in 1,6-anhydro-2,3,4-tri-O-trimethylsilyl- $\beta$ -D-glucopyranose and the assignment problem has hunted us ever since. Prof. Harris et al.<sup>2,3</sup> succeeded in assigning some of the shifts in other pertrimethylsilylated monosacharides. Unfortunately, none of the spectroscopically "pure" methods of assignments used<sup>2,3</sup> was applicable to our compound except for the selective mono-deuteration but that was not up to the taste of our chemists. Hence we had to resort to substituent effects.

Since  $^{29}\text{Si}$  chemical shifts correlate relatively well with  $\sigma^*$  constants in the  $\text{Me}_3\text{SiOR}$  compounds it was no surprise to find an excellent correlation for "rigid" 1,6-anhydro- $\beta$ -D-glucose derivatives. Using the correlation for trimethylsiloxy group bound to C - 3 carbon the signal at  $\delta = 17.57$  (in  $\text{CDCl}_3$ ) should be assigned to the trimethylsiloxy group on this carbon atom. From a comparison with the spectrum of 1,6-anhydro-2-O-tosyl-3,4-di-O-trimethylsilyl- $\beta$ -D-glucopyranose ( $\delta = 19.81$  and  $18.54$ ) we could assign the signals at  $\delta = 18.52$  and  $17.78$  to the groups on C - 4 and C - 2 carbons, resp.



1,6-anhydro- $\beta$ -D-glucopyranose skeleton

Sincerely yours,

*Jan*  
Jan Schraml

1. Schraml J. et al.: Coll.Czech.Chem.Comm. 41, 360 (1976)
2. Grale D.J., Haines A.H., Harris R.K.: OMR 7, 635 (1975)
3. Haines A.H., Harris R.K., Rao R.C.: OMR 9, 432 (1977)



Rijksuniversiteit Utrecht

## Organisch chemisch laboratorium

Croesestraat 79  
3522 AD Utrecht  
Telefoon 030 - 882311

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

Datum 5 November 1981

Dear prof. Shapiro,

It has been known for some years, that coupling constants are solvent dependent, i.e. changing the solvent will change the coupling constant even when no conformational changes occur in the solute.

A major factor in this solvent dependency (which is in the order of less than 3% for  $^1J_{C-H}$ ) is attributed to an electric field effect. Recently the electric field dependency has been studied by Watanabe c.s. for  $^1J_{C-H}$  in a number of chlorine substituted ethanes<sup>1</sup> and haloethanes<sup>2</sup> dissolved in a series of solvents with dielectric constants ranging from 2.24 to 191.3. Of the several models which describe the induced electric field distribution in the solute<sup>3-4-5-6</sup> Watanabe uses the "solvation" or "solvaton" model<sup>6</sup>. Theoretical values for  $^1J_{C-H}$  are derived from finite perturbation INDO and/or CNDO/2 approximations.

Though the fit of the observed data and the theoretical values in the studied solvent ranges are far from perfect\*, Watanabe concludes that, after scaling of the theoretical data, the solvation model is at least as satisfactory as the reaction field model.

As we had done some preliminary studies on the solvent dependency of  $^1J_{C-H}$  in various compounds, but did not obtain very satisfactory results, we decided to study the old workhorse of electric field dependency of NMR parameters, PARALDEHYDE.

For this compound the shift dependency on the reaction field has been

\*and in our opinion incorrectly the dielectric constants of the solvents are used for the calculations.



well established<sup>7</sup> ; we measured all coupling constants and shifts of this compound for a range of solutions (approximately 25%v/v) with dielectric constants varying from 2.75 to 42.44 (solvent  $\epsilon$  is 1.89 to 109).

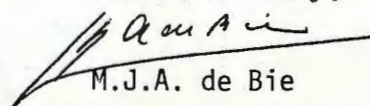
We plotted the coupling constants against a number of dielectric functions, i.e.:

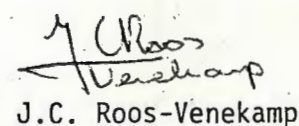
$$\epsilon, \frac{\epsilon-1}{\epsilon}, \frac{\epsilon-1}{\epsilon+2.86}, \left(\frac{\epsilon-1}{\epsilon+2.86}\right)^2 \text{ and } \frac{(\epsilon-1)(2\epsilon+1)}{\epsilon}$$

We found that there are discrepancies in the curves for solutions with dielectric constants above or below the dielectric constant of paraldehyde. This is not unreasonable because, according to the review article by S.L.Smith<sup>8</sup>, one should gradually change from an electric field in the solute cage caused by the reaction field to one which is due to the Stark-effect<sup>9</sup>. This is clear from the figure in which we plotted for our preliminary data both dependencies on  $\frac{(\epsilon-1)(2\epsilon+1)}{\epsilon}$  (Stark term) and  $\frac{\epsilon-1}{\epsilon+2.86}$  (reaction field term).

It has to be noted that no significant changes occur in the conformation of the solute, because the  $^3J_{C-D-C-H}$ , which in this dihedral angle region is very sensitive to the conformation, remains essentially constant around an average value of  $2.14 \pm 0.03$  Hz, whereas the  $^1J_{C-H}$  ranges from 158.1 to 162.1 Hz. Our data show that, at least for paraldehyde, for a description of the observed effects, there is no need to resort to essentially point charge models, but that a macroscopic "solvent cage" type of model is completely satisfactory. Presently we are working on calculations for these systems.

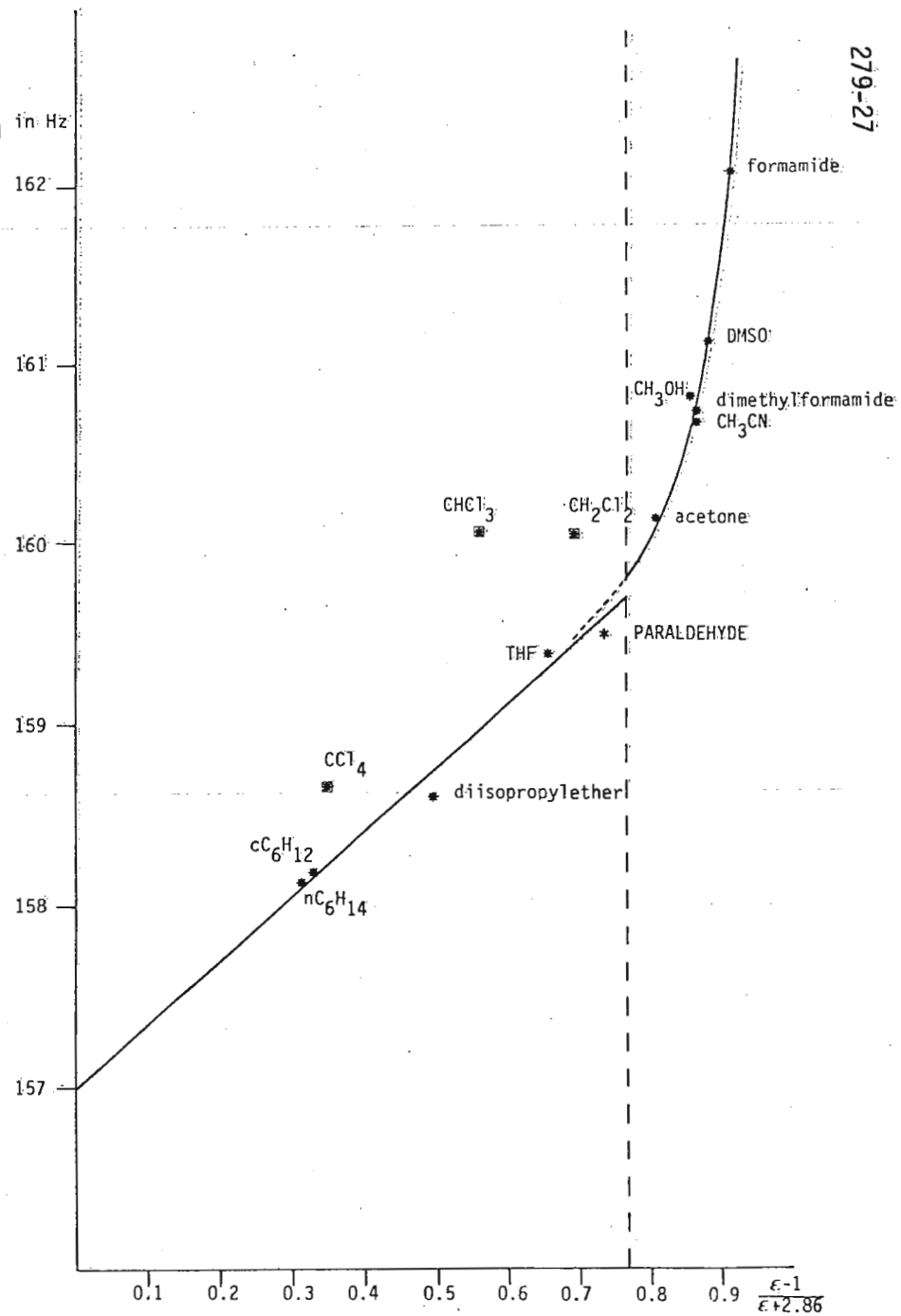
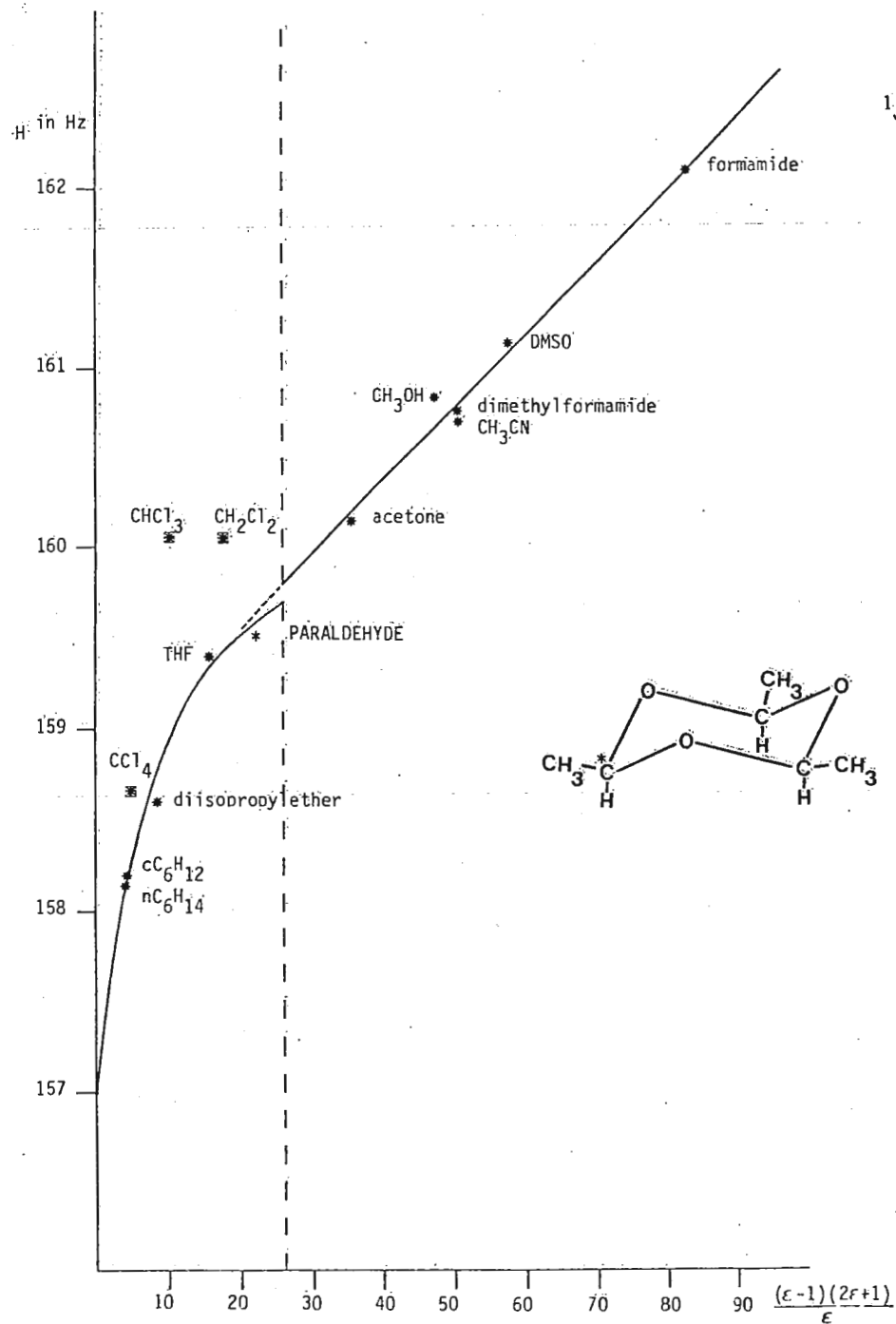
Yours sincerely,

  
M.J.A. de Bie

  
J.C. Roos-Venekamp

1. S.Watanabe and I.Ando, Bull. Chem. Soc. Jpn., 53, 1257 (1980)
2. M.Kondo, S.Watanabe and I.Ando, Mol. Phys., 37, 1521 (1979)
3. M.D.Johnston and M.Barfield, J. Chem. Phys., 54, 3083 (1971)
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NOTE: Data indicated by \* are used for the calculation of the curves.





# University of Durham

Department of Chemistry

Science Laboratories, South Road, Durham, DH1 3LE  
Telephone: Durham 64971 (STD code 0385)

10th November, 1981.

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

Dear Barry,

Computer program for pulsed NMR spectrometer control

At last we are responding to the stream of coloured paper from you!

About two years ago we contributed a PDP11 program for operating an NMR FFT spectrometer. Now a much improved version can be offered. It runs under RT11 or TSX+ (with the latter the timesharing facilities can still be used) and requires an FP-11 processor to be present, though a version can be supplied which does not need this. Currently we are working on a version which will drive more than one spectrometer simultaneously. The program can be supplied as source files on an RX01 floppy disk which contain instructions for assembly and use. Necessary peripherals, as before are an AR11 for display and some timing, a DR11 for data input and output to the pulse programmer (drawings of which can be supplied) ADC and digital plotter.

Yours sincerely,

A. Royston.R.S. Matthews.

DEPARTMENT OF CHEMISTRY  
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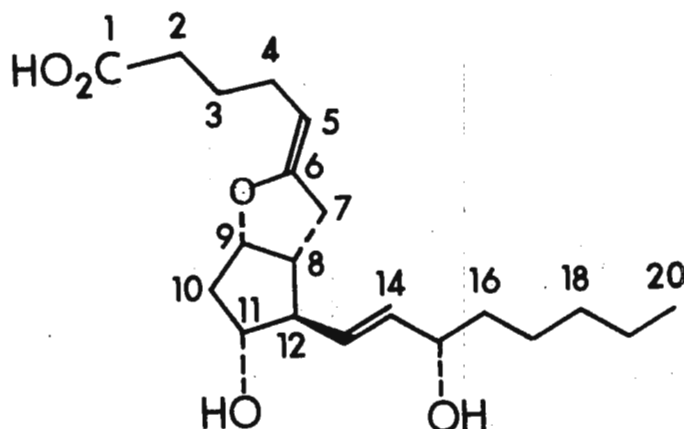
November 9, 1981

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

### $^{13}\text{C}$ $T_1$ Measurements on Prostacyclin

Dear Professor Shapiro:

In our continuing studies of the structure-activity relations of the prostaglandins, specifically of prostacyclin and its derivatives (1,2), we have carried out detailed  $^{13}\text{C}$   $T_1$  measurements on prostacyclin.



The  $^{13}\text{C}$  resonances were readily assigned using the  $^{13}\text{C}$  spin echo technique with gated proton decoupling (3). These line assignments are in good agreement with those observed for the prostacyclin methyl ester in  $\text{CDCl}_3$  (4) with the exception of C1 to C3, as expected. The  $NT_1$  values for C5 to C15 are nearly equal within experimental error, indicating that this portion of the molecule has a longer correlation time than is observed for C2, C3 and C16, C18, C19. This conclusion is in agreement with our results based on the  $^1\text{H}$  relaxation rates (1). The present results are in agreement with  $^{13}\text{C}$  data for prostaglandin  $\text{F}_{2\alpha}$  (5,6), which has one five-membered ring between C8 and C12.

TABLE  
 $^{13}\text{C}$  Chemical Shifts and Relaxation Times ( $NT_1$ ) for Prostacyclin (0.085 M) in Glycine Buffer (0.20 M, pH = 10.4,  $T = 4^\circ\text{C}$ ).

Carbon	Shift(a) (ppm)	$NT_1$ (b) (sec)
1	186.26	-
2	39.86	0.60

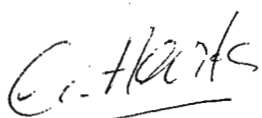
3	29.17	0.56
4(17)	27.53	-
5	100.30	0.23
6	156.29	-
7	34.96	0.30
8	47.60	0.25
9	86.35	0.29
10	42.47	0.36
11	78.75	0.26
12	56.36	0.23
13	134.67	0.32
14	138.13	0.27
15	75.44	0.30
16	38.88	0.38
17(4)	27.53	-
18	33.89	0.74
19	24.98	1.48
20	16.31	-

- a. With respect to TSP-d<sub>4</sub> measured at 100.6 MHz. Resolution = 1.221 Hz/pt.
- b. The NT<sub>1</sub> values represent an average value based on 2-4 experiments. Error limits on T<sub>1</sub> are ~10%. A line broadening of 10 Hz was used. The measurements were carried out on degassed samples.

#### References

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Yours sincerely,



G. H. M. Aarts



T. T. Nakashima



G. Kotovych



## UNION CARBIDE CORPORATION

P. O. BOX 8361, SOUTH CHARLESTON, W. VA. 25303

RESEARCH AND DEVELOPMENT DEPARTMENT

Technical Center

November 11, 1981

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

Re: "Increased  $^{13}\text{C}$  sensitivity by a new modulation method"

Dear Professor Shapiro:

A 543:1 signal-to-noise ratio for  $^{13}\text{C}$  90% ethylbenzene (12 mm standard sample) has been obtained on our Varian XL-100 (Figure 1) and we routinely achieve 500:1 or better. Prior to this, the maximum  $^{13}\text{C}$  S:N achieved was 170:1 (Varian specification 120:1). Other experimental results, using a variety of compounds, confirm a signal strength increase of a factor of three. This improvement is due to a recently developed modulation method for proton decoupling.

A more suitable power spectral density of the decoupling radio-frequency field is achieved by a modulation technique that successively modulates the r-f with two frequencies having a frequency ratio of four-to-one. The circuit is shown schematically in Figure 2. Our Varian XL-100 NMR spectrometer (vintage 1975) equipped with the standard random noise modulation was used to develop and evaluate this double modulation scheme. The only modification involved the 100 MHz modulator/power amplifier circuit (schematic 87-126-860). In this module, the input r-f coaxial cable was cut and fitted with BNC connectors to provide a means of connection to the modulation circuit.

Our best results were realized by first phase modulating the r-f with a square-wave frequency of 128 Hz followed by a second phase modulation with a frequency exactly one-fourth of the first frequency (32 Hz).

A full report of this work is scheduled to be published in the February, 1982 issue of the Journal of Magnetic Resonance.

Sincerely,

Robert W. Dykstra

RWD/lc

Attachment



## DEPARTMENT OF HEALTH &amp; HUMAN SERVICES

Public Health Service

Building 2, Room B2-08

National Institutes of Health  
Bethesda, Maryland 20205

November 12, 1981

Dr. Barry Shapiro  
NMR Newsletter  
Texas A&M University  
College Station, Texas 77843

Dear Barry:

Re:  $^{31}\text{P}$  NMR and DNA Conformation

Further evidence for the alternating (zig-zag) phosphodiester backbone conformation of poly(dAdT)·poly(dAdT) is provided by the effects of increasing salt concentration on its  $^{31}\text{P}$  NMR spectrum.

The doublet ( $\Delta\delta = 22$  Hz) originally described for 145 bp material derived from semi-synthetic chromatin cannot be resolved in the spectrum of polymeric synthetic material because the lines are too broad (1). However, it can be resolved in material which has been sonicated to smaller size ranges (2,3). The doublet of poly(dAdT)·poly(dAdT) is observed well below the melting temperature determined by UV absorbance and  $^{31}\text{P}$  NMR studies. This doublet indicates distinct conformations for dApdT and dTp dA sequences in the co-polymer (1-4).

Addition of NaCl (2) or CsF (Figure) causes an increase in the separation of the doublet which is linear with salt concentration. Marky *et al.* (5) were able to resolve the doublet of synthetic poly(dAdT)·poly(dAdT) in 1 M tetramethylammonium chloride, but not in 1 M or lower concentrations of NaCl. This discrepancy with our results probably arises from the larger sized commercial material they used. The changes in the relative areas of the two components observed on addition of NaCl could arise from a changeover from a strictly alternating conformation, or possibly also from aggregation. With increasing CsF concentration the relative areas of the two components remain approximately equal (Figure).

Kypr *et al.* (6) and Patel *et al.* (7) have both concluded recently that poly(dAdT)·poly(dAdT) can exist in two forms depending on the salt concentration. Since they were unable to resolve the doublet of synthetic poly(dAdT)·poly(dAdT) in low salt, Patel *et al.* concluded that there was a fast non-cooperative transition with  $\text{Cs}^+$  and other cations from a regular B-form in low salt, represented by a singlet, to an alternating form in high salt, represented by the doublet (7). Kypr *et al.* (6) also observed the doublet with sonicated material in low salt, however they explained the increased peak separation in high salt by the existence of a "strange double helix." The linear shift changes for the doublet peaks with increased salt concentration that we have observed indicate a fast non-cooperative transition via a continuum of structures involving DNA winding (8) from a zig-zag B-form to a zig-zag C-form. Further details of conformational aspects of salt effects on alternating d(AT) and other sequences will be given in a forthcoming publication (4).

David Foxall has arrived from Oxford, to replace Lev Jacobson, just as our Nicolet-Oxford 500 MHz spectrometer has become operational.

Yours sincerely,

*Jack S. Cohen & Chi-wan Chen*  
Jack S. Cohen & Chi-wan Chen  
Developmental Pharmacology Branch  
National Institute of Child  
Health and Human Development

JSC:ell



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2. J. S. Cohen, J. B. Wooten and C. L. Chatterjee. Biochemistry **20** 3049, 1981.
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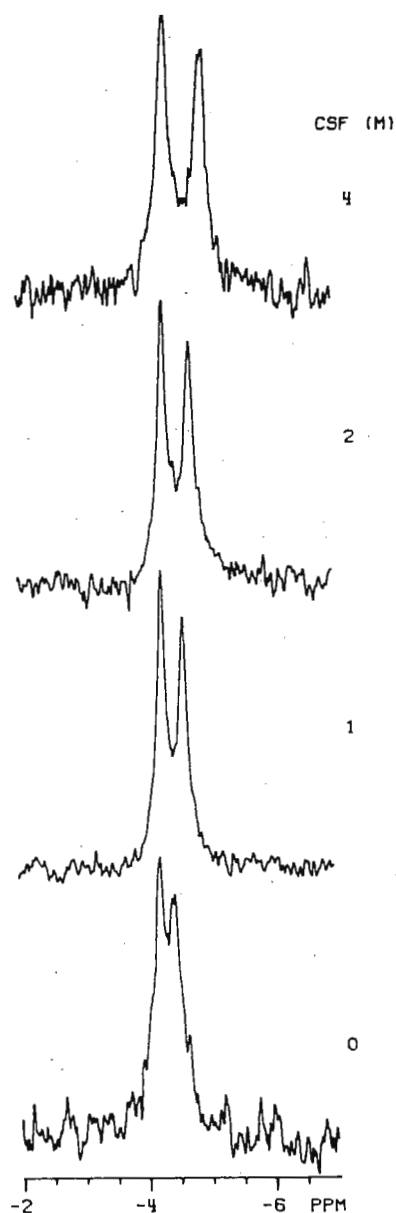


Figure Legend: Dependence of  $^{31}\text{P}$  spectra at 109.3 MHz of sonicated poly(dAdT) on CsF concentration at  $37^\circ\text{C}$ .



Eidgenössische  
Technische Hochschule Zürich

Laboratorium  
für Physikalische Chemie

ETH-Zentrum November 15, 1981  
CH-8092 Zürich  
Durchwahlnummer 01 / 256 4368  
Telefonzentrale 01 / 256 22 11

0430

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

"Optical Line-Narrowing" in Magic Angle NMR

Dear Dr. Shapiro,

All readers familiar with magic angle spinning know how elusive that mythical angle really is. Although the stability of Andrew-Beams rotors is quite satisfactory, the axis of rotation is not well defined. In practice, this axis often deviates significantly from the symmetry axis of the conical stator, thus making accurate mechanical control of the latter's position meaningless. The actual axis of rotation varies with spinner speed, rotor material, sample packing and temperature of the driving gas. The angle is best calibrated by observing the linewidth of a signal with large anisotropy (such as the carbonyl resonance in glycine), but painstaking adjustments may become useless after changing the sample.

We have recently implemented a simple optical device to adjust the angle of the actual axis of rotation. An inexpensive low-power laser source (Spectra Physics model 136) is mounted between the "horns" of the magnet cryostat, with the beam directed vertically down the bore of the superconducting magnet. This beam is first deflected by a polished aluminium mirror, mounted at about 1 cm from the rotor. The surface of the 8 x 12 mm mirror lies at an angle of  $54.7^\circ$  with respect to the vertical magnetic field, parallel to the rotor axis. The laser beam is then deflected by the cap of the spinning Andrew-Beams rotor. Although we normally use (per-deuterated) plexiglas which is quite transparent, it is sufficient to polish the outer surface of the screw-on cap to obtain adequate reflection, in spite of the screwdriver-slit in this surface. (The greatest part of the beam helps to keep the sample warm and colourful).

The beam travels back up the magnet bore, is reflected by a  $45^\circ$  mirror fastened to the laser source (the primary beam travels through a hole in this aluminium mirror), and projects an image on the wall.

The total path length after deflection on the rotor cap is 6 m, hence a deviation by  $\pm 0.1^\circ$  causes the image to move by  $\pm 1$  cm. Deviations of the rotation axis perpendicular to the plane spanned by the magnetic field and the spinner axis do not affect resolution, and corresponding excursions of the laser image (vertical in our arrangement) may be ignored. In practice, the surface of the screw-on cap may not be perfectly normal to the axis of rotation. As a result, the laser image describes a circular or elliptical path in the course of sample rotation, typically with a diameter of about 10 cm. The linewidth of the carbon-13 resonance correlates reproducibly with the horizontal excursions of the laser image as shown in Fig. 1. The device has turned out to be useful if the sample must be changed frequently, or if spectra must be obtained with different spinning speeds (e.g. to unravel overlapping sidebands). Fig. 2 shows how the lineshape degrades upon acceleration from 2000 Hz (bottom) to 4000 Hz (middle). A straightforward realignment of the laser image yields excellent lineshapes without trial-and-error (top). Note that the amplitude of the centreband is enhanced at the expense of the sidebands (not shown).

The infrared spinner-speed detector of our Bruker CXP-300 is mounted sideways, directed towards the rotor segment which protrudes from the rf coil.

We've found research to be more enjoyable with our device, particularly in our recent attempts to combine magic angle spinning with two-dimensional spectroscopy.

Yours sincerely

*Geoffrey Bodenhausen*

Geoffrey Bodenhausen

*P. Caravatti*

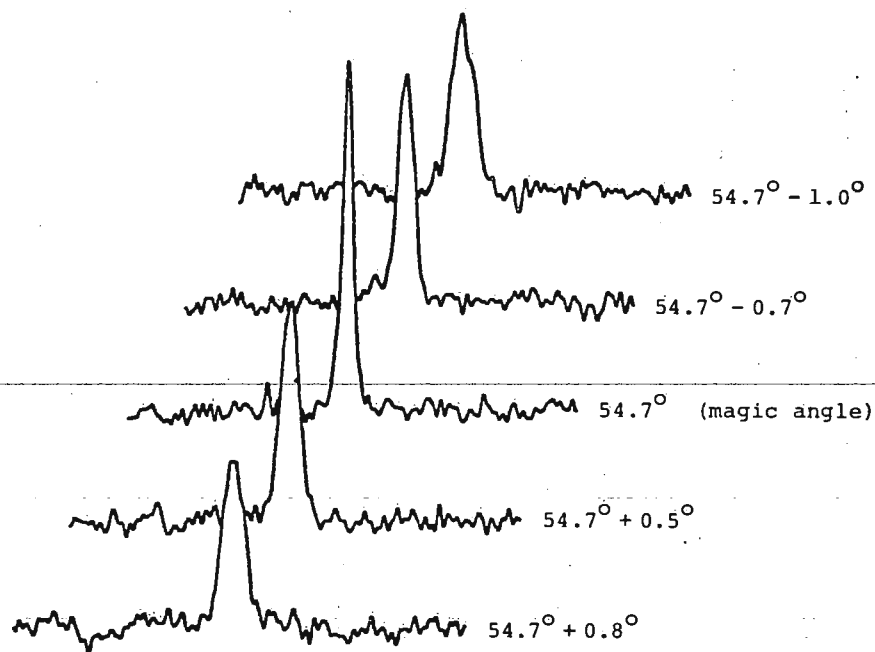
Pablo Caravatti

*János Deli*

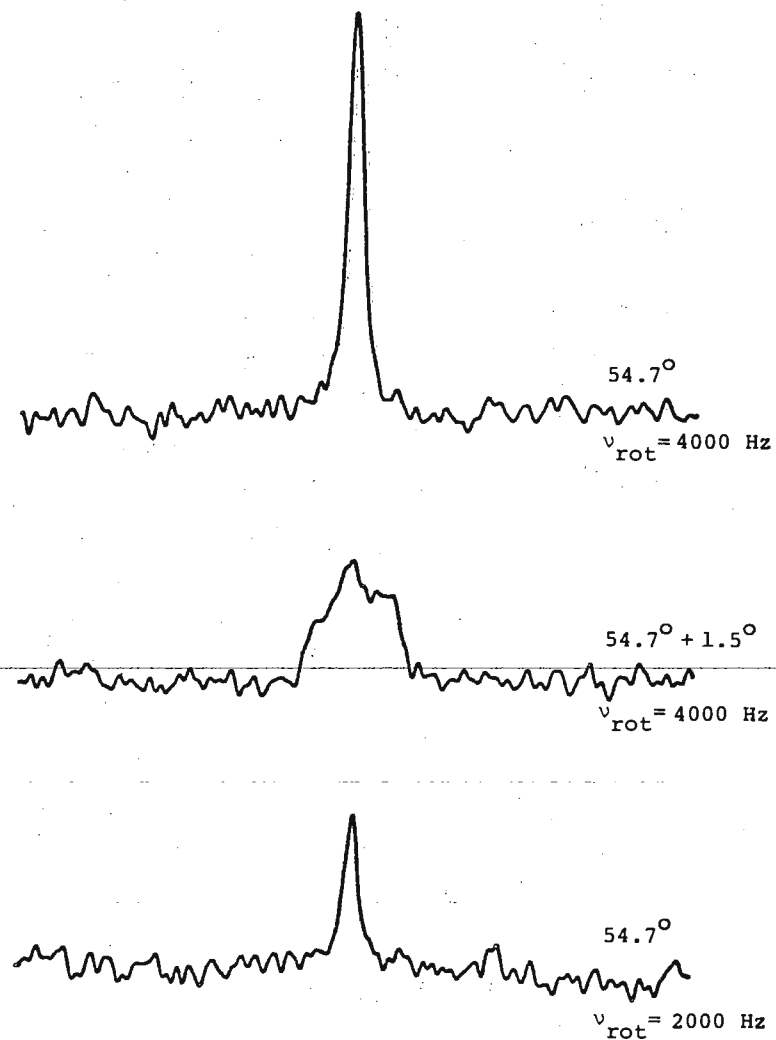
János Deli

*R.R. Ernst*

R.R. Ernst



**Fig. 1** Carbon-13 resonance of carbonyl in glycine, observed at 75 MHz with cross-polarization, high-power decoupling and 4000 Hz rotation speed, shown as a function of the actual angle of the rotor axis. The deviations of the laser image were (from top to bottom) -10, -7, 0 +5 and +8 cm from the optimum. The linewidths are 85, 50, 30, 50 and 85 Hz (expanded plots cover 1500 Hz, Lorentzian broadening 10 Hz).



**Fig. 2** Lineshape of carbonyl resonance in glycine (same conditions as Fig. 1). Below: 2000 Hz rotation speed, with angle adjusted optically. Middle: after acceleration to 4000 Hz, the laser image indicates a deviation by +1.5°. Top: optical realignment yields excellent resolution (30 Hz + 10 Hz Lorentzian line-broadening).



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

Paris, November 18, 1981

LABORATOIRE DE CHIMIE  
ORGANIQUE PHYSIQUE

J.-E. DUBOIS, *Directeur*

BT/CR. N° 406

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

Dear Professor Shapiro,

Title : Magnetic Pollution at the Jussieu Campus, Paris, France.

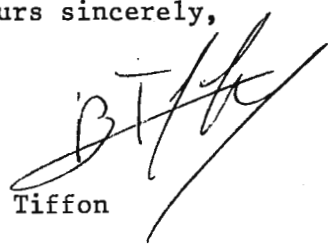
It is known that due to its intrinsic stability, a superconducting magnet does not require a nuclear lock system even for long term accumulations, at least for spins  $> 1$ . However our BRUKER WP 200, when it is not locked, shows a random drift of c.a 10-15 Hz at 200 Mhz within a few minutes around a constant value. This precludes any unlocked accumulation.

After extensive trouble shooting (exchange of the master oscillator, cancellation of the room temperature shim system, etc..) together with switching off of all electric apparatus in the vicinity of the spectrometer, we concluded that an external random magnetic field of a few gauss was responsible for this drift. Indeed a permanent magnet HITACHI-PERKIN ELMER R 24 spectrometer located in the same building shows a similar drift. This random magnetic field can have two causes :

- 1) Two subway lines (600 volts D.C) run under the campus.
- 2) Our laboratory is in a concrete building but we are located close to a very large steel building (the main part of the campus) in which a permanent magnet VARIAN EM 360 spectrometer shows even greater drift. Moreover, if the magnet axis is rotated by  $90^\circ$ , the resolution cannot be stabilized. There are certainly random electrical currents running in the steel framework which induce random magnetic fields inside the building and perhaps outside, at least on short distance.

Recently, a BRUKER WM 250 superconducting spectrometer has been installed at the campus in another concrete building. Contrary to its colleagues, this spectrometer is perfectly stable. Indeed the WM 250 is further from the steel monster than our WP 200. Moreover the WM 250 is installed on the 7th floor and in fact rather far from the subway lines. This place is really the 7th heaven for NMR spectrometers !

Yours sincerely,

  
B. Tiffon

Professeurs et Maîtres de recherche :

P. BAUER, J. CHRÉTIEN, G. DODIN, J.-P. DOUCET, J.-E. DUBOIS, P.-C. LACAZE, C. LION, H. MIR-HEDAYATULLAH, M.-F. RUASSE, J. TOULLEC.



## CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING  
GATES AND CRELLIN LABORATORIES OF CHEMISTRYJOHN D. ROBERTS  
INSTITUTE PROFESSOR OF CHEMISTRYDr. Bernard L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, TX 77843

November 19, 1981

180° Pulse Lengths for Solutes Containing  $^{15}\text{N}$  as a Function of Solvent

Dear Barry,

The recent letter from Dr. Ziessow published in TAMU (July 1981, No. 274-5) about the solvent dependence of RF pulse lengths piqued our interest. As we often take nitrogen-15 spectra of samples at the natural-abundance level of  $^{15}\text{N}$  or of samples with very low concentrations of  $^{15}\text{N}$ -labeled compounds, we usually use the 90° pulse length of a standard sample of 90% formamide/DMSO- $\text{d}_6$  to determine the optimum pulse length, regardless of solvent. To test the validity of this procedure, we measured the 180° pulse length for  $^{15}\text{N}$ -labeled benzamide dissolved in various solvents using an XL-200. The results follow:

<u>Solvent</u>	<u>Concentration, mM</u>	<u><math>\epsilon</math> (20-25°)</u>	<u>180° pulse, <math>\mu\text{s}</math></u>
$\text{C}_6\text{H}_6$	ca. 10	2.3	50
$\text{CHCl}_3$	40	4.8	47
$\text{CH}_3\text{OH}$	40	32.7	48
$\text{H}_2\text{O}$	40	80.4	48
$\text{H}_2\text{O} + 0.5\text{M NaCl}$	40	-	51
90% formamide/DMSO- $\text{d}_6$			49

One can see that the 180° pulse length is relatively constant over a wide range of solvents. When Dr. Ziessow's 180° pulse lengths are plotted against the dielectric constant, the points fall on a straight line except for the point for HMTA in  $\text{H}_2\text{O}$ . This was the only measurement of a solute in a solvent. Fortunately, it seems that the 180° pulse length for  $^{15}\text{N}$  in a solute is not an important question of the solvent's properties.

Sincerely,



Michael Nee



John D. Roberts

# GX-400

WITH  
The "plexus" system from JEOL



**You couldn't ask  
more from an NMR...**  
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The GX-400 represents a totally new design concept, based on years of JEOL technical experience. It's not an NMR that uses a computer or — a computer that uses an NMR. But, a completely integrated spectrometer that employs a 400 MHz Solenoid which, of course, provides outstanding sensitivity, resolution and dispersion.

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And, if all this isn't enough to convince you of how serious we are about providing the

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*You might ask more from a great NMR and there is more. To find out how much more, call or write ...*

# JEOL

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

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December 4, 1981

(303)491-6480

Department of Chemistry

Colorado State University  
Fort Collins, Colorado  
80523

Setting the Magic Angle Using a Quadrupolar Nuclide

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

Dear Barry:

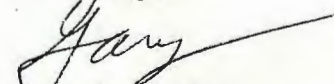
As an increasing portion of our Center's activities revolve around solid-state experiments, details of magic-angle spinning (MAS) have become very important in the Center. Essentially all of our MAS work has used the bullet design spinner (Bartuska and Maciel, *J. Magn. Reson.*, 42, 312 (1981)). One of the annoying characteristics of this design, which is shared with the mushroom-type spinner, is the uncertainty in setting the angle (spinning axis) for each experiment. A common procedure in  $^{13}\text{C}$  work is to set the angle with hexamethylbenzene (HMB), and then use the same (or hopefully identical) spinner with the sample of interest in it. This presupposes that the density and packing characteristics of the sample are sufficiently close to those of HMB that the HMB angle setting is valid. If lines that are broader than expected are obtained, one sometimes repeats the run once or twice with slightly different angle settings to determine whether off-axis spinning is responsible for the line broadening--an annoying waste of time.

Jim Frye has developed a method of using the MAS spectrum of  $^{79}\text{Br}$  in KBr as a means of setting the angle in a  $^{13}\text{C}$  experiment. The  $^{79}\text{Br}$  resonance frequency is so close to that of  $^{13}\text{C}$  that both resonances can be observed without retuning the probe. A small sample of KBr can be placed at the bottom of the spinner without appreciably degrading the effective volume of the sample.

It has been demonstrated recently, especially by Oldfield and coworkers, that MAS provides useful narrowing of the resonance lines of half-integer quadrupolar nuclei, providing spectra that often have rich sideband patterns (see attached figure). We have found that a convenient parameter in the  $^{79}\text{Br}$  spectrum for setting the angle is the ratio of intensities of the second-order spinning sideband and the central peak. The accompanying figure shows a plot of this parameter against angle, together with a corresponding plot of aromatic-to-aliphatic intensity ratios in the HMB  $^{13}\text{C}$  spectrum.

We have found this technique to be routinely useful and convenient, and are exploring other half-integer quadrupolar nuclides for related purposes.

Sincerely,

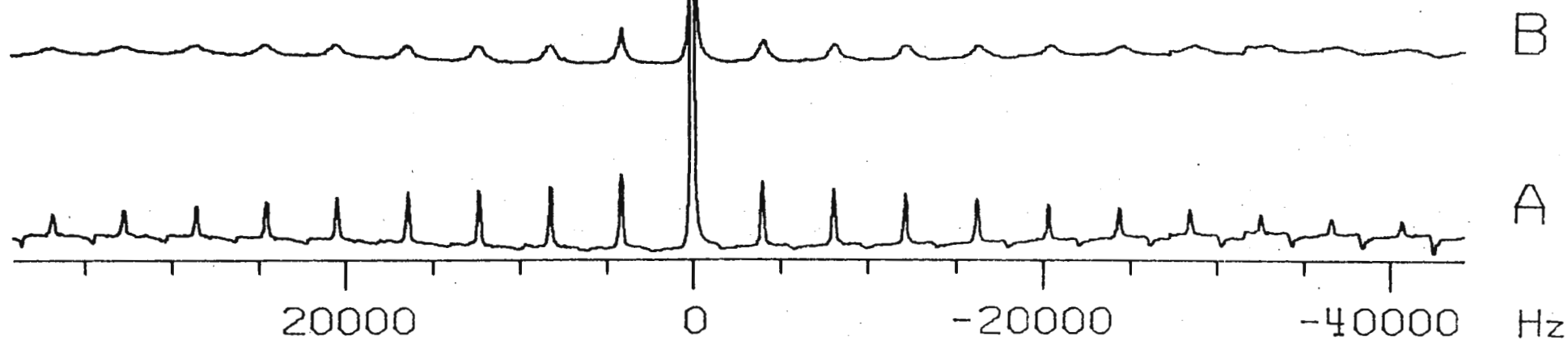


Gary E. Maciel  
Professor of Chemistry, and  
Director of the Regional NMR Center

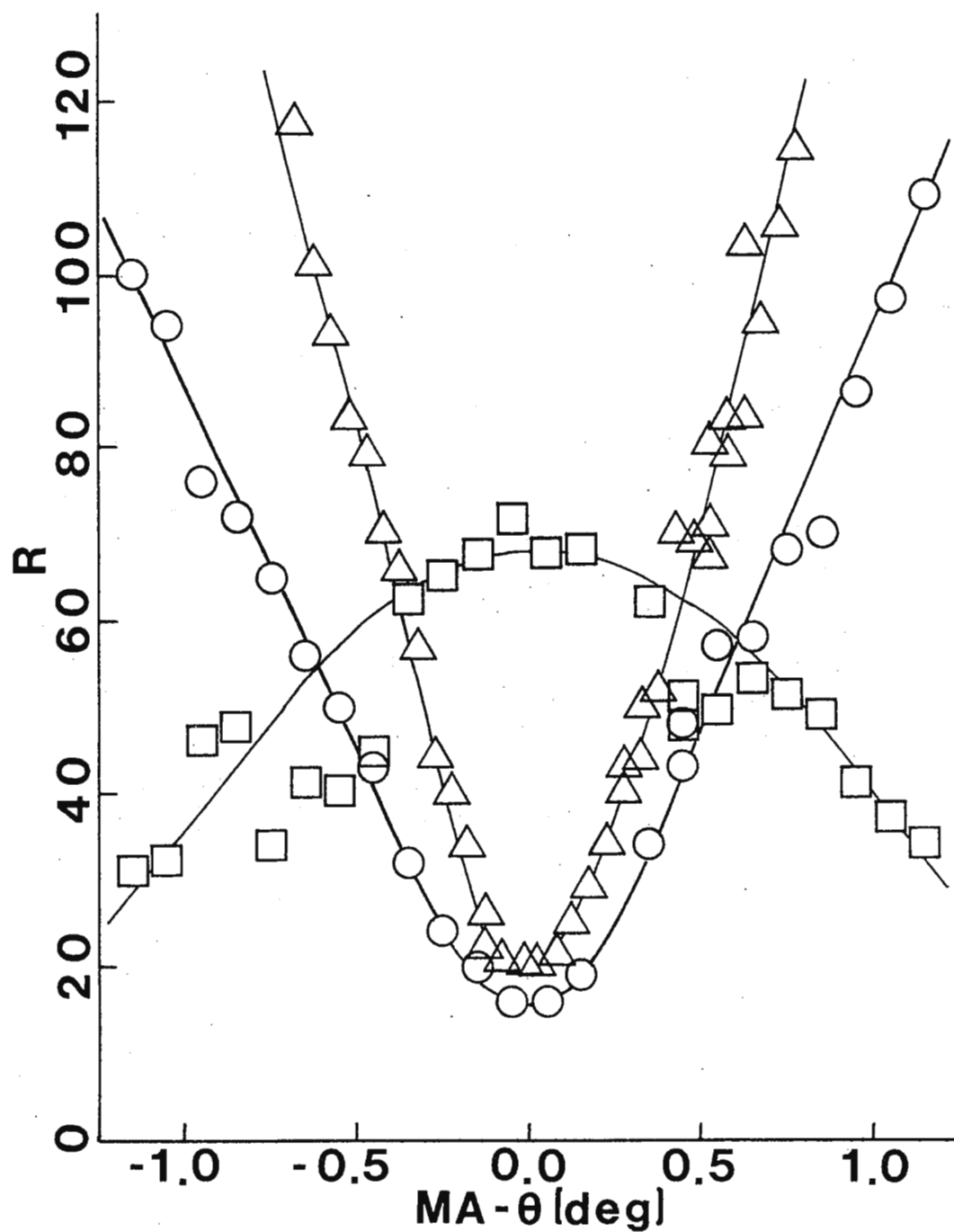
GEM:lb

\* External Organ of the Mile High PENIS Laboratory

FT/MAS  $^{79}\text{Br}$  spectrum of KBr at the magic angle (A) and  $0.5^\circ$  off angle (B), at 37.6 MHz. 1000  $3\text{-}\mu\text{s}$  pulses were taken with a 70-ms repetition time. Extensive aliasing of high-order spinning side bands is evident in A.







Plot of peak height ratio vs deviation from magic angle. For KBr,  $R = (\text{average height of second-order spinning sidebands})/(\text{height of central peak})$  with powdered ( $\circ$ ) and crystalline ( $\Delta$ ) samples. For HMB ( $\square$ ),  $R = (\text{height of aromatic peak})/(\text{height of methyl peak})$ .

School of Studies in Chemistry

Bradford West Yorkshire BD7 1DP England  
Telephone Bradford 33466 (STD Code 0274)  
Telex 51309 UNIBFD G

16th November, 1981

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

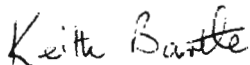
Dear Professor Shapiro,

ORGANIC GEOCHEMISTRY OF TURKISH ASPHALTITES

In collaboration with Turkish colleagues at Ankara (A.Olcay & F.Ozel) and Istanbul (E.Ekinci), we have recently made use of  $^1\text{H}$  and  $^{13}\text{C}$  NMR in solution to aid studies by GC, mass-spectrometry, etc. of hydrocarbon fractions extracted from two Turkish asphaltites. These minerals (typical analyses: C, 50-57; H, 4-6; N, ~1; S, 7-8; volatiles 28-47%) have analogies with North American tar sands and can be processed to yield fuels and chemical feedstocks.

The Soxhlet-extracted bitumens were separated from the asphaltites by solvent extraction (*n*-pentane, benzene, methanol) and silica-gel column chromatography<sup>1</sup>; molecular-sieve adsorption of *n*-alkanes<sup>2</sup> enabled the branched/cyclic fraction to be separated from the total alkane fraction of Avgamasya asphaltite. The biggest fractions (over 80%) of the bitumens are neutral benzene-soluble aromatic materials, either soluble (viscous oils) or insoluble (solid asphaltenes) in *n*-pentane.  $^1\text{H}$  and  $^{13}\text{C}$  NMR<sup>3</sup> show that these fractions contain small polynuclear aromatic entities linked by heteroatoms and substituted with naphthenic groups and alkyl chains. Characteristic structural parameters<sup>4</sup> have been derived (Table ), while several statistical average structures for the oils have been devised, representative of the very many molecules present, covering a molecular-weight range 200-2000. Aromatic and alkane compositions of these predominantly aromatic asphaltites are consistent with geochemical origins as petroleum migration followed by biodegradation and other maturation processes.

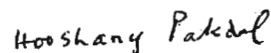
Yours sincerely,



K.D.Bartle  
(Dept. of Phys.Chem.,  
Leeds University)



D.W.Jones



H.Pakdel

## References:

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Table

STRUCTURAL PARAMETERS, CALCULATED AS DESCRIBED PREVIOUSLY<sup>4</sup>, CHARACTERISING NEUTRAL AROMATIC FRACTIONS OF ASPHALTITE BITUMENS

	Harbolite		Avgamasya asphaltite	
	<i>n</i> -pentane solubles <sup>a</sup>	asphaltenes <sup>a</sup>	<i>n</i> -pentane solubles <sup>a</sup>	asphaltenes <sup>a</sup>
Average molecular formula	C <sub>47.7</sub> H <sub>66.2</sub> S <sub>1.9</sub> O <sub>0.5</sub>	C <sub>133.5</sub> H <sub>157.2</sub> N <sub>1.1</sub> S <sub>6.2</sub> O <sub>1.1</sub>	C <sub>27.3</sub> H <sub>32.3</sub> S <sub>0.9</sub> O <sub>0.1</sub>	C <sub>104.1</sub> H <sub>107.1</sub> N <sub>1.1</sub> S <sub>3.3</sub> O <sub>1.3</sub>
Number average molecular weight	710	1990	390	1500
Aromaticity: from <sup>1</sup> H	0.37	0.48	0.55	0.58
<sup>13</sup> C	0.34	0.47	0.50	0.52
Degree of alkyl substitution, $\sigma$	0.48	0.50	0.43	0.47
Average alkyl chain length	5.0	4.3	2.5	6.4
Peripheral carbon, C <sub>p</sub>	18.3	52.6	13.3	26.1
Ring carbon, C <sub>R</sub>	19.2	71.9	16.1	65.9
$\frac{C_p - 6}{C_R - 6}$ <sup>b</sup>	0.93	0.71	0.73	0.34

<sup>a</sup> Benzene clusters.

<sup>b</sup> Parameter describing degree of condensation of aromatic nuclei, which decreases with increasing condensation and is invariant with molecular weight for a given homologous series.



UNION CARBIDE CORPORATION  
P. O. BOX 8361, SOUTH CHARLESTON, W. VA. 25303  
RESEARCH AND DEVELOPMENT DEPARTMENT  
Technical Center

November 18, 1981

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

Dear Professor Shapiro:

Ruthenium NMR

We have been interested in developing ruthenium NMR in our laboratories<sup>1,2,3</sup> and thought your readers might be interested in some of our observations. Using our modified Varian FT-80A, a variety of ruthenium resonances have been observed. (See Figure.)

After finding Larmor frequencies for Ru-101 and -99, we were surprised to discover a Ru-99 resonance which was closer to K-39 and Ag-109 resonances than it was to our selected reference  $[\text{Ru}(\text{CN})_6]^{4-}$ . Based on other metal nuclide information, we expect the chemical shift range to be even greater than the 7000 ppm observed to date.

Sincerely yours,

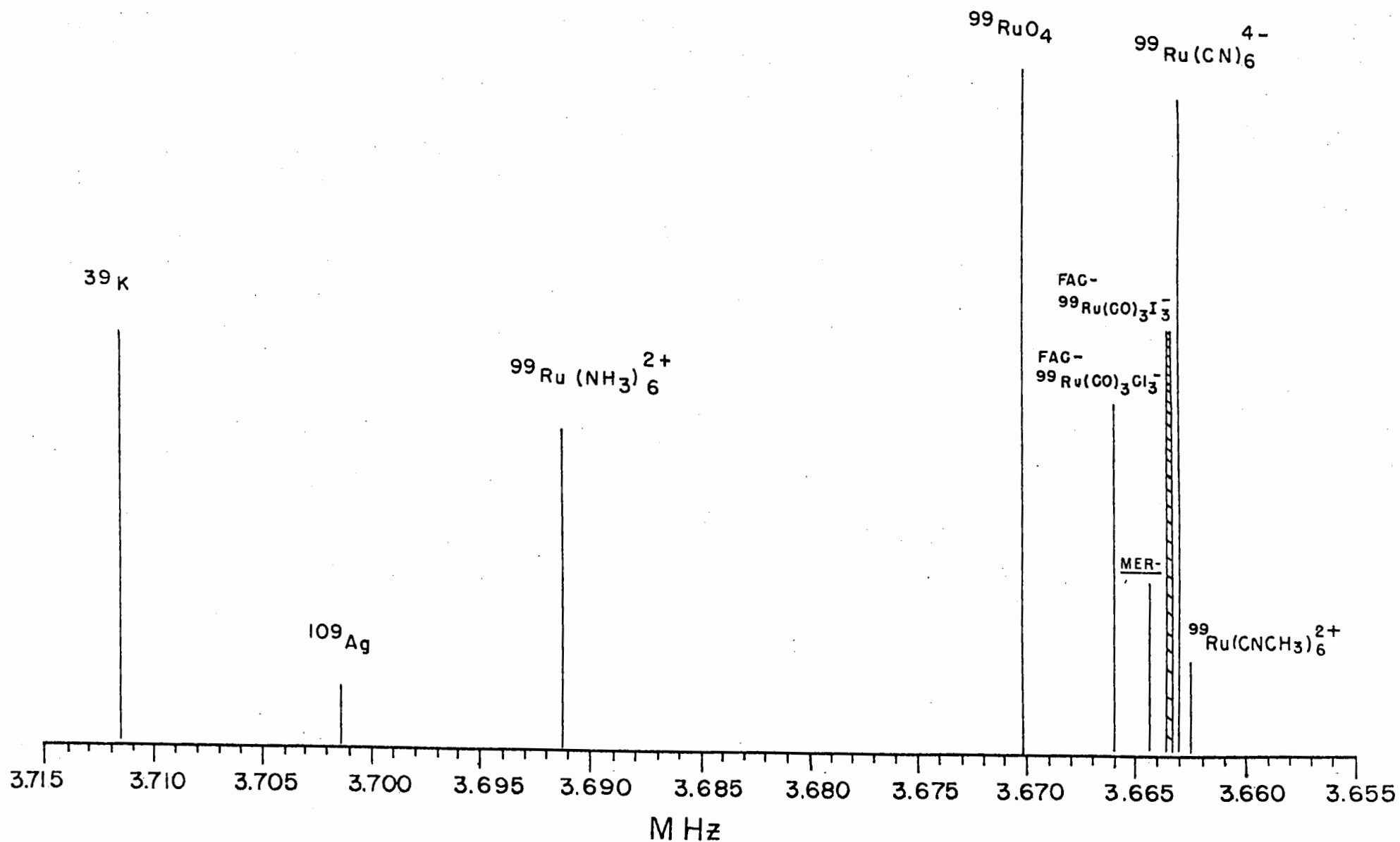
Arnold M. Harrison

Robert W. Dykstra

AMH/RWD:ps

- 
1. Robert W. Dykstra and Arnold M. Harrison, J. Magn. Reson., 45(1), 108(1981).
  2. Robert W. Dykstra and Arnold M. Harrison, J. Magn. Reson., in press.
  3. Robert W. Dykstra, presentation at Midwest NMR Discussion Group, December 6, 1980, Purdue University, West Lafayette, Indiana.

"NMR" FREQUENCIES OBSERVED ON  
A MODIFIED VARIAN FT-80A



Dr. E. Haupt

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College Station, TX 77843  
USAFernsprecher: 41 23-3135 }  
Behördennetz: 9.38. ( " ) } Durchwahl

Telex-Nr.: 2 14732

Datum und Zeichen Ihres Schreibens

Aktenzeichen (bei Antwort bitte angeben.)

Datum

Nov. 20, 1981

Betreff Determination of 90°-Pulses

Dear Professor Shapiro,

the successful use of modern pulse-sequences depends on the accuracy of the 90°(-180°)-pulse-length. This determination is done either by signal-nulling methods or the time-consuming intensity measurements on a standard sample with all its inaccuracy (e.g. TAMUN 274-5).

Therefore it seems desirable to have a simpler method, which gives a direct access to this value especially for those experiments, where higher concentrations are necessary and a BB-decoupled spectrum can be reached with one pulse.

If one runs two times a spectrum, where the pulse-length of the second experiment is twice the length of the first,  $\alpha_1$  can be determined:

$$\begin{aligned} I_1 &\sim M_0 \cdot \sin \alpha_1 \\ I_2 &\sim M_0 \cdot \sin \alpha_2 \end{aligned} \quad (I \triangleq \text{intensity})$$

$$t_{p_2} = 2 t_{p_1} \Rightarrow \frac{I_1}{I_2} = \frac{\sin \alpha_1}{\sin \alpha_2} = \frac{\sin \alpha_1}{\sin 2\alpha_1} = \frac{1}{2 \cos \alpha_1}$$

$$\boxed{\cos \alpha_1 = \frac{I_2}{2 I_1}}$$

The 90°-pulse is then calculated as:

$$\boxed{t_p(90) = \frac{90 \cdot t_{p_1}}{\alpha_1}}$$



The example is for the proton-pulse ( $\text{CHCl}_3$ ) on an WH-90.

The calculated values are:

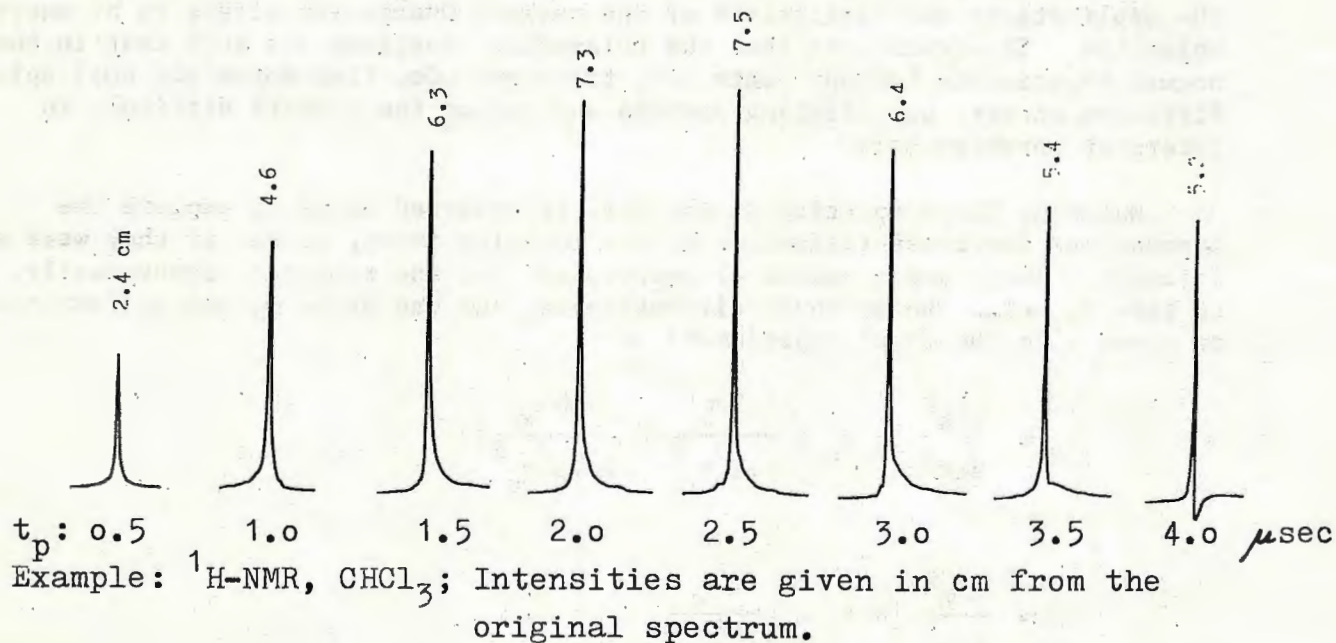
$t_{p1}$	$t_{p2}$	$t_p(90)$
0.5	1.0	2.7
1.0	2.0	2.4
1.5	3.0	2.3
2.0	4.0	2.6

$$\overline{t_p} = 2.5 \mu\text{sec}$$

This agrees well with the observed result of the intensity measurement.

Another example may be taken from a spectra-catalogue (WP-80) for  $^{13}\text{C}$  (Ethylbenzene), if the calculation is restricted to the CH-carbons. The calculated values are in the range between 6.79 and 6.91  $\mu\text{sec}$ , while the estimated value is 7  $\mu\text{sec}$ .

This procedure is very fast, because a plot is no longer necessary if a computer-printout is available. With this intensity information the procedure will be done automatically when phase-correction-programs are available.



Please credit this contribution to the account of Prof. Leibfritz.

Yours sincerely

*E. Haupt*  
E. Haupt

## Carnegie-Mellon University

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November 30, 1981

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

Dear Barry:

Greetings from all of us at Mellon! Christine continues to aid and abet the cause of NMR spectroscopy, (do not forget the shower curtains with yellow swans) the most recent occasion being the time we were watching her on the ice performing a camel spin.

As you know, we and others have been occupied for some time in exploring the applications and limitations of the nuclear Overhauser effect in biomacromolecules. The trouble is that the relaxation equations are such that in the normal experiments (steady state nOe, transient nOe, time-dependent nOe) spin diffusion occurs, complicating matters and making the effects difficult to interpret unambiguously.

Watching Chris rotating on the ice, it occurred to me to explore the expressions for cross-relaxation in the rotating frame, to see if they were more friendly. There are a number of approaches, but the simplest, conceptually, is to take  $T_1\rho = T_2$ . Under these circumstances, one can write  $\sigma_2$  and  $\rho_2$  (analogous to  $\sigma$  and  $\rho$  in the usual experiment) as

$$\rho_2 = \frac{\gamma^4 \hbar^2}{20\pi^6} \left\{ 5 \tau_c + \frac{9 \tau_c}{1 + \omega^2 \tau_c^2} + \frac{6 \tau_c}{1 + 4\omega^2 \tau_c^2} \right\}$$

$$\sigma_2 = \frac{\gamma^4 \hbar^2}{20\pi^6} \left\{ 4 \tau_c + \frac{6 \tau_c}{1 + \omega^2 \tau_c^2} \right\}$$

Introducing these into the usual nOe equations, one finds that the cross-relaxation is similar to that in the extreme narrowing limit (as though the spins were seeing only  $H_1$ ). We have tried this experiment, and it appears to work.

The trial experiment went as follows. We used a concentrated glucose solution in  $D_2O$  as a sample (very gooey, long  $\tau_c$ ) and verified that it gave a negative Overhauser effect with abundant spin diffusion. Then we applied a  $90^\circ$  pulse followed immediately by a spin-locking pulse of 0.3 secs duration along the y. Accumulation of FID and transformation gave spectrum 1. Repetition of this experiment, but with preliminary inversion of the  $\alpha$  anomeric proton signal using a soft DANTE-like sequence, gave spectrum 2. The difference is shown in spectrum 3. Behold! A selective positive NOe. The spectra are not very pretty because they are all single-scan spectra, and because we do not have a very powerful spin-locking field as yet, but they are reproducible and give other effects as predicted (invert  $\alpha 2$ , observe  $\alpha 1$  change) as well.

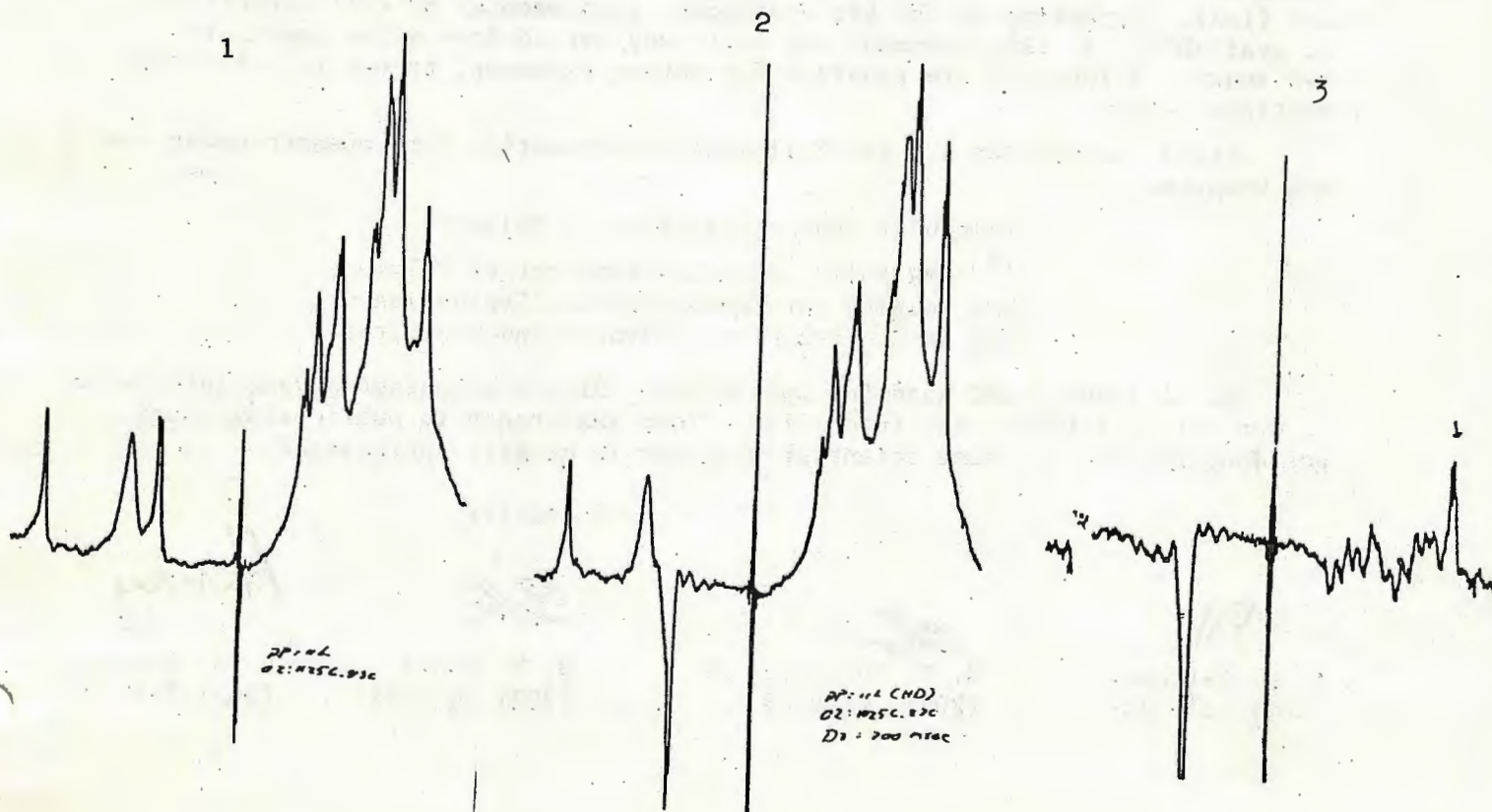
It takes no great effort to see that this could easily form the basis of a 2-D method (simply wait  $t_2$  between application of  $90^\circ_x$  and spin locking y pulses).

A name? How about camel-spin (Cross-relaxation Appropriate for Mini-molecules Emulated by Locked Spins)? Don Bennett and Joe Dadok put together the necessary gates, amplifiers, and phase shifters so that we could do this experiment, and they, Rich Stephens and I spent many hours combating and overcoming some peculiar phase glitches introduced by the DO command in our Bruker. We are working on improving the experimental set-up. Best regards to Lee.

Sincerely,

*Aksel*

Aksel A. Bothner-By







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

IN REPLY REFER TO:  
6120-505:ANG:mjt

3 December 1981

Postdoctoral and Visiting Scientist Programs

The Naval Research Laboratory has programs for both postdoctoral and visiting scientists. We are writing, on behalf of the Polymer Diagnostics Section, to inform TAMUN Newsletter readers of some of these opportunities.

The NRL postdoctoral program is administered by the National Research Council (NRC) and the applications are approved on a competitive basis. The present stipend is \$22,400 per year. Relocation expenses and a professional travel allowance are provided. The applicant must be a U.S. citizen. Appointments are for two years. The following attraction has been added recently: a third year of contractual support may be available from the Office of Naval Research for selected NRC associates who continue research in post tenure positions at academic institutions. Application and research proposal forms are available from NRC at the following address and must be completed and returned to NRC by 15 January 1982.

Associateship Office, JH 610-PC  
National Research Council  
2101 Constitution Avenue, N.W.  
Washington, D. C. 20418

Announcement of awards is usually made in April with tenure normally beginning within six months of the awards, but not later than 1 February 1983.

The Laboratory also 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, travel to scientific meetings, etc.

Within the Section are the following opportunities for research under the NRC program.

Molecular Characterization of Polymers  
<sup>13</sup>C NMR Solid State Spectroscopy of Polymers  
NMR Imaging for Nondestructive Evaluation  
NMR in Electroactive Polymers and Graphites

The 15 January NRC deadline approaches. Please encourage anyone interested to contact us directly and informally. Your assistance in publicizing these postdoctoral and visiting scientist programs is greatly appreciated.

Sincerely,

*AI*

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*Bill*

W. B. Moniz  
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*Henry*

H. A. Resing  
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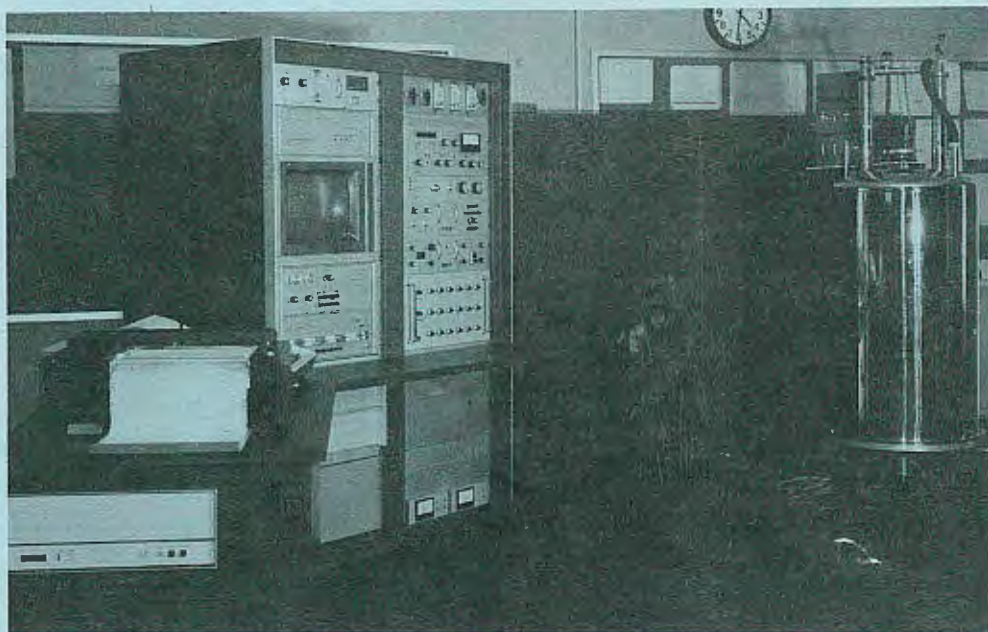
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- Automated  $T_1$  and  $T_2$  measurements.
- Chemical dynamics studies.
- Temperature-programmed experiments.
- $^{31}\text{P}$  experiments on living organs.

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