TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

NO. 306

MARCH 1984

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No. 307 ----- 2 April 1984

No. 308 ------- 7 May 1984

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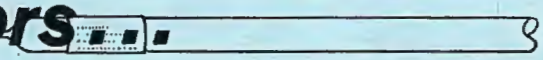

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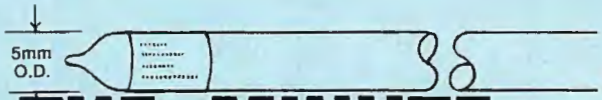

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All Newsletter Correspondence
Should be Addressed to:

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

AUTHOR INDEX ----- TAMU NMR NEWSLETTER NO. 306, MARCH 1984

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SCHOOL OF PHARMACY
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY
(415) 666-1937

SAN FRANCISCO, CALIFORNIA 94143

January 31, 1984

Dear Barry,

We have continued our protein studies of the interaction of ^{129}Xe with the O_2 binding myoglobin. Previous results with the metmyoglobin derivative indicated at least two distinguishable binding sites with an estimated kinetic off rate (18°C) from the main site of 10^5 sec $^{-1}$ (Tilton and Kuntz, 1983). Our latest low temperature results on deoxy myoglobin also indicate two binding environments (a broader upfield resonance and a downfield resonance) which is similar to the met- derivative. Although the kinetics have not been measured directly, the temperatures of the two maxima are similar to metmyoglobin, suggesting similar rate constants. (fig. 1) On the other hand, the cyanometmyoglobin low temperature profile displays only a single line broadening event with an accompanying downfield chemical shift. (fig. 2) Two interpretations of this data are 1) the equilibrium constant of one of the sites (presumably the main site proximal cavity identified with the upfield resonance) has been greatly reduced or 2) all of the sites in this ferric low spin (Fe^{+3}, $S = ½$) derivative have similar chemical shifts and kinetics and hence are not resolvable. Experiments are underway to help clarify this issue.

On a different note, we have measured T_1 data on a number of myoglobin derivatives to compare the effect of the Fe state on ^{129}Xe relaxation (Table I). Although the experiments are run under fast exchange conditions and the specific sites and binding constants of the different derivatives are still not fully understood, the results indicate a T_1 range spanning from 15 msec in the met-state to over 800 msec in the carbon monoxy state. This wide range is surely due to the paramagnetic effects of the Fe.

Sincerely

Bob Tack

R.F. Tilton and I.D. Kuntz

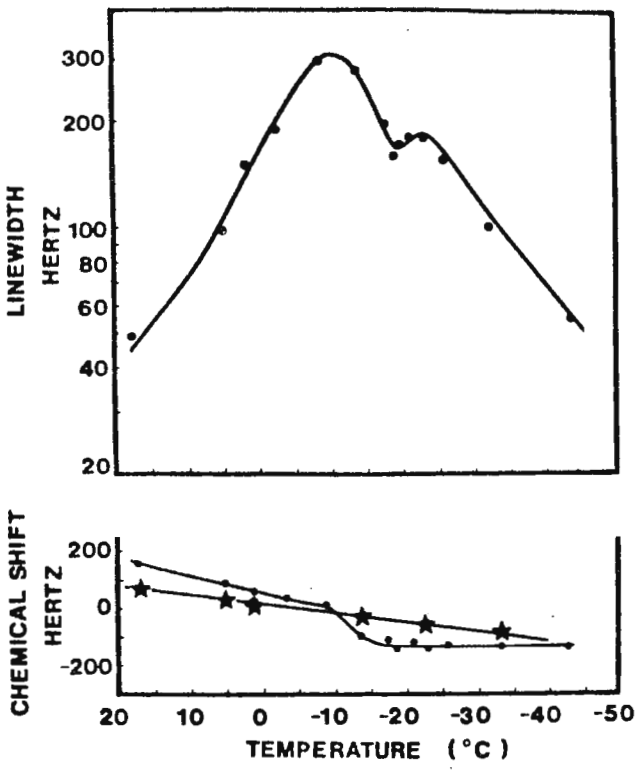


Fig. 1 (Upper Panel) Temperature dependence of ^{129}Xe linewidth for deoxymyoglobin solution (130 mg/ml) solution. (Lower Panel) Temperature dependence of ^{129}Xe chemical shift in cryosolvent (★) and deoxymyoglobin (●).

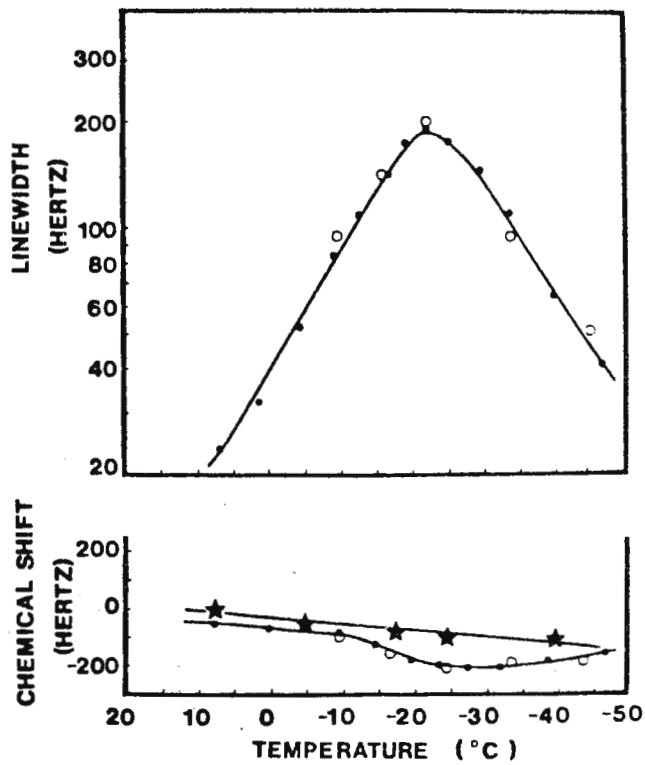


Fig. 2 (Upper Panel) Temperature dependence of ^{129}Xe linewidth for ferric-cyanomyoglobin (110 mg/ml) solution. Open circles indicate data obtained during warming of the sample from -40 C rather then cooling. (Lower Panel) Temperature dependence of ^{129}Xe chemical shift in cryosolvent (★) and ferric-cyanomyoglobin (●).

Table I: T_1 Relaxation Data

Derivative	Fe State	T_1 (msec)
Metmyoglobin	Fe^{+3};S= 5/2	17
Deoxymyoglobin	Fe^{+2};S= 2	410
Ferric-Cyanomyoglobin	Fe^{+3};S= ½	580
Carbonmonoxy-myoglobin	Fe^{+2};S= 0	~865
HgI_3^- - Metmyoglobin	Fe^{+3};S= 5/2	144
Methemoglobin	Fe^{+3};S= 5/2	335
Benzene	-	~2700

*Fast exchange between protein and solvent.
Protein concentration 100mg/ml

DOW CHEMICAL U.S.A.

February 2, 1984

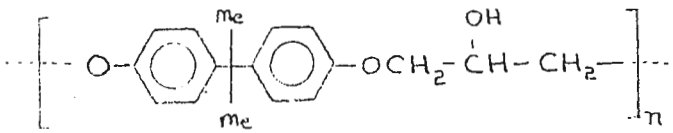
TEXAS DIVISION
FREEPORT, TEXAS 77541

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

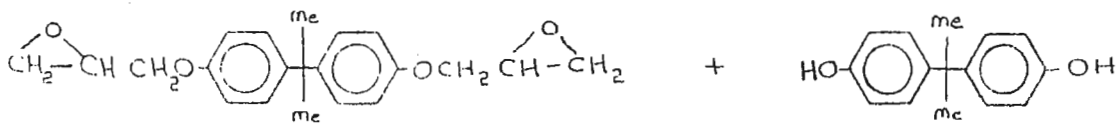
BRANCHING IN EPOXY RESINS

Dear Barry,

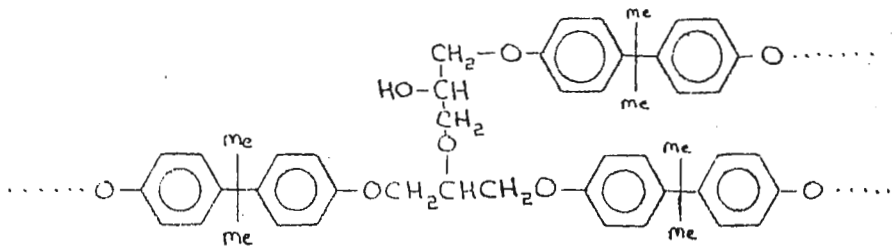
In general, the epoxy structure



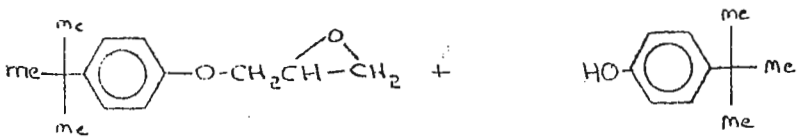
is formed from the reaction of



however there is always the possibility that a structure such as



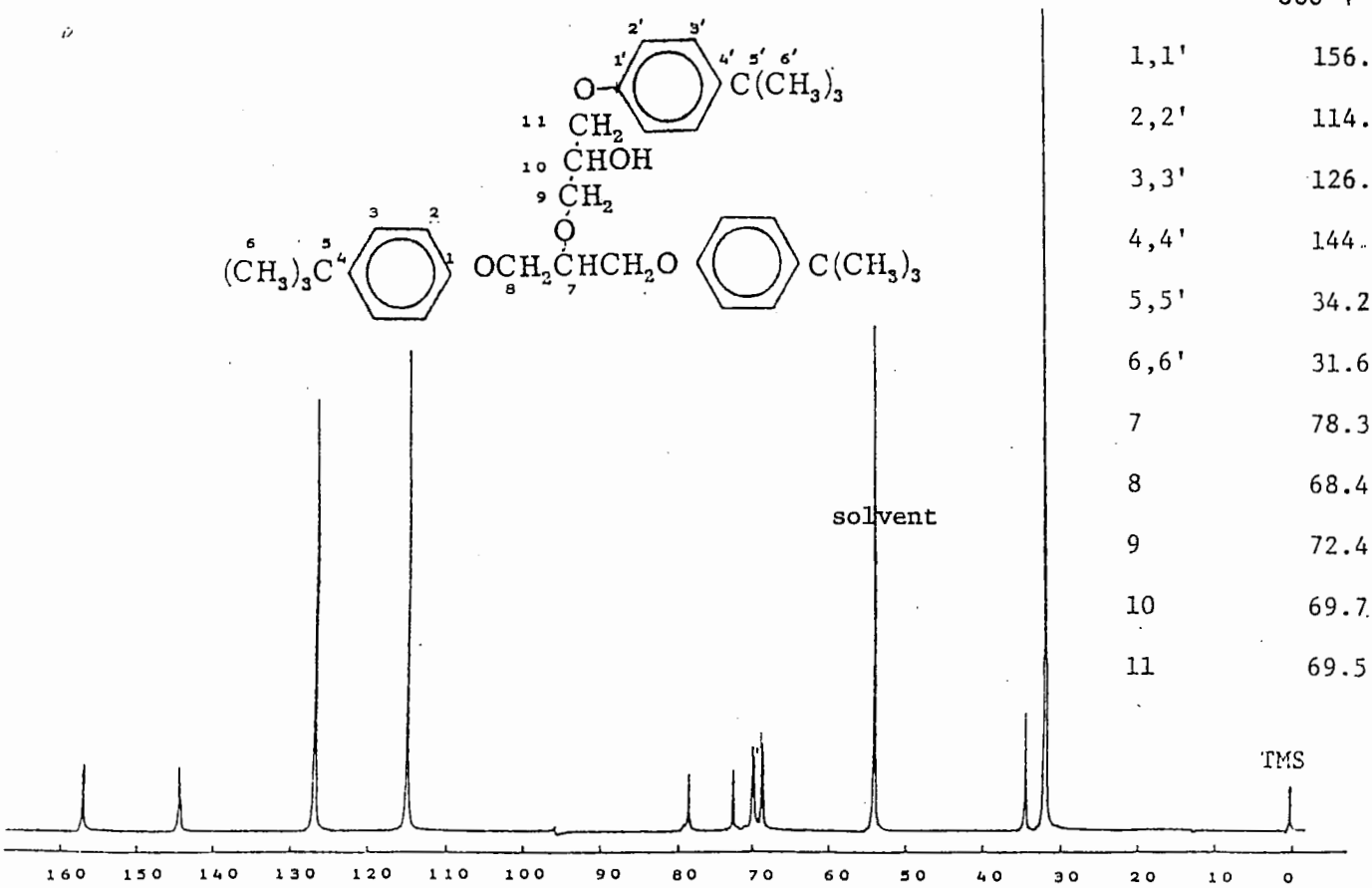
will be formed by reaction of the glycidyl ether with the secondary hydroxyl of the epoxy backbone. In order to investigate the carbon spectrum of the branch point we isolated two model compounds from the reaction



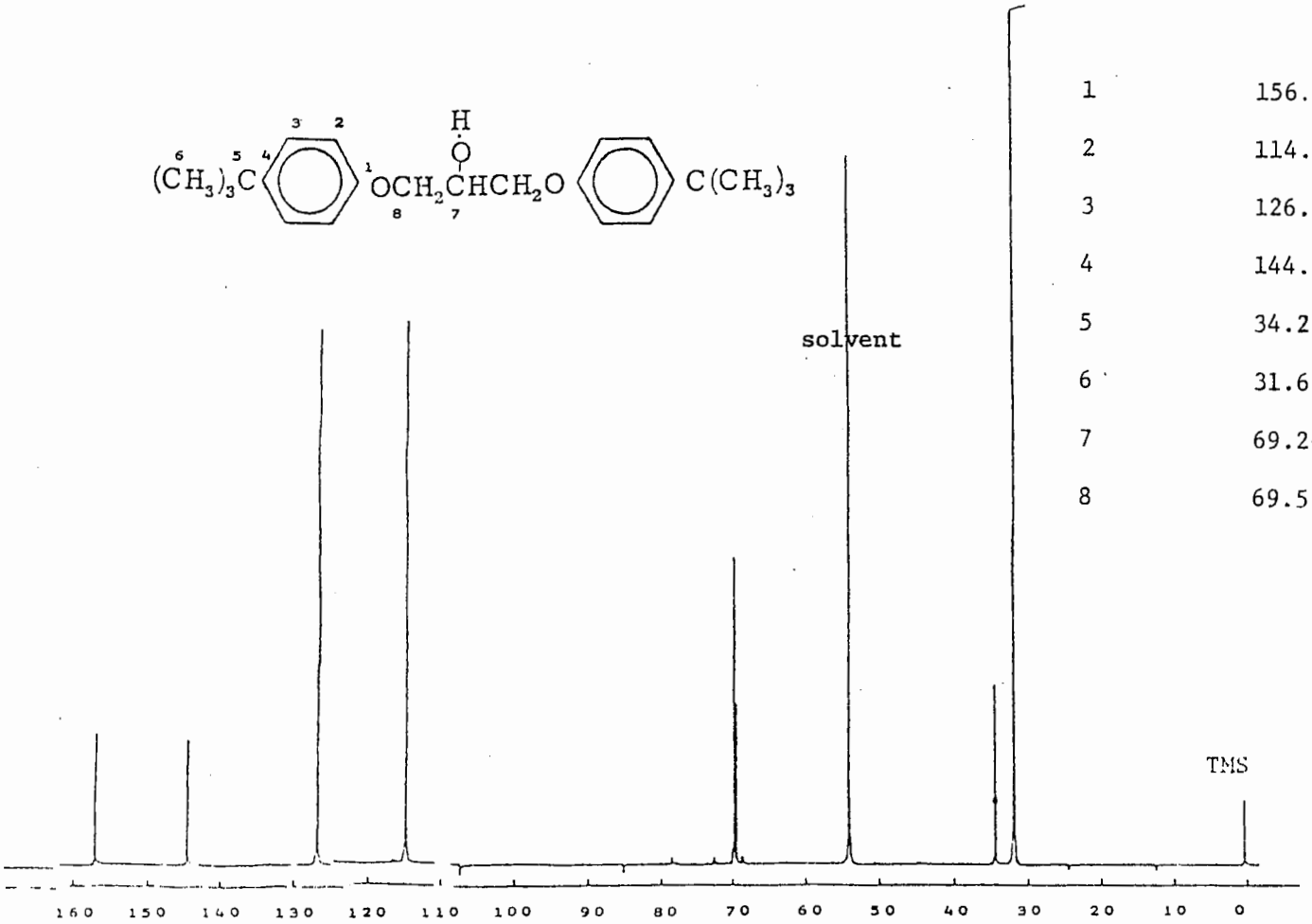
Prior to our acquisition of a superconducting magnet, spectra of the two compounds were taken by Jerry Heeschen on a 360 MHz NMR at the Michigan Division of Dow Chemical Company. The assignments are based on APT experiments as well as chemical shifts. Using our new JEOL GX-270 NMR here in Texas we have been able to detect small peaks at about 78 ppm (from TMS) attributable to branching in various commercial resins dissolved in acetone:CCl_4 (2:1). Work is continuing to characterize what are apparently different types of branch points.

Ray VanderWal
R. P. VanderWal

Michael D. Meadows
M. D. Meadows



1,1'	156.8
2,2'	114.5
3,3'	126.5
4,4'	144.2
5,5'	34.2
6,6'	31.6
7	78.3
8	68.4
9	72.4
10	69.7
11	69.5



1	156.8
2	114.5
3	126.5
4	144.2
5	34.2
6	31.6
7	69.2
8	69.5

306-5

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February 3, 1984

Dr. B. L. Shapiro
Texas A & M Nmr Newsletter
College of Science
College Station, TX

"New ICONS for Nmr"

Dear Barry:

As many of your readers know, new computer systems such as the Apple Macintosh and Lisa feature icons instead of command tables. For example, if you want to perform a function such as filing, you point a cursor to a picture (icon) of a file cabinet, and if you wish to delete your work, you point to a picture of a trash basket.

Ever wishing to be at the forefront of a new trend, whether valid or not, we at Bruker therefore propose a new system for the next generation of nmr software using icons instead of lengthy lists of commands or verbose help messages. We hope that these nmr icons will be adopted and embraced by the entire nmr community, particularly by our competitors.

Sincerely,

Elaine Braun-Keller Leo Joncas John Janigan and

as ever,

Jim Cooper

enc:

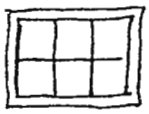
JWC/c

PROPOSED LIST OF NMR ICONS


Sweep Field


Spin Sample


Pulse


Window Function


DeLay


GO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Fourier Transform


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Plot


Plot with Title


Inversion Recovery


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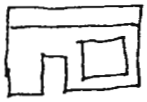
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February 15, 1984

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

Re: First results on an NMR Imaging Spectrometer

Dear Barry:

It seems that the US Mail is doing a pretty good business between College Station and Houston, and they must be tired of carrying the different reminders that you kept sending me. Thanks anyway.

As your new neighbor, I am now in charge of the NMR program at University of Texas Medical School in the Department of Radiology. We are currently building an NMR Imaging Spectrometer using a Nalorac 33 cm 2 Tesla horizontal bore magnet, a VAX-11/750 computer, a CDA array processor and various other components such as PTS synthesizers, Amplifier Research RF amplifiers and Tecmag NMRkit transceiver and filter boards. We have designed and built our own pulse programmer and ADC board.

This system will be used primarily for research and will have imaging AND spectroscopic capabilities. Being broadbanded, the observation of nuclei such as P-31, Na-23 or C-13 will be no problem. After 4 months of hard work, we have now a working console (we got our first spectrum using a 0.47 Tesla permanent magnet) and we should receive our magnet soon (?). Be assured that we will let you know the latest development on this instrument, and we will try to keep a balanced budget as far as letters between our two institutions are concerned.

Yours sincerely,

Jean

Jean L. Delayre
Assistant Professor
Director, NMR Program

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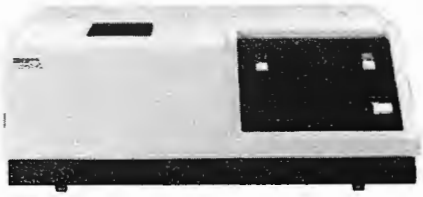

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DEPARTAMENTO DE QUIMICA

February 8, 1984

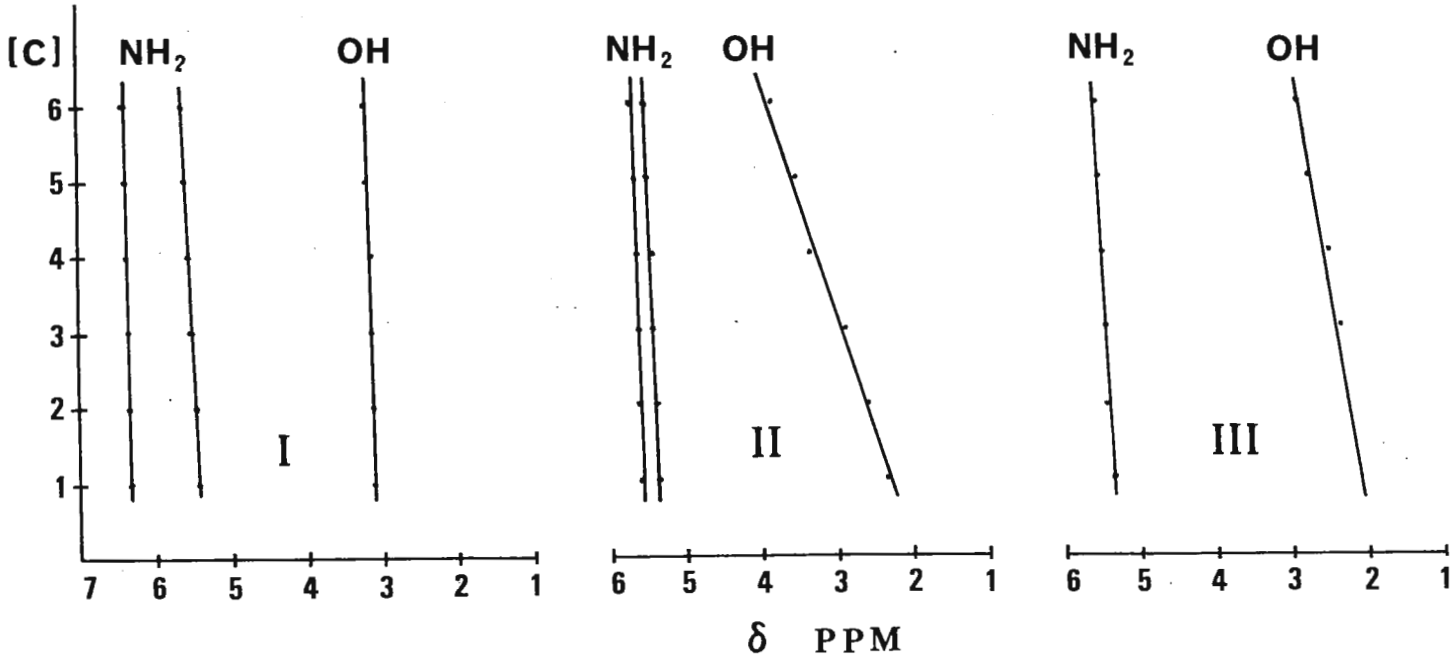
Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas
U. S. A. 77843

Non-equivalence of hydrogens in aliphatic primary amides.

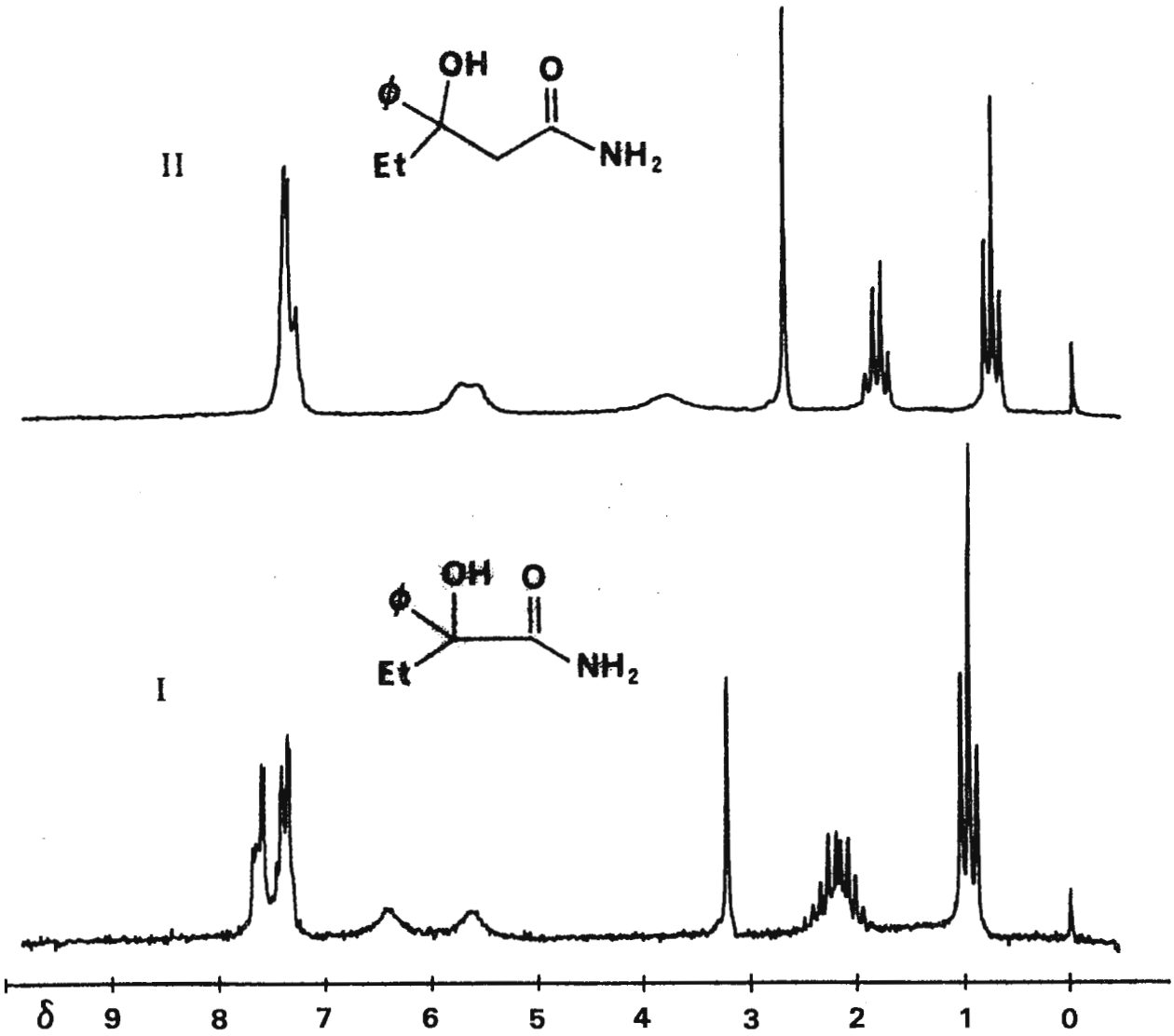
Dear Professor Shapiro:

In the context of a synthetic study leading to the preparation of γ-hydroxy-γ-phenyl-caproamide (III) analogues[1] for biological evaluation, a collegue requested us to verifie samples of α-hydroxy-α-phenyl-butyramide (I) and β-hydroxy-β-phenyl-valeramide (II). By doing this on our EM-390 spectrometer using $CDCl_3$ solutions, it immediately became clear that there are two well defined signals for the two hydrogen atoms of the primary amides in I and II. Since this behavior is in contrast to the fact that the amide protons in III provide only one signal[1], a more detailed study of I and II at lower concentration was undertaken.

Pulse-FT measurements on our XL-100 system provided the data given in the plots, in which [c] is concentration, expressed in mg/0.4 ml $CDCl_3$.



1.- P. Joseph-Nathan, G. Massieu, G. Carvajal and R. Tapia, Rev. Latinoamer. Quím., 9, 90 (1978).



These data suggest that an important hydrogen bonding is present in I, while in II this interaction is weaker. In III there is no evidence for such situation.

It should also be pointed out that hydrogen nonequivalence in primary amides has previously been reported for $CDCl_3$ solutions in aromatic molecules such as benzamides[2]. In a more general context, the nonequivalence is well known in strongly acidic media[3], where protonation of the amide oxygen atom increases the C-N double bond character, thus inhibiting the free rotation. In the case of I a somewhat equivalent situation is caused by the hydrogen bonding.

Sincerely yours,

Pedro Joseph-Nathan

Josefina Espiñeira

2.- D.J. Calvert and C.H. O'Connor, Aust. J. Chem., 32, 337 (1979).
3.- W.E. Stewart and T.H. Siddall III, Chem. Rev., 70, 517 (1970); M. Liler, J. Chem. Soc. Perkin II, 816 (1972).

THE UNIVERSITY OF ARIZONA
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COLLEGE OF ARTS & SCIENCES

FACULTY OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY

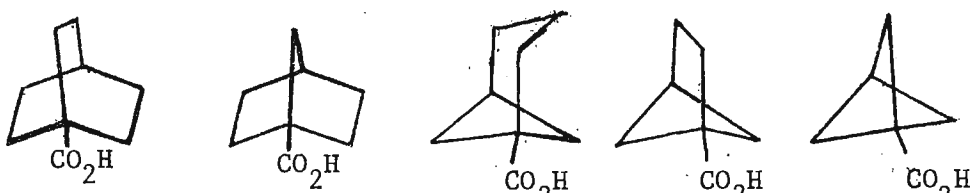
February 9, 1984

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

Dear Barry:

"Natural Abundance Studies of the ^{13}C-^{13}C Coupling between the Bridgehead Carbons in Bicycloalkanes"

In collaboration with Ern Della of the Flinders University of South Australia we have been looking at a variety of coupling constants in the bicycloalkane series. Of particular interest are the trends in the experimental and calculated ^{13}C-^{13}C bridgehead coupling constants in the series 1-5.



1 2 3 4 5

	J_{C1-C4}	J_{C1-4}	J_{C1C5}	J_{C1-C4}	J_{C1-C3}
expt	13.21	7.38	(-)8.74	(-)4.48	(-)25.15
calc	14.24	2.50	- 9.63	- 3.90	- 24.83

Experimental values were determined in natural abundance from ^{13}C satellite spectra or from the INADEQUATE double quantum coherence technique (1). Signs, which are assumed on the basis of the number of geminal and vicinal paths, are consistent with the calculated INDO-FPT values. The determination of the coupling in 5 resulted from a very fortuitous isotopic shift (See Figure 1).

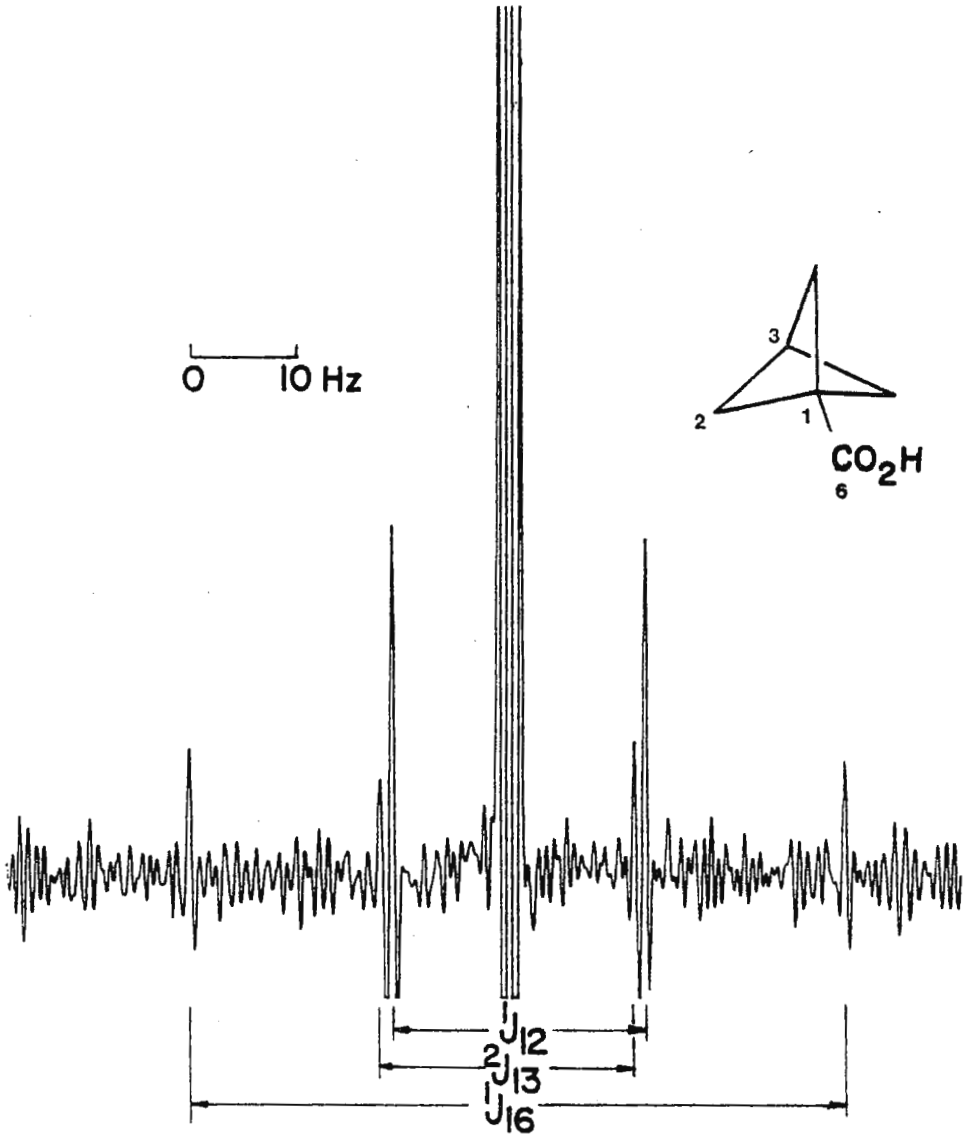
Sincerely yours,

Mike

Mike Barfield

MB:crd

(1) A. Bax, R. Freeman, and S.P. Kempsell, J. Am. Chem. Soc., 102, 4849 (1980).


0
10 Hz
3
2
1
CO2H
6
1J12
2J13
1J16

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TEL. DIRETTO

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

OLEFIN TYPE ANALYSIS USING SPECTRA EDITING TECHNIQUES

Dear Prof. Shapiro,

with the development of pulse sequences, new powerful methods are the disposal of the spectroscopist[1]. Although these sequences are becoming popular as precious aids in the resonances assignment and in the delucidation of structures, their use in quantitative analysis is lacking and subjected to some controversy (TAMU NMR Newsletter 289-17 and 295-24).

Here we want to make a little contribution to the argument, examining the possibility of using some of the new sequences (GASPE[2], DEPT[3]) in ^{13}CNMR for the quantitative characterization of complex organic mixtures.

By appropriate combination of addition and subctraction of spectra obtained at different τ values (corresponding to $1/J_{CH}$, $1/2\ J_{CH}$, $1/4\ J_{CH}$, $3/4\ J_{CH}$) it is possible to estract spectra containing only the quaternary carbons, the methines, the methylenes or the methyls.These sequences work very well when the J_{CH} value doesn't change from one to another carbon. From the integration of the sub-spectra the carbon type distribution is obtained.

We have use this approach to characterize complex olefin mixtures in terms of the different unsaturated carbon atoms, -CH=, CH_2= and $>$C=. The analysis of these mixtures by ^{1}HNMR in terms of olefin types is difficult. The usual ^{13}C NMR spectrum only allows differentiation of the CH_2= carbon, which resonates quite apart from the -CH= and $>$C = signals.

To verify the feasibility of GASPE and DEPT sequences in quantitative analysis, we have examined an olefinic mixture containing the three types of unsaturated carbons. The test mixture is simple enough (see table 1) to let us obtain quantitative data even using the normal broad band spectrum and the APT sequence[4].

The results and the conditions of measurements are shown in Table 2. The data obtained are reproducible and in good agreement with the theoretical ones, supporting the validity of the quantitative approach for the pulse sequences considered. For very complex mixture GASPE and DEPT sequences give more information than BB and APT sequences and can be applied with confidence. Furthermore GASPE is superior to DEPT as it gives a direct means of evaluating the quaternary carbons. Fig. 1a, 1b show the spectra obtained by BB and DEPT sequences of a very complex olefin mixture (propylene trimers and tetramers). The method has been used to determine the composition of the C_9-C_{12} olefinic fraction before and after acid catalyzed reaction with phenol to produce alkylated phenols.

The data (Table 3) support the higher reactivity of the CH_2= carbon with respect to the other unsaturated carbons.

Yours sincerely,

E. Santoro P.L. Cantini

References

1) R. Benn and H. Günter, "Angew. Chem.", 95, 381 (1983)
2) D.J. Cookson and B.E. Smith, "Org. Magn. Res.", 16, 111 (1981)
3) D.M. Doddrell, D.T. Pegg and M.R. Bendall, "J. Magn. Res.", 48, 323 (1982)
4) S.L. Patt, "J. Magn. Res.", 46, 535 (1982)

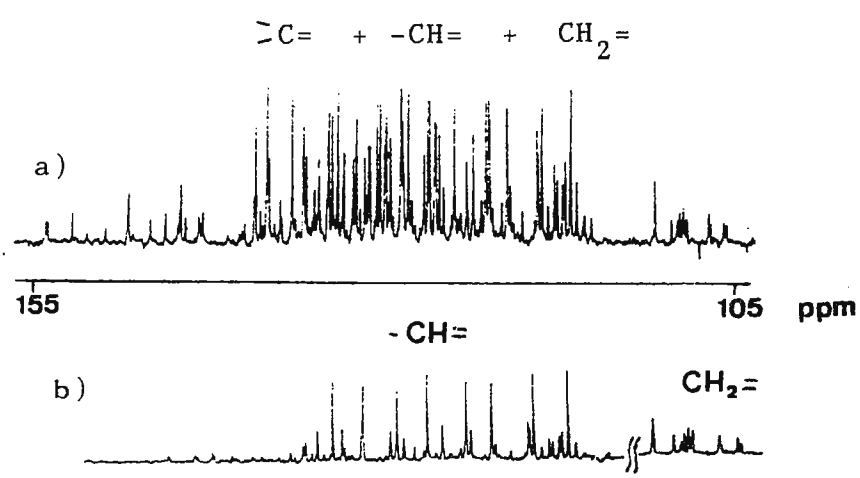

Fig. 1 - ^{13}CNMR spectra (olefinic region) of a sample of propylene trimers-tetramers in $CDCl_3$ as solvent: a) BB spectrum; b) DEPT spectra.

Table 1 Test mixture

Compound	% by wt.	Unsaturated carbon atom distribution (%)		
		-CH=	CH_2=	⟩C=
1-nonene	24.9			
cis and trans 2-octene	25.4			
cis and trans 4-octene	24.8	63.0	24.2	12.8
2,4,4 trimethyl 1-pentene	24.9			

The concentration of the mixture in $CDCl_3$ was 30% ca. Some of the samples were also 0.04 M in Cr $(AcAc)_3$

Table 2 Quantitation of unsaturated carbons with different pulse sequances (*)

Carbon type	Calculated % Carbon	Experimental % carbon BB	APT	GASPE	DEPT
CH_2=	24.2	24.1	25.4	23.0	22.0
-CH=	63.0	62.6	65.0	61.5	64.6
⟩C=	12.8	13.4	13.7	15.5	(13.4) (**)

(*) BB = Broad band ^{13}C spectrum with inverted gated decoupling; APT = Attached Proton Test; GASPE = Gated Spin Echo; DEPT = Distortionless Enhancement by Polarization Transfer. The time interval between each series of pulses is several times the relaxation times involved; J_{CH} considered: 160 Hz.

(**) BB and DEPT spectra have been compared to determine the amount of quaternary carbons.

Table 3 Quantitation of unsaturated carbons of propylene trimers - tetramers sample before (A) and after (B) reaction with phenol

Carbon type	% carbon A	B
CH_2=	6	1
-CH=	43	51
⟩C=	51	48

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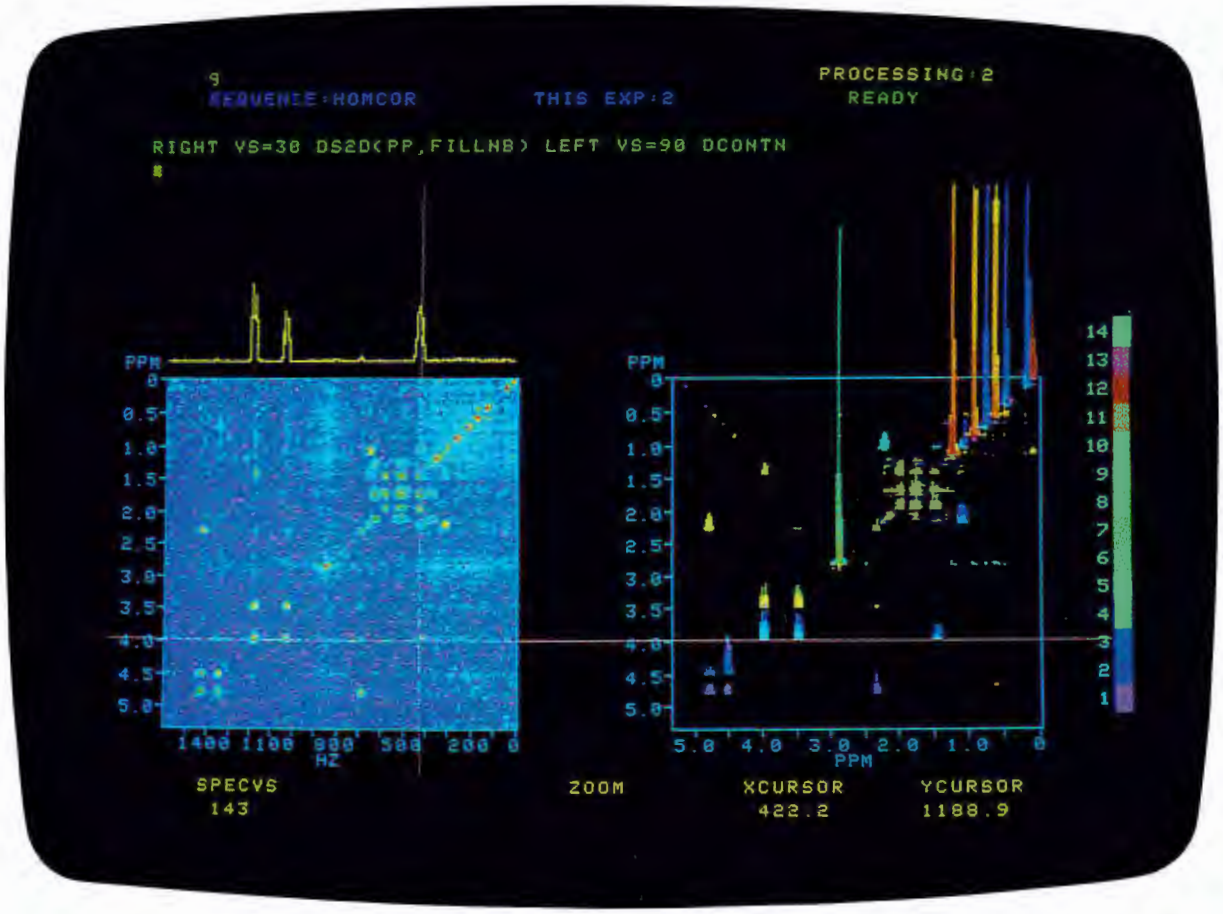

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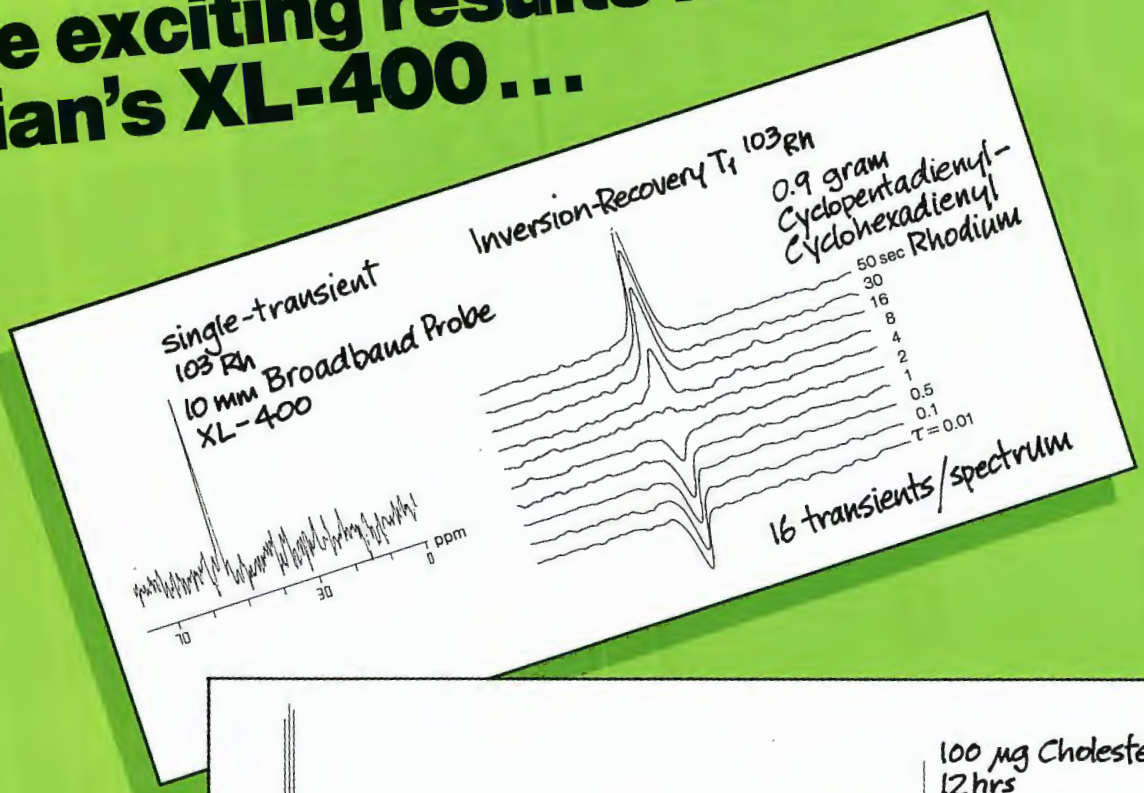

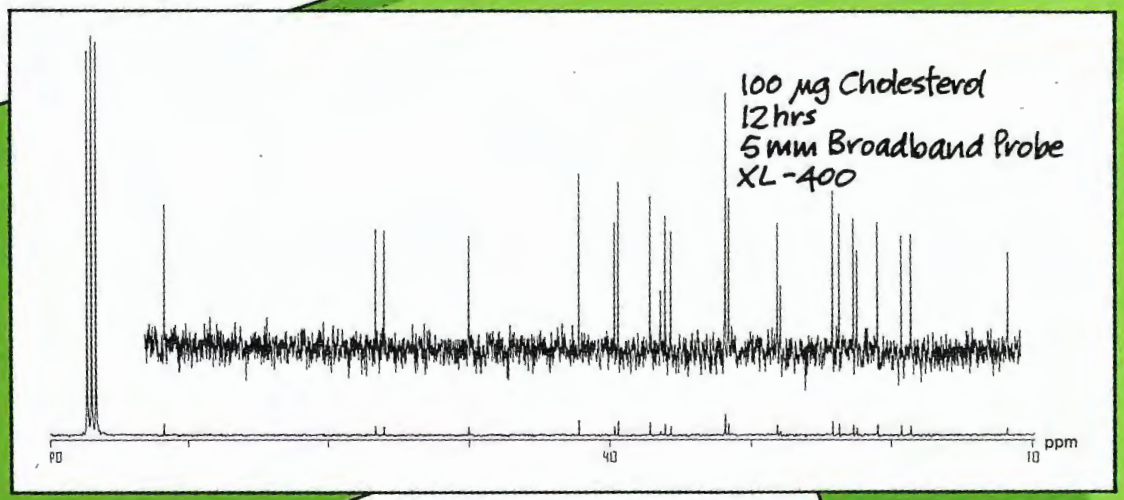

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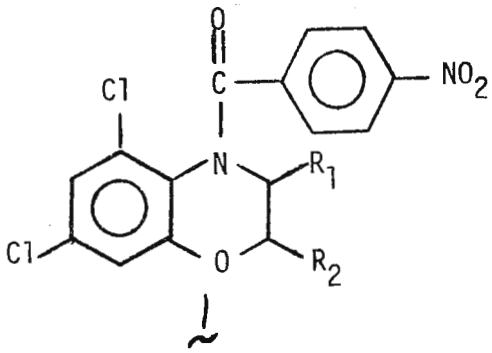
February 20, 1984

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

Title ^{13}C NMR Observation of Dynamic Processes in Benzoxazine Derivatives

Dear Barry,

We recently performed some structure determinations on a series of 4-H-2,3-dihydro-1,4-benzoxazine derivatives (1) for Professor Harold Heine and Barbara Barchiesi of Bucknell University. Most of the compounds



1

studied exhibited slow rotation about the amide N-C(=O) bond at ambient temperatures. One of these compounds, where R_1=H and R_2=$(pCH_3O)C_6H_5$ showed an additional, independent process which was slow on the NMR time scale at -30°C. We have tentatively attributed this to ring inversion of the benzoxazine ring. The ^{13}C NMR spectrum is shown in the Figure. Four distinct carbon resonances can be seen for most carbon atoms in the molecule. Of course, as the sample is heated the peaks coalesce until at 80°C only single, sharp peaks are observed for each carbon atom. The spectrum was obtained on our Varian XL-300 operating at 75.4 MHz (20KHz spectral width, 32K data points). We are currently investigating these processes for a whole series of these compounds.

Sincerely,

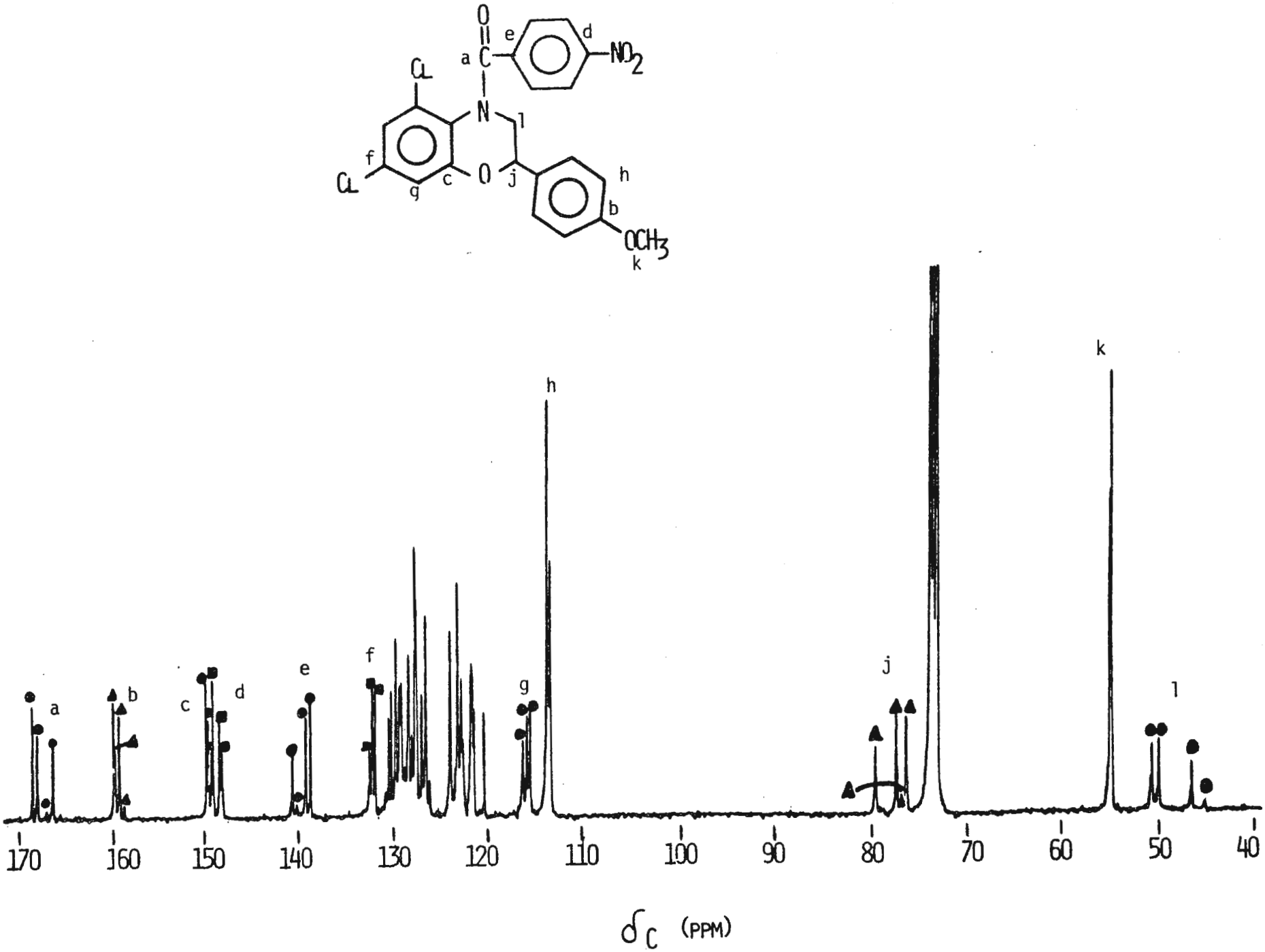
E. A. Williams

P. E. Donahue

J. F. Smith

/ldr

Materials Characterization Operation
R&D Applications Operation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δC (PPM)

R-2-D-1

Première circulaire

Une Ecole d'Eté Francophone sur la **Théorie et les Applications de la Résonance Magnétique Nucléaire à Deux Dimensions R-2-D-1** se tiendra à Orléans du **27 août au 8 septembre 1984.** L'enseignement comportera des cours, des tables rondes et des travaux pratiques (Spectromètre BRUKER 200 MHz).

Les thèmes suivants seront abordés :

- Principes de base d'une expérience à deux dimensions
- Expériences à une dimension liée à la RMN 2D - Modèle Vectoriel
- Transfert d'aimantation et de cohérence
- Traitement du signal
- Corrélations J-δ et corrélations δ-δ homo et hétéronucléaires (COSY, SECSY)
- Spectroscopie à plusieurs quanta
- Corrélation par la relaxation et l'échange chimique (NOESY)
- Applications chimiques et biochimiques.

L'accord de principe des conférenciers suivants est acquis :

R. FREEMAN (Oxford) ; G. MORRIS (Manchester) ; M. LEWITT (E.T.H. Zürich) ; O. SORENSEN (E.T.H. Zürich) ; D. CANET (Nancy) ; G. POUZARD (Marseille) ; J.Y. LALLEMAND (Gif-sur-Yvette) et A. BRIGUET (Lyon).

Les frais d'inscription et d'hébergement -en Cité Universitaire- seront de l'ordre de 1.900 F. Un petit nombre de bourses de 1.000 F sera accordé à des jeunes chercheurs. Le nombre de participants sera limité à 60.

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Université d'Orléans
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306-21

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AMV:PG

10th February 1984

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

Cross polarization investigation of pyridine soaked coal

Dear Barry,

As part of our investigation into the structure and reactivity of coals, we have been studying the interaction of pyridine with a bituminous coal, and have found that a significant amount of pyridine is cross polarizable under the conditions used to obtain a ^{13}C spectrum of coal (Fig. 1). Free, unbound pyridine does not give a spectrum under these conditions (phase alternation of 90° pulse in the spin-locking sequence with alternating acquisition polarity) since any Bloch decay signals which are generated by the pulse are negated by the following acquisition. Signals from those pyridine molecules which are bound and thus more rigid, are seen however since their spin systems follow the phase inversion of the spin locking pulse used in the cross polarization pulse sequence. Accurate settings of the phase and amplitude of the r.f. transmitter pulse are mandatory.

If the same experiment is repeated with the initial 90° pulse in the spin locking sequence disabled and the signals co-added, only those spins which respond to a single carbon pulse are seen, i.e. only mobile or "liquid-like" spins are detected. Fig. 2 shows the pyridine coal system spectrum under these conditions. The number of scans (200) is the same in both cases but the signal-to-noise ratio is vastly greater in Fig. 2 because of the excess of free pyridine. The broad resonance under the sharper pyridine lines is still under investigation but it is thought to arise from those structures in the coal that have been freed from conformational rigidity by the swelling action of pyridine.

Sincerely,

A.M. Vassallo M.A. Wilson

A.M. Vassallo and M.A. Wilson

Fig 1

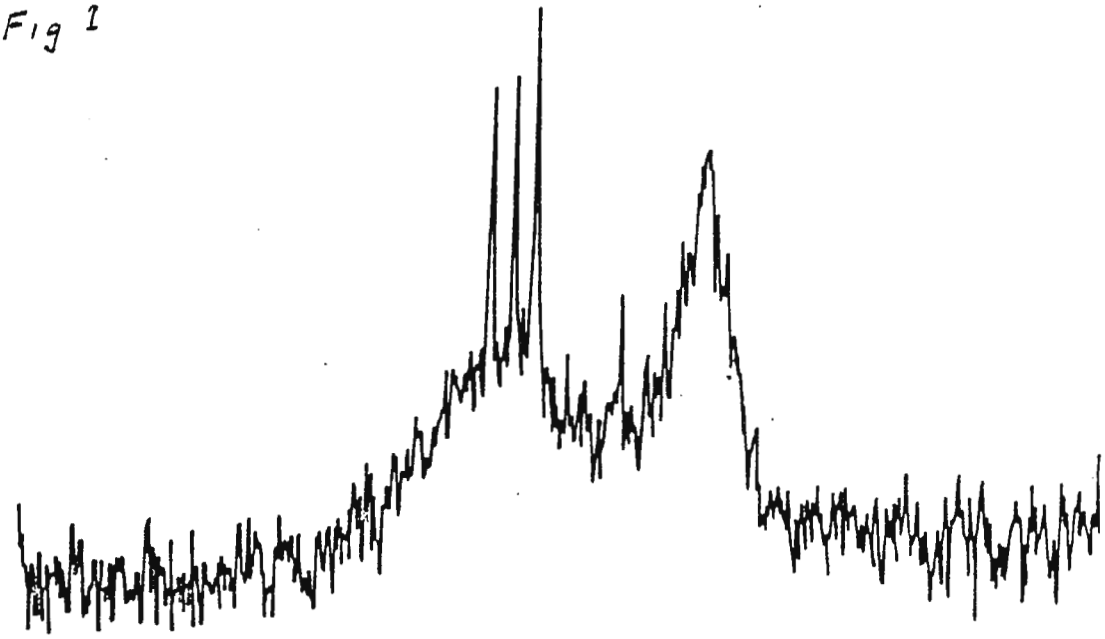
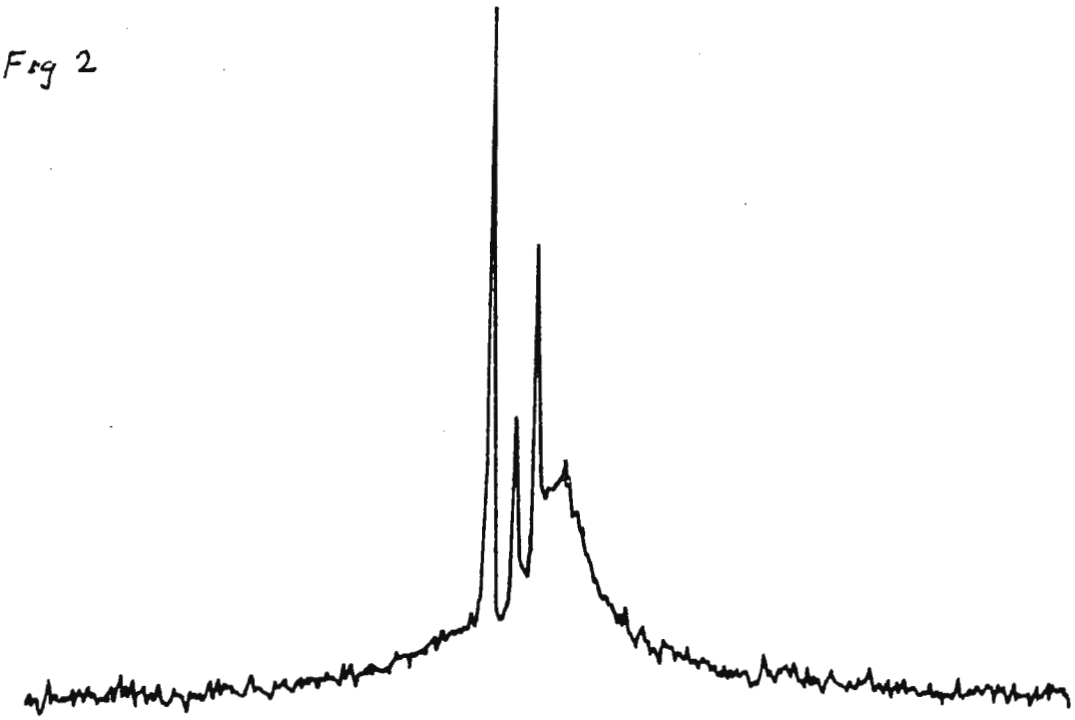


Fig 2



The University of Western Ontario

Department of Chemistry
Chemistry Building
London, Canada
N6A 5B7

February 10, 1984

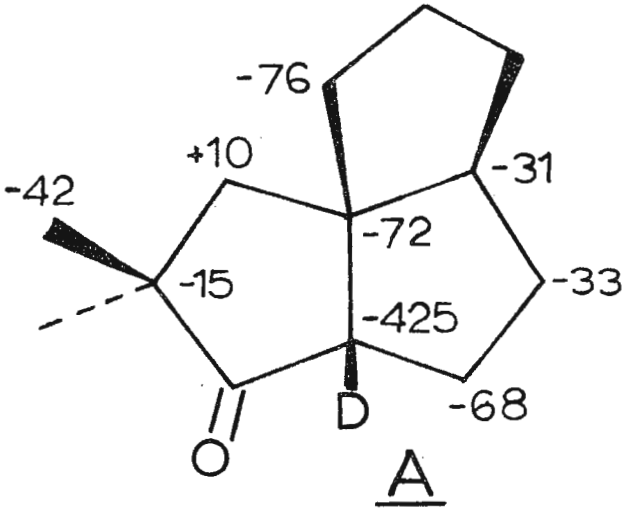
Dr. B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, Texas 77843,
U.S.A.

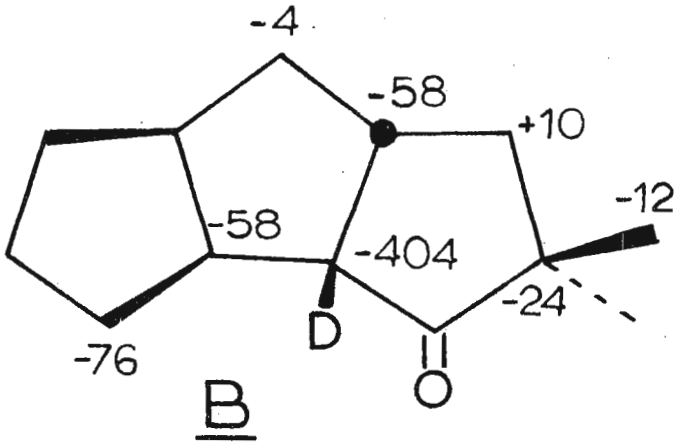
More on Intrinsic $^{2}H/^{1}H$ Isotope Effects on ^{13}C Shieldings

Dear Barry:

All too soon your barrage of colored notes has descended on me and my subscription requires reinstatement. For this purpose, perhaps a couple of applications of three-bond deuterium isotope effects as an assignment aid will suffice. As background, you may recall the finding of the stereochemical dependence of such effects in saturated systems which were described some time ago [TAMU Newsletter 286, 42 and JACS 104, 4677 (1982)]. The useful feature of this tendency is the fact that a sp^3 carbon syn-periplanar to deuterium exhibits an isotope shift comparable to geminal effects and the isotope shift decreases with an increase in the dihedral angle relating the two nuclei. In connection with studies directed toward the synthesis of some tricyclic natural products, these effects have been helpful for assignment purposes since in most cases, sufficient material is not initially available for successful INADEQUATE experiments.

Two examples are:





Dr. B.L. Shapiro,
Page 2,
February 10, 1984.

The isotope shifts are given in ppb with an estimated error of ± 3 ppb. These were measured with 1:1 mixtures of each with its protio analog. Our recently commissioned XL-300 certainly renders these measurements easier but, thankfully, the data originally obtained on the XL-200 for A agreed very nicely with those more recently recorded with the 300. Each of A and B have one methylene carbon eclipsing the deuterium and both exhibit shifts of 76 ppb. In each case the shifted signal is a poorly resolved triplet indicating J_{CCCD} to be ca. 0.8 Hz. In both compounds, a four-bond isotope shift is observed for one of the methyl carbons which I presume is the β-methyl as drawn although this has not been confirmed. Perhaps even more surprising is the fact that one of the vicinal methylene carbons, that in the ring containing the carbonyl group, displays a small but definitive downfield shift. The isotope shifts for the carbonyl carbons were not measured, since these are of little interest for practical purposes. In any event, the vicinal isotope shift found for eclipsed (or nearly so) carbons is quite helpful for signal assignments in systems such as these. It may be noted that antiperiplanar vicinal arrangements generally result in more readily resolved triplets although the isotope shifts tend to be much smaller.

I trust that these notes will reinstate my subscription.

Sincerely,

Jake

J.B. Stothers

JBS/aadg

Jake: You are reinstated. Stop grousing about our gentle reminders or you will be forced to drink nothing but 100 P-----s for 6 years.

Barry

Senior Research Association position available in the Department of Chemistry, Villanova University. Responsibilities will include supervision, instruction, routine maintenance, and operation on Varian XL-200 and Perkin-Elmer R-32 NMR instruments. Some teaching will be required. Collaborative or individual research is expected. Ph.D. required. Salary about $17,000. Start June 1. Applicants should send a resume and two references by April 15, 1984 to Dr. Amos J. Leffler, Chemistry Department, Villanova University, Villanova, Pennsylvania 19085. An EO/AA Employer.

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(617) 732-1879

February 9, 1984

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

SIMULTANEOUS QUANTITATION OF
INTRA- AND EXTRACELLULAR ^{23}NA
IN HUMAN ERYTHROCYTES

Dear Barry:

We have used aqueous shift reagents to discriminate the intra- and extracellular $^{23}Na^+$ NMR signals in suspensions of human erythrocytes. We have quantitated the amounts of Na^+ by calibrating the NMR spectrometer with standards of known concentration and have compared these results with quantitation by flame emission photometry on aliquots of the same samples used for NMR. The figure shows the results plotted against one another and the line of unit slope. The values for intra- and extracellular Na^+ are clearly labelled and the category of blood sample is also indicated. A sample of whole blood was used along with suspensions of washed erythrocytes. The latter allowed us to vary the extracellular concentration over a wide range. Before the FP analysis of intracellular Na^+, the cells were washed by two centrifugations (4°C) after the NMR analysis.

It is clear that there is no significant "NMR invisibility" of intra- or extracellular ^{23}Na ($I = 3/2$) in such suspensions of human erythrocytes. One should not, however, extrapolate this finding to other nuclei and/or other cells. A similar quantitation must be conducted for each new case.

A routine ^{23}Na NMR analysis of whole blood could certainly be completed within one half hour of venipuncture. The details of our experiments will appear in the May issue of the American Journal of Physiology.

Best regards,

Charlie

Martin M. Pike

Eric T. Fossel

Thomas W. Smith

Charles S. Springer, Jr.
Visiting Assoc. Prof.
of Medicine
Harvard Medical School

Martin M. Pike
Research
Assistant

Eric T. Fossel
Asst. Prof. of
Radiology
Beth Israel
Hospital

Thomas W. Smith
Professor of
Medicine
Harvard Medical
School

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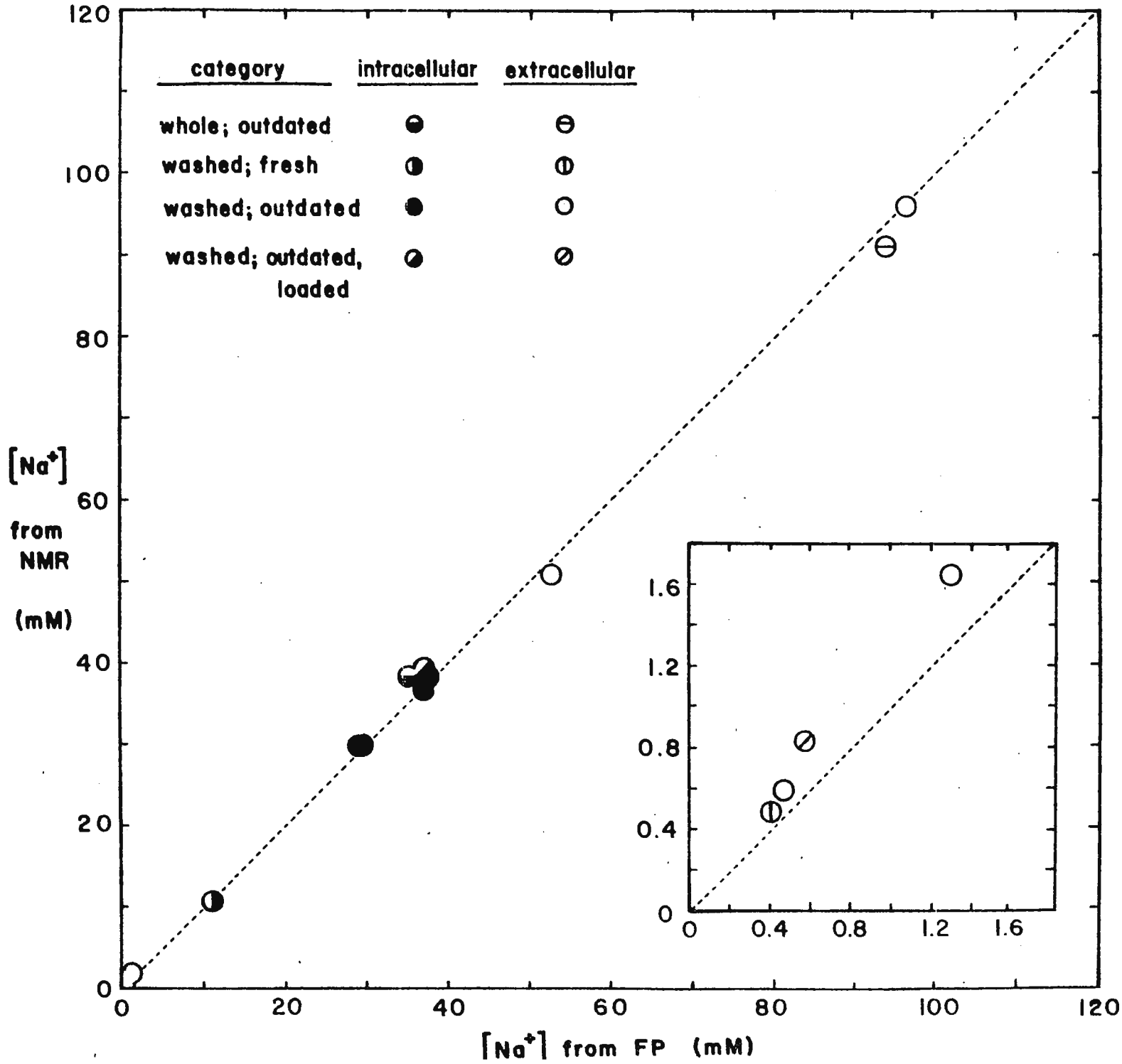
P.S. Please credit this contribution to the Harvard Medical School NMR Laboratory subscription (c/o Joanne Ingwall and Jim Balschi).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University of Illinois at Urbana-Champaign

Eric Oldfield BSc PhD DSc CChem FRSC
Professor of Physical Chemistry
Telephone 0101 (217) 333-3374

School of Chemical Sciences
505 South Mathews Avenue
Urbana, IL 61801, USA

February 13, 1984

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

Dear Barry:

Homebrew to Nicolet Conversion

We recently found it necessary to make our "home-built" 12 Tesla NMR spectrometer "look-like" a Nicolet spectrometer, in order to make effective use of most of the software features of the NIC-1280 data system. This has enabled us to do efficient programming for 2D and MQ studies, and may be of use to others.

In our system, phase shifts at the NMR frequency (F_1) in the observe channel are achieved by mixing phase-shifted 30 MHz (IF) rf pulses with pulses at ($F_1 \pm 30$) MHz. Until recently, phase shifted pulses were generated by gating 4 independent channels (0°, 90°, 180° or 270°) using 4 different Sp outputs from our NIC 293B. Due to this, we could not use the phase expression letters associated in the NIC 1280 software. This meant that fully phase cycled programs could get to be very long.

The interface shown here facilitiates the usage of phase expression letters, such as @ A, for effecting automatic phase cycling of the observe channel rf pulses. A similar interface has also been incorporated into our decoupling channel, the only difference being that Sp13, Sp16, and Sp17 outputs, respectively, are used instead of Sp0, Sp18, and Sp19. The functioning of the interface can be easily visualized by knowing that the $P_1/1$, $P_1/2$, and $P_1/3$ commands bring respectively the Sp18, Sp19 and Sp(18 + 19) outputs high while Sp0 is brought high by $P_1/0 \leftrightarrow 3$.

Yours sincerely,

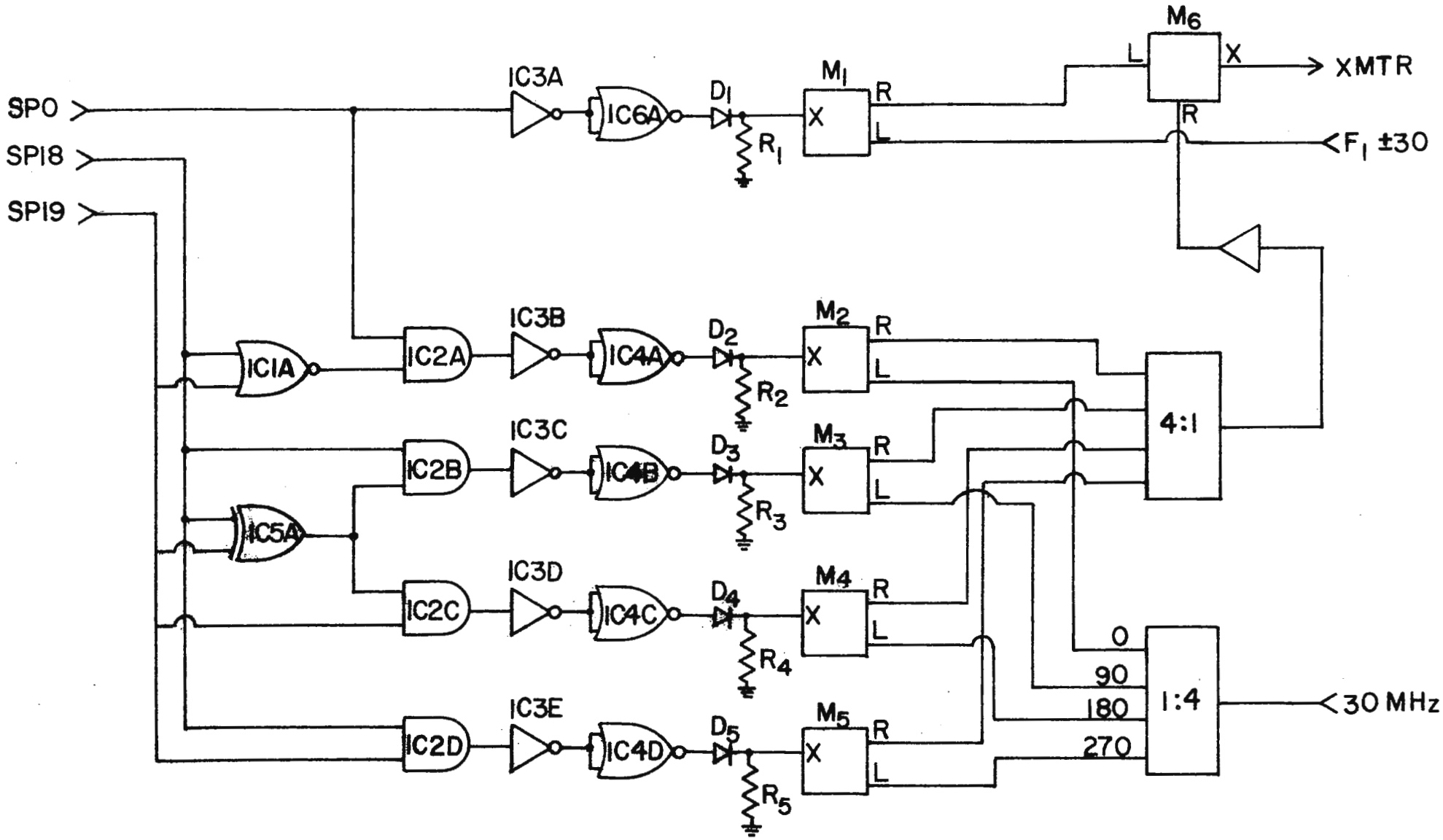
R. Ramachandran
R. Ramachandran

Jeff Forbes
Jeff Forbes

Ben Montez
Ben Montez

Eric Oldfield
Eric Oldfield

ch
Enclosures



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DUPONT

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

February 16, 1984

Sub: C-13 shifts for phthalaldehydic acid-assignments revised on the basis of results from 2-D INADEQUATE experiment

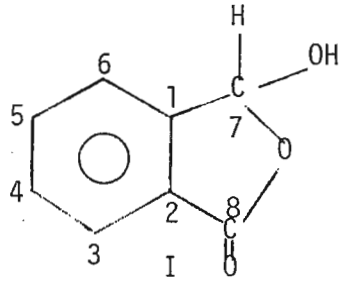
Dear Prof. Shapiro:

We had reported in our earlier communication (TAMU NMR Newsletter No. 260) on the subject of the C-13 chemical shifts for phthalaldehydic acid(I) in a variety of solvents; those were derived on the basis of known substituent effects for benzene substituents and from data for related compounds. However, some of the shifts were close to each other with the possibility of interchangeability of their assignments. An opportunity came to verify those assignments employing a 2-D INADEQUATE experiment on the sample by seeing the C-C connectivities. Since C-1 resonance was unambiguously known, the rest of the carbons were automatically identified from the above experiment; indeed, three of the earlier assignments (C-3, C-4 and C-6) had to be revised!

While exact assignments of such closely-spaced resonances (e.g. C-3 & C-6) might only be of academic interest in the present case, there may be instances such as reaction mechanism or biosynthetic studies wherein it may be very important.

A contour plot of the 2-D INADEQUATE spectrum is shown on the following page, indicating the C-C connectivities.

I express my sincere gratitude to Dr. Hermann Bleich and Ms. Joyce Wilde of IBM Applications Laboratories, IBM Instruments, Danbury, CT, who carried out the above experiment on their SY-270 Spectrometer.



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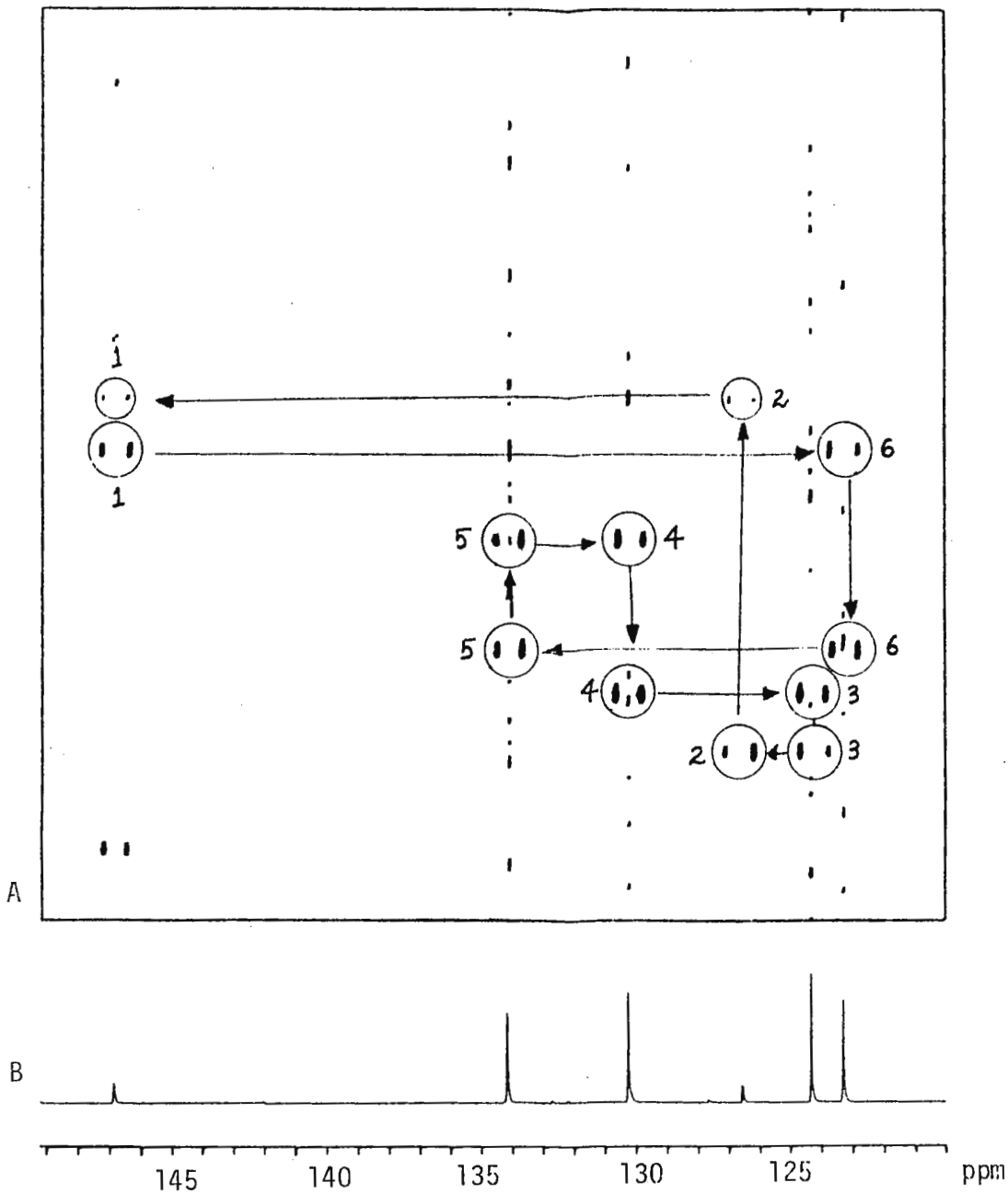
With best regards,

Sincerely yours,

P. R. Srinivasan

549 Albany Street, Boston, Massachusetts 02118 Telephone 617-482-9595 Telex 94-0996

Contour plot of 2-D INADEQUATE spectrum of phthalaldehydic acid (50% w/v solution in acetone-d_6): A-contour plot; B-1-D plot of the noise-decoupled spectrum.



Princeton University DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08544

February 21, 1984

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

Title: High Resolution, Long Accumulation Spectra in Unlocked Mode

Dear Professor Shapiro:

We have been running high resolution ^{2}H spectra at natural abundance on some naturally occurring organic molecules, and are interested in obtaining the best resolution possible. Samples are run in unlocked mode on a Bruker WM250 spectrometer whose magnet drift is small but noticeable on these typically overnight runs. The accompanying spectrum of β-pinene demonstrates a method we have found to be very useful for minimizing the effect of long-term magnet drift on line widths.

FID's are collected in blocks, where the magnet drift over the time for one block accumulation is less than 0.2 Hz. Enough blocks are accumulated to give adequate signal-to-noise. Each block is transformed, then the resulting spectra are shifted to compensate for field drift, and co-added to give the final spectrum. The spectrum below was collected using ca. 1 watt of broad-band, ^{1}H decoupling to remove ^{1}H couplings that were especially noticeable on the methyl signals. FID's were collected as 8 blocks of 512 scans each, digital resolution was 0.25 Hz per point, and the entire run took slightly over 5 hours. In this particular case, the total magnet drift over the period of the experiment was approximately 0.8 Hz, which would have

been acceptable, but for our typically overnight (16-20 hr) runs, the pair of signals at 1.96δ and 1.91δ would not be resolvable without block averaging.

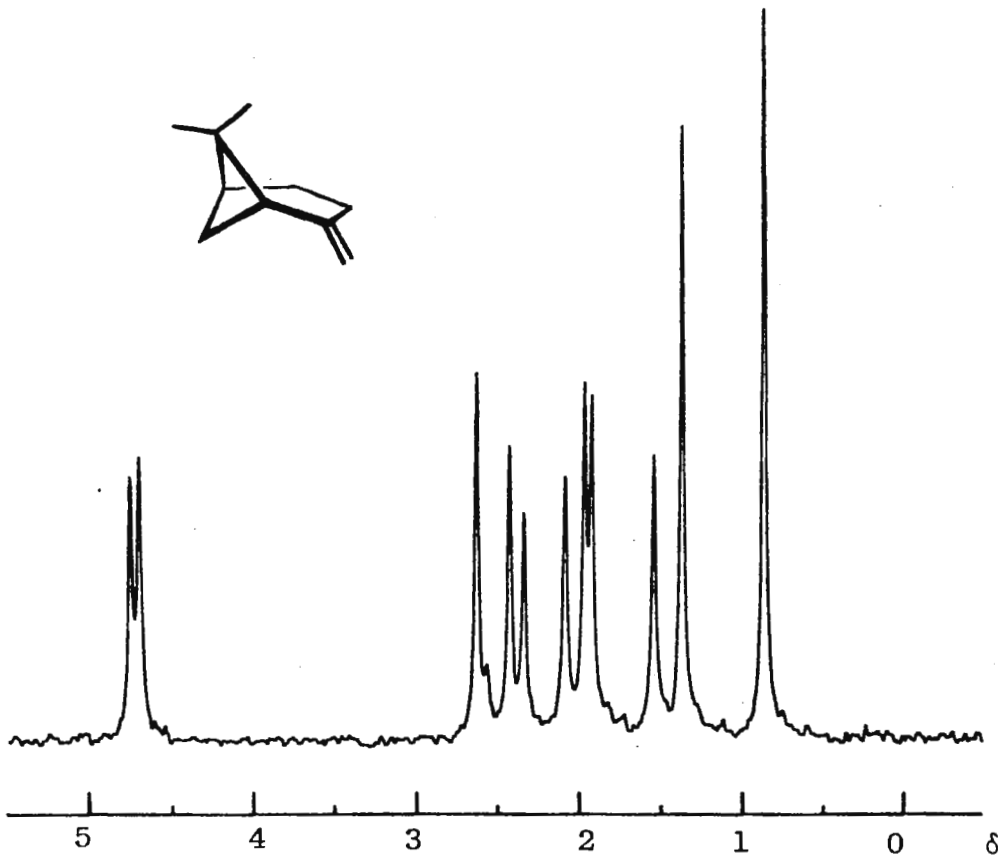
Sincerely,

Mary W. Baum Robert Pascal Jr.

Mary W. Baum*, Robert A. Pascal, Jr.

gc

Natural Abundance ^{2}H NMR spectrum of β Pinene



306-35

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Afdeling Biophys.Chemie

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

Uw kenmerk	Uw brief van	Ons kenmerk	Datum
		84690/CHW/ro	22 February 1984

Onderwerp

Binding sites for spermidine on tRNA.

Dear Professor Shapiro,

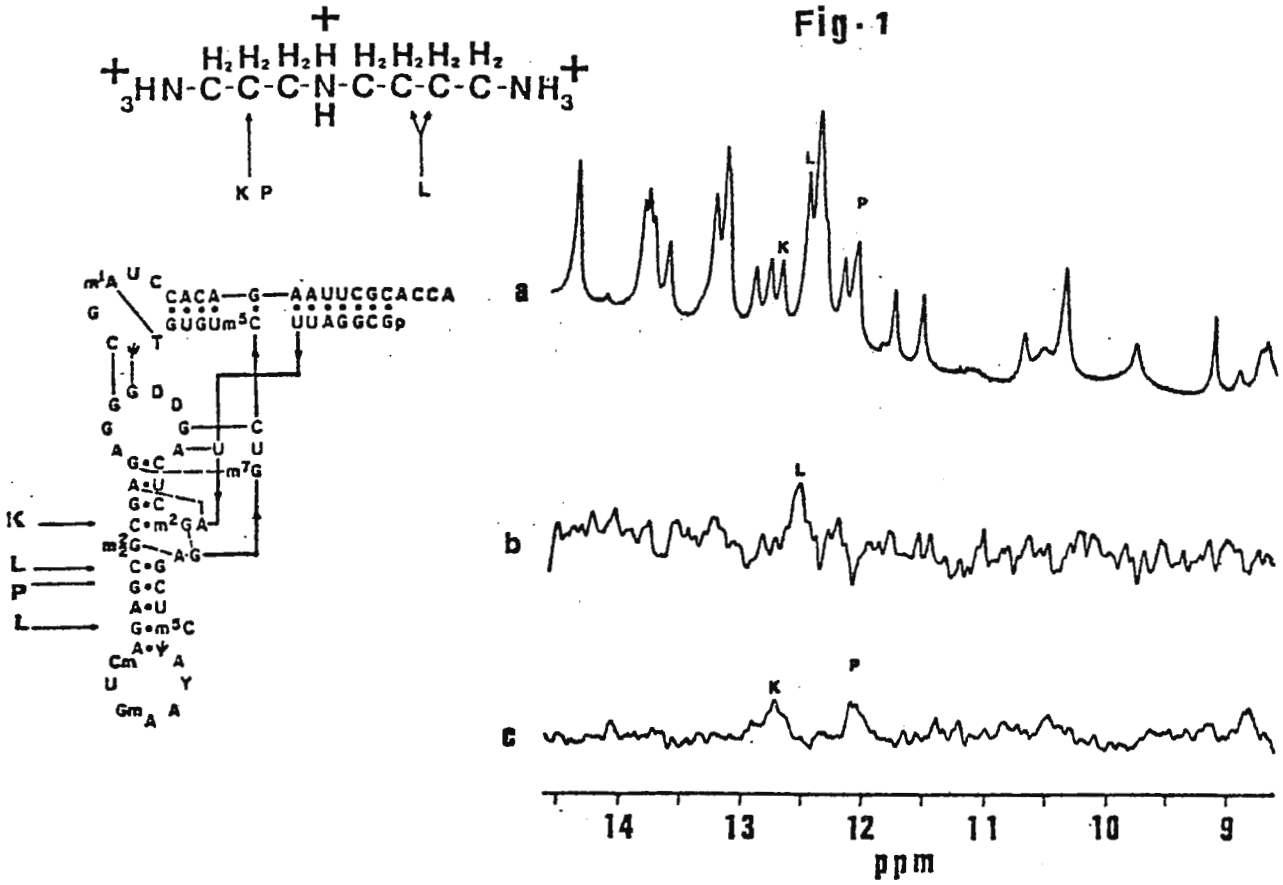
Transfer RNA's (MW 28000) are biomacromolecules which play a crucial role during protein synthesis. NMR has been used quite extensively to investigate the structure of these molecules in solution. In these studies the hydrogen bonded imino protons, situated in Watson Crick base pairs which form the frame work of the molecular structure, have received special attention. The resonances from these imino protons are found at low field positions (15 - 10 ppm downfield from Dss) and are therefore quite well-resolved from the bulk of the proton resonances of the molecule.

Because these imino protons exchange quite rapidly with solvent it has been difficult to assign their resonances but recently by making use of nuclear Overhauser effects between the imino protons of adjacent base pairs it has been possible to achieve this identification (1 - 4).
One of the following interesting problems to look at, concerns the interaction of transfer RNA with molecules important for its functioning. An important class of molecules is formed by the polyamines. The presence of these molecules is a prerequisite for the proper course of protein synthesis.
For one of these polyamines, spermidine we have determined the binding site on yeast $tRNA^{Phe}$ by using nuclear Overhauser effects between spermidine protons and the imino protons of the tRNA. This is demonstrated in Fig. 1. Spectrum (a) represents a normal imino proton spectrum of yeast $tRNA^{Phe}$. After preirradiation (during 1 sec.) of the protonspins L of the spermidine molecule (see Fig. 1 top left) we see Overhauser effects at 12.5 ppm (difference spectrum b in Fig. 1) and after preirradiation of protonspins KP we see nuclear Overhauser effects at 12.1 and 12.8 ppm (difference spectrum c). The imino protons in the tRNA corresponding with these Overhauser effects are indicated by arrows in the tRNA structure (left). From these results we may conclude that the spermidine binds preferably at the D-stem anticodon stem junction and that there are two different binding sites for spermidine in this molecular region.

Sincerely Yours,

A. Heerschap — J.A.L.I. Walters — C.W. Hilbers

J.A.L.I. Walters — C.W. Hilbers



The spermidine/tRNA ratio in these experiments is ∿ 1

1. Tropp, J. and Redfield, A.G. (1981). Biochemistry 20, 2133.
2. Roy, S. and Redfield, A.G. (1983). Biochemistry 22, 1386.
3. Heerschap, A., Haasnoot, C.A.G. and Hilbers, C.W. (1982). Nucleic Acids Research 10, 6981.
4. Heerschap, A., Haasnoot, C.A.G. and Hilbers, C.W. (1983). 11, 4883 and 4501.

Chemistry

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Professor B L Shapiro
Department of Chemistry
Texas A & M University
College Station TX77843
U S A

28 February 1984

Dear Barry,

THE LAW OF MORE or A "CHOOSE YOUR OWN DIRECTION" SHIFT REAGENT

We have been continuing our work on attempting to improve shift reagents for ^{23}Na and ^{39}K spectra and have found a remarkable bidirectional shift reagent. With the ^{23}Na shift reagent developed by the Guptas, $Dy^{3+}/^{23}Na$ tripolyphosphate, it is possible to obtain shifts in excess of 35ppm. We thought it might be fun to examine other polyphosphates.

First of all we tried Dy^{3+}/diphosphate which gives appreciable ^{23}Na shifts (5 to 10ppm). Given that two phosphates gave good shifts, three phosphates even better shifts, we decided to try four phosphates using linear sodium tetrapolyphosphate. This is an adaptation of the "Law of More" taught to me by my old school chemistry teacher, 'If some is good, more is better'. This law, as he pointed out, although believed in by most schoolboys, is almost always wrong. At school you soon find out that if some ice cream is good, more is not always better! Later in life we also find for example if some beer is good, more is not always better! This applies in chemistry too.

The Figure shows titrations of Dy^{3+} against Sodium tetrapolyphosphate, recording the ^{23}Na chemical shift as a function of added Dy^{3+}. The chemical shift variation is, at first sight, quite remarkable. With this reagent you can choose the direction in which you shift the sodium (+ve or -ve frequency) by choosing the stoichiometry of your $Dy^{3+}/PPPP^{6-}$ mixture. This is to our knowledge the only bidirectional shift reagent known.

Each of the curves plotted for different concentrations of Na_6PPPP follows the same stoichiometric relationship as all the others. Slopes, intercepts, maxima and minima are all in the correct ratios for the relative amounts of reagents. Quite clearly, several different complexes of Dy^{3+} with Na^+ and $PPPP^{6-}$ are involved, each having a differing geometric relationship between Dy^{3+}, the phosphate and the Na^+ ions.

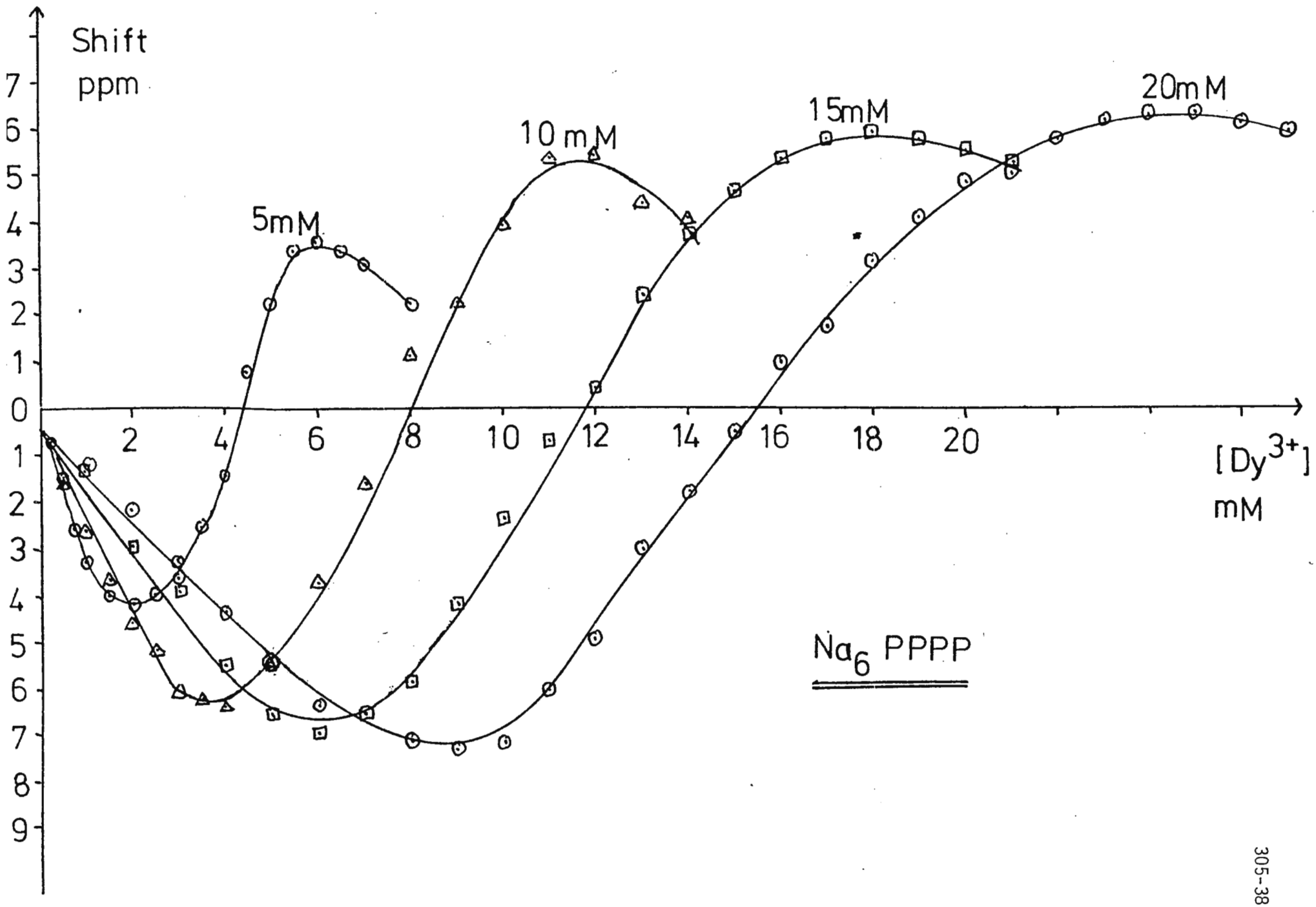
Perhaps somebody will find a use for this unusual behaviour?

Yours sincerely,

Frank

Dr F G Riddell

M K Hayer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[Dy3+]
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15mM
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Na6 PPPP

305-38

Orchard Park
PO Box 332 Danbury CT 06810

Telephone: 203 796 2500

February 1, 1984

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

Selective Observations of Non-Protonated and Methyl Carbon NMR Resonances in Solids

Dear Professor Shapiro:

I am enclosing a preliminary report describing some pulse sequences that I have been studying. I believe that these pulse sequences will be useful in studying molecular systems where large differences in T1's occur, particularly for molecules with methyl groups and for soft/hard segment polymers. I am planning to submit a much more detailed discussion to a Journal shortly.

The results of applying these experiments to an ideal molecular system, p-Di-tert-butylbenzene, are shown in Figures 1 and 2. The rf pulse sequences and mechanics are drawn in Figure 3. The numbers besides the pulse sequences in Figure 3 correspond to the NMR spectra in Figures 1 and 2.

This molecule is particularly favorable since the T1 of the methyl carbons is approximately 0.2 sec which is about 25 times shorter than the next shortest carbon T1. This molecule is also very useful in verifying the proper tuning and operation of the proposed rf pulse sequences.

Please credit this letter to the account of Richard Schwemm of IBM Instruments.

Cordially,

Paul

Paul D. Murphy

/lw
Enclosure

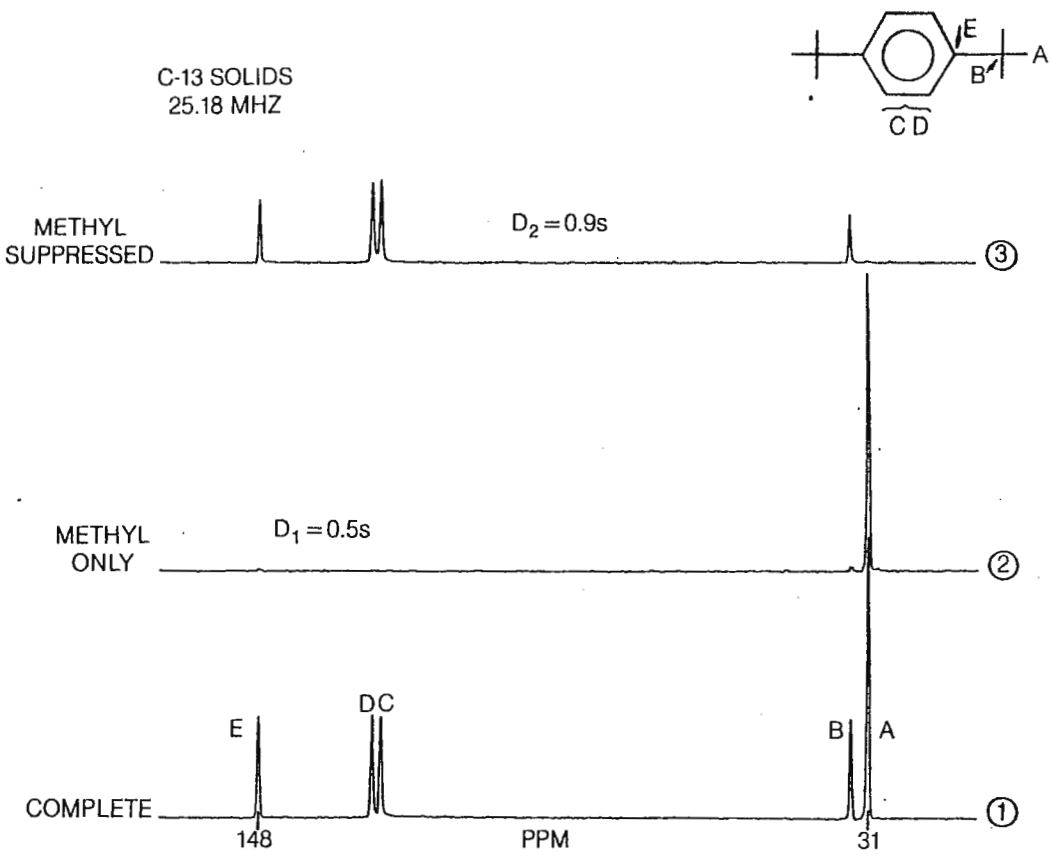

Figure 1. C-13 NMR spectra of p-Di-tert-butybenzene obtained using pulse sequences drew in Figure 3. Methyl resonance are manipulated.

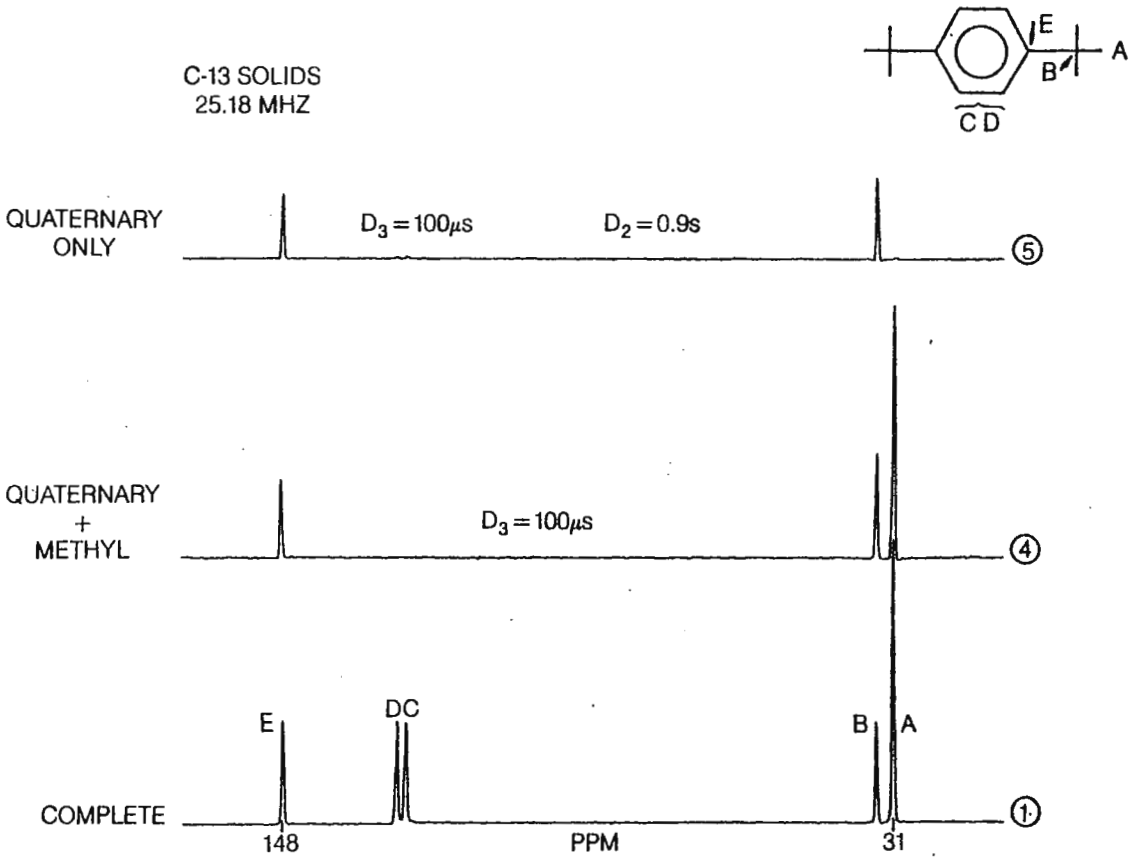

Figure 2. C-13 NMR spectra of p-Di-tert-butybenzene obtained using pulse sequences drawn in Figure 3. Methyl suppression is combined with dipolar dephasing.

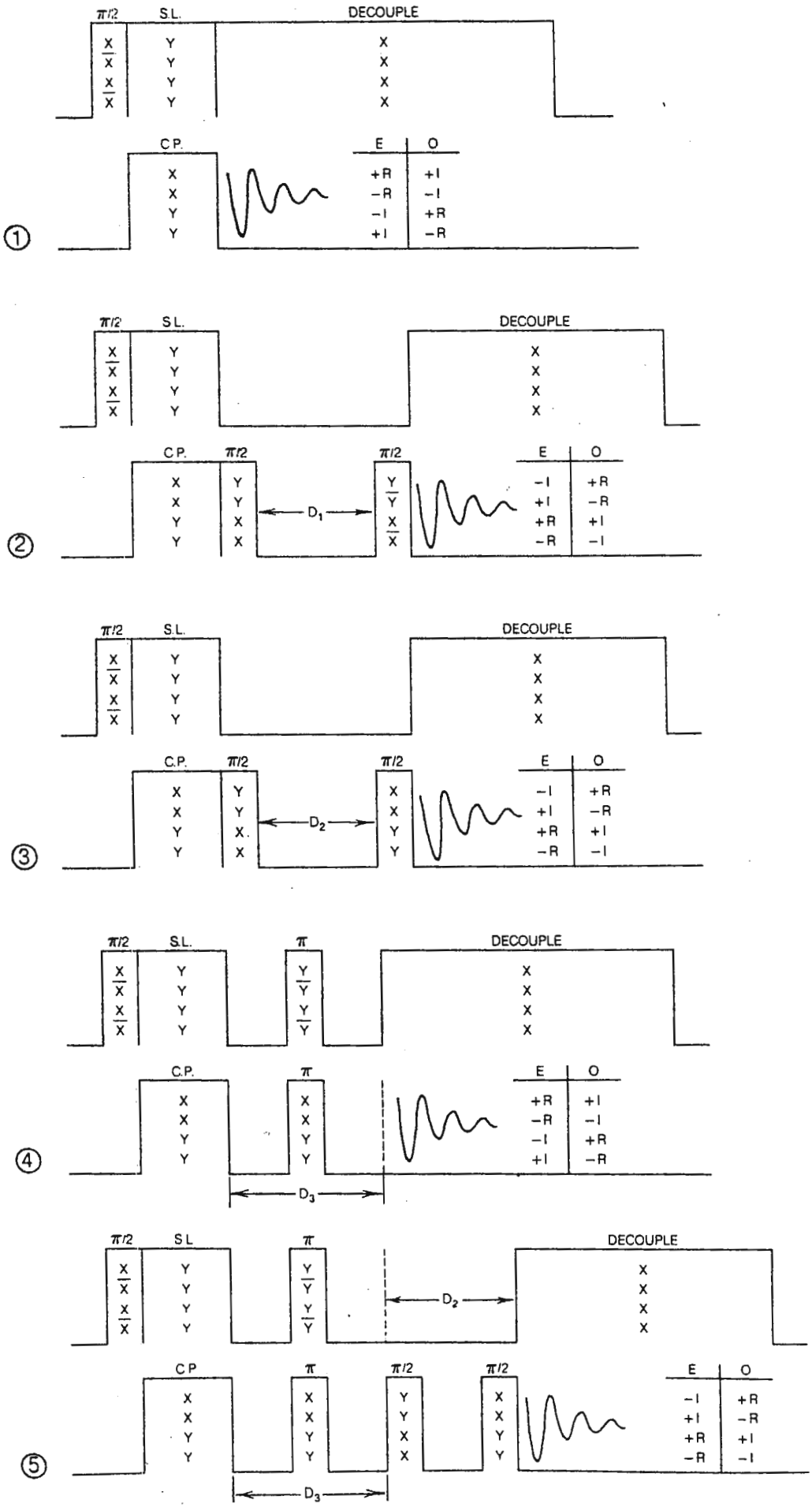

Figure 3. Schematic representation of rf pulse sequences and phase cycling used to excite spectra shown in Figures 1 and 2.

Los Alamos
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Los Alamos, New Mexico 87545

Group INC-4, Mail Stop C345
Ref.: INC-4:84-127
22 February 1984

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

Dear Dr. Shapiro:

Hidden Signals and Lineshapes in High Resolution Solid State NMR

For a while we have been using a double air bearing probe made by Doty Scientific, Inc. This is not meant to be a recommendation or indictment of that probe (like most pieces of equipment it has its strong and weak points). In order to obtain the highest spinning speeds the manufacturers recommend using Vespel endcaps on a sapphire cylinder. Since there is a rather infamous case in the literature in which rotor signals were misinterpreted [1,2], I would like to pass on some data on Vespel. Vespel is a DuPont polyimide, a generic structure of which is shown at the top of Figure 1. The spectrum in the figure was obtained from a "variable temperature" rotor which has the two endcaps and a 1.8 mm screw down the middle. This spectrum is the result of a total of 7168 scans. This is the result of block averaging 7 spectra which were used to estimate the proton T_1 and the T_{IS}. I have only made a rough estimate of these parameters but T_{IS} is about 1 ms which is reasonable for such a polymer. The proton T_1 is greater than 15 s which is rather long and simply implies that the polymer is rather rigid. Since I was spinning fairly slowly ($\approx$ 2.3 kHz) there are a lot of sidebands. It is not entirely clear whether there is any aliphatic intensity, i.e., if there is an R group in this particular polyimide. The point of all of this is that if the Hartmann-Hahn condition is carefully met, if a contact time of 2 or 3 ms is used, and if a repetition time of 10 s is used, one can obtain a quite good spectrum in less than 1024 scans. As a point of comparison, on my spectrometer, I obtain a signal to noise of about 90 to 1 on the methyl carbon of hexamethylbenzene with a 2 ms cross polarization contact in 8 pulses.

This leads into another little warning; I have been playing around with the single peak curve-fitting routine in the Bruker software. I have not investigated the details of their curve fitting but it has become quite clear

that the peaks are better fit by a Gaussian than a Lorentzian function. This is true whether the compound is quite rigid with a narrow line like the peaks in solid sugars or if the compound is something more mobile and broader like hexamethylbenzene. In fact this is not surprising because we have pointed out that the majority of the linewidth in solids is due to a dispersion of chemical shifts [3]. It is likely that the dispersion of chemical shifts is more Gaussian than Lorentzian. Figure 2 shows the curve fit of both the Lorentzian and Gaussian to the methyl peak of hexamethylbenzene as an illustration of this fact. Note that the Lorentzian fits very poorly in the wings as might be expected.

Sincerely,

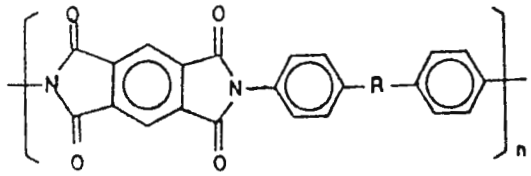
Bill.

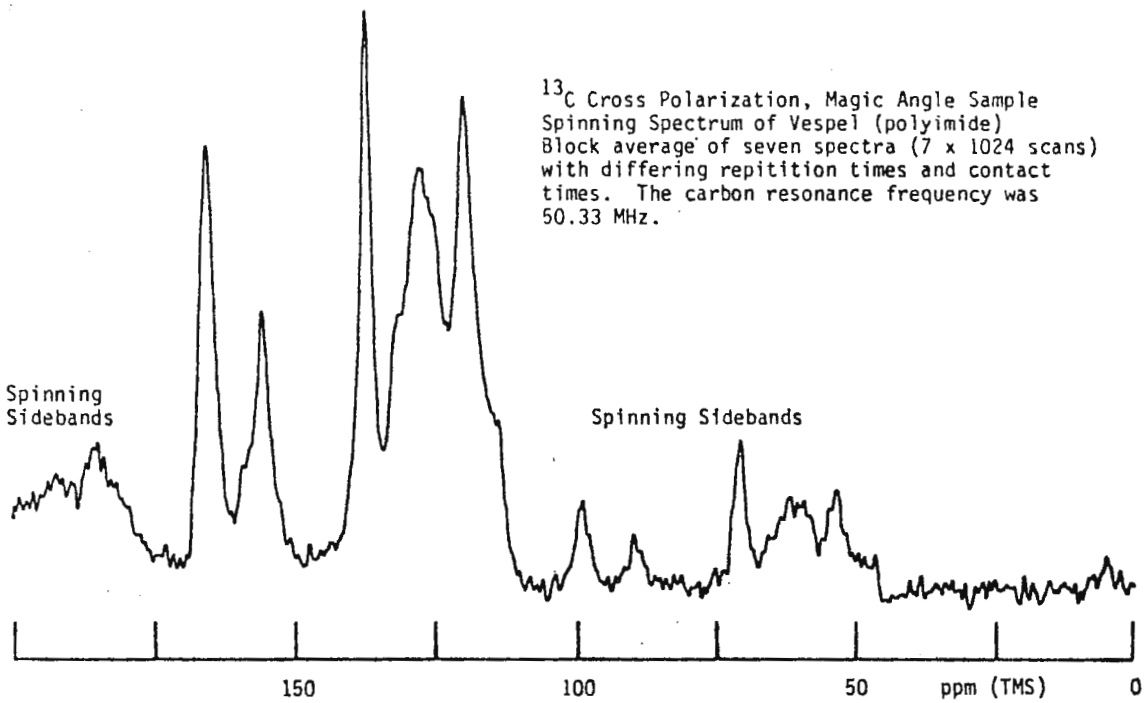
William L. Earl

WLE:msf

1. D. Vučelić, N. Juranić, and D. Vitorović, Fuel 58, 759 (1979).
2. M. T. Melchior, K. D. Rose, and F. P. Miknis, Fuel 59, 594 (1980).
3. D. L. VanderHart, W. L. Earl, and A. N. Garroway, J. Magn. Reson. 44, 361 (1981).

FIGURE 1

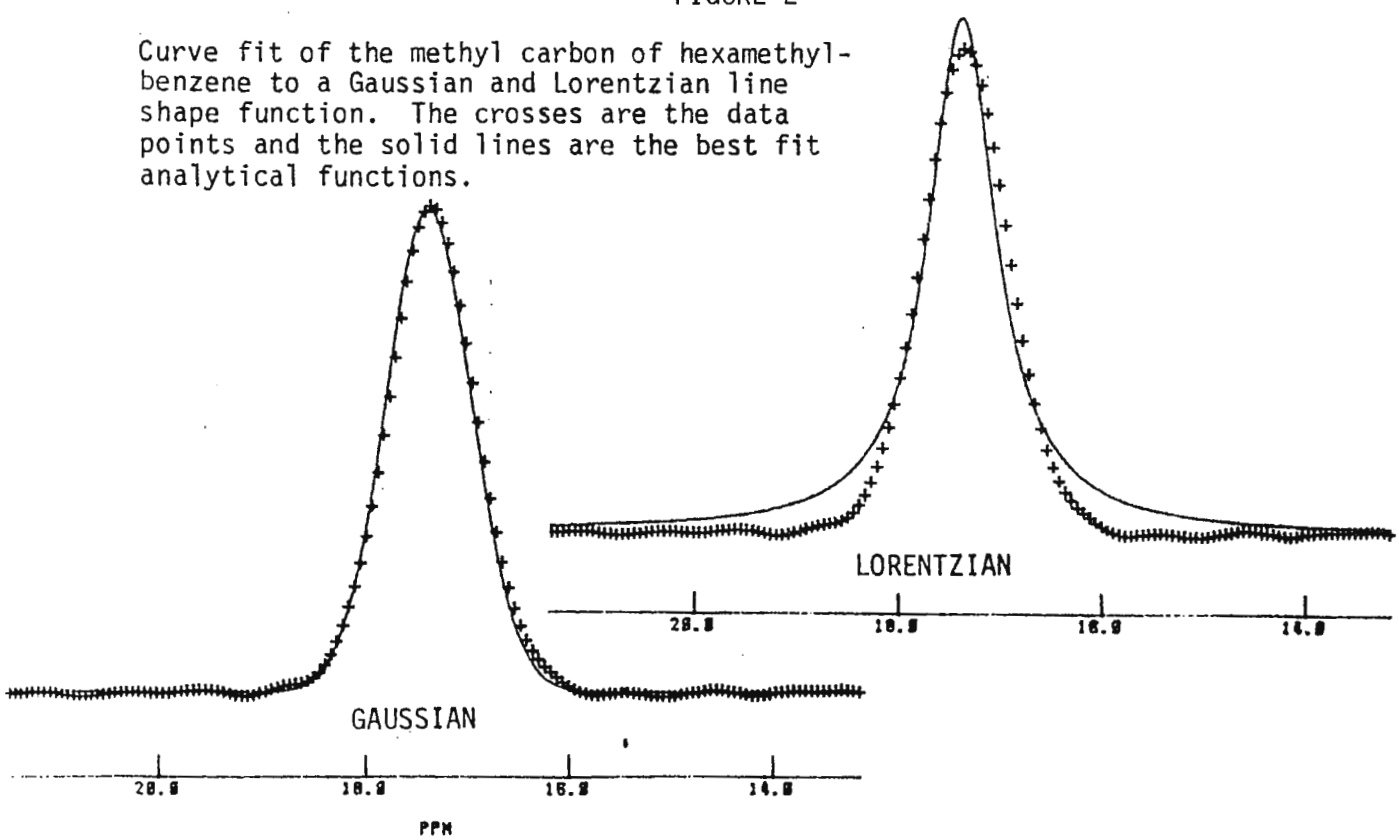




^{13}C Cross Polarization, Magic Angle Sample Spinning Spectrum of Vespel (polyimide) Block average of seven spectra (7 x 1024 scans) with differing repitition times and contact times. The carbon resonance frequency was 50.33 MHz.

FIGURE 2

Curve fit of the methyl carbon of hexamethylbenzene to a Gaussian and Lorentzian line shape function. The crosses are the data points and the solid lines are the best fit analytical functions.



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DEPARTMENT OF CHEMISTRY BERKELEY, CALIFORNIA 94720

February 24, 1984

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

Dear Barry:

A Postdoctoral Research Associate position is available for an applicant with a Ph.D. in chemistry, physics, or biochemistry, with extensive hands-on experience in magnetic resonance, particulary multiple pulse 2-D-FT, and multiple quantum techniques, and a strong interest in pursuing applications to organic and organometallic chemistry.

The successful candidate will collaborate closely with the groups of Professors Paul Bartlett, Robert Bergman, Clayton Heathcock, and Peter Vollhardt. The applicant should have interest in applying state-of-the-art NMR techniques to "wet" chemical problems in the bio-organic, synthetic organic, and synthetic and mechanistic organometallic areas. The candidate should have a strong interest in identifying and defining problems as they might occur within the research groups of the principal investigators mentioned above, and in collaborating with graduate students in their solution.

The NMR laboratories at the Department of Chemistry include multinuclear instruments with Nicolet data systems and 180 MHz wide-bore, and 200, 250 and 300 MHz standard bore magnets. A Bruker 500 MHz system is expected to be operational before midyear.

Interested applicants should submit a complete resume, including list of publications, and have two or more letters of reference forwarded to my attention, Chemistry Department, U.C. Berkeley, Berkeley, CA 94720, telephone (415) 642-6417.

Sincerely yours,

Rudi Nunlist

Rudi Nunlist

RN:ja

HERCULES

Hercules Incorporated
Research Center
Wilmington, DE 19899
(302) 995-3000

January 4, 1984

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

Dear Dr. Shapiro:

Position Available

Hercules Incorporated is seeking a Ph.D. chemist to work and provide technical leadership in a group applying NMR spectroscopy to problems of corporate interest. Current equipment includes two superconducting NMR instruments (8.4 tesla), and an ESR instrument with a state-of-the-art computer. Research areas include studies of polymers in solution, development of analytical NMR methods, and application of multinuclear NMR techniques.

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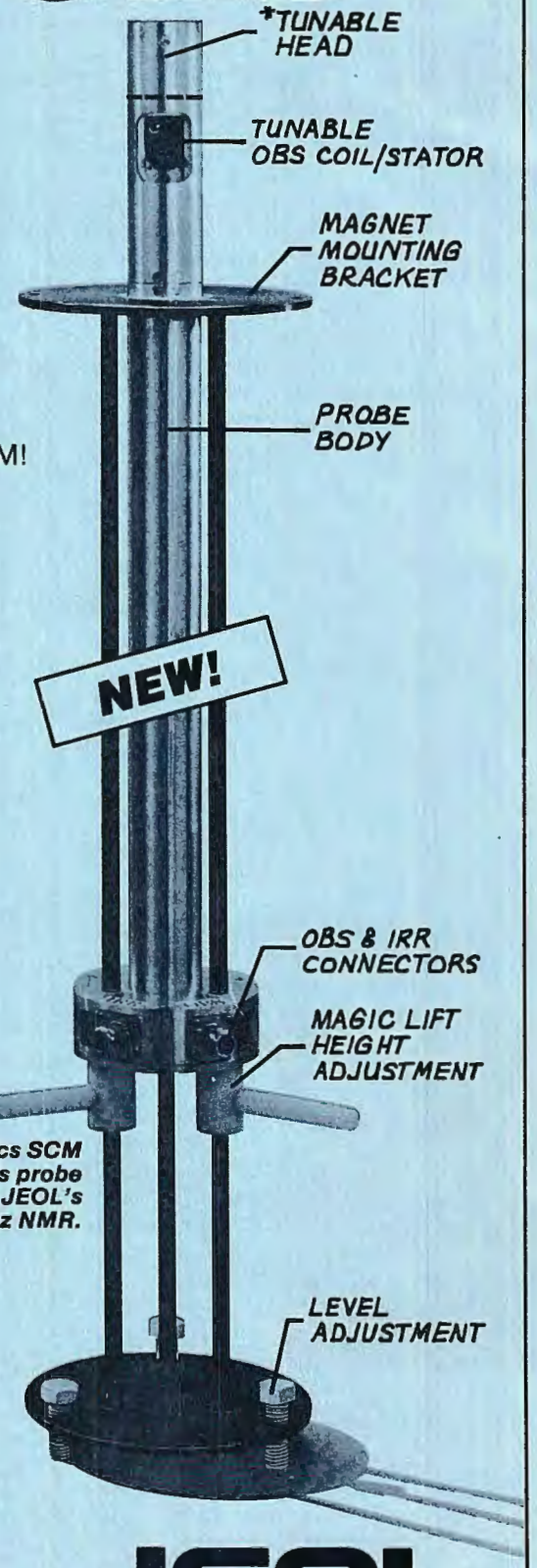

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