TEXAS A&M UNIVERSITY

NMR NEWSLETTER

NO. 305

FEBRUARY 1984

(continued on page i)

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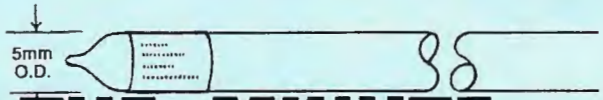

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	WGH-61	95% Orthodichlorobenzene + 5% TMS	Resolution	
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Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843 U.S.A.

DEADLINE DATES

No. 305 ------ 5 March 1984
No. 3D6 ------ 2 April 1984

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Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Group INC-4, Mail Stop C346

December 22, 1983

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

Improvements for Cross Polarization NMR (Especially on Bruker CXP's)

Dear Dr. Shapiro:

At times it is convenient to perform an NMR measurement as a function of B_1. On the Bruker CXP instruments, the final output stage is a pair of 4CX350 tubes and the rf power is varied by varying the screen grid voltage on those tubes via the "gain" knob on the front of the transmitters. It is very simple to access a voltage in the amplifier which is proportional to the screen grid voltage and thus proportional to the rf output. In the final stage amplifier there is a switch on the back which can be switched between "tune", "high voltage", and "400 v". We have simply soldered a pair of wires to the switch such that we have the "400 v" on the wires. In fact, one does not obtain 400 volts but rather some arbitrary voltage determined by a voltage divider in the amplifier. We simply bring the pair of wires out the back of the amplifier and go to a digital 0 to 200 mv voltmeter. In our case we measure a voltage of about 0 to 80 mv for the total range on the gain knob. Note that the rf output is not linear in the voltage measured but it is resettable through this measurement. We have made this modification to both the proton and multinuclear amplifier. In use, the system is quite simple. We can set the Hartmann-Hahn matching condition at several different B_1's with adamantane, noting the carbon and proton voltages. We change samples and dial in the same voltage pairs with the gain knobs and expect to get a good match in all cases. There are three other conditions which must be met: the spinning speed must be reset to nearly the same value, the probe must be accurately tuned, and the tubes must not have deteriorated between the calibration and the final use. A qualitative measure

of the settability obtained with this technique can be given by saying that using adamantane and a 1 ms contact time, one does not always return to the optimum Hartmann-Hahn match but setting the match on adamantane with 1 ms contact, replacing it with hexamethylbenzene with 1 ms contact I cannot detect the deviation from the optimum match. I think that this means that the resettability is better than about 0.2 dB. In any case, for those people using Bruker MAS probes, the matching condition varies significantly with the details of the pulse sequence used. Presumably, this is due to the high Q of the probe and some component whose value varies with temperature thus changes with the duty cycle.

We have made another modification or improvement to our CXP-200. The decoupler frequency is generated in two phase lock loops which produce about 20 MHz. That frequency is tripled to produce 60 MHz and then mixed with 140 MHz to finally generate the 200 MHz desired. Both of the phase lock loops are potentially noisy and in our case one of them is noisy. This effectively inserts phase noise on the decoupler rf which means that it is not possible to hold a good proton spin lock with the decoupler. Thus, S/N is lost in cross polarization and it is not possible to measure good proton $T_{1\rho}$'s via cross polarization. It turns out that the fix to this problem is relatively simple and we have to thank Mark Mattingly for suggesting it. There is an SMB connector in the HP Decoupler module labelled "30 MHz from f2". In fact this has 20 MHz on a CXP-200. Simply disconnect the cable and put a good clean 20 MHz sine wave into the module at this point. We are using a relatively old GR synthesizer which we had available for the 20 MHz. We have locked this to the main PTS synthesizer in the console and we insert 1 volt peak to peak at 20.043280 MHz into the HP Decoupler as described. This bypasses both of the phase lock loops and gives us a nice clean decoupler channel. Of course the phase noise will depend on the 20 MHz source used so the cleaner the better. This modification essentially disables the 02 command so changes in the 200 MHz decoupler must be made manually on the synthesizer which sits on top of our console. Since we are using a 10 Hz synthesizer and then must go through the tripler we have a resolution of only 30 Hz but that could be easily remedied with a different synthesizer, if necessary. To date we have not found the manual nature of this setup to be a problem but I have been told that it would be possible to use a PTS synthesizer, purchase another interface from Bruker and then the SY command in the software would set the second (decoupler) synthesizer.

Sincerely, Bill

William L. Earl

DELFT UNIVERSITY OF TECHNOLOGY
Laboratory of Organic Chemistry
Julianalaan 136
2628 BL DELFT
The Netherlands

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

U.S.A.

Delft, January 3rd, 1984
JAP/mk/04

Dear Professor Shapiro,

Detection of impurities in $Ln(fod)_3$ shift reagents

Previously, we have shown that commercial lanthanide shift reagents of the type $Ln(fod)_3$ sometimes are contaminated with substantional amounts of the binuclear complex $Ln(fod)_3.Mfod$ (M = alkali ion)[1].

For the heavier lanthanides, these impurities can easily be detected with the use of ^1H NMR. For example, contaminated $Yb(fod)_3$ shows two t-butyl peaks in the ^1H spectrum: one for $Yb(fod)_3$ ($CDCl_3$, δ = 5.23) and another one for $Yb(fod)_3.Mfod$ (δ = 0.98).

In e.g. $Eu(fod)_3$ contaminated with $Eu(fod)_3.Nafod$, however, fast exchange of the fod ligands occurs between both complexes: only a single set of fod signals is observed in the 200 MHz ^1H, 50 MHz ^{13}C, and 188 MHz ^{19}F spectra at ambient temperature.

Some time ago Johnston and Caines suggested ^{23}Na NMR as a tool for the detection of $Ln(fod)_3.Nafod$ impurities, but with the use of that technique they could not detect a ^{23}Na signal in some of their off-the-shelf $Eu(fod)_3$[2].

Recently, we measured the ^{23}Na NMR spectrum (52 MHz) of almost pure $Eu(fod)_3.Nafod$ (0.6 M in $CDCl_3$). A very broad ^{23}Na signal ($w_{\frac{1}{2}}$ = 4000 Hz) was observed. Therefore, the detection of small amounts of that impurity in $Eu(fod)_3$ shift reagents will be rather difficult, in particular with the use of low field spectrometers.

In our opinion mass spectrometry[1,3] and atomic absorption[4] are more suitable techniques for the detection of the binuclear impurities in $Eu(fod)_3$ shift reagents.

Please credit this contribution to J.A. Peters.

Sincerely yours,

D.J. Raber J.A. Peters

[1] J.A. Peters, P.J.W. Schuyl, W.M.M.J. Bovée, J.H. Alberts, and H. van Bekkum, J. Org. Chem. 13, 2784 (1981).
[2] M.D. Johnston, Jr., and G.H. Caines, TAMU NMR Newsletter 292, 24 (1983).
[3] J.A. Peters, P.J.W. Schuyl, and A.H. Knol-Kalkman, Tetrahedron Lett. 23, 4497 (1982).
[4] D.J. Raber, TAMU NMR Newsletter 295, 3 (1983).

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ROCHE

4 January 1984

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

NMR Measurements of Optical Purity

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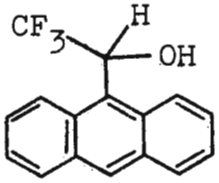
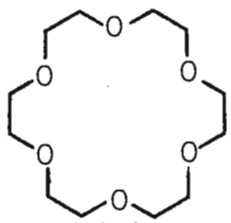
Dear Barry

A problem arising increasingly in our nmr laboratory concerns the measurement of optical purity of novel compounds. To this end, rather than the chiral lanthanide complexes which we find generally disappointing, particularly with amines, we have been using the chiral anthryl alcohol (1) first introduced by Pirkle et al[1]. Using molar ratios from



(1) (+) or (-) isomer



(2)

1:1 to 10:1 (reagent:substrate) in a variety of compounds we have almost invariably managed to completely separate at least one pair of ^{1}H or ^{13}C signals, sufficiently to obtain an integral. For compounds such as amine salts, which are insufficiently soluble in $CDCl_3$, chemical derivitisation is not ideal due to the risk of racemisation during synthesis. We have found that in some cases, use of a solubilising agent e.g. 18-crown-6 (2) allows the optical purity of otherwise insoluble compounds to be determined in admixture with reagent (1). A simple example is shown in the Figure, where DL-alanine methyl ester hydrochloride with about four or eight times the molar equivalent of (1) is readily dissolved in $CDCl_3$ containing some crown ether. Gated decoupling removes the large singlet in the ^{1}H spectrum due to 18-crown-6. This method has proved very reliable on a routine basis, and levels down to ~1% optical impurity can be measured, particularly by comparison with ^{13}C satellites of the main peak. Other solubilising agents may well be used for the same purpose, allowing a much greater range of compounds to be examined.

With best wishes.

Yours sincerely

W A Thomas I W A Whitcombe P J Gilbert

1. Pirkle, W.H., Rinaldi, P.L.: J. Org. Chem. 1978, 43, 14475. Aldrich Chemical Co., No. 21, 134-6 and 21, 135-4.

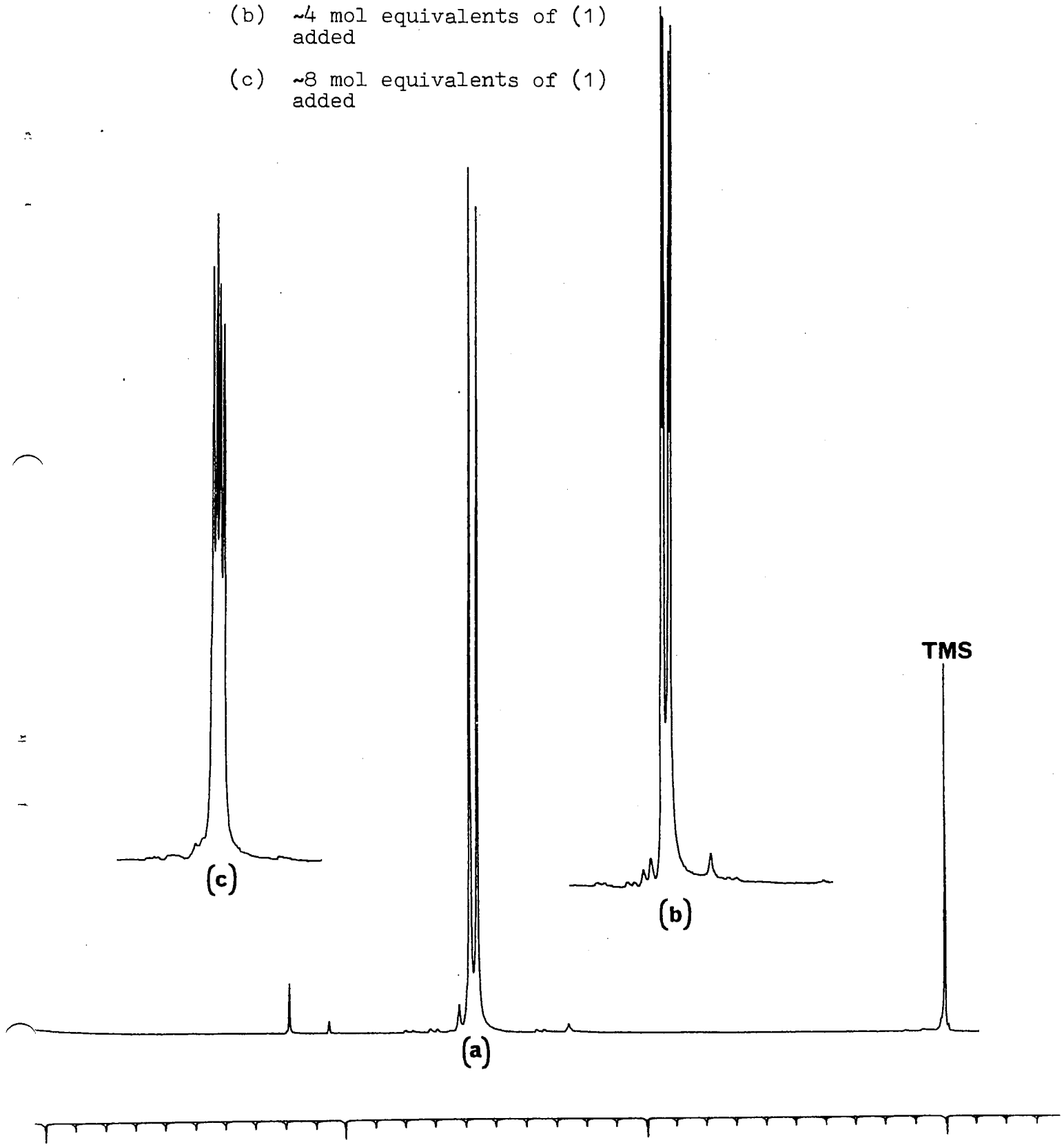
FIGURE

β-Methyl proton resonance of (±) Alanine methyl ester hydrochloride (10mg/ml) in $CDCl_3$ + 18-crown-6 (> molar equiv.)

(a) normal 300 MHz ^1H spectrum

(b) ~4 mol equivalents of (1) added

(c) ~8 mol equivalents of (1) added



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January 4, 1984

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

Modification of the Bruker CXP-300 Proton HP Decoupler for ^{19}F (282 MHz) Operation

Dear Professor Shapiro:

We have been using ^{19}F MAS-NMR extensively to study the surface chemistry of fluoridation of hydroxyapatite and dental enamel. These studies have yielded a wealth of information about the structural features of the fluoride atoms on the surface of hydroxyapatite.[1,2] However, in order to observe selectively the phosphorus atoms on the surface, we needed to carry out cross-polarization MAS-NMR of the ^{31}P nuclei by the ^{19}F nuclei. To do so, we reconfigured the high-power proton decoupler on our Bruker CXP-300 spectrometer to operate at the ^{19}F frequency. This was accomplished by: (a) Replacing the 70 MHz intermediate frequency source (from f_2 generator) with 64 MHz from an external frequency synthesizer and (b) replacing several of the fixed capacitors in the decoupler mixer with variable capacitors, which simplified tuning of the high-power decoupler between 282 MHz (^{19}F frequency) and 300 MHz (^{1}H frequency). In addition to the RF filters normally placed between the probe and the preamplifiers, we added a 282 MHz bandpass cavity filter before the ^{19}F input of the modified MAS probe to minimize saturation of the ^{31}P preamplifier by the ^{19}F transmitter.

As of this writing, we have been successful in observing significant differences between the ^{31}P-^{19}F cross-polarized MAS-NMR spectra of fluoroapatite and fluoride-treated hydroxyapatite (see figure 1).

On a personal note, one of us (JPY) will be leaving Procter & Gamble Co. shortly to take up a new post as Manager of the Southern California NSF Regional NMR Facility at CalTech. Therefore, please address all future P&G TAMU correspondence to Fouad S. Ezra.

Sincerely yours,

C. D. Sazavsky James Yesinowski

C. D. Sazavsky J. P. Yesinowski

1. Yesinowski, J. P., Wolfgang, R. A.,and Mobley, M. J., "Adsorption on and Surface Chemistry of Hydroxyapatite"; Misra, D. N., Ed.; Plenum Press: New York, in press.

2. Yesinowski, J. P. and Mobley, M. J., "^{19}F MAS-NMR of Fluoridated Hydroxyapatite Surfaces"; JACS, 1983, 105, 6191.

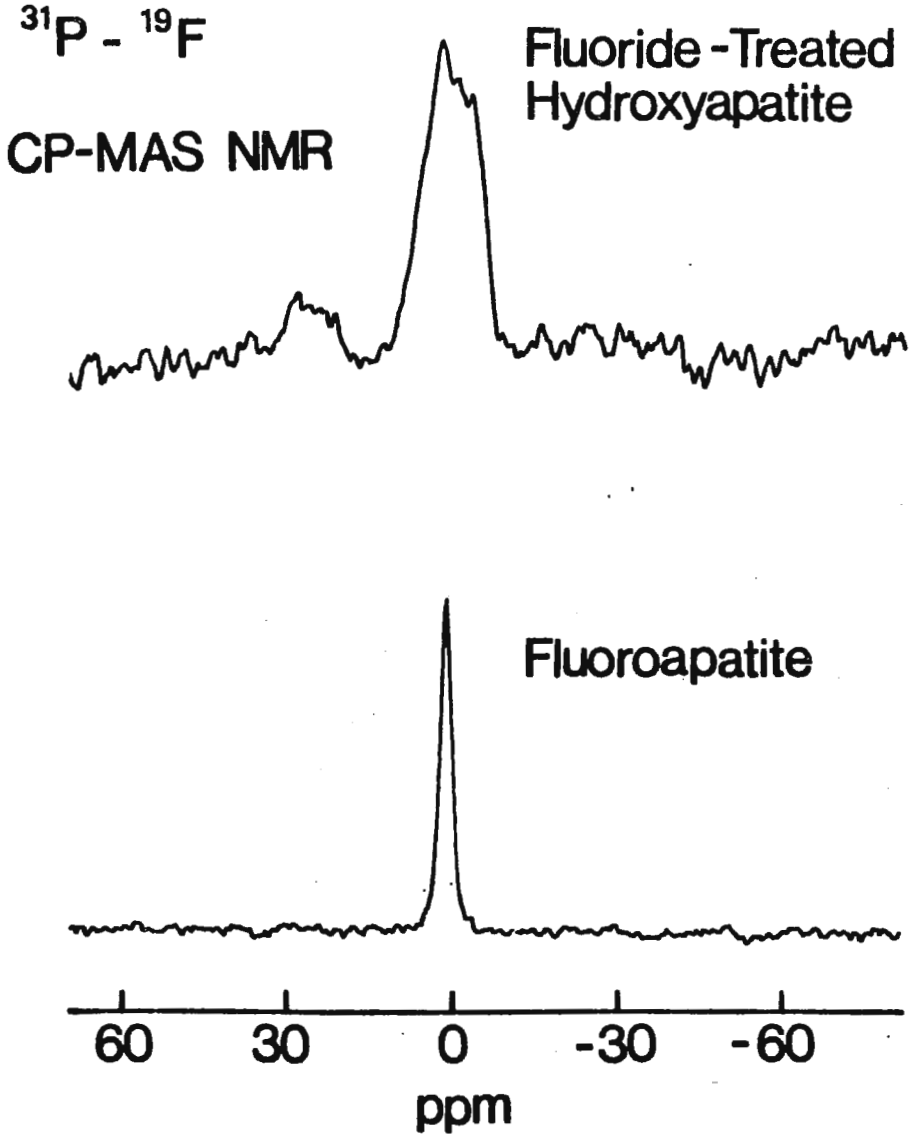
^{31}P - ^{19}F
CP-MAS NMR
Fluoride-Treated
Hydroxyapatite
Fluoroapatite
60
30
0
-30
-60
ppm

Figure 1

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January 24, 1984

Dr. B. Shapiro
NMR Newsletter
Chemistry Department
Texas A&M University
College Station, Texas

Title: Paramagnetic metalloporphyrins as potential contrast agents in NMR imaging.

Dear Barry:

I take the opportunity of your timely reminder to mention some work on relaxation time (T_1) measurements of water in the presence of several water-soluble paramagnetic metalloporphyrins.

We chose to study these compounds for several reasons:
(a) they are analogues of common biological compounds,
(b) they do not show the aggregation effects of many porphyrins since they contain ionic groups,
(c) both porphyrins and metalloporphyrins are known to show selective retention by different tissues, notably tumors,
(d) they are not as toxic as free metal ions,
(e) they are chemically and biochemically stable,
(f) unlike many metal chelates their axial water ligands usually exchange quite rapidly, thus averaging the paramagnetic effect with the bulk water.

The results (1) indicate that compounds of this type should have great potential as contrast agents in NMR imaging.

Please note that in addition to the positions I described in a recent letter to you I have several fellowships available.

Sincerely,

Jack S. Cohen
Biophysical Pharmacology Section
Clinical Pharmacology Branch
National Cancer Institute

JSC:ell

Reference 1. Chen, Cohen, Myers & Sohn, FEBS Letters, in press.

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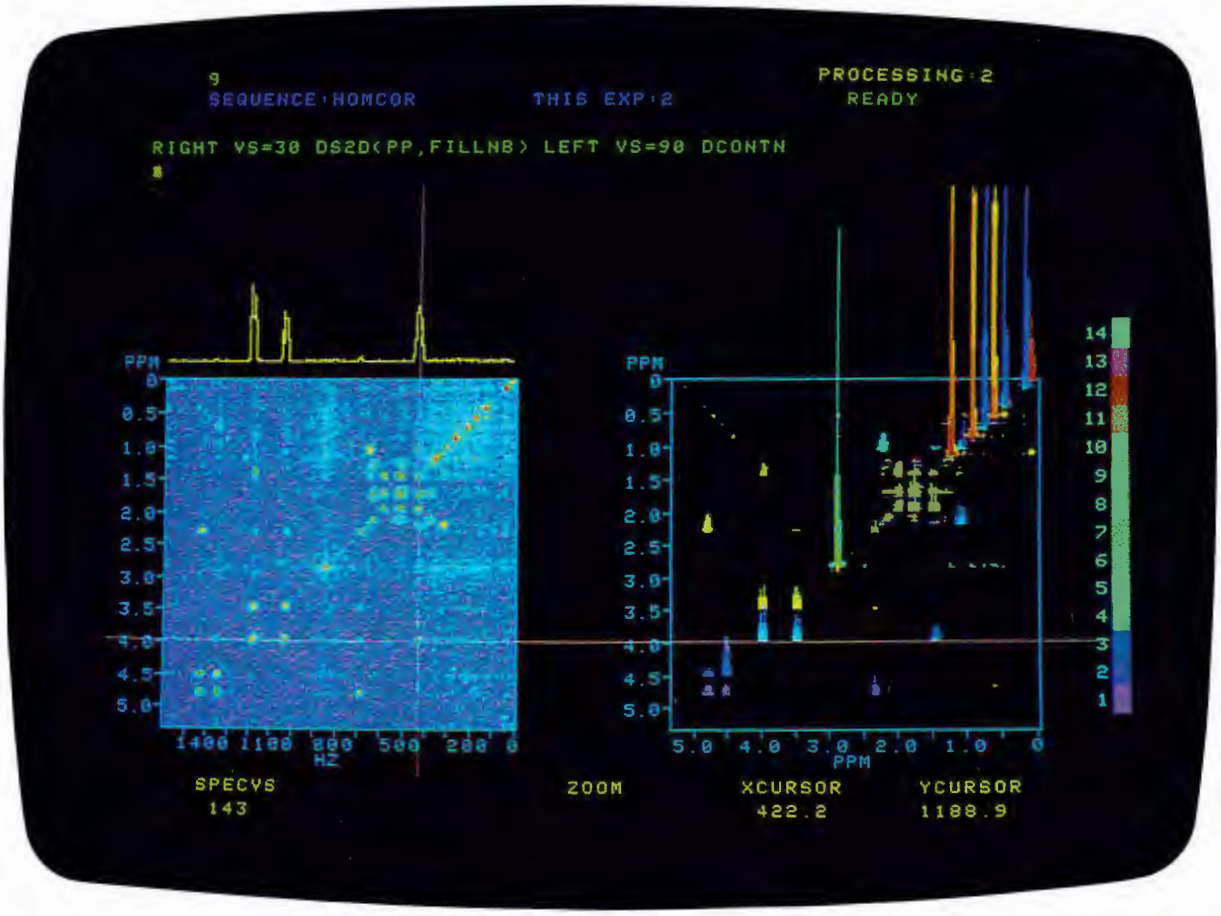

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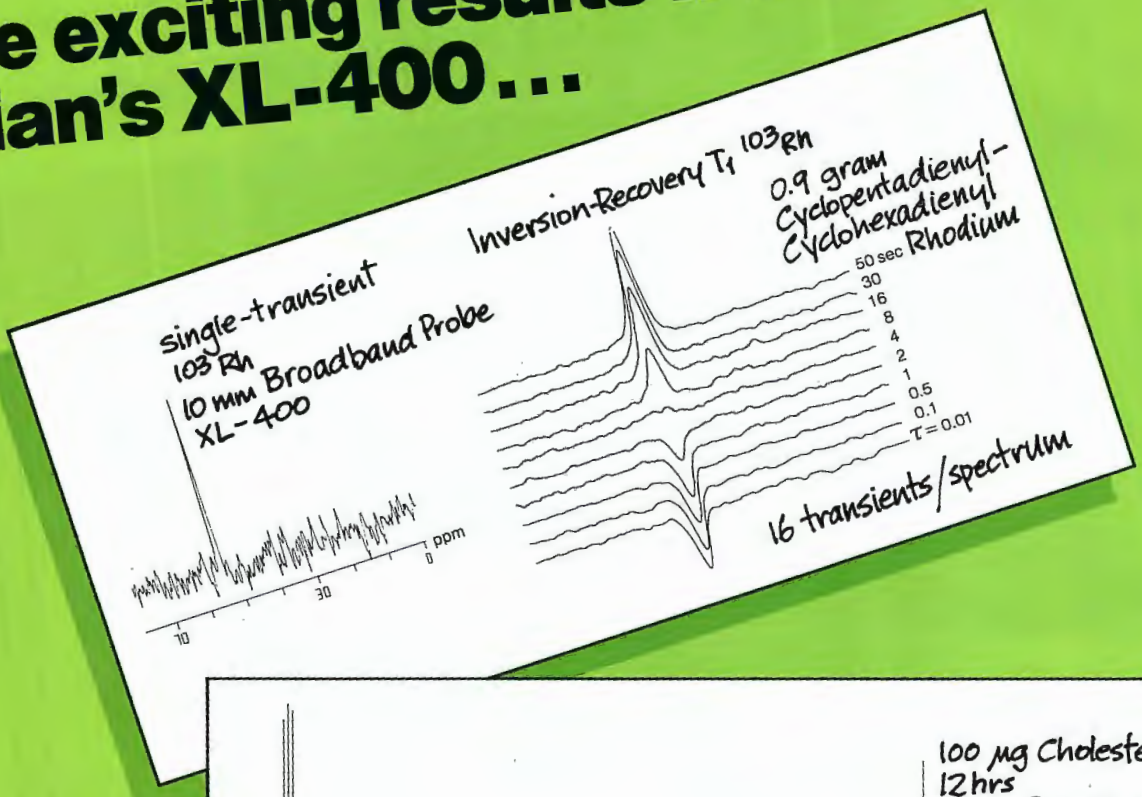

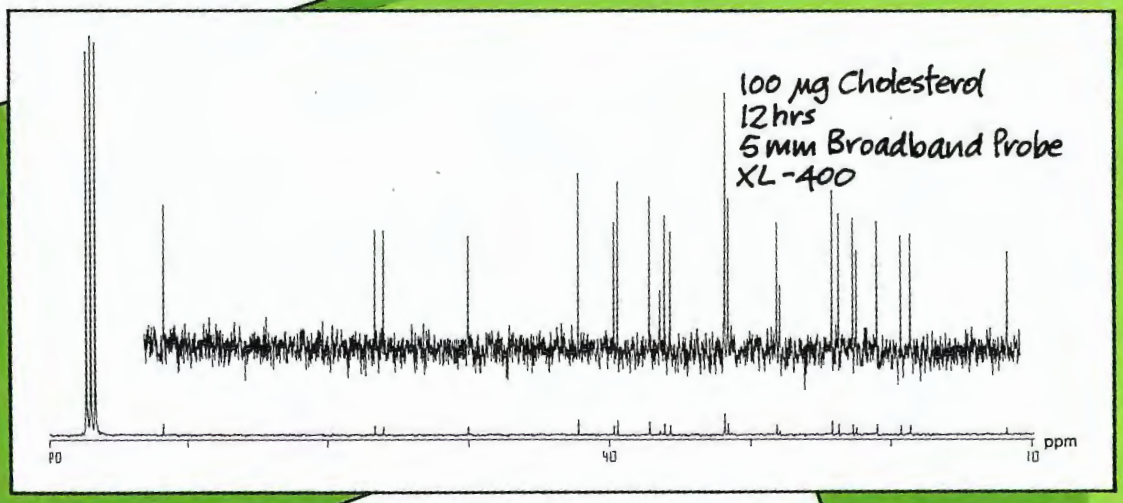

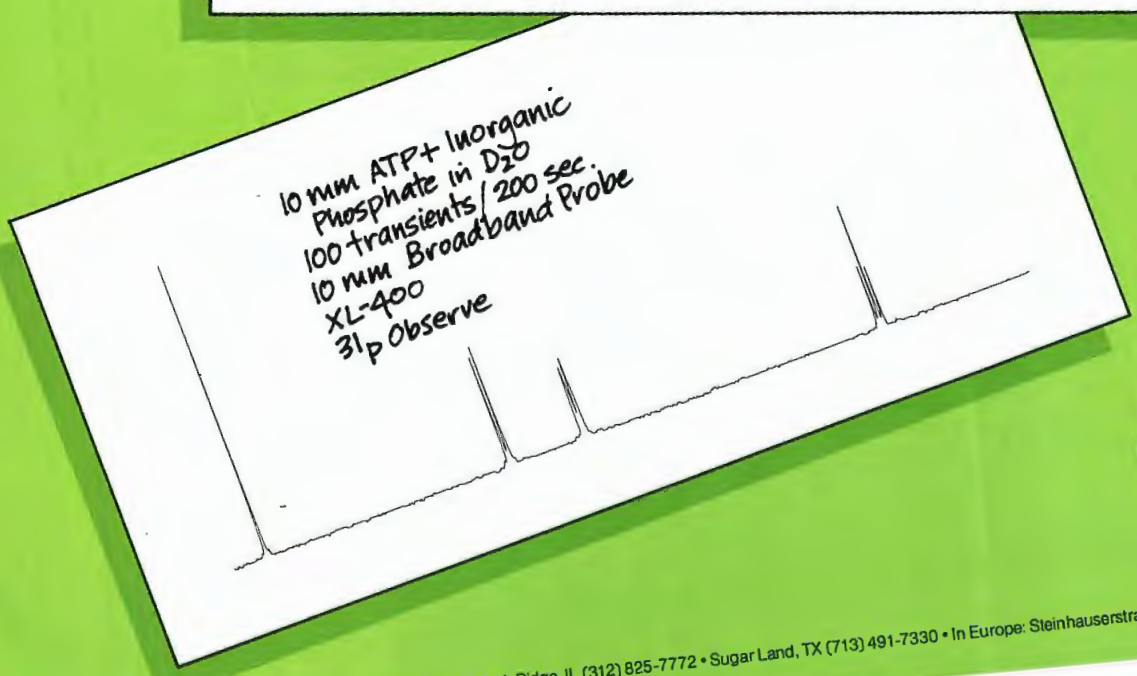

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Wageningen
Department of Molecular Physics

Your reference
Your letter of
Our reference 84/4 mh/mk
Date December 30th,1983
Enclosure(s)

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

Subject selective excitation in high-resolution solid state NMR

Dear professor Shapiro,

After writing our previous letter (our reference 83/839 mh/mk of November 30th, 1983) we found an article by Caravatti, Bodenhausen and Ernst (J. Magn. Reson. 55, 88-103, 1983) dealing with the same subject and describing the same pulse technique as we have employed. This is to fully acknowledge their contribution and to make clear that at the time we wrote our letter we could not be aware of their work, because our copy of the issue of the *Journal* was delayed by a postal strike in the Netherlands.

Recently, we have employed the technique of selective saturation as described by Caravatti et al. to a sample of freeze-dryed Tobacco Mosaic Virus (TMV). It is found that easily holes can be burned in the ^{13}C MAS NMR spectrum, demonstrating that the resonances must be strongly inhomogeneously broadened. This effect that probably arises from isotropic chemical shift distributions, may severely impede the application of MAS NMR techniques. Further investigations are directed towards a study of the origin of this effect.

Sincerely yours,

Marcus A. Hemminga Rolf M.J.N. Lamerichs P. Adrie de Jager

Agricultural University/Transitorium, De Dreijen 11/6703 BC Wageningen/The Netherlands/Tel. (08370) 82044/82634

Universiteit van Amsterdam
ANORGANISCH CHEMISCH LABORATORIUM
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Professor B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
COLLEGE STATION, TEXAS 77843,
U. S. A.

AMSTERDAM, January 6th 1984

TITLE: Five-Coordinate Tin and Chirality.

Dear Professor Shapiro,

Recently we have been busy with two projects concerning the coordination properties of organo-tin halides. One of these is the study of species in which one of the organo groups has a built-in donor function , generally $-NMe_2$ .In this way it had been shown that it was possible to isolate chiral , pentacoordinate , triorganotin halides.[1] The well-defined nature of these complexes has prompted a thorough NMR (^{1}H,^{13}C and ^{119}Sn) study and some typical ^{119}Sn results are given below. It has been long known that ^{119}Sn NMR was a useful technique for investigating the coordination number of tin but studies are hampered more often than not by uncertainty as to the exact nature of some of the species present in solution when organotin halides interact with donor molecules. In the series we have studied this problem does not exist and we can identify not only the large highfield shift on going from 4- to 5-coordinate tin but also the dependence of this shift on the size of the chelate ring that is formed. Introduction of a chiral grouping into one of the organo groups can lead to two diastereoisomers with different NMR spectra.[2] The enclosed spectrum shows that ^{119}Sn is a very suitable nucleus for studying the subtle effects of chirality. The linewidths here are typical for these 5-coordinate species and appear to result from incompletely resolved coupling to ^{14}N.

Yours Sincerely,

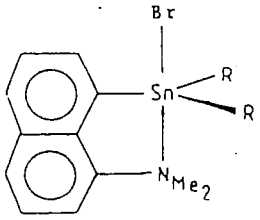
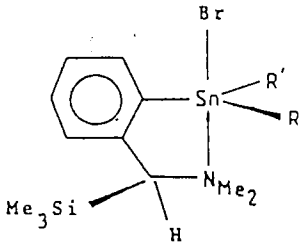
David M. Grove.

D.M. Grove

1) G. van Koten and J.G. Noltes, JACS 98,5393(1976) .

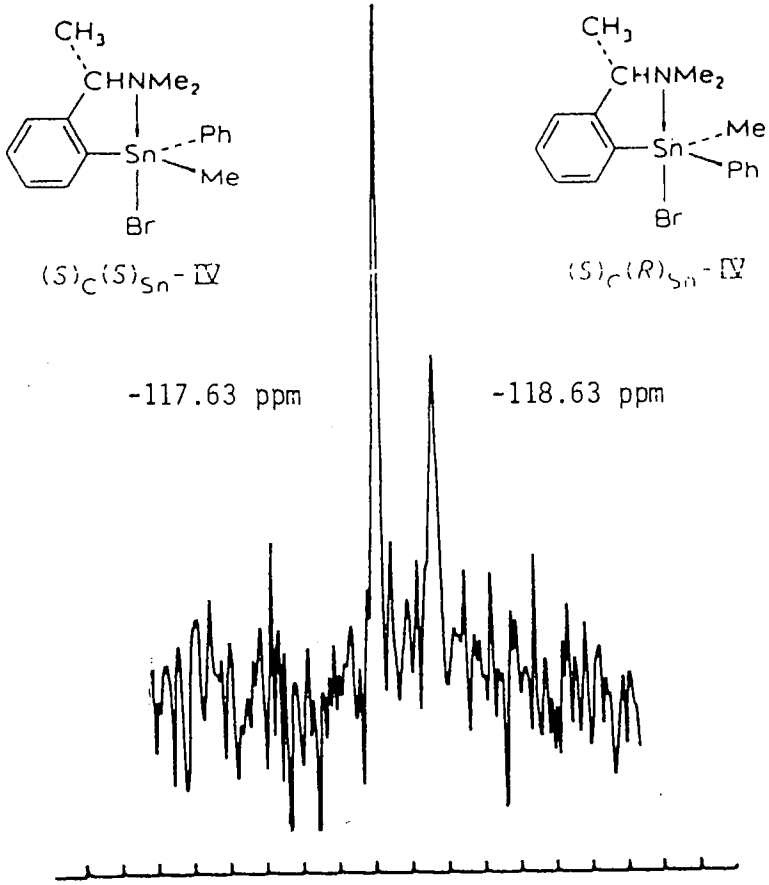
2) G. van Koten et al. , JACS 100,5021(1978).

^{119}Sn NMR Data - $CDCl_3$, 270K , 93.28 MHz

COMPOUND	R=R´=Me	R=Me, R´=Ph	R=R´=Ph
	-38.7	-97.5	-165.1
	+3.1	-70.0	-135.9

Shifts relative to $SnMe_4$ (0 ppm)

93.28 MHz ^{119}Sn NMR Spectrum (CH_2Cl_2/d_8-toluene;288K;rel. to $SnMe_4$)



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

Villeurbanne, January 12, 1984

Cher Docteur Shapiro

MINISPECTROMETER PC20 - APPLE II WEDDING !

Nous utilisons depuis plusieurs années un spectromètre PC 20 BRUCKER pour mesurer des temps de relaxation T_1 et T_2 dans des milieux physiologiques ou des échantillons d'origine biologique (grains de pollen). Si cet appareil nous a donné satisfaction au niveau de la précision et de la reproductibilité des mesures, en revanche il nous semble nettement insuffisant au niveau du traitement des données. Ceci est d'autant plus vrai lorsque la relaxation se manifeste comme une somme d'exponentielles. Manifestement dans ce cas une visualisation des signaux RMN est nécessaire pour permettre un ajustement des paramètres d'interprétation des courbes de relaxation.

Nous avons donc installé une carte d'acquisition sur un microcalculateur APPLE II, ce qui à partir du signal analogique obtenu à la sortie du PC 20, nous permet un traitement plus fin des courbes de relaxation.

Les caractéristiques de cette carte d'acquisition sont les suivantes :

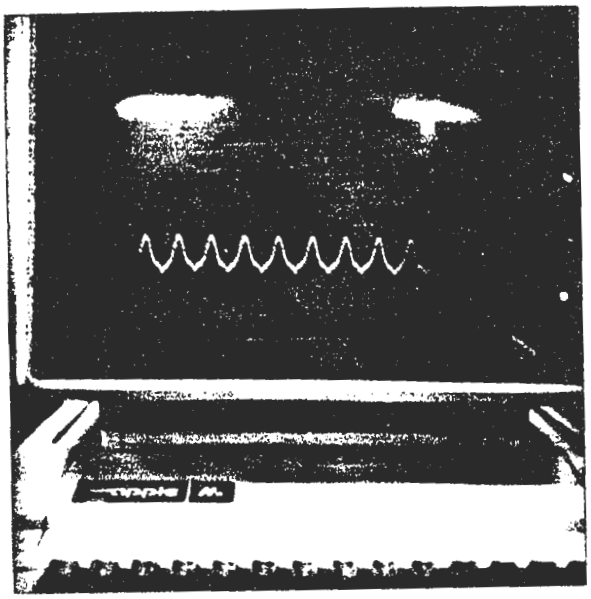
- vitesse d'échantillonnage : 208 µs
- nombre de points : 4096.

Nous avons mis au point un programme de création de fichiers stockés sur "disquette" et des programmes de traitement comportant en particulier une recherche de maxima pour obtenir les valeurs maximales des échos de spins dans la séquence C.P.M.G.

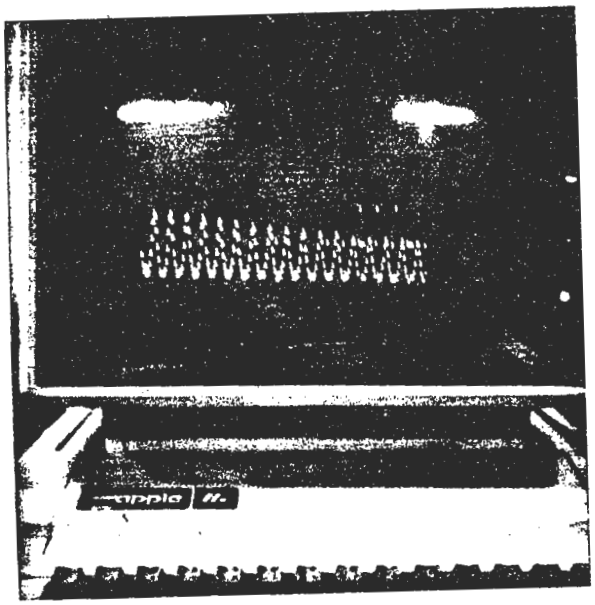
La figure montre un exemple d'échos de spins et la courbe des maxima à partir de laquelle pourra être déterminée la valeur de T_2 dans une séquence C.P.M.G.

La carte d'acquisition adaptable en interface entre l'APPLE II et le Spectromètre PC 20 a été établie par Y. BOURDON (Sté ERIM - Lyon) Nous sommes disposés à donner toutes indications concernant ce travail qui peut intéresser les utilisateurs du spectromètre PC 20.

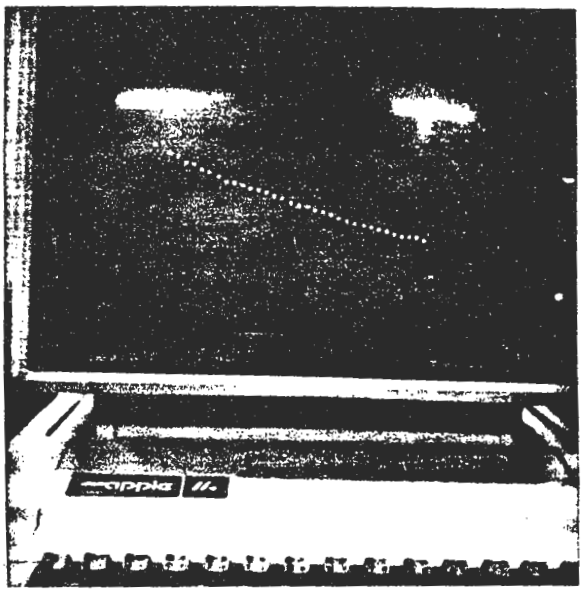
A. BRIGUET J. DELMAU J.C. DUPLAN



Enregistrements des échos de spins



Courbe des maxima des échos de spins.



University of Edinburgh

Department of Chemistry

West Mains Road, Edinburgh, EH9 3JJ Scotland.

Yr. ref.:
Our ref.: IHS/mfh

Telex 727442 UNIVED G
Telephone 031 - 667 1081
Ext. 3676

16 January 1984

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

Dear Professor Shapiro,

A simple modification to Bruker Spectrometer spinner turbines for low temperature work

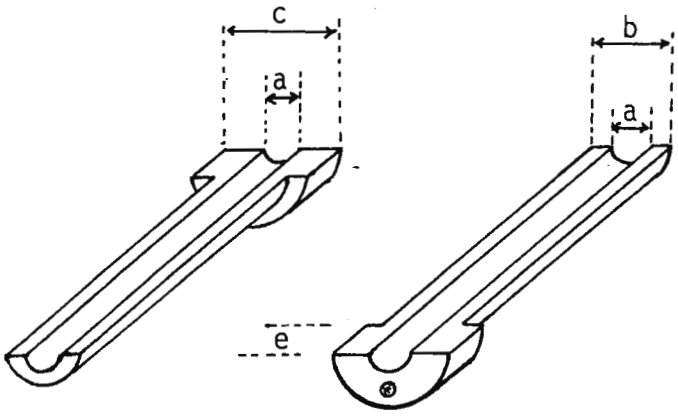
A significant amount of our work requires us to run sealed samples which decompose rapidly if allowed to warm above *ca.* -70°C. The samples may obviously be stored below -90° and be run in the spectrometer at similar temperatures. The problem arises in putting the spinner turbine on the tube, which instantly frosts over on removal from a dewar of liquid nitrogen, without breaking it or allowing it to warm up too much. This problem is rarely considered by spectrometer designers.

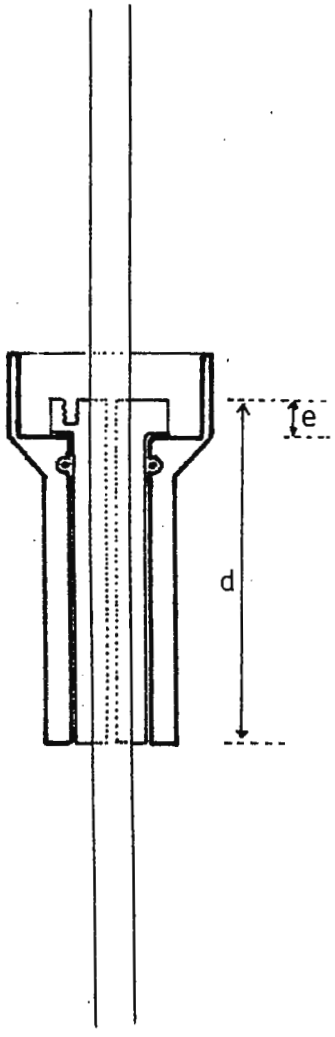
Fortunately the outer dimensions of the spinner turbines for use with the Bruker WH, WM, WP series spectrometers is independent of the diameter of the sample tube they are designed to hold so that the use of a spinner for a larger diameter tube together with two semi-annular cross section spacers overcomes the low temperature sample problem above. The design of these spacers is shown in the diagram and they can conveniently be made by machining a complete annulus from Delrin and slicing this in half. This arrangement allows the spinner plus one spacer to be placed in position over the sealed end of the tube while the lower end containing the sample remains surrounded by liquid

nitrogen. The second spacer is then slid into position. The tube with its spinner can be transferred to the spectrometer much more quickly with almost negligable frosting, which also reduces the likelihood of the sample refusing to spin. To facilitate removal of the spinner after the experiment the top of one spacer is partially drilled and threaded for the insertion of a screwed rod. We have made spacers for using 5 mm tubes in a 10 mm spinner and 10 mm and 12 mm tubes in a 15 mm spinner and have had no problems with these provided they are reasonably carefully machined.

Yours sincerely,

Ian H. Sadler.





Dimensions (mm)	Tube Size 5 mm	10 mm	12 mm
a	5	10	12
b	10	15	15
c	15	19	19
d	43	43	43
e	5	5	5

McMASTER UNIVERSITY
Department of Biochemistry

HEALTH SCIENCES CENTRE,
1200 MAIN STREET WEST,
HAMILTON, ONTARIO, CANADA.
L8N 3Z5
TEL. (416) 525-9140 EXT. 2457

January 13, 1984

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

Dear Dr. Shapiro:

Re: Selectivity of the DOUBTFUL double-quantum experiment

The DOUBTFUL double-quantum pulse sequence (1) is a useful technique for resolving overlapped multiplets (usually AX spins systems) in ^1H NMR spectra and frequently is used in our studies of oligoribonucleotides to determine the connectivity of the H-6 and H-5 protons on pyrimidine bases (2). We have completed an analysis of the selectivity of this experiment (3) and present here a summary of our results. The DOUBTFUL pulse sequence creates double-quantum coherence and detects the resulting signal in the same way as the INADEQUATE experiment. The double-quantum evolution time, t_1, is incremented in regular intervals and the spectra obtained for each t_1 are added together. The intensity of the resulting signal is proportional to the product $\sin(2\pi J\frac{\tau}{2})\cdot\cos(2\pi\nu t_1)$ where ν is the double-quantum frequency relative to the carrier. If the carrier is on the double-quantum frequency for an AX system the signals will add coherently while all other spin systems will eventually cancel. If the final value of t_1 is constant ($t_1 = t_f$) the signal intensity will have a sin(x)/x dependence on the offset of the double-quantum frequency, ν. The intensity will be a maximum for $\nu = 0$, it will decrease and go through zero when $\nu_f = \frac{1}{2t_f}$ and then become negative (Figure 1). Therefore the selectivity of the experiment may be defined as the zero-crossing frequency $\nu_f = \frac{1}{2t_f}$. Any multiplet whose double-quantum frequency lies within $\pm\nu_f$ of the carrier will be detected as a positive signal. Multiplets with double-quantum frequencies between ν_f and $2\nu_f$ will also appear in the spectrum as negative peaks and have reduced intensity.

An example of how this analysis of the DOUBTFUL experiment can select specific multiplets is provided by the 250 MHz spectra obtained at 70°C of the triribonucleotide, UpUpC. Figure 2 shows an expansion of the single pulse spectrum displaying the pyrimidine H-5 base protons and the ribose anomeric proton doublets. An AX system results from three bond coupling between the protons at positions 5 and 6 on the pyrimidine base. From Figure 1, placing the carrier 4.0 Hz to high field of the cytidine H-6(7.859)/H-5(6.084 ppm) double-quantum frequency should produce positive CH-5 signals with near maximum intensity. The large offset from the U(1)H-6(7.808)/H-5(5.867) and U(2)H-6(7.837)/H-5(5.899) double-quantum frequencies should result in

Professor B.L. Shapiro January 13, 1984

negative signals of low intensity. This was confirmed in the spectrum shown in Figure 3 where signals from both CH-5 and U(1)H-5 were observed while the U(2)H-5 was nulled. This analysis makes it possible to assign several AX connectivities in a single experiment.

Please credit this to the account of J.I.A. Thompson.

Sincerely yours,

Donald W. Hughes R.A. Bell

Alex D. Bain
Bruker Spectrospin
Canada Ltd.

Donald W. Hughes

Jan M. Coddington
Dept. of Chemistry
Univ. of California,
San Diego

Russell A. Bell

1. P.J. Hore, R.M. Scheek, A. Volbeda, R. Kaptein, and J.H. van Boom. J. Magn. Reson. 50, 328 (1982) and J. Am. Chem. Soc. 104, 4286 (1982).

2. D.W. Hughes, T. Neilson, J.M. Coddington, and R.A. Bell. Can. J. Chem., in press (1984).

3. A.D. Bain, D.W. Hughes, J.M. Coddington, and R.A. Bell. J. Magn. Reson., in press (1984).

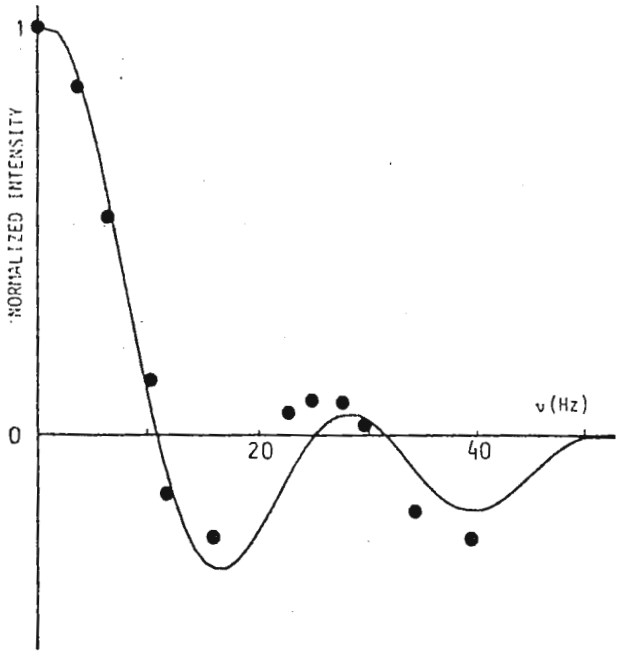
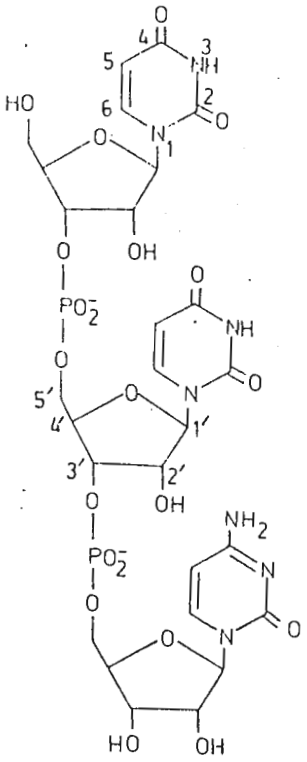


FIGURE 1



UpUpC
1 2 3

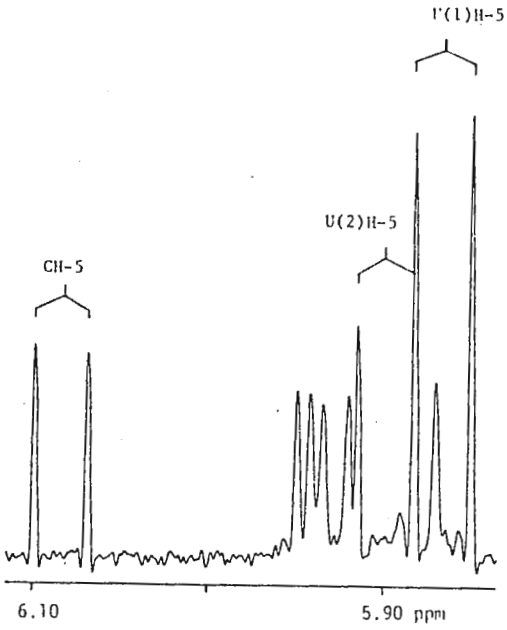


FIGURE 2

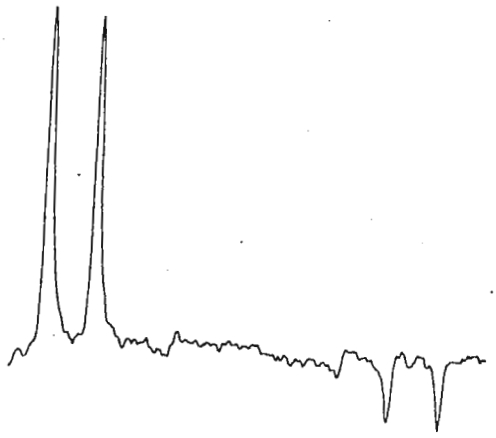


FIGURE 3

UNIVERSITY OF BRADFORD

305-22

Bradford West Yorkshire BD7 1DP England.
Telephone Bradford 733466 (STD Code 0274)
Telex 51309 UNIBFD G Ext. 317 or 498

Dr. Derry W. Jones,
School of Studies in Chemistry

(messages 480)

4th January, 1984

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

Dear Professor Shapiro,

Long-range Deuterium Isotope Effects on ^{13}C Chemical Shifts in a Polycyclic Hydrocarbons

Attention has been drawn recently by Ernst (1,2) to isotope effects, induced by deuterium in substituent trideuteromethyl groups, on ^{13}C shifts of polycyclic hydrocarbons and to the value of such effects as aids to spectral assignment. Earlier, Martin *et al.* (3) measured $^{13}C_{\alpha}$-D and $^{13}C_{\beta}$-C-D *ortho* isotope shifts and noted evidence for $^{13}C^{\alpha}$-C-C-D *meta* and $^{13}C_{\gamma}$-C-C-D *peri* couplings in several specifically deuterated but otherwise unsubstituted hydrocarbons. J.D.S. has detected isotope effects by a ring deuterium on carbons two, three and four bonds distant in spectra of 7,12-dimethylbenz[*a*]anthracene(7,12-DMBA).

100.6 MHz ^{13}C spectra of 7,12-DMBA and 5-D-7,12-DMBA in deuterated chloroform solution enabled the assignment (3) of C-5 to be revised and other ambiguities to be removed. Positive substituent shifts in (ppb) due to the 5-deuterium were evident over one bond (C-5, 28), two bonds, (C-6, 128; C-4a, 65), three bonds (C-4, 50; C-6a/C-12b,9) and four bonds (C-12a, 7; C-7, 5; C-3, 4). In addition, apparently significant negative isotope shifts of -5 ppb for the methyl carbons at C-7 (5bonds) and C-12 (6 bonds, by two paths) suggest small hyperconjugation or possibly through-space contributions in opposite sense to the contributions due to vibronic-energy-level changes and thought to be predominant over short paths. The molecular structure of 7,12-DMBA is known to be appreciably non-planar in the crystal (4).

Deuteration at position 5 led directly to the assignment of the 126.11 p.p.m. resonance (with its weak triplet) in 5-D-7,12-DMBA rather than that (5) at 125.514 p.p.m. to C-5. *Ortho* isotope shifts supported the allocation of C-4a to the 133.04 p.p.m. line (rather than 132.63 p.p.m.) and of C-6 to 123.671 (unchanged). Magnitudes of isotope shifts also facilitated probable discrimination between assignments of individual resonances within the groups C-4a, C-6a, C-12a, C-12b; C-7, C-7a, C-11a, C-12; and C-2, C-3.

We are grateful to Dr. B.E. Mann and the Brüker WH-400 SERC service at Sheffield University for spectra and to Professor M.S. Newman (O.S.U.) for the sample of 5-D-7,12-DMBA.

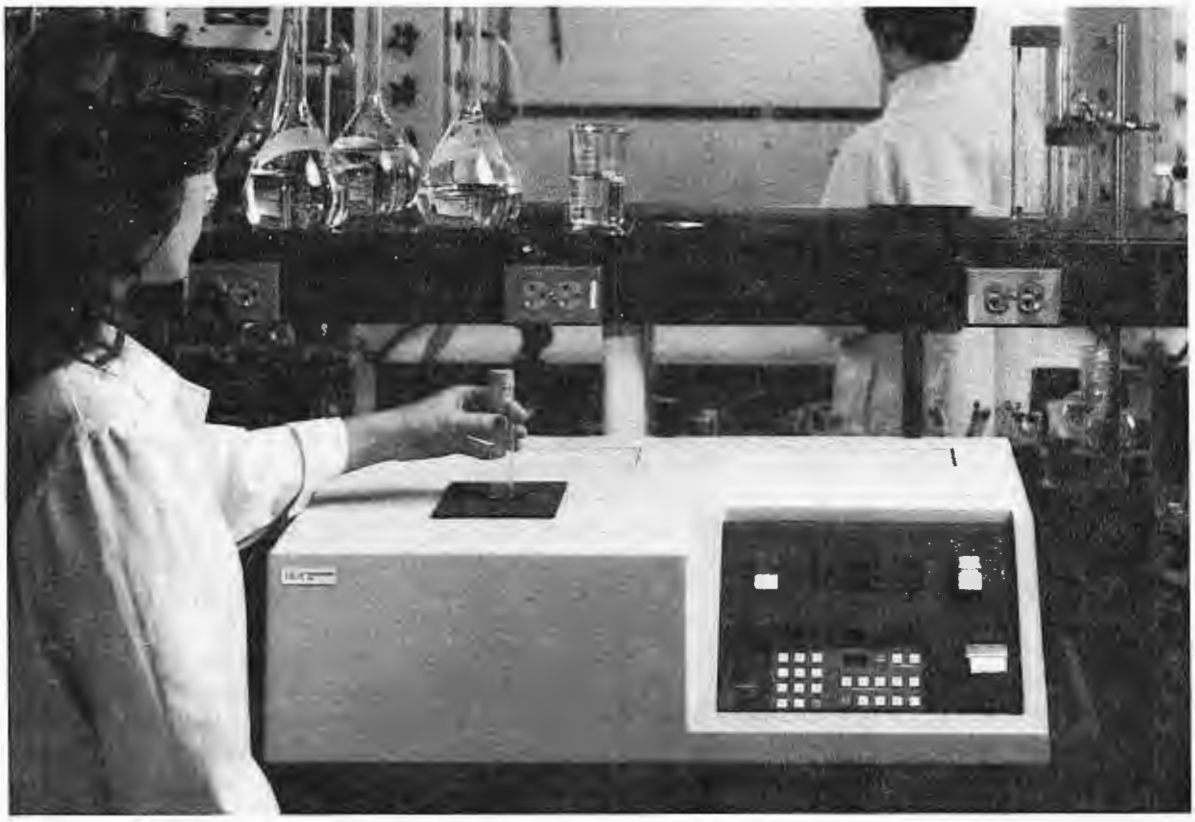
Yours sincerely,

D.W. Jones J.D. Shaw

K.D.Bartle,
(Leeds University)

1. L. Ernst, TAMU NMR Newsletter No. 297, 15 (June, 1983)
2. L. Ernst, H. Hopf and D. Wullbrandt, *J. Amer. Chem. Soc.*, 105, 4469 (1983)
3. R.H. Martin, J. Moriau and N. Defay, *Tetrahedron*, 30, 179 (1974).
4. J. Iball, *Nature*, 201, 916 (1964).
5. R.S. Ozukbo, G.W. Buchanan and I.C.P. Smith, *Can. J. Chem.*, 52, 2493 (1974).

Determine oil, fat or moisture content in seconds



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The Monospec model with pre-programmed module control for routine repetitive analysis.

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OX1 3QZ

1st February, 1984

7th European Experimental NMR Conference

The conference will be held in Altavilla Milicia, near Palermo, Sicily, beginning on Tuesday 29th May and closing on Friday 1st June at noon. Participants will be accommodated in the hotel Torre Normanna, which will also provide the lecture facilities and poster exhibition.

The programme of the 7th E.E.N.C. will cover experimental and instrumental aspects of NMR spectroscopy. It comprises invited lectures and poster sessions. Each poster is on display during the entire conference and may be mounted as early as Tuesday morning. The language of the conference will be English. Further information and registration forms may be obtained from M. Delfini, Dipartimento Chimica, Università di Roma, P. le Aldo Moro 5, Rome, Italy.

Ray Freeman

Ray Freeman

IOWA STATE UNIVERSITY

Biochemistry and Biophysics Department
Ames, Iowa 50011

D. J. Graves (515) 294-4456
D. E. Metzler (515) 294-2828

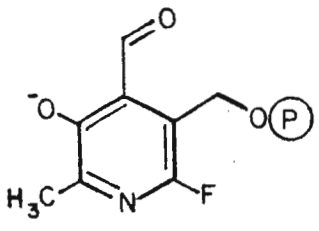
January 17, 1984

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

Title: Interaction of a Fluorinated Coenzyme with an Enzyme

Dear Barry:

We have a Bruker WM-300-WB spectrometer which is shared by the departments of Chemistry and Biochemistry & Biophysics. NMR measurement on high molecular weight proteins (of interest to biochemists) are made difficult by the slow tumbling rates of these molecules and the abundance of resonances. We have studied aspartate aminotransferase (MW 92,688) in solution using ^{19}F NMR. Although ^{19}F does not naturally occur in this molecule, vitamin B_6, as its coenzyme pyridoxal 5'-phosphate (PLP), is tightly bound and can be replaced[1] by a fluorinated analog of the vitamin, 6-FPLP. The resulting "modified" protein is 40% as catalytically active as the unmodified. The ^{19}F linewidth of the 6-FPLP increases from 8 Hz to 200 Hz upon binding to the protein and T_1 decreases[2] from 1.5s to 0.5s. The catalytic process of this enzyme entails the formation of enzyme-substrate intermediates[3]. Some of these intermediates may be trapped using substrate analogs. The analog erythro-3-hydroxyaspartate binds to the enzyme and stabilizes 2 intermediates (Fig. 1). The NMR spectrum consists of bands at -34.4 and -36.6 ppm from external TFA. Although the UV-spectrum of the naturally occurring protein does not change with temperature, that of the modified protein spectrum does. We have used this change in spectrum to assign the two peaks in the NMR spectrum by collecting at both 2 and 20°C, (Fig. 2). At 20°C the -36 ppm peak is 10% larger than at 2°C. This parallels the behavior of the quinonoid band in the absorption spectra. Thus the peak at -36 is assigned to the quinonoid form while the peak at -34 may be a Michaelis complex.



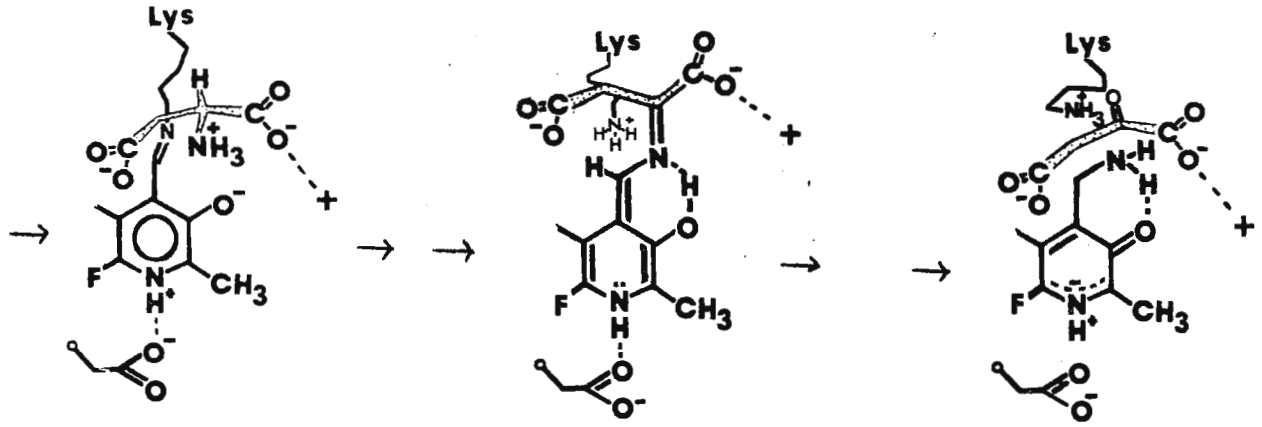
6F-PLP

We hope to continue using ^{19}F NMR to study interactions of this enzyme. Monitoring only one resonance per monomer of the protein makes assignment possible, and the sensitivity and chemical shift range of ^{19}F render even broad peaks useful.

Please credit this to the account of Dr. D.H. Huang.

Sincerely,

R.D. Scott
Y.C. Chang
D.H. Huang
D.J. Graves
D.E. Metzler



Substrate Michaelis Complex — Quinonoid — Product Michaelis Complex

Figure 1. Structures of intermediates of aspartate aminotransferase containing 6-fluoropyridoxal-5'-phosphate (6FPLP) and acting on L-aspartate. Erythro-3-hydroxyaspartate forms similar intermediates but with a larger amount of quinonoid form.

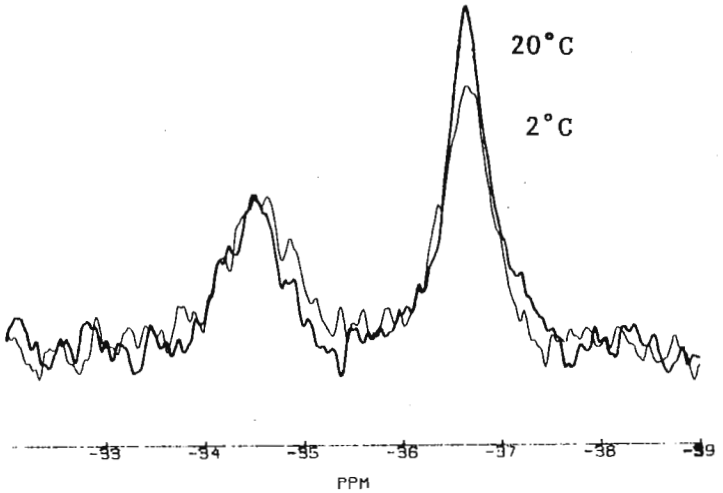


Figure 2. Variation with temperature of ^{19}F NMR spectrum of aspartate aminotransferase (80 mg/L) containing 6-FPLP; pH 5.4 in the presence of 20 mM erythro-3-hydroxyaspartate.

References:

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2. R.D. Scott, Y.-C. Chang, D.J. Graves, and D.E. Metzler in "Chemical and Biological Aspects of Vitamin B_6 Catalysis" (A.E. Evangelopoulos, ed.), Part B. Alan R. Liss, New York, pp. 247-253, (1984).
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TEXAS A&M UNIVERSITY

DEPARTMENT OF CHEMISTRY

COLLEGE STATION, TEXAS 77843-3255

6 February 1984

Dr. W. B. Moniz, Code 6120
Polymeric Materials Branch
Chemistry Division
Naval Research Laboratory
Department of the Navy
Washington, D.C. 20375

Re: Warning Letters (see letter on p. 28)

Dear Bill:

No, we have not ceased the practice of warning letters. Our records show that we sent you a Reminder in May 1983, an Ultimatum letter in July, a Final Ultimatum letter in August, and cancelled you two or three months after that.

Perhaps the notices got caught in an entropy loop involving some of the large cast of characters who signed your contribution of December 30. It ight solve more than one problem if two or three of them could be induced to block for Mr. Riggins, but I doubt it.

Our scoreboard for your subscription indicates that your next technical contribution is due by April 1984. If your mail service and/or science does not get too involved in the USFL activities, you will be able to make this target date.

With all best regards,

Yours sincerely,

Bernard L. Shapiro
Editor and Publisher

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

IN REPLY REFER TO:
6120:722:CFP:cfp
30 December 1983

Dr. Barry Shipiro
Mr. Russell Kirk
TAMU Newsletter
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Automated Crystal Rotator for the FX60Q

Dear Barry,

Have you ceased the practice of warning letters?

Over the past 18 months we have been quite pleased with the Carbon-13 NMR results we obtain from solid graphites (i.e.,intercalated HOPG) measured on our JEOL FX60Q spectrometer system. However, chemical shift vs. orientation studies were rather tedious, requiring us to manually rotate the sample after each run and restart the accumulation routine.

To automate this procedure we fabricated a sample rotator from a Superior Electric Slo-Syn motor (M061-FD-311) and translator module (STM101). The triggers for the translator module are generated by a loop written into a standard pulse routine in the JEOL PG200 pulse programmer. The pulses come out on line K, and are accessible, on our instrument, through a connector which was part of a field modification for cross polarization supplied by JEOL.The stepping pulses are applied to the translator module through a transistor buffer amplifier. The motor and module are mounted on aluminum rails which rest on the top of the magnet cabinet. The motor can be moved to the rear for normal spectrometer operation. The cost of the motor and conditioner was around $300.

In use, we load the modified single pulse program, set the parameter, LOOP, which governs the angle through which the sample is to be rotated between each accumulation,set up the rest of the accumulation parameters, program the STACK routine for the number of orientations we wish to measure and start. We currently analyze the data with the JEOL PROCESS routine, using a large value for COMP. So far we have not been able to override the X-axis offset in the PROCESS plotting routine. (Anyone have any suggestions?)

Our best wishes for the New Year from Washington (REDSKINS) DC.

H.A. Resing
B.S. Holmes
C.F. Poranski
W.B. Moniz

Sharon Graybill (Va. Poly. Inst. & State Univ.)
Dan Stec, III (NRL/NRC Reaserch Associate)
Dave Farrar (Univ. of Maryland)

P.S. Please send the back issues you held up, thanks.

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

January 20, 1984

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

Dear Barry:

Computer Simulation of NMR Experiments

Some 15 years ago, I and several others (notably Ernst and Meakin) worked out NMR simulation computer programs based on numerical integration of the Bloch equations. Mine used an HP9100 calculator which, although slow, produced excellent plots of spectra and FIDs for systems of uncoupled nuclei.

Interactive use of these programs was not easy, and I finally gave them up because I was not interested in batch-mode operation. The recent advent of the HP9000, a 32-bit machine with, presumably, about the computing power of a VAX 750 (and said to approach a VAX 780 with additional CPUs), along with my involvement with NMR imaging in connection with the Huntington Medical Research Institutes in Pasadena, revived my interest in computer simulation of NMR experiments, especially because of the long-term need for educating a large group of medicos in what NMR is all about.

Much programming will be required (especially of coupled systems), but I have progressed far enough to simulate a multipulse experiment (90^{o}-1sec-180^{o}-2sec-180^{o}-2sec-180^{o}-2sec) as shown in the figure. The algorithm is based on a third-order Runge-Kutta numerical integration and requires 400 sec for the second run-through (in the first run, the extended HP BASIC is

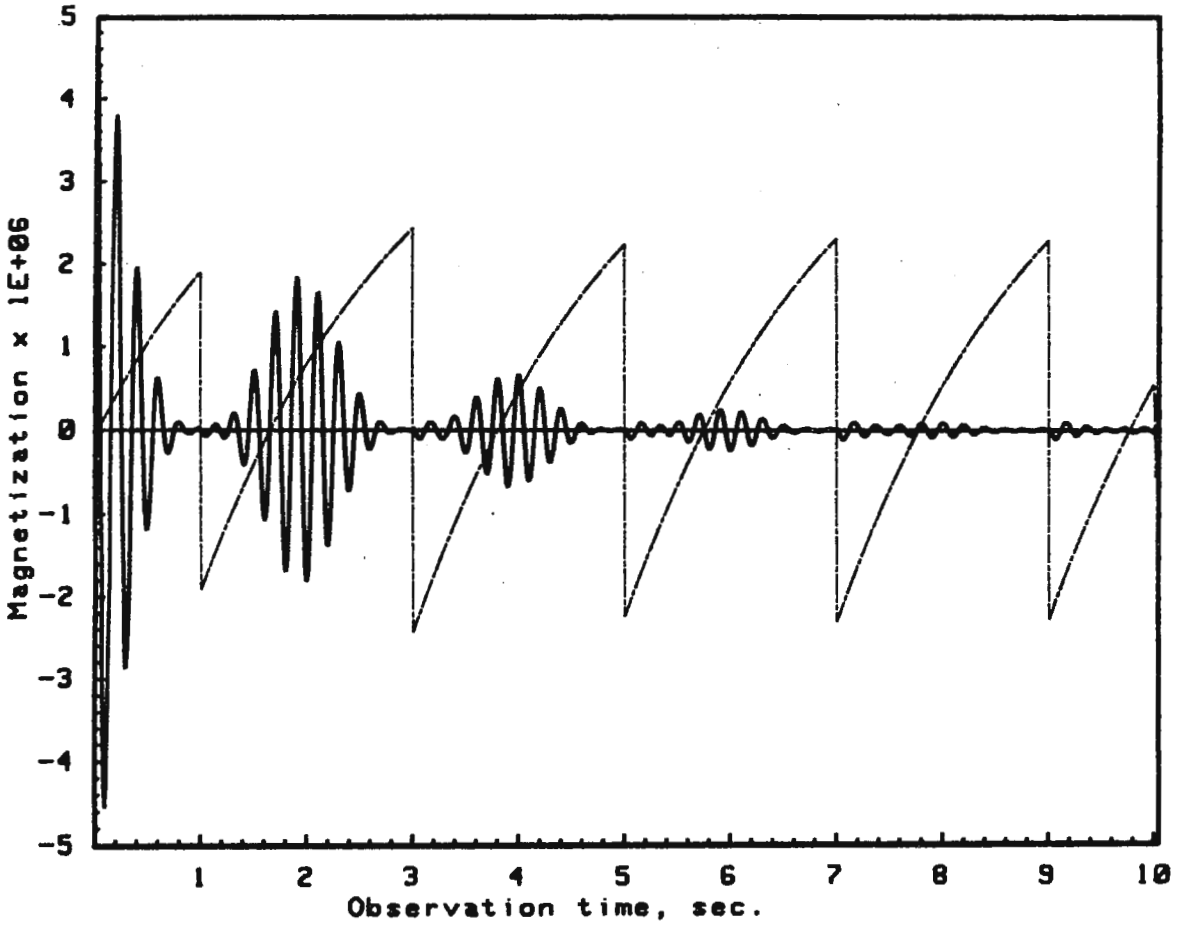
compiled). The calculation shown here illustrates an echo produced by 20 nuclei with a mean shift of 5 Hz and gaussian distribution of shifts from the mean so as to have a standard deviation from the mean of 1.0 Hz, $T_1=T_2=2$ sec, and the 90° pulse time is 0.001 sec.

While the operating system on the HP9000 hardly combines all of the best features of the earlier HP computers I have used (HP9100, 9830, 250 and 85), entering and editing of programs is very facile, the black and white and color graphic capabilities are fantastic, and one can shift back and forth between several programs running simultaneously with a keystroke.

With all good wishes,

Very truly yours,

Jack



305-31

OSU

The Ohio State University

Department of Chemistry
140 West 18th Avenue
Columbus, Ohio 43210
Phone 614 422-2251

January 12, 1984

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

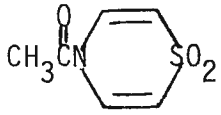
RE: d - orbital overlap in a cyclic sulfone; NIC 500; Postdoctoral position

Dear Barry:

In response to your different colored notes.

Our NIC 500 has been here for some weeks. In addition to the usual vicissitudes of start-up I have a couple of comments. The field is apparently high enough so that shift anisotropy broadens the ^{13}C lines for some of our organolithium compounds enough to obscure and partically average the ^{13}C, ^{6}Li coupling. This is very bad if one is interested in structure of $(RLi)_n$ species and the dynamics of C, Li bond exchange.

I may have communicated some time ago that the N-acyl sulfone I,



I

has an unusually low barrier (11.4 kcal) to amide rotation. We have now traced this via IR and X-ray crystallography to a loose (C-N) amide linkage. Gaussian 80 (STO 3G*) calculations of the barrier show extensive $3d_{xz}(S)$ $2p_z(C)$ overlap in some higher bonding orbitals, of the twisted amide (transition state for rotation) and reproduce the barrier at 11.7 kcal.

Finally I announce that a postdoctoral position will be available in my laboratory by June for someone interested in NMR line-shape analysis of dynamic phenomena in and among organolithium compounds and their complexes in solution. Some expertise is acquired in organometallic synthesis and expected in NMR technology.

Best wishes for the new year.

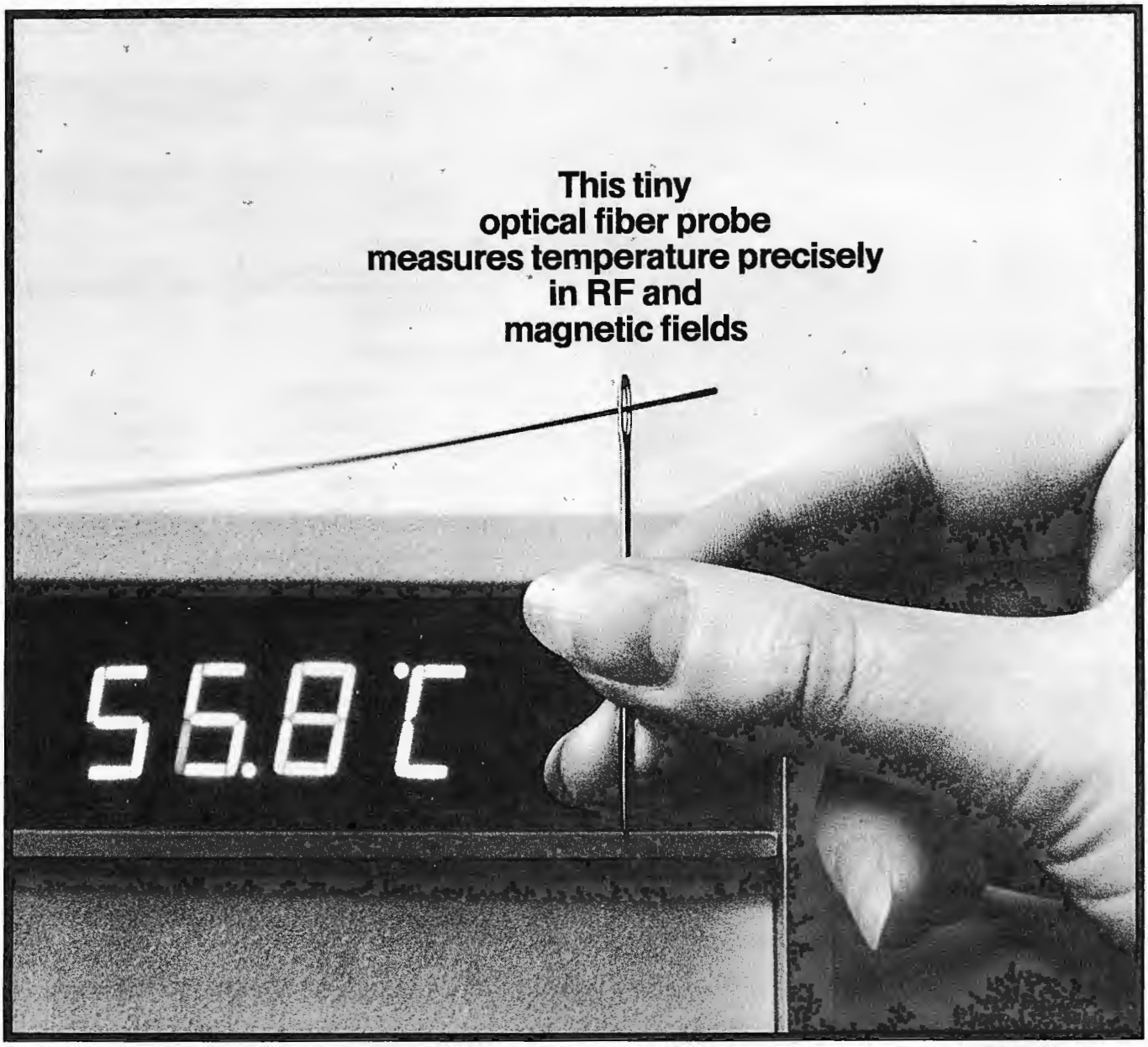
Yours sincerely,

Gideon

Gideon Fraenkel
Professor of Chemistry

ls

BREAKTHROUGH



Did you ever wonder how you could measure temperatures during NMR studies? Whether you are doing bioeffects studies, investigating patient heating effects during NMR imaging or making fundamental measurements on temperature-sensitive materials of biomedical interest, Fluoroptic™ Thermometry by Luxtron provides an important new investigational tool. Autoclavable probes are nonconducting, minimally perturbing and small enough to be inserted through an 18 gauge catheter. With our new automatically calibrated Model 1000B, accuracies of 0.1°C are readily achievable. Call or write for the complete story.

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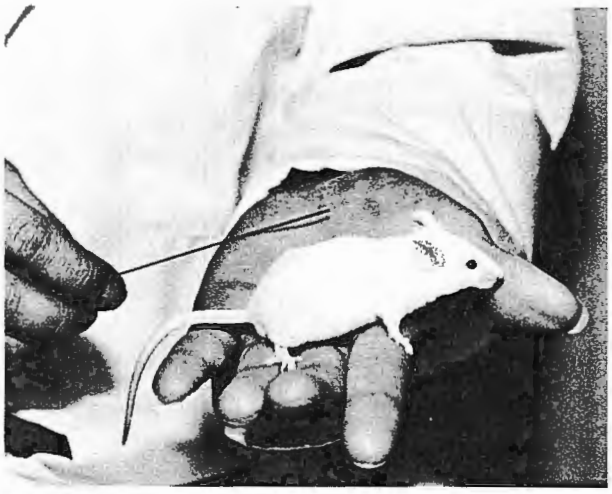
Model 1000B Applications

Several characteristics of Luxtron's fiber optic probe distinguish it from conventional temperature sensors and permit creative biomedical researchers to tap new realms of temperature data. These distinctive characteristics include: autoclavability for direct insertion into tissue; local sensing for pin-point readings; slender size for insertion via 18 guage catheter needles; versatile lengths for routing through apparatus or into screen rooms; total safety for isolated, non-electrical sensing; small thermal mass for rapid readings; RF/microwave immunity for non-perturbance in or by electromagnetic fields.



Benefits of Fluoroptic™ probe for small animal research include: small size, autoclavable, fast response, localized sensing, non-contaminating.

Model 1000B Specifications

SYSTEM PERFORMANCE

Temperature Range:
0° to 80°C (32° to 176°F)

Precision (Repeatability):
±0.1°C with 1 second measurement time

Resolution of Display:
0.1°C or °F

Resolution of Outputs (Analog and digital):
0.01°C; 0.02°F

Method of Calibration:
Automatic using 2 reference points within hyperthermia range (37° to 50°C)

Accuracy:
Using Floating Internal Temperature References:
1. 37-50°C: ±0.25°C
2. 0° to 20°C: ±1.2°C
3. Remainder of Range: ±0.6°C

Using Optional Precision External Temperature References:
1. 37-50°C: ±0.1°C
2. 0° to 20°C: ±1.0°C
3. Remainder of Range: ±0.5°C

Stability:
Less than 0.2°C change per degree change in ambient from 15° to 35°C

Measurement Times:
⅓, 1 or 4 seconds, operator selectable

PROBE

Materials:
Single strand plastic clad optical fiber with black PFA Teflon® external jacket.

Lengths:
2 meter lengths standard; longer probes and extensions available with some reduction of performance.

Diameter:
Less than 0.7mm throughout, excluding connector. Sensor can easily pass through the sheath of an 18 gauge I.V. catheter placement unit.

Flexibility:
While the fiber is quite flexible, the sensor end is sufficiently stiff to be self-guiding during insertion into catheter or placement unit.

Sterilization:
Because of the unusually hardy materials and construction techniques used, probes can be sterilized by autoclaving.

INSTRUMENT

Front Panel Indicators:
LED display for temperature in °C or °F plus overrange, underrange, probe fault and lamp out indicators, warm-up and calibration status indicators.

Internal Selectors:
°C or °F; measurement time; calibration mode and settings; output parameters.

Rear Panel Analog Output;
10mV per degree C or F with adjustable zero offset; BNC connector.

Rear Panel Digital Output (Optional):
RS 232C Serial with switch-selectable BAUD rates. An optional conversion to IEEE standard 488 output also available.

Temperature References:
Two floating temperature reference wells, accurate to 0.25°C, are provided within the instrument for routine calibration. A high precision temperature reference, with two fixed point wells, is also available as an option.

Packaging:
RF-shielded and filtered, bench-style instrument with tilt-up bail. With standard shielding, displayed temperature will not change by more than ±1.0°C with a radiation flux density of 10mW/cm² at frequencies up to 2.45 GHz. Optional heavy-duty shielding also available to reduce this RF field susceptibility to ±0.1°C.

ENVIRONMENTAL SPECIFICATIONS

Temperature:
Operating 10°C to 40°C; storage −55°C to 75°C

Humidity:
10° to 25°C, 95% RH; 25° to 40°C, 75% RH

Vibration:
Meets requirements of MIL-T-28800 for Style E Class 6 equipment

Size and Weight:
16¾" wide by 13" deep by 4" high;
18 pounds (8.2 Kg)

Power:
100, 120, 220, 240 VAC ±10%; 50-60 Hz; 60 Watts

LUXTRON

Fluoroptic™ Temperature Sensing
1060 Terra Bella Avenue, Mountain View, California 94043
Telephone (415) 962-8110, Telex 348-399 KARMIGA

Printed in U.S.A. 4/82

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- Spectrométries de Résonance Magnétique
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- Mesures de Susceptibilité magnétique
- Recherche Océanographique

SADIS BRUKER SPECTROSPIN, Boîte Postale N 67160 WISSEMBOURG

Professor B.L. SHAPIRO
Department of Chemistry
TEXAS A & M University
College Station

TEXAS 77843
U.S.A.

N./Réf. 84 01 43 CB/AMB

V./Réf.

Wissembourg, le February 1st 1984

90° pulse measurement

Dear Barry,

Life is beautiful, as are your multi-colored reminders.

Life is rather tuff when comes the measurement of the 90° pulse for very insensitive, low frequency, long T_1, dipolar isotopes (typically an overnight run !).

We found useful the following sequence :

```
1 ZE
2 D1                          ; 5 T1
3 P1                          ; initial pulse value
4 LO TO 3 TIMES I             ; actual pulse value indexed to the
                                number of the experiment via the
                                I loop
5 GO = 2                      ; PW = 0, RD = 0
6 WR #1
7 IF #1
8 IN = 1
9 EXIT
```

Provided that T_{1x} is long (> 1 second), there is no influence of the extra delay introduced by the looping process on the measured $PW_{90°}$ value.

May I follow Pierre Laszlo suggestion (TAMU n° 299 p 10) by proposing you, when in Europe, to extend your trip from Belgium to Ilhaeusern, nearby Strasbourg, at "l'Auberge de l'Ill", one of the three stars Michelin restaurants in France.

See you then !

Christian

Dr. Christian BREVARD

January 18, 1984

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

Dear Professor Shapiro:

Title: Using the JEOL Shimplex with an Automatic Sample Changer; Report on the Nicolet 1280 Co-processor

The JEOL Shimplex is a microprocessor-controlled device which uses the simplex method to optimize and maintain Z_1 and Z_2 homogeneity. Unfortunately, the unit in our FX-270 spectrometer occasionally stops working (and turns on the "BEST" lamp) before it has found optimum values for Z_1 and Z_2.

We have discovered a procedure, described below, which circumvents this problem and also enables the Shimplex to obtain homogeneity from much poorer starting values of Z_1 and Z_2 than are normally usable. The method apparently works by "tricking" the Shimplex into increasing its starting search ranges for Z_1 and Z_2:

1. RESET the Shimplex.
2. Obtain a suitable lock signal level for the Shimplex.
3. Reduce the lock gain by one 3-dB step.
4. Start the Shimplex (RUN mode). Wait 4 seconds.
5. Restore the original lock gain.
6. Monitor the lock signal intensity for 2 or 3 minutes:
   a) If the lock intensity decreases by more than 10 percent, HOLD the Shimplex and then RUN.
   b) If a Shimplex ERROR occurs: HOLD, reduce the lock gain and then RUN again.

Although this procedure can be carried out manually, we have interfaced a Commodore-64 computer to the Shimplex in order to automate the method. The computer is part of an automatic control system we have designed for the FX-270 spectrometer. The system includes an automatic lock, a circuit to adjust the observe receiver gain, a spinner speed controller and a Zymark laboratory robot for changing samples. Our JEOL FX-270 now automatically obtains both proton and ^{13}C spectra from samples dissolved in a variety of lock solvents.

Dr. Bernard Shapiro
January 18, 1984

On another matter, we are happy to report the fine performance of the new Nicolet 1280 co-processor, which has been installed in our home-built solid-state instrument for the past 6 weeks. This array processor will do a fast Fourier transform and phase correction on a 64K data set in 3.5 and 1.0 seconds, respectively. These times are compared with 43.6 and 7.9 seconds before installation of the co-processor.

Please credit this contribution to the Kodak Research Laboratories subscription.

Very truly yours,

Stanley Gross

SG/NZ/keh

Stanley Gross

N. Zumbulyadis

Nicholas Zumbulyadis
Analytical Sciences Division
Research Laboratories

305-37

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

January 23, 1984

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

Dear Dr. Shapiro,

Ref: 400 MHz ^{1}H NMR Analysis of PCA Extracts from a RIF-1 Tumor

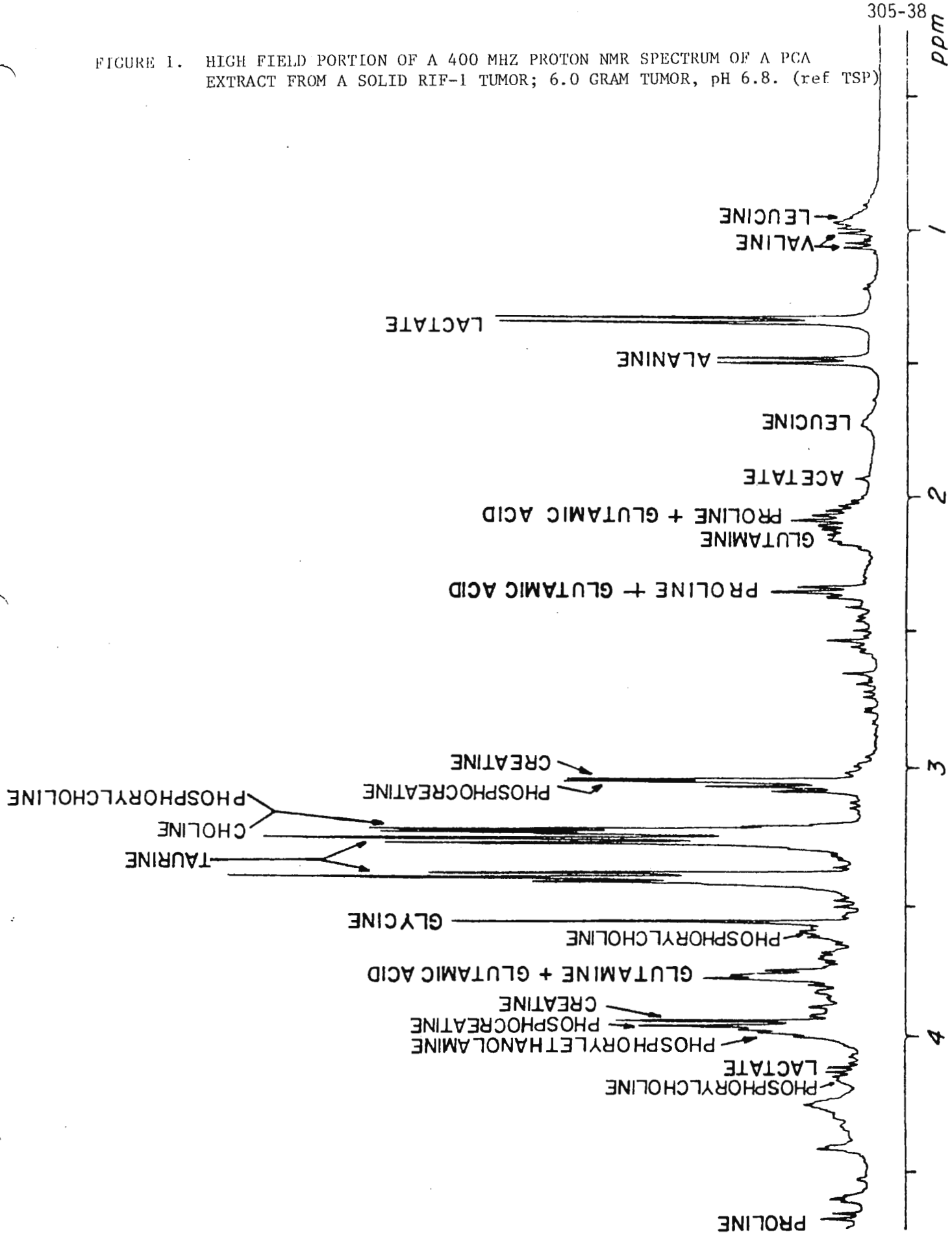
As we await the arrival of the "final ultimatum" (i.e. the yellow letter), we take time to write about our continuing work in the area of in vivo NMR of solid tumors. We recently have concluded a PCA extract analysis of solid radiation-induced fibroblast (RIF-1) tumors. This study consisted of ^{1}H, ^{13}C, and ^{31}P NMR, automated phosphate analysis, HPLC analysis, and amino acid analysis. Figure 1 shows the high field portion of a ^{1}H NMR of a PCA extract from a RIF-1 tumor. A great many compounds can be readily identified. In addition, phosphocreatine can be distinguished from creatine at 3.95 ppm. Interestingly, the most intense resonance for both the ^{1}H and ^{13}C NMR spectra was identified as taurine, a sulfur containing amino acid. We have also observed this compound in PCA extracts of brains, hearts, and muscle. This is only new from a identification viewpoint, it is not a new discovery. Taurine has long been known to be present in these and other tissues. Its purpose, however, is still not fully understood.

These results should soon appear in a full paper submitted to B.B.A.

Magnetically yours,

William T. Evanochko Jerry D. Glickson Thian C. Ng Ted T. Sakai

FIGURE 1. HIGH FIELD PORTION OF A 400 MHZ PROTON NMR SPECTRUM OF A PCA EXTRACT FROM A SOLID RIF-1 TUMOR; 6.0 GRAM TUMOR, pH 6.8. (ref TSP)



305-39

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
McCORMICK ROAD
CHARLOTTESVILLE, VIRGINIA 22901

January 25, 1984

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

Dear Professor Shapiro:

^{13}C T_1 and $T_{1\rho}$ Studies of Dipalmitoylphosphatidylcholine Bilayers

We have measured acyl chain methylene ^{13}C spin-lattice (T_1) relaxation times of dipalmitoylphosphatidylcholine (DPPC) bilayers at seven different magnetic field strengths (15-126 MHz) (1,2), have derived relaxation expressions based on reasonable models for acyl chain motion, and have fit the data to these models.

The models considered (3) are:

(i) Diffusion - carbons undergo isotropic or anisotropic rotational diffusion, characterized by one or more correlation times, a diffusion tensor anisotropy parameter, and an orientational order parameter;

(ii) Noncollective - two types of motion occur, fast and slow, each of which can be characterized by an order parameter and a correlation time;

(iii) Collective - again, two types of motion are assumed, fast and slow; however the slow motions are presumed to be more collective in nature than in (ii) and are characterized by a continuous distribution of correlation times.

The fast motions in models (ii) and (iii) are presumed to be due largely to bond rotations, whereas the slow motions may represent whole molecule movements. As one can see in Figure 1, the data are inconsistent with the diffusion model, but can be fit by both the collective and noncollective models. This work will appear in J. Chem. Phys.

In collaboration with M. Sefcik, J. Schaefer, E. Stejskal, and R. McKay of the Monsanto Corporation, we are extending our ^{13}C spin-lattice relaxation measurements (4) and theoretical work to the kHz regime. $T_{1\rho}$'s measured at 50 MHz with spin lock fields of 25-50 kHz are approximately an order of magnitude lower than the corresponding T_1's and are dependent on the spin lock field. At present, the T_1 and $T_{1\rho}$ data suggest that the collective model is most satisfactory, and further studies of lipid bilayers and biomembranes are in progress.

Postdoctoral positions are available in our research group. Inquiries are invited.

Jeff Ellena
NMR Spectroscopist

Michael Brown
Assistant Professor of Chemistry

REFERENCES

1. TAMU NMR Newsletter 302-37.
2. M. F. Brown et al., Proc. Natl. Acad. Sci. USA 80, 4325 (1983).
3. M. F. Brown, J. Chem. Phys. 77, 1576 (1982).
4. M. D. Sefcik et al., Biochem. Biophys. Res. Commun. 114, 1048 (1983).

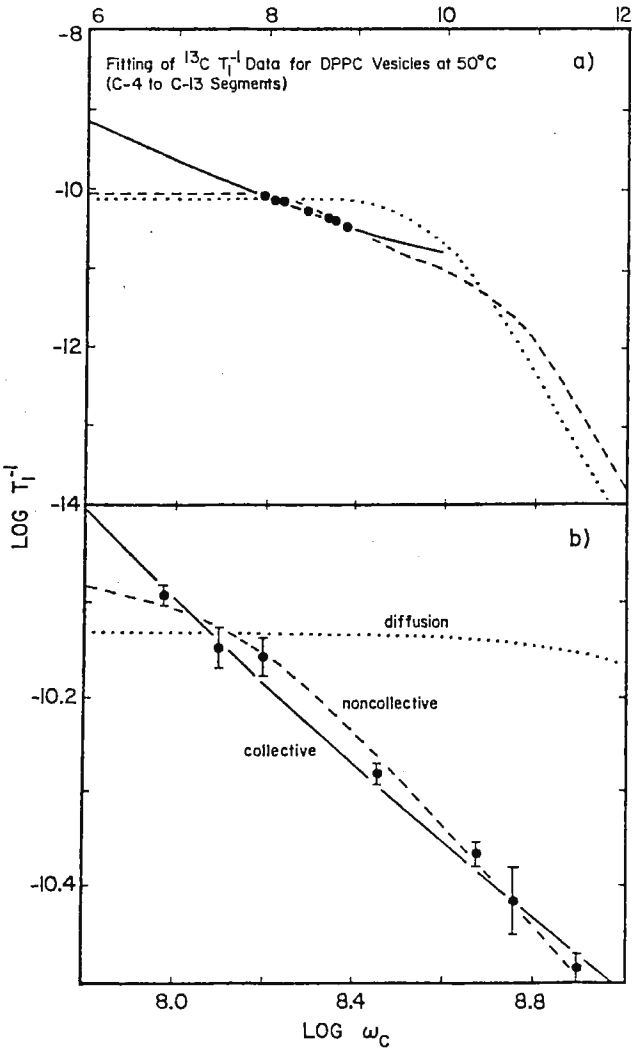


Fig. 1. Nonlinear regression best fits of models for lipid bilayer dynamics to ^{13}C T_1 relaxation times of unilamellar DPPC vesicles, as a function of the resonance frequency ω_C at 50°C. Data for the $(CH_2)_n$ resonance corresponding to the C-4 to C-13 fatty acyl chain segments are indicated. The T_1^{-1} rates have been scaled by dividing by $N_H(\gamma_C\gamma_H h/r_{CH}^{0\,3})^2$, with a value of r_{CH}^0 = 1.14 Å. (• • •) Fit of diffusion-type model. (- - -) Fit of noncollective model. (——) Fit of collective model. The upper panel (a) shows plots over the frequency range log ω_C = 6 to 12; the lower panel (b) shows expanded plots from log ω_C = 7.8 to 9.0.

305-41

National Research Council Canada
Conseil national de recherches Canada

Division of Biological Sciences
Division des sciences biologiques

Ottawa, Canada
K1A 0R6

23 January 1984

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

Dear Professor Shapiro:

The Division of Biological Sciences of the National Research Council of Canada has a staff position available in the Immunochemistry and Microbiology section. This research officer is required to provide a high resolution NMR service. The duties will include routine operation and maintenance of a Bruker AM-500 spectrometer together with at least one other lower field instrument. The successful candidate must be prepared to develop active collaborations with the present members of the section and will be encouraged to apply modern instrumentation and spectroscopic techniques to the solution of a variety of biological projects.

Current research interests in the section centre upon structural studies and synthesis of bacterial antigens, which are carbohydrates. Of particular interest are methods for the structural elucidation of bacterial polysaccharides, conformational studies of bacterial antigens supported by computer modelling and receptor-ligand binding with particular reference to antigen-antibody interactions.

The minimum qualifications for this position are a Ph.D., preferably in chemistry, with several years of post-doctoral research. Preference will be given to candidates who have specialized knowledge of carbohydrate chemistry and extensive experience in the application of NMR techniques, ideally carbohydrate systems. In particular, previous use of two dimensional NMR and experience in quantitative aspects of conformational analysis are highly desirable. Experience of computational methods for assessing conformational preference and the interpretation of NMR data in these terms will be judged an asset. In addition the disposition to work with a large cross-section of biologists and chemists is indispensable. Salary will be commensurate with qualifications.

Canada

Prospective applicants should write to me for application forms and at the same time name two senior scientists familiar with their abilities.

Yours sincerely,

David Bundle

David Bundle.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMISTRY
CAMBRIDGE, MASSACHUSETTS 02139

January 9, 1984

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

Dear Professor Shapiro:

Post-Doctoral Positions Available

I would like to alert your audience to two post-doctoral positions available in my laboratory at M.I.T.

(1) An opening is available immediately for an individual interested in in vivo NMR studies of methanogens (focussing on carbon-flow and nitrogen assimilation in these bizarre archaebacteria). Experience with anaerobic techniques would be useful, although not necessary.

(2) A position will be available in May/June for an individual interested in physical studies of various phospholipid aggregates (short chain lecithin micelles, bilayer vesicles, minilipoproteins, etc.) and phospholipases. QLS (quasielastic light-scattering) as well as NMR will be emphasized.

Anyone interested in either opening should phone (617-253-1820) or write me.

Sincerely,

Mary F. Roberts

THE UNIVERSITY OF SYDNEY

DEPARTMENT OF BIOCHEMISTRY

SYDNEY N.S.W. 2006
AUSTRALIA

TELEPHONE: (02) 692-2222
TELEX: FISHLIB 20056

26 January, 1984

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

"Inversion Transfer ^{31}P NMR Spectroscopy using the DANTE Pulse Sequence"

Dear Professor Shapiro,

Recently we have used the Bruker WM400 Spectrometer at the University of Sydney for studies on the in vitro and in vivo kinetics of glycolytic enzymes. One aspect of this work is the use of inversion and saturation transfer techniques to study the kinetics of phosphate group exchange among substrates in the glycolytic pathway.

Previous workers in this field [1] have used a second ^{31}P decoupling frequency to selectively saturate or invert one of the phosphate resonances. As our WM400 spectrometer lacks a ^{31}P decoupling channel we have resorted to using the DANTE sequence to selectively saturate and invert phosphate resonances [2].

Fig. 1 shows spectra from an inversion transfer experiment on rabbit muscle phosphoglyceromutase which catalyses the reaction

3-phosphoglycerate (3PG) $\rightleftharpoons$ 2-phosphoglycerate (2PG)

Resonance A (3PG) was selectively inverted with a DANTE pulse sequence using the following parameters: pulse width 0.9 μs, delay between pulses 333 μs and number of pulses 40. After a variable delay time (shown next to each spectrum) a non-selective 90° pulse was applied and the spectrum recorded. The inversion was transferred to resonance B (2PG).

Inversion of resonance A was selective and resonance B was unaffected by the DANTE pulse although the chemical shift difference is only 93 Hz. We found no need to attenuate the transmitter power in either saturation or inversion experiments. The non-selective 180° pulse using our ^{31}P probe is 36 μs.

Our experiments have shown that the DANTE sequence works well and recommend it to other workers in this field who lack a ^{31}P decoupling channel on their spectrometers.

Yours sincerely,

Philip W. Kuchel — Gae Robinson — B E Chapman

P.W. Kuchel — G. Robinson — B.E. Chapman

[1] Brown, R.J. and Ogawa, S. (1977) Proc. Nat. Acad. Sci. USA 74, 3627
[2] Morris, J.A. and Freeman, R. (1978) J. Mag. Res. 29, 433.

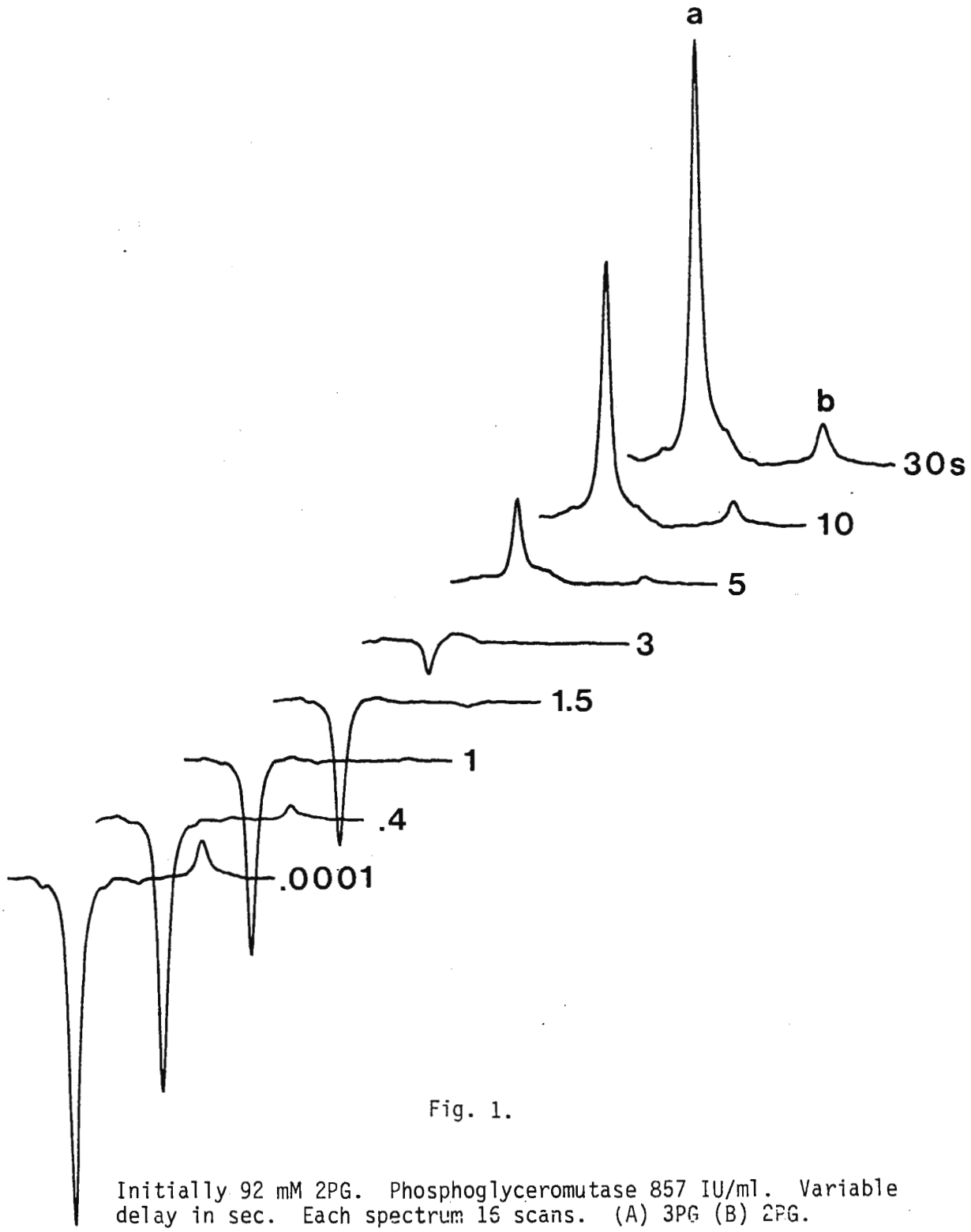


Fig. 1.

Initially 92 mM 2PG. Phosphoglyceromutase 857 IU/ml. Variable delay in sec. Each spectrum 16 scans. (A) 3PG (B) 2PG.

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Naturwissenschaften II (Chemie/Biologie)

Universität-Gesamthochschule-Siegen · Postfach 101240 · 5900 Siegen

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

5900 Siegen, Jan 27, 1984
Adolf-Reichwein-Straße
Postfach 10 12 40
Telefon (02 71) 7401
Durchwahl 740–

^{2}H-^{13}C Chemical Shift Correlation

Dear Barry,

we apologize for the delay in answering your threatening letters, but . . .

Last year we continued our adoption of modern pulse techniques for deuterated compounds in collaboration with Dr. R. Bendall and a paper that describes complete editing of subspectra for CD, CD_2, CD_3, CHD, CHD_2, and CH_2D groups on the basis of polarisation transfer achieved with the UPT sequence (a member of the DEPT family) in combination with a J(CH) modulated spin echo sequence is presently in print (JMR).

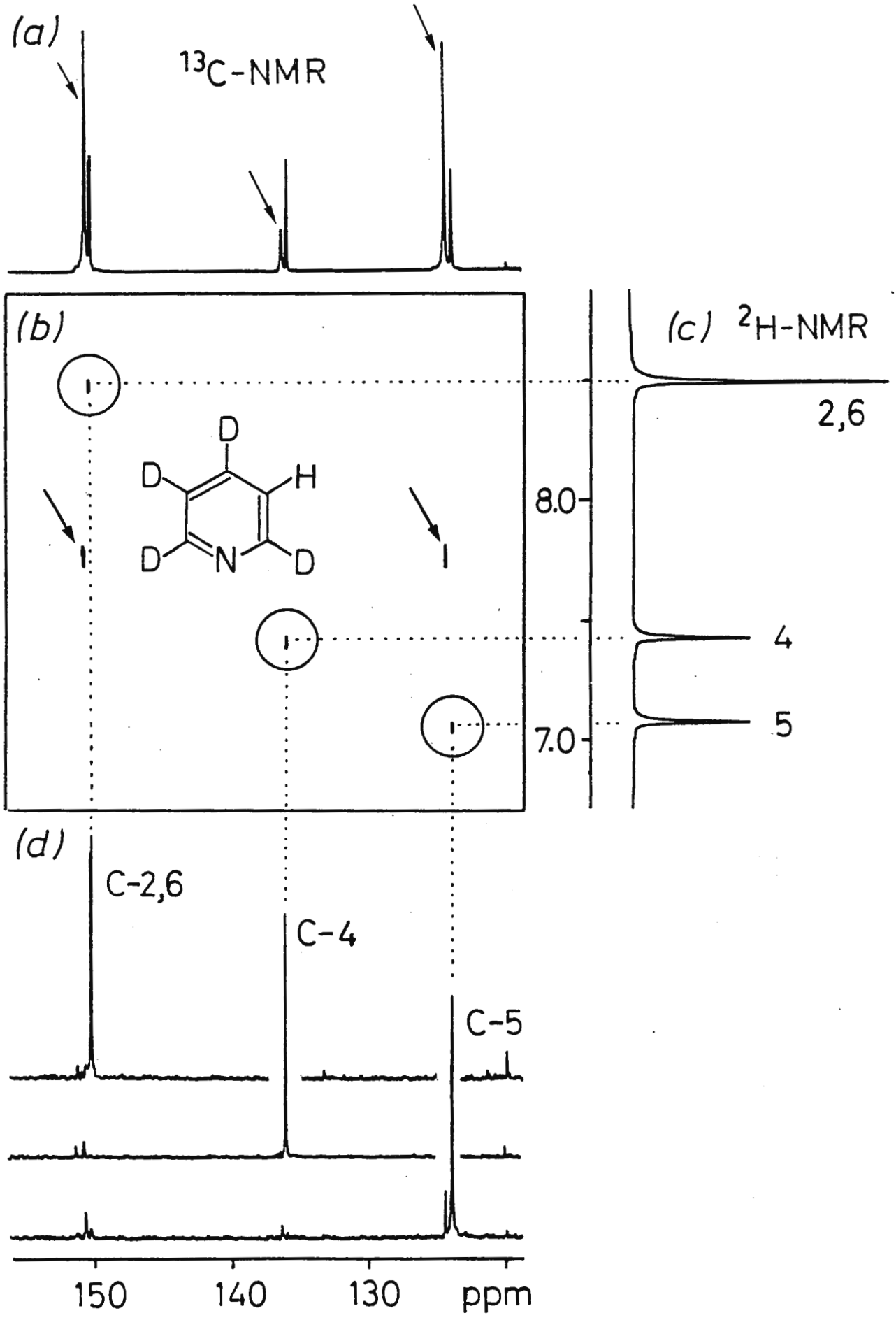
The latest addition to these experiments is ^{2}H-^{13}C shift correlation, a straightforward extension of the polarisation transfer work. The details are described in a communication submitted to OMR. Preprints are available upon request.

The 2D shift correlation technique is of particular advantage if small amounts of deuterated material are to be analyzed in the presence of a large excess of non-deuterated compounds. This aspect is best demonstrated with the enclosed figure, that shows the results for a solution of 50 mg pyridine-d_4 dissolved in 3 g pyridine. Trace (a) shows a polarisation transfer experiment where, due to imperfections, the signals of the "protonated" carbons are not fully eliminated (arrows). These signals are suppressed in the 2D experiment (C-4) or fall on the F_1=0 axis (C-2,6, C-5) (b). They are easily identified through the ^{2}H nmr spectrum, where the corresponding signals are missing (c). The lines of the deuterated carbons are thus firmly established. They can be recorded sperately from the appropriate traces of the 2D diagram (d).

Hope this puts us back on the mailing list! Kind regards

Yours sincerely,

J. R. Wesener P. Schmitt H. Günther


(a)
^{13}C-NMR
(b)
D
D
H
D
N
D
(c) ^{2}H-NMR
2,6
8.0
4
7.0
5
(d)
C-2,6
C-4
C-5
150
140
130
ppm

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GBF
Gesellschaft für Biotechnologische Forschung mbH
Abteilung
Physikalische Meßtechnik & Pflanzliche Zellkulturen

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

Ihre Nachricht vom	Telefon 05 31/70 08-1	Telefondurchwahl	Datum
		05 31/70 08 /362	27. 01. 1984

^{31}P NMR of plant cell suspension cultures

Dear Professor Shapiro,

Over the past 18 months we have been looking at the ^{31}P nmr spectra of plant cell suspension cultures. After identifying the various phosphorus containing compounds from spectra of perchloric acid extracts, treated for paramagnetic ions, we have established a method of taking in vivo spectra. As these compounds are in much smaller concentrations than in animal cells spectra must be accumulated over long periods of time and hence aeration of the medium is necessary. Although various other groups are using perfusion methods to look at excised plant tissue we have found that bubbling air through the medium directly in the nmr tube using a fine concentric capillary at a rate of 2-5 ml min^{-1} allows satisfactory spectra to be recorded over long periods of time without spinning. Our initial results with Nicotiana tabacum grown in shake flasks have been reported (Z. Pflanzenphysiol. 112, 215 (1983)).

The method is not only of physiological interest but its biotechnological application is of considerable importance as the scale-up of fermentations relies on knowing details of the physiological state of the cells prior to transfer. At the moment the optimal timing of this process is difficult to ascertain by other methods. Most recently we have been taking spectra of cultures of Catharantus roseus which were recorded for samples taken directly from a fermentation without prior treatment of the cells. An example of these spectra, taken at various times during the fermentation, are shown in the figure. The spectra give us not only information about the physiological condition of the cells but allow us to monitor the disappearance of inorganic phosphate from the cell vacuole. This is of importance as inorganic phosphate is known to influence growth and the regulation of secondary metabolism, and hence antibiotic synthesis, in these systems.

Yours sincerely,

Victor Wray
Victor Wray

Jochen Berlin
Jochen Berlin

Otmar Schiel
Otmar Schiel

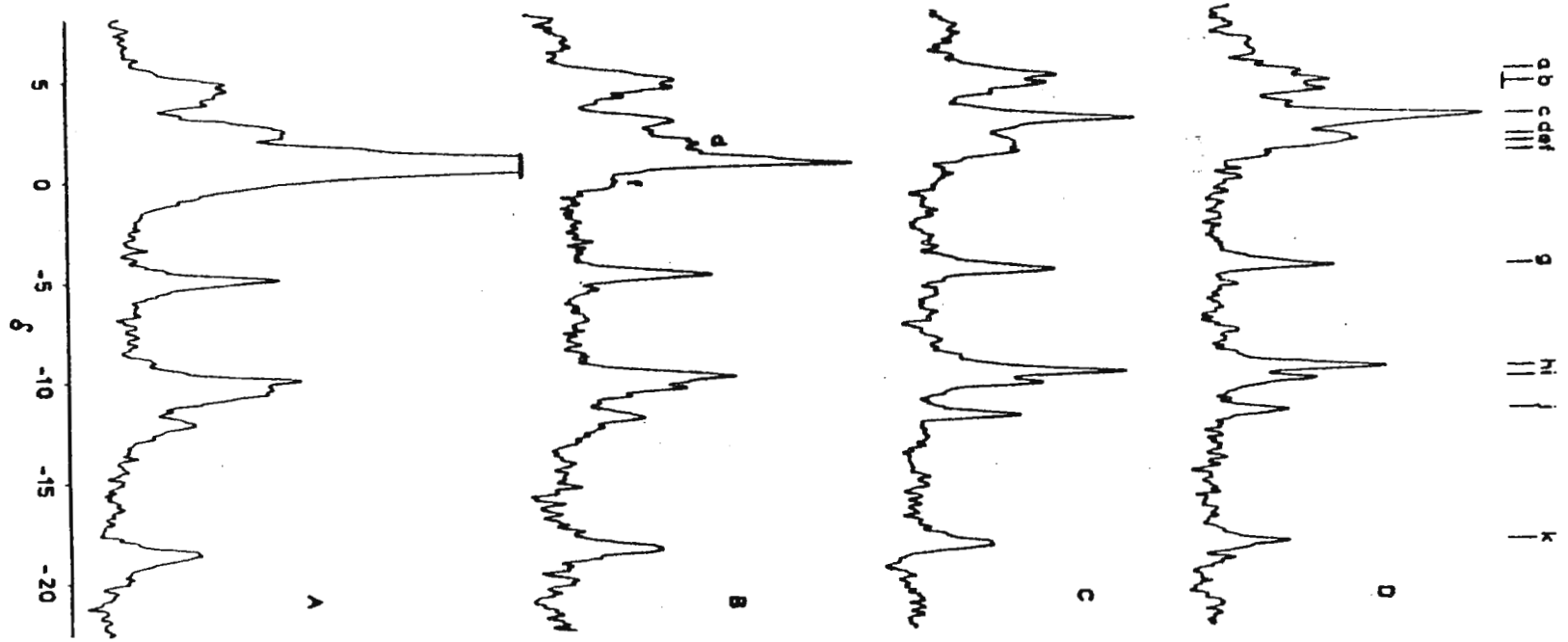


Figure. In vivo ^{31}P nmr spectra of samples taken from a 75l fermentation of a cell suspension culture of Catharantus roseus after A 2 days, B 5 days, C 9 days and D 12 days fermentation. The signals are assigned as follows: a = glucose-6-phosphate, b = sugar phosphates, c = cytoplasmic inorganic phosphate, d and f = unidentified signals, e = vacuolar inorganic phosphate, g = γ-ATP (Mg^{2+} complex), h = α-ATP (Mg^{2+} complex), i and j = nucleoside diphosphoglucose and k = ß-ATP (Mg^{2+} complex). Spectra were accumulated for 14 hours per spectrum on average.

305-49

Western Research Institute
P.O. Box 3395, University Station
Laramie, Wyoming 82071
307 721-2011

December 5, 1983

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

Dear Barry:

I would like to call readers' attention to the Preliminary Announcement for the 26th Rocky Mountain Conference to be held in Denver, Colorado, August 5-7, 1984. Symposium on NMR and EPR will again be featured this year. The NMR Symposium will feature sessions on NMR techniques in solids and NMR applications to studies of zeolites, catalysts, surfaces, quadrupolar nuclei, fossil fuels and polymers. Poster papers in all areas of NMR are welcome.

The 7th International EPR Symposium, organized by Gareth and Sandra Eaton will also be held. It will feature sessions on EPR imagery, pulsed EPR and EPR of Transition Metals. The International Conference on Coordination Chemistry will be held in Boulder, Colorado, the week prior to the Rocky Mountain Conference.

Anyone wishing to present a paper in the NMR or EPR symposium can use a xerox copy of the form on the announcement and send it to me (NMR) or Gareth Eaton (EPR).

Best regards,

Fran Miknis

Fran Miknis
Chairman
NMR Symposium
Rocky Mountain Conference

Preliminary Announcement and Call for Papers

305-50

26th ROCKY MOUNTAIN CONFERENCE

August 5-9, 1984

Denver Convention Complex
Denver, Colorado

Sponsored jointly by:

Rocky Mountain Section
Society for Applied Spectroscopy

and

Rocky Mountain Chromatography
Discussion Group

Conference Chairman:
Jan Gurnsey
5531 Bitterbush Way
Loveland, Colorado 80537
Telephone (303) 669-9216

Abstracts of no more than 200 words must be submitted on a Rocky Mountain Conference abstract form or a standard ACS abstract form. These forms may be obtained from the conference or symposia chairmen.

ABSTRACT DEADLINE is MARCH 14, 1984

Submit abstracts to the specific symposium chairman. Abstracts for the GENERAL SESSION should be submitted to the conference chairman.

General papers and poster sessions in all areas of chemistry are planned along with the following specific symposia:

- APPLICATIONS OF CHROMATOGRAPHY TO BIOLOGY, MEDICINE AND BIOTECHNOLOGY - K. Brooks, Dept. of Chemistry, University of Colorado at Denver, 1100 14th St., Denver, CO 80202. (303) 629-3201
- ATOMIC SPECTROSCOPY - T. Niemczyk, Dept. of Chemistry, University of New Mexico, Albuquerque, NM 87131. (505) 277-5319
- CHROMATOGRAPHY - K. Brooks, Dept. of Chemistry, University of Colorado at Denver, 1100 14th St., Denver, CO 80202. (303) 629-3201
- COMPUTER APPLICATIONS - A. Lewis, Exxon Nuclear-Idaho, P.O. Box 2800, CPP602B, Idaho Falls, ID 83401. (208) 526-3680
- ELECTROCHEMISTRY - C. Koval and M. Elliott, Dept. of Chemistry, Box 215, University of Colorado, Boulder, CO 80309. (303) 492-5564
- ENVIRONMENTAL - M. Reddy, USGS, 5293 Ward Rd., Arvada, CO 80002. (303) 234-3975
- EPR - G. Eaton and S. Eaton, Dept. of Chemistry, University of Denver, Denver, CO 80208. (303) 753-2507
- IR & FLUORESCENCE SPECTROSCOPY - M. Goldberg, USGS, P.O. Box 25046, MS 424, Denver Federal Center, Denver, CO 80225. (303) 234-6425
- ION CHROMATOGRAPHY - A. Hedley, USGS, 5293 Ward Rd., Arvada, CO 80002. (303) 234-3975
- MASS SPECTROSCOPY - M. Bergeron, Rockwell International, P.O. Box 464, Golden, CO 80401. (303) 497-4793
- NMR - F. Miknis, University of Wyoming Res. Corp., Box 3395, Laramie, WY 82071. (307) 721-2307
- SURFACE ANALYSIS - B. Phillips, Perkin-Elmer, 6509 Flying Cloud Dr., Eden Prairie, MN 55344. (612) 828-6411

If you are interested in receiving a pre-registration program with titles of papers and further conference information and/or if you wish to submit a paper or a poster, please return this form to Jan Gurnsey.

Name _____

Title _____

Organization _____

Address _____

City, State, Zip _____

Telephone ( ) _____

Type of presentation ☐ Paper ☐ Poster

- ☐ General Session
- ☐ Applications of Chromatography to Biology, Medicine and Biotechnology
- ☐ Atomic Spectroscopy
- ☐ Chromatography
- ☐ Computer Applications
- ☐ Electrochemistry
- ☐ Environmental
- ☐ EPR
- ☐ IR & Fluor. Spect.
- ☐ Ion Chromatography
- ☐ Mass Spectroscopy
- ☐ NMR
- ☐ Surface Analysis

Paper/Poster Title _____

305-51

Western Research Institute
P.O. Box 3395, University Station
Laramie, Wyoming 82071
307 721-2011

January 9, 1983

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

SUBJECT: NMR spectroscopist position

Dear Barry:

A position in NMR spectroscopy is available at the Western Research Institute (WRI). The minimum qualifications are a B.S. degree in Chemistry and/or Physics and knowledge in the operation of FT-NMR spectrometers. Preferred qualifications are a Masters degree and in depth knowledge of theoretical and practical NMR, and knowledge of multiple-pulse sequence experiments with analytical application to quantitative NMR. Some electronic experience as related to NMR instrumentation is also preferred.

The position function is to provide NMR services to the research staff at the Institute as well as develop and apply new NMR techniques to fossil fuel characterization.

Depending on qualifications, the position will be at the Technician IV or Scientist II level with a starting salary in the range of $20,000-$27,000, possibly more. We offer a competitive benefit program and relocation expense assistance may be provide. Opportunities also exist for advance degrees at the University of Wyoming.

Interested candidates should write to Mr. William VanLente, Manager of Personnel Services for the Institute. Include in the letter a complete résumé with references.

Sincerely,

Dan

Daniel A. Netzel, Manager
Spectroscopic Research and
Applications Division

EASTERN RESEARCH CENTER | Stauffer CHEMICALS | Stauffer Chemical Company
Dobbs Ferry, New York 10522 / Telephone (914) 693-1200

January 16, 1984

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

Dear Barry:

NMR Position Available

We have a challenging position available in the Analytical Department at the Eastern Research Center of Stauffer Chemical Company for a solids NMR spectroscopist. We currently have an XL-300, an EM-360 and a PE R600 high resolution NMR spectrometer and are planning the purchase of a solids spectrometer.

The successful applicant will have a Ph.D. in chemistry with good knowledge of and experience in the application of multinuclear solids NMR to the solution of challenging problems. The individual will be responsible for the evaluation, selection and acquisition of the solids system and the application of the technique to a wide range of problems in catalysis, materials science, polymers, biochemistry and inorganic and organic chemistry. The position requires good communication skills and the ability to work closely with a diverse group of technical people.

Stauffer Chemical Company is an equal opportunity employer, offers an excellent compensation package and opportunity for professional growth. Please reply, in confidence, to Mr. G. DeMunnik, Manager Administrative Services at this location, or directly to the undersigned.

Sincerely,

Dave Marr

D. H. Marr, Manager
Analytical Research

DHM/hc

305-53

CYANAMID

American Cyanamid Company
Stamford Research Laboratories
1937 West Main Street
P.O. Box 60
Stamford, Conn. 06904 – 0060
Tel. (203) 348-7331

January 13, 1984

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

Dear Dr. Shapiro:

Your assistance is requested in suggesting possible candidates for a job opening in our NMR laboratory.

We are seeking a person with at least a Ph.D. in NMR-related research. Extensive experience in the application of NMR to organic problems is essential, together with a strong background in organic chemistry. Experience with solid state NMR, nuclei other than C and H, and supercon instruments is desirable. The job involves organic problem-solving in support of discovery and research and development projects using one or more NMR instruments, including a supercon.

Our approach to problem-solving is interdisciplinary and the candidate should have a background in fields such as infrared, mass spectrometry, etc., to effectively interact with our specialists in those fields. Original research will also be expected.

If you know of suitable candidates who merit your favorable recommendation, please have them contact us.

Your cooperation is greatly appreciated.

Very truly yours,

F. Santacana
Manager, Spectroscopy and
Physical Chemistry
Scientific Services Dept.
Chemical Research Division

INDEPENDENCE MALL WEST PHILADELPHIA, PA. 19105, U.S.A. TELEPHONE (215) 592-3000
CABLE ADDRESS: ROHMHAAS TELEX 845-247

REPLY TO:
RESEARCH LABORATORIES
RING HOUSE, PA. 19477
(215) MI 3-0200
(215) CH 2-0400

ROHM AND HAAS COMPANY

January 17, 1984

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

Dear Professor Shapiro:

The Rohm and Haas Company, a leading multinational chemical company, has an opening for a PhD physical or analytical chemist at our corporate research headquarters located in Spring House, PA, an attractive suburb of Philadelphia. An NMR spectroscopist is needed in the spectroscopy group of our Analytical Research Department, which supports the entire research effort of the Rohm and Haas Company.

This position involves working with applications of NMR to a wide variety of systems, ranging from small molecules through polymers. Techniques now applied include 2-D NMR, multinuclear studies, relaxation studies, solids NMR, and other sophisticated methods in addition to standard techniques. The laboratory presently has Varian XL-100 and XL-200 NMR spectrometers, and a 400 MHz instrument is expected in the lab by mid-year. Previous experience with solids NMR would be a plus for this position.

The scientist will have a major responsibility for the instruments involved, but will not be limited to them. A full range of state-of-the-art analytical techniques are available which can be applied in conjunction with NMR to solve analytical problems requiring a broad approach. Time is also available for the development of new technology. In addition to technical skills, good communication and interpersonal skills are important for interaction with scientists in diverse areas of product and process research. Rohm and Haas offers an excellent salary and benefits program, including relocation assistance and high visibility in an active research environment conducive to professional advancement. Interested persons should send a detailed resume and references to:

Recruiting and Placement
Rohm and Haas Company
Independence Mall West
Philadelphia, PA 19105

Rohm and Haas Company is an equal opportunity employer.

Sincerely,

Edward C. Greer

Edward C. Greer

305-55

Varian / 611 Hansen Way / P.O. Box 10800 / Palo Alto / California 94303 / U.S.A.
Tel. (415) 493-4000
Telex 348476

varian

January 23, 1984

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

Dear Barry:

ADVANCED FT-NMR WORKSHOP, MAY 22-25, 1984

I'd like to bring the above workshop to the attention of your readers. It will be held in Rahway, New Jersey and is designed to cover the principles, techniques and applications of modern FT-NMR. Heavy emphasis will be placed on new experiments such as APT, INEPT, DEPT as well as two-dimensional homonuclear and heteronuclear experiments. Faculty include Stan Smith (University of Kentucky), Bob Santini (Purdue), Steve Patt (Varian Associates, Florham Park, NJ), Peter Rinaldi (recently joining Varian as Applications Scientist in Florham Park, NJ) and Jim Shoolery (Varian Associates, Palo Alto, CA). The program is given below. The workshop fee is $500 for four days. Interested parties can inquire by phone (408) 734-5370, ext. 406 or by mail to Varian NMR Workshop, Box D-070, Palo Alto, CA 94303.

See you at ENC,

George

George A. Gray
NMR Applications Laboratory
Varian Associates

GAG/by

1984 ADVANCED NMR WORKSHOP PROGRAM

● MAY 22-25, RAHWAY, NEW JERSEY

FIRST DAY

Interpretation of ^1H and ^{13}C NMR Spectra
Chemical shift trends and tables. Spin coupling patterns. Spectral assignment techniques. Examples of spectral interpretation as related to structure determination.

Principles of Pulsed Fourier Transform NMR
Behavior of the nuclear magnetism in a strong static magnetic field under the influence of a single radio frequency pulse. Detection of the resulting signals, analog-to-digital conversion, the sampling theorem, aliasing (or folding) quadrature detection, data processing.

Relaxation Times and Nuclear Overhauser Effects
Theory of spin-lattice and spin-spin relaxation. Typical relaxation times for protons and ^{13}C nuclei. Correlation of molecular motion with relaxation times. Measurement of relaxation times. Effect in multipulse experiments. Proton-proton NOE and applications. Proton-carbon NOE. Effect on quantitative NMR measurements and methods for improving quantitative accuracy.

Spin Coupling, Decoupling, and the Use of J-Modulation Spectral Editing
Proton-proton coupling constants, the Karplus equation, homonuclear decoupling. Proton-carbon coupling constants, direct J_{CH} and long-range $^3J_{CCH}$ and $^3J_{CCCH}$. Broadband decoupling, MLEV and WALTZ decoupling, selective decoupling, gated decoupling, off-resonance CW and noise-modulation decoupling, behavior of signal intensities as a function of time for various J values in the J-modulated APT experiment. Spectral editing and assignments. Coupled spectra.

SECOND DAY

Choosing Spectral Parameters
Multipulse experiments, data accumulation, effect of spin-lattice relaxation time, T_1, and the transverse relaxation time T_2, choice of acquisition time and pulse repetition rate, effect of pulse length or tip angle, the Ernst angle, spectral resolution and digital resolution, spectral width.

Applications of ^1H and ^{13}C NMR to Chemical Problems
Examples of the use of NMR measurements to solve a variety of chemical structure problems. General approach to problem-solving and choice of experimental techniques.

New Methods of Pulsed Excitation
Description of the elements of pulse sequences, their purpose, and behavior of nuclear magnetization during pulses and delays. Pulse imperfections and resulting problems and solutions. Effect of rf "phase" of pulses and detectors. Use of phase cycling in sequences. Refocussing pulses, composite pulses, the APT experiment.

NMR of Other Nuclei
Survey of active nuclei. Quadrupolar nuclei and the effect of quadrupole moment on the NMR signals. Examples of generally useful nuclei, their chemical shift ranges, relative sensitivities, relaxation behavior, spin coupling behavior, methods for observing.

THIRD DAY

NMR Data Processing
Exponential multiplication for resolution or sensitivity tradeoffs, use of apodization function, Gaussian, sine-bell and pseudo-echo processing, optimum Gaussian filtering, integer and floating-point processing, practical considerations, hardware and software requirements.

Polarization Transfer INEPT and DEPT
Principles of polarization transfer. Use of protons and special pulse sequences to transfer polarization to weak nuclei. Advantages and limitations of the techniques. Use in spectral editing.

Principles of Two-Dimensional NMR
General structure of all two-dimensional NMR experiments. Basic categories, such as J-resolved and shift correlation experiments. Data handling, such as Fourier transformation, matrix transposition, and the second Fourier transformation. Presentation and plotting of data. Practical considerations. Advantages and limitations of the techniques.

NMR of Solids
Dipolar broadening in solids, use of high-power decoupling, chemical shift anistropy and Magic Angle Spinning (MAS), Cross-Polarization (CP), spinning sidebands and methods for handling them, typical results and applications, advantages and limitations, hardware considerations. Considerations in choice of magnetic field strength.

FOURTH DAY

2-D Homonuclear Correlation Spectroscopy
Purpose of the experiment. Principle of operation. Types of data display. Stacked and contour plots. Use of color. Elimination of artifacts. Interpretation and application to practical problems involving analysis of proton-proton coupling patterns. COSY, NOESY.

2-D Homonuclear and Heteronuclear 2D-J Spectroscopy
Use for obtaining H-H coupling. Direct and long-range X-H couplings. Techniques for data processing and selective 2D-J versions.

Multiple Quantum 2-D NMR and Applications
Use of pulse sequences to generate zero or multiple quantum coherences. Use of such sequences to discriminate between various spin systems. The carbon-carbon connectivity experiment, CCC2D. Use of partial connectivity data with other NMR data to solve problems. Advantages and limitations, hardware and software requirements.

2-D Heteronuclear Correlation Spectroscopy
Correlation of chemical shifts of coupled nuclei. Direct and long-range correlations. Effects of the polarization transfer properties in choosing parameters. Advantages, limitations, and applications. RELAY. Hardware and software considerations. Deciding which experiment to use.

Structure Determination by ^1H and ^{13}C NMR
An assortment of structural problems solved by NMR to illustrate the foregoing methods.

305-57

Iowa State University of Science and Technology Ames, Iowa 50011

Department of Chemistry
Telephone: 515-294-6342

Jan. 18, 1984

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

Dear Professor Shapiro:

There is an immediate opening for the following position at the Iowa State University.

Instrumentation Specialist

Professional staff position for individual with experience in maintaining chemistry analytical instrumentations. This person will also be involved in maintenance and circuit design for various NMR spectrometers, FT-IR and GC/MS spectrometers. Experience in RF and digital electronics is desirable. Very competitive salary and fringe benefits.

Interested candidates should write to:

Tom Lyttle, Manager
Research Instrument Services
Department of Chemistry
Iowa State University
Ames, Iowa 50011

I.S.U. is an EO/AA employer.

Sincerely yours,

Dee-Hua Huang

WASHINGTON UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY

January 27, 1984

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

MAGNETIC RESONANCE SPECIALIST

Dear Barry:

The Department of Chemistry of Washington University is searching for a Ph.D. level scientist to manage its magnetic resonance facilities, the core instrument of which will be a 500 MHz spectrometer to be delivered in summer/fall of 1984. Responsibilities and salary will be competitive and will depend upon the experience and qualifications of the applicant.

The ideal candidate should have extensive "hands-on" experience in magnetic resonance, preferably solution-state high resolution proton and carbon NMR, as well as familiarity with spectrometer design, operation and maintenance. In addition to administrative aspects, this position will offer an excellent opportunity for the pursuit of both collaborative and individual research with state-of-the-art instrumentation. In addition to the 500 MHz spectrometer, relevant Departmental instrumentation includes Bruker WH 360 and CPX 200 NMR spectrometers, an IBM ESR spectrometer, FT IR and laser Raman spectrometers, and a VAX 11/780 computer. The Department has pending a proposal for a 300 MHz spectrometer which will be administered as part of the NMR Facility. Interested candidates should send a complete resume and have three letters of recommendation forwarded to: Professor William D. Phillips, Chairman, Department of Chemistry, Campus Box 1134, Washington University, St. Louis, Missouri 63130. Washington University is an equal opportunity affirmative action employer.

Sincerely,

William D. Phillips
Professor of Chemistry
and Department Chairman

/jm

305-59

DEPARTMENT OF BIOCHEMISTRY

THE UNIVERSITY OF ALBERTA
MEDICAL SCIENCES BUILDING
EDMONTON, CANADA T6G 2H7

PHONE: (403) 432- 5460

January 24, 2984

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

Dear Barry:

Re: Solvent Isotope Shift Referencing

We have been involved in the biosynthetic incorporation of fluoro-amino acids into proteins and their study using ^{19}F NMR (1). In particular, we have used the H_2O/D_2O solvent isotope shifts (SIS) of the ^{19}F NMR resonances of these amino acids to measure the "exposure" in the protein under various conditions. The question arises as to an appropriate reference for these ^{19}F chemical shift measurements. We have avoided external references because of susceptibility problems, and have in essence used the ^2H NMR resonance of D_2O/HDO (the lock) as a reference (2). Two assumptions are implicit in this procedure: 1. that we know the SIS for H_2O, and 2. that the ratio of ^1H and ^2H is constant as a function of the % H_2O so that we can calculate the SIS for the lock.

The SIS for H_2O has been determined by observing the ^1H NMR of H_2O and HDO in acetone (3). Holmes *et al.* (3) reported that HDO resonates upfield of H_2O by 0.030 ± 0.003 ppm. We have repeated this and get the same value (0.033) ppm.

Frait and Gemperle (4) measured the ratio γ_D/γ_H as a function of % H_2O and state a value of 0.153506076 ± 0.000000046. We have measured the ^1H NMR of H_2O/HDO as a function of % H_2O while locked on the ^2H NMR of HDO/D_2O, and find this to be constant to within ±0.5 Hz (0.0017 ppm). Given ν_H = 270,003,950 and ν_D = 41,447,250, this gives λ_D/λ_H = 0.153506087.

Best regards,

Heather

Heather D. Dettman

Brian

Brian D. Sykes

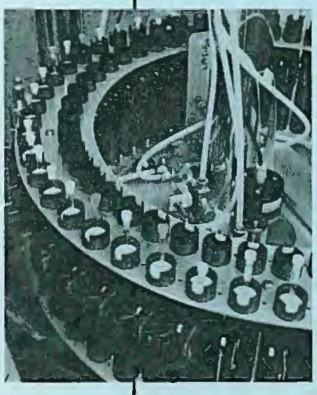
1. Biophys. J. 37: 243 (1982)
2. Biochem. 18: 2007 (1979)
3. J. Chem. Phys. 37: 150 (1962)
4. Czeck, J. Phys. B 22: 1259 (1972)

Find out how friendly and versatile NMR can be.

The QE-300 spectrometer was specifically developed for high efficiency, high-throughput carbon and hydrogen NMR. It provides a complete range of routine and high resolution capabilities with a 300 MHz (7 Telsa) superconducting magnet, synthesizer based frequency control, quadrature phase detection, high-speed pulse programming, and a dual $^{13}C/^{1}H$ switchable probe. To make operation dramatically simple, the QE-300 also features auto-locking, auto-shimming, and auto-spectral phasing plus an incredible menu driven software package called CHARM.

And now, to make the QE-300 even more versatile, we've added a number of accessories to make your work faster and more efficient than ever before.

Around-the-clock data acquisition and processing



First, there's the QE-300 Automatic Sample Changer for unattended, sequential analysis of up to 100 samples. It lets you collect spectra continuously—overnight and even over weekends. So, instead of facing a stack of samples when you walk into your lab in the morning, you have a stack of results, completely phased and annotated to your specifications.

Multiple megabyte speed and power

Winchester and other optional hard disk accessories for the QE-300 dramatically expand your data handling capacity. And to speed up Fourier Transforms and spectral phasing, you can add a high-powered array processor as well.

Remote data stations for multi-user productivity

Increased data requires more data processing capability. To meet that need, you can add a remote, interactive data station to the QE-300. It communicates directly with the QE-300 as well as other Nicolet 1280-based NMR spectrometers and enables you to process NMR data off-line while the main spectrometer is being used to acquire spectra.

VT capability for temperature dependent studies

A new microprocessor controlled Variable Temperature accessory for the QE-300 allows acquisition of experimental data at differing sample temperatures. The controller ranges from +160C to −100C with ±0.1C precision.

Enhanced ^{13}C sensitivity

An optional dual 10mm ^{13}C/5mm ^{1}H switchable probe increases ^{13}C sensitivity to more than three times that of the standard $^{13}C/^{1}H$ probe.

Broadband console electronics and X nucleus probes

Broadband console electronics and X nucleus probes for the QE-300 are offered for observing nuclei other than ^{13}C and ^{1}H, including a dual 5mm $^{31}P/^{1}H$ switchable probe for analyzing phosphorous in biological, medical, and related applications.

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The QE-300 with CHARM. Friendly, *versatile* NMR for the laboratory that has alot of work to do.

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GENERAL ELECTRIC

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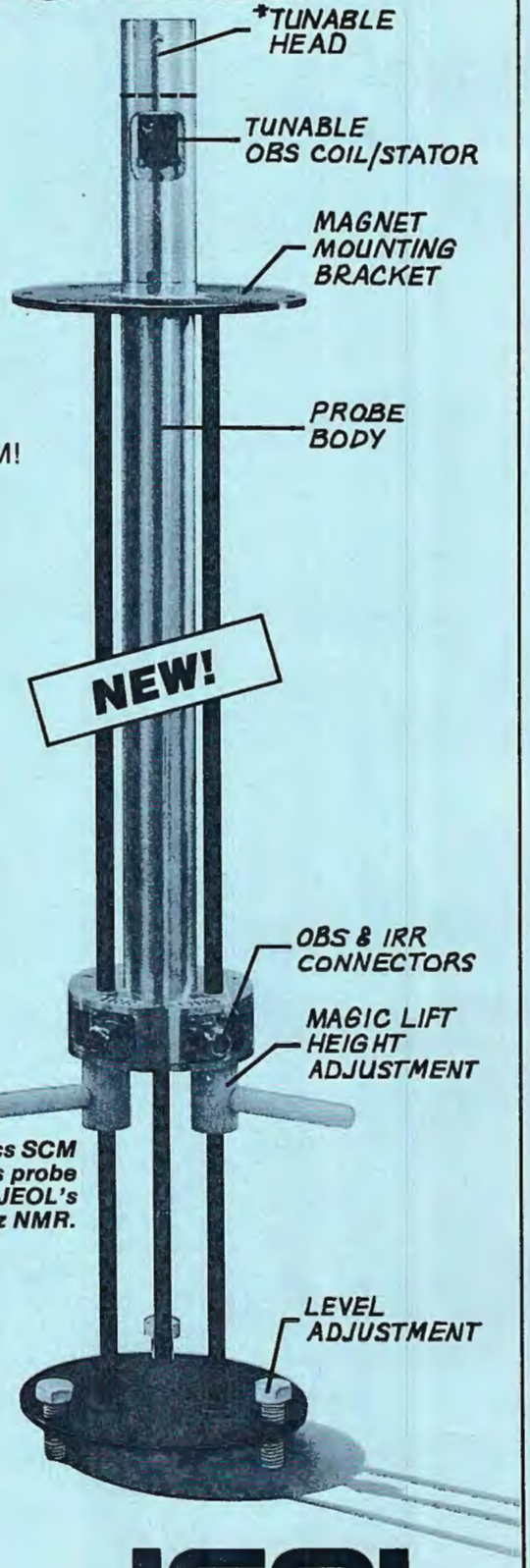

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- WIDE BORE MAGNET WITH VARIABLE TEMPERATURE SOLIDS FOR THE GX-270/89

JEOL

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