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NMR NEWSLETTER

NO. 302

NOVEMBER 1983

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College Station, Texas 77843 U.S.A.

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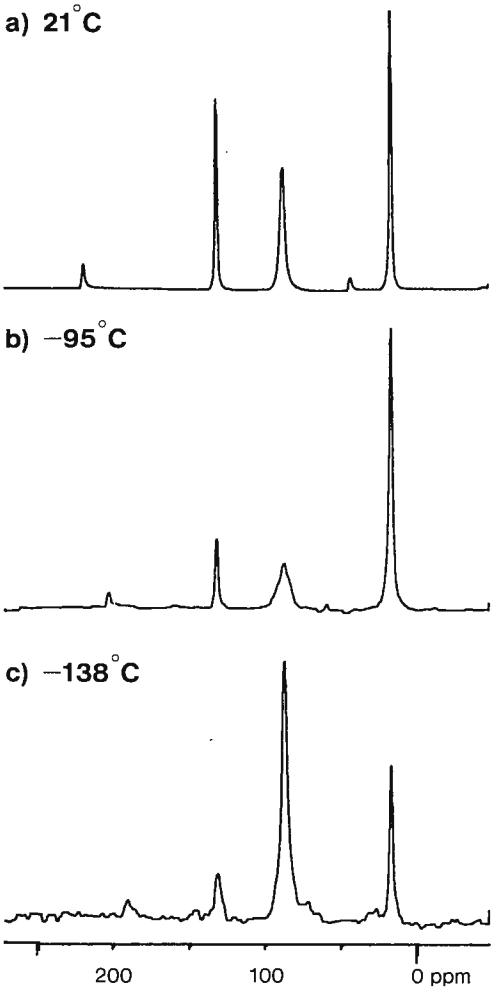
Variable Temperature CP-MAS with the GX Series FT NMR Spectrometers



^{13}C (50.1 MHz) VT/MAS spectra of hexamethylbenzene. a) and c) ^{1}H-^{13}C cross polarization. b) Bloch decay. The peak at ~ 90ppm is due to the Delrin rotor.

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2nd August 1983

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

Dear Professor Shapiro,

Two conformations of a protein at 500 MHz

In the course of our studies of drug binding to the enzyme dihydrofolate reductase we found two years ago that the complex of the enzyme with the inhibitor trimethoprim and the coenzyme $NADP^+$ exists in an equilibrium between the two conformational states (Gronenborn et al, Nature 290, 273, 1981; Molec. Pharmacol., 20, 145, 1981). One of the pieces of evidence for this was the observation that, at 270 MHz, the C2-proton resonances of two of the histidine residues were split into two peaks at low temperature which broadened and coalesced as the temperature was increased.

With the advent of a 500 MHz spectrometer at the MRC Biomedical NMR Centre here, we have taken another look at this complex. As shown in the Figure, the deconvoluted 500 MHz ^1H spectrum shows that in fact six of the seven histidine C2-proton signals are 'split', by amounts varying from 0.008 to 0.035 ppm. Only resonance C (from His 64) is unaffected. This striking instance of the increased information content of high-field spectra demonstrates that the difference in conformation between the two states is not localised to the active site region - two of the histidine residues affected are on the opposite side of the protein from the active site. We are now searching other regions of the 500 MHz ^1H spectrum for other 'split peaks' so that we can characterise the conformational difference in more detail.

Yours sincerely,

Barry Birdsall Jim Feeney Gordon Roberts

B. Birdsall J. Feeney G.C.K. Roberts

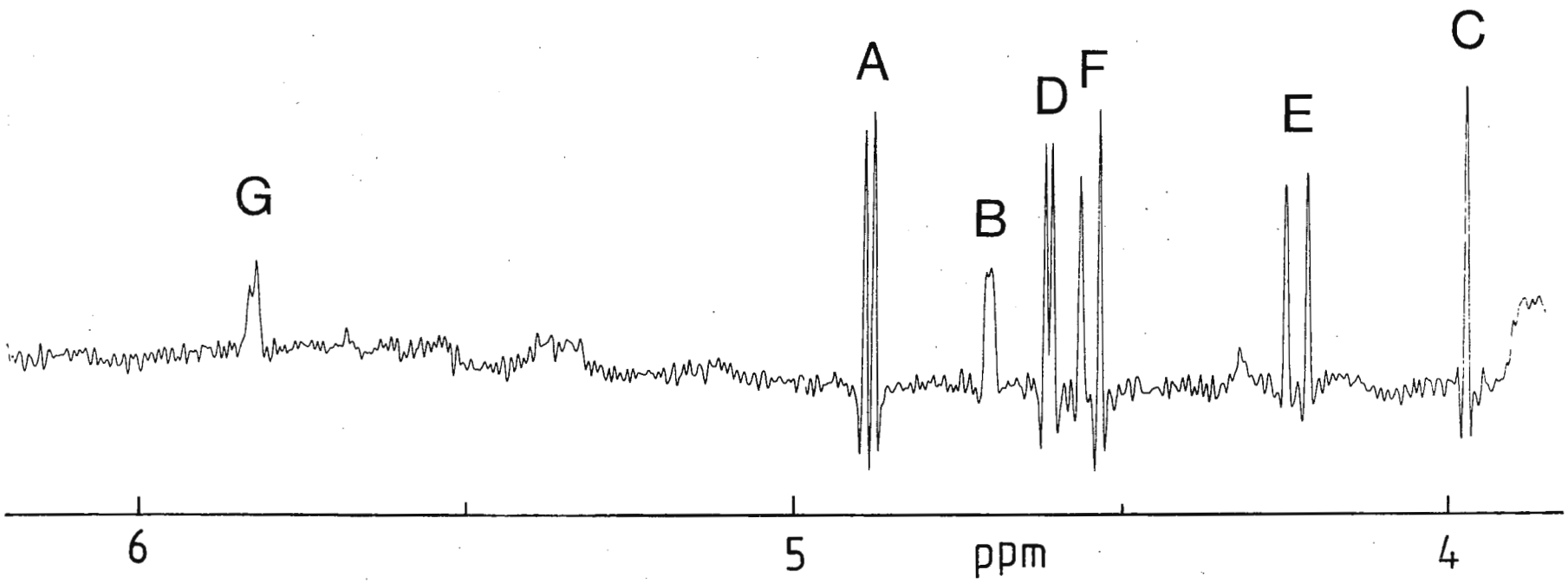

Figure . Part of the deconvoluted 500 MHz ^{1}H spectrum of the dihydrofolate reductase-trimethoprim-$NADP^{+}$ complex, showing the C2-proton resonances (labelled A-G) of the seven histidine residues. Deconvolution was by the Gaussian multiplication method. Chemical shift ppm from dioxan.

Prof. Dr. F.H. Köhler
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3109 Prof. Köhler

Prof. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77 843

Title: Variable Temperature NMR and thermal equilibrium in a CXP instrument

Dear Professor Shapiro,

an increasing number of colleagues interested in $J > 1/2$ nuclei perform solution NMR experiments with high power spectrometers such as the CXP series. This is only one field where broad resonances and a large shift range must be overcome. For several years now my group has the same problems in paramagnetic NMR. Clearly, for paramagnetic molecules a good deal of information comes from temperature dependent studies. Since the NMR spectral changes with temperature are very pronounced one runs into trouble if the measurements suffer from systematic errors. This led us to test the Bruker high power probe heads, and your readers might be interested in our findings.

For convenience of liquid sample handling saddle coils instead of solenoids are usually preferred. Originally Bruker placed the thermocouple in the dewar insert chamber where the gasflow enters. This leads to large temperature gradients between the probe and the thermocouple; now we have it just below the bottom of the NMR tube.

Fig. 1 shows a typical high temperature jump. The probe temperature was measured with a resistance thermometer which was placed in a NMR tube such that the active part was surrounded by toluene and situated just in the middle of the coil. The fat curve and scale of the Figs. refer to this temperature, the others to the temperature measured by the thermocouple of the B VT 1000 variable temperature unit. Among other things, Fig. 1 shows that a waiting time of 30 min is necessary for thermal equilibrium after a 10 to 15 °C step upwards. Also, a low temperature series cannot be startet soon after high temperature experiments (and vice versa) since the probe approaches room temperature only after 4 h (cf. Fig. 1). Additional cooling may save 1 h.

Fig. 2 shows that in a low temperature series run under computer control regulation problems occur near room temperature. This arises because the cooling gas flow is determind by the deepest temperature setting. Thus, computer control of the gas flow is desirable to shorten waiting times.

Please credit this letter to Prof. H.P. Fritz.

Yours sincerely

(Prof. Dr. F.H. Köhler) (Ren de Cao)

PS. Ren de Cao just returned to China before your reminder arrived. I hope you do not mind that his picturesque signature is missing.

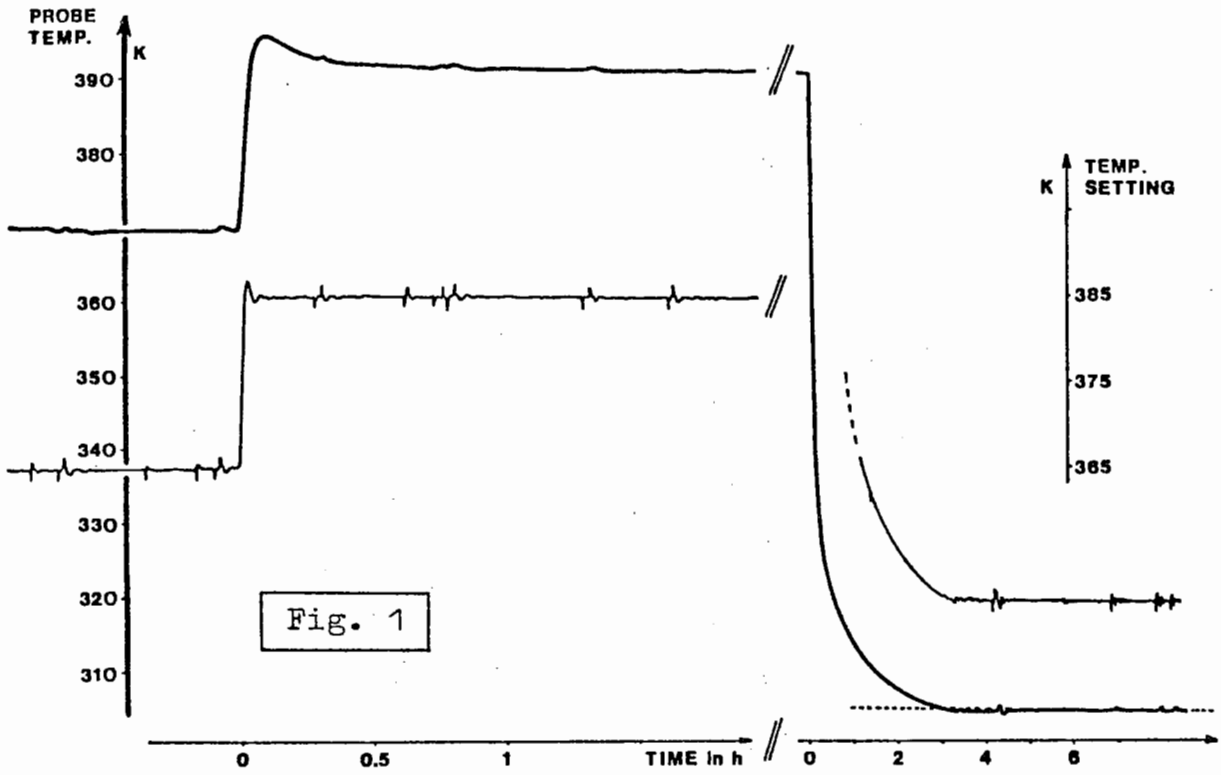
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Fig. 1

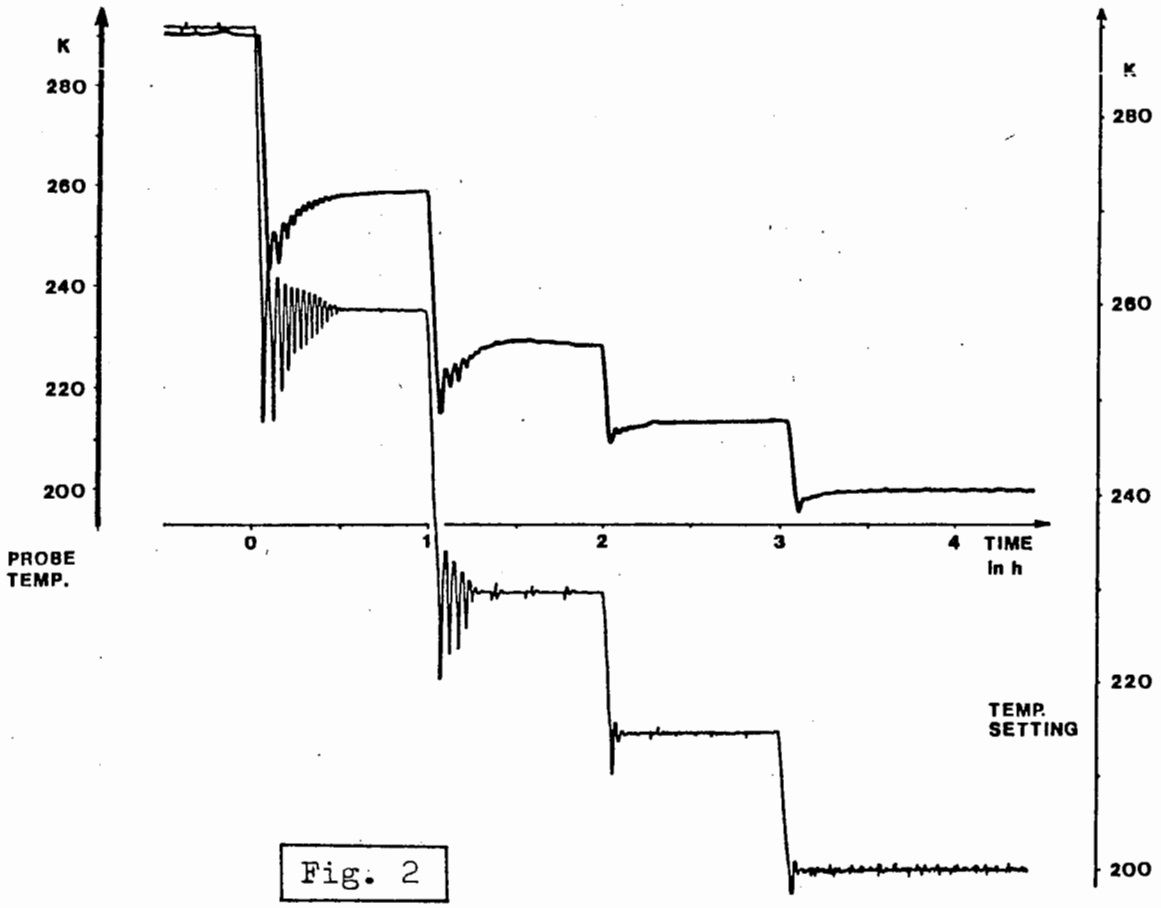
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Fig. 2

Shell Development Company
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Westhollow Research Center
P. O. Box 1380
Houston, Texas 77001

October 3, 1983

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

Dear Barry:

SUBJECT: INDUSTRIAL APPLICATIONS OF NMR IMAGING

In 1973 Lauterbur (1) demonstrated that the spatial distribution of hydrogen containing fluids in an object can be mapped using NMR. A decade of research has now passed, resulting in the successful development of a number of NMR imaging techniques for producing two and three dimensional in vivo images through the human body with unprecendented contrast and clarity. While the medical applications of this new imaging modality are difficult to overemphasize, we believe there are a number of important industrial applications for this technique as well. In 1982, Shell acquired a prototype NMR Imaging instrument from Bruker. The system is electromagnet based, operating at a resonant frequency of 35.7MHz for ^{1}H.

Figure 1 represents one of the first applications of NMR imaging to a polymeric system (2). In this study, the distribution of water absorbed in two glass fiber reinforced epoxy-resin composites was mapped. Both composites were based on a BPA epoxy resin; Composite A was cured with an aromatic amine while Composite B utilized an anhydride curing agent.

One inch diameter rods of Composite A and B were placed in a 93°C water bath for 70 and 90 days, respectively. Following this exposure, the two NMR images shown in Figure 1 were produced. The water distribution (unnormalized) is encoded on a 32 level gray scale; white represents regions of greatest water concentration in the sample. Both images clearly show a very nonuniform distribution of absorbed water. For Composite A, the water is preferentially positioned through the center of the rod (this sample contained a small shrinkage crack in the center of the rod), while for Composite B the water is preferentially distributed about the rod perimeter.

---

1) P. Lauterbur, Nature 242, 190(1973).
2) W. P. Rothwell, D. R. Holecek, and J. A. Kershaw, Submitted for Publication.

This example provides a simple, but effective, demonstration of one application of NMR imaging to polymer science. Within this context, the method provides a rapid, noninvasive means of mapping the macroscopic distribution of absorbed fluids. Since the technique is nondestructive, one may perform physical tests on a sample following measurement or, perhaps, even during measurement. Further, NMR relaxation maps of the absorbed fluids may be made, providing a means of distinguishing different absorption environments. Further applications of NMR imaging to polymer science will undoubtedly be forthcoming.

Please credit this to C. A. Reilly's account.

Yours truly,

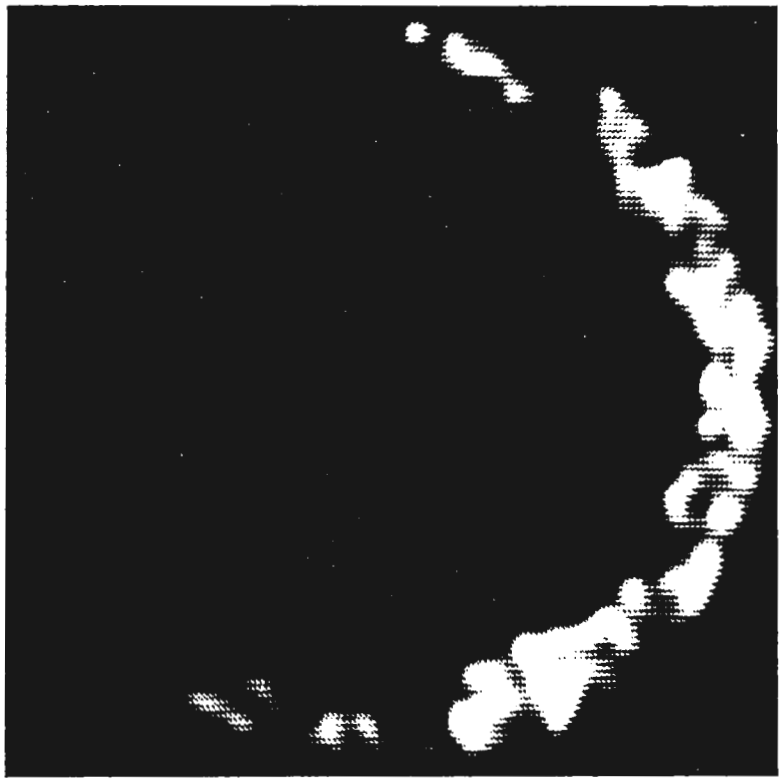
Bill

W. P. Rothwell
Research Chemist

WPR/pkm

Attachment

Composite A



Composite B

Figure 1. NMR Images Mapping the Concentration of Absorbed Water in Two Glass-Reinforced Epoxy Resin Composites
Rods were placed in a 93 C water bath for 70 days *(Composite A)* and 90 days *(Composite B)*.

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J.-E. DUBOIS, *Directeur*

Professor B.L. Shapiro
Department of Chemistry
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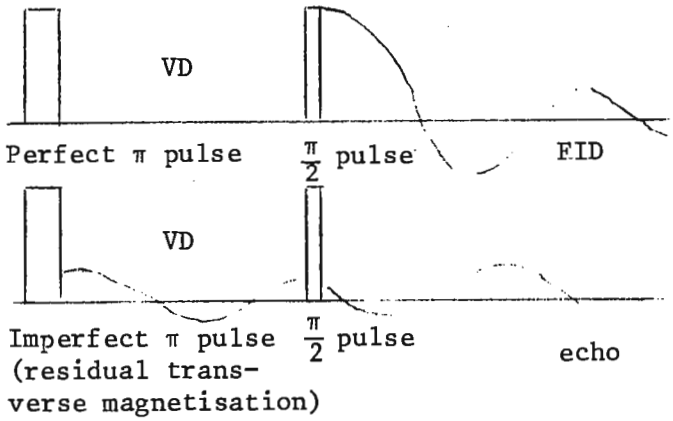
Dear Professor Shapiro,

Undoubtedly deuterium is a very interesting nucleus, notonly for the purpose of locking. Although it is a quadrupolar nucleus its relaxation times, $T_1 = T_2$, cannot be generally determined from linewidth, owing to the maquet inhomogeneity component. The Inversion-Recovery method can solve the problem, but it has been known for a long time that for short time delays between the inversion pulse and the measuring pulse, intensity anomalies occur, arising from echo formation. Phase alternation of the inversion pulse cancels these anomalies but this requires at least two accumulations. Unfortunately as reported some time ago (TAMU, 279, 38, 1981) a time-dependent magnetic field at the Jussieu Campus, Paris, precludes any unlocked accumulation on our WP 200. Thus, we recorded the recovery curve shown on Fig.1 (perdeuterated hexamethylenetetramine 0.1M in $CHCl_3$ at 243°K, $T_1 \simeq 0.04$ sec) modulated by the offset frequency of the deuterium line (71 Hz). Fig.2 shows the same phenomenon obtained with a 180° phase shift on the inversion pulse. Finally, a double accumulation with phase alternation (a skilful operation requiring complete decorrelation between pulses and subway trains) leads to the expected exponential recovery curve (Fig.3). We call this phenomenon EMIR (Echo Modulated Inversion Recovery).

Sincerely yours,

B. Tiffon

The actual phenomenon can be split in the following way :



ν = frequency offset

if VD = $n \times \frac{1}{\nu}$
echo and FID are in phase

if VD = $(n + \frac{1}{2}) \frac{1}{\nu}$
echo and FID are out-of-phase

Echo Modulated Inversion Recovery

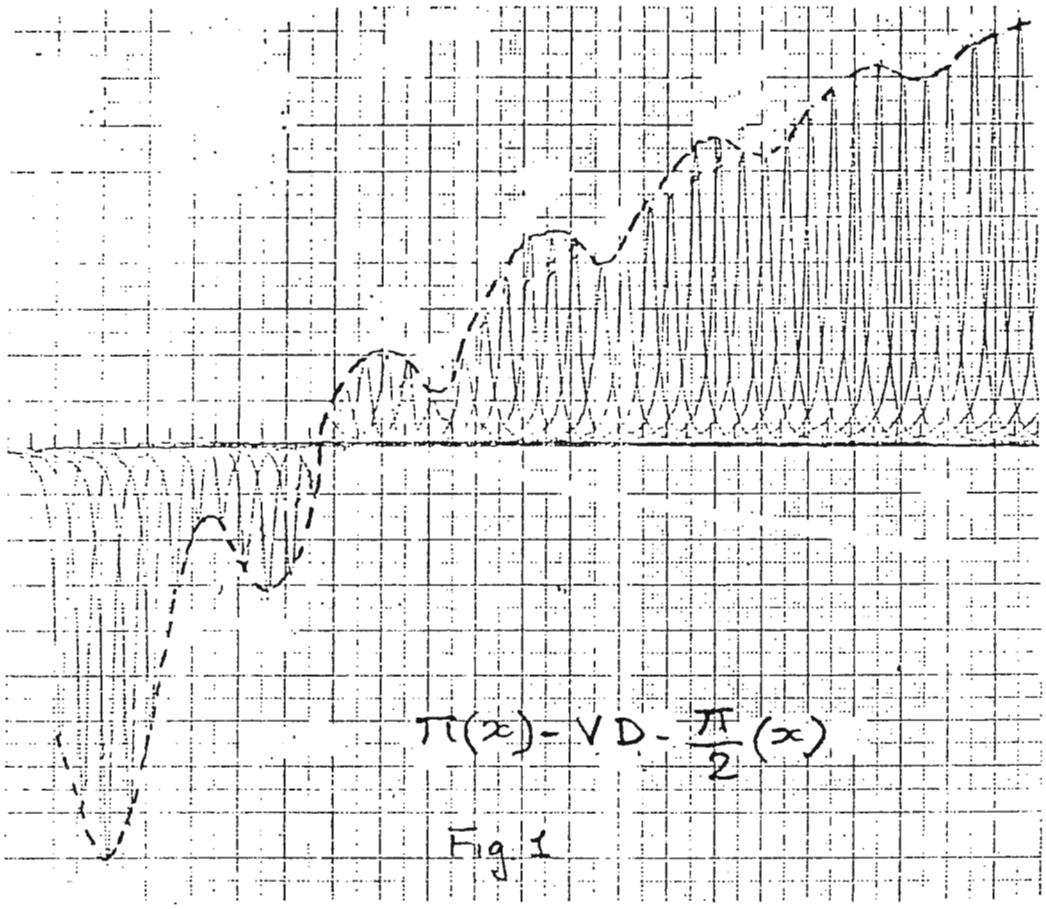


Fig 1

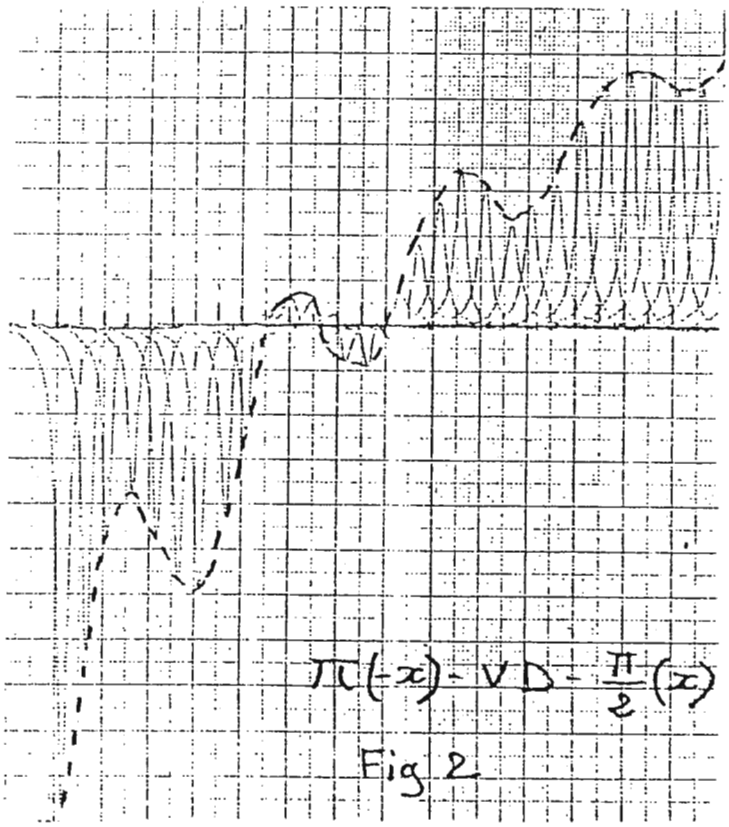


Fig 2

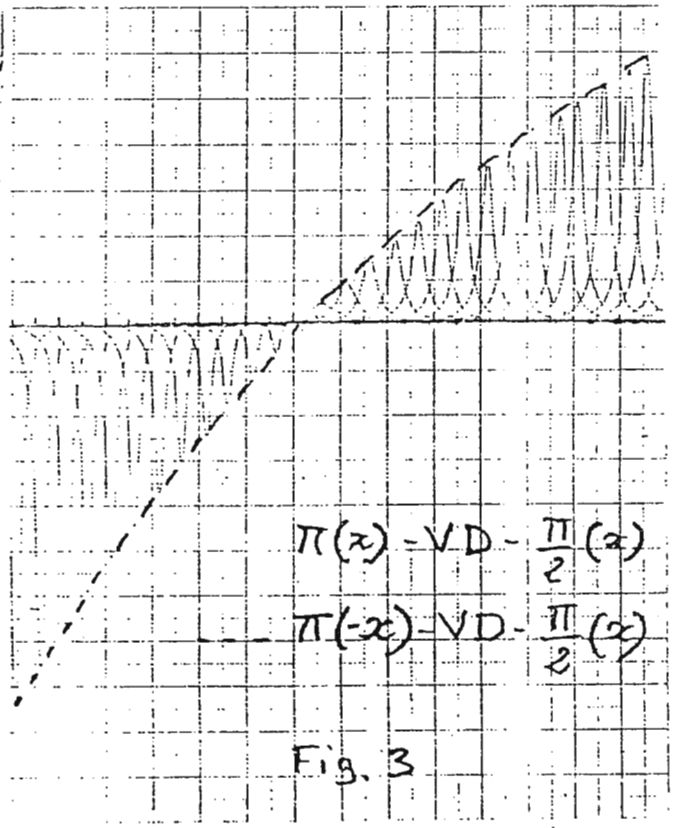


Fig. 3

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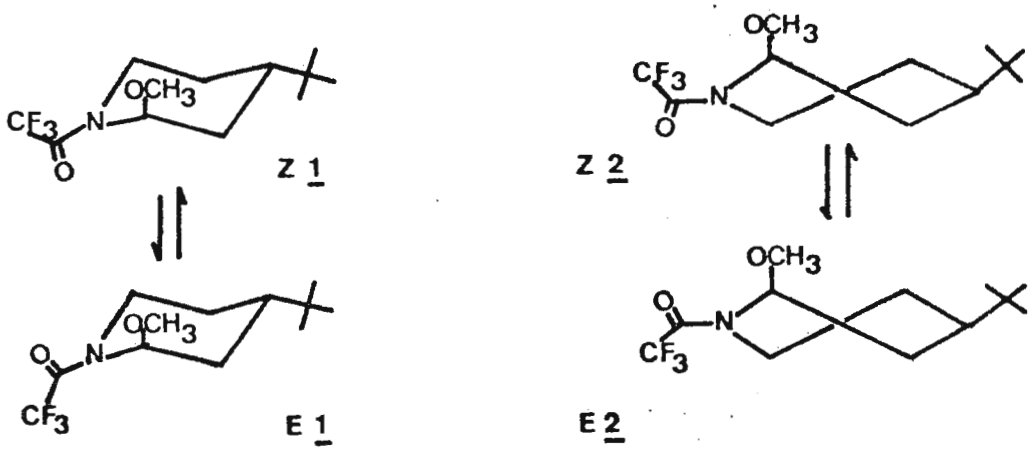
Prof. B.L. SHAPIRO
Dept. of Chemistry
Texas A & M University
College Station TX 77843
U. S. A.

Dear Barry,

Recently, we have measured the rotation barrier around the amide bond in trans-(1) and cis-N-trifluoroacetyl-2-methoxy-4t.butylpiperidine (2) with ^{13}C NMR. The Z/E ratio for these two compounds are 64:36 (r.t.) for the trans (1) and 79:21 (-20°C) for the cis isomer (2).



Because of the difference in energy between the Z and the E rotamer, we have used the method of H. Shanan-Atidi and K.H. Bar-Eli (1970)[1] for obtaining the free energy of rotation. An advantage of this method is that no time consuming detailed line-shape analysis is required. We needed only the measured values of T_c and $\delta\nu$ in order to calculate the rotational barrier. The value of log $[X/2\eta(1 \pm \Delta P)]$ can be deduced from a graph[1] for any particular value of ΔP.

Results are for a) trans-N-trifluoroacetyl-2-methoxy-4-t.butylpiperidine (1): T_c = 358°K ; $\delta\nu$ = 35.4 Hz ; ΔP = 0.28 solvent $Cl_2CH\text{-}CHCl_2$, giving $\Delta G^{\neq}_{358(Z\rightarrow E)}$ = 18.5 kcal/mol and $\Delta G^{\neq}_{358(E\rightarrow Z)}$ = 18.0 kcal/mol.

and b) cis-N-trifluoroacetyl-2-methoxy-4-t.butylpiperidine (2): T_c = 291°K ; $\delta\nu$ = 33.0 Hz ; ΔP = 0.58 ; solvent $CDCl_3$, giving $\Delta G^{\neq}_{291(Z\rightarrow E)}$ = 15.3 kcal/mol and $\Delta G^{\neq}_{291(E\rightarrow Z)}$ = 14.6 kcal/mol.

One can state that whereas the ground state of the trans isomer will be close to a chair conformation, the cis isomer however must possess pronounced twist-boat character. We therefore assume that the differences in free energy of rotation (resp. 3.1 kcal for the Z rotamer and 3.5 kcal for the E rotamer) represent roughly the differences between the chair and TB conformation of these two N-trifluoroacetyl-2-methoxy-4-t.butylpiperidines.

Reference :

(1) H. Shanan-Atidi and K.H. Bar-Eli, J. Phys. Chem. 74, 961-963 (1970).

Prof. M. Anteunis.

F. Borremans.

D. Duquet.

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Dear Professor Shapiro

SPI vs. SELECTIVE DECOUPLING

We have been busy the last couple of months to familiarise ourselves with the capabilities and new possibilities of our new Bruker WM500 n.m.r. spectrometer. After about a year we are very pleased and satisfied with the trouble free operation of our newest addition.

One of the first problems we looked into was the structure elucidation of Phomopsin A ($C_{36}H_{45}ClN_6O_{12}$), a mycotoxin isolated from Phomopsin leptostromiformis. ^{13}C n.m.r. spectroscopy and amino acid analysis indicated that this compound is basically a cyclic peptide. From 500 MHz ^{1}H n.m.r. spectra the different amino acid structural units could be recognised.

In order to deduce the amino acid sequence the couplings existing between the amide hydrogen and the carbon atoms, especially the carboxyl carbon atoms, must somehow be detected. We first try the established method[1] of selective decoupling of the different amide protons while observing the 125 MHz ^{13}C n.m.r. spectra in the difference mode. We could not detect any change in the ^{13}C resonances. ^{13}C-{^{1}H} SPI experiments, however, supplied us with the required information. The 125 MHz ^{13}C n.m.r. spectra (difference mode[2]) from two such SPI experiments are shown in Fig. 1. The structure of Phomopsin A, with all the ^{13}C-{^{1}H} SPI experiments performed and the detected effects, are depicted in Fig. 2.

Yours sincerely

P.L. WESSELS
SENIOR CHIEF RESEARCH OFFICER

1. M.A. Khaled and D.W. Urry, J. Chem. Soc., Chem. Comm., 1981, 230.

2. A.A. Chalmers, K.G.R. Pachler and P.L. Wessels, J. Magn. Reson., 15, 415 (1974).

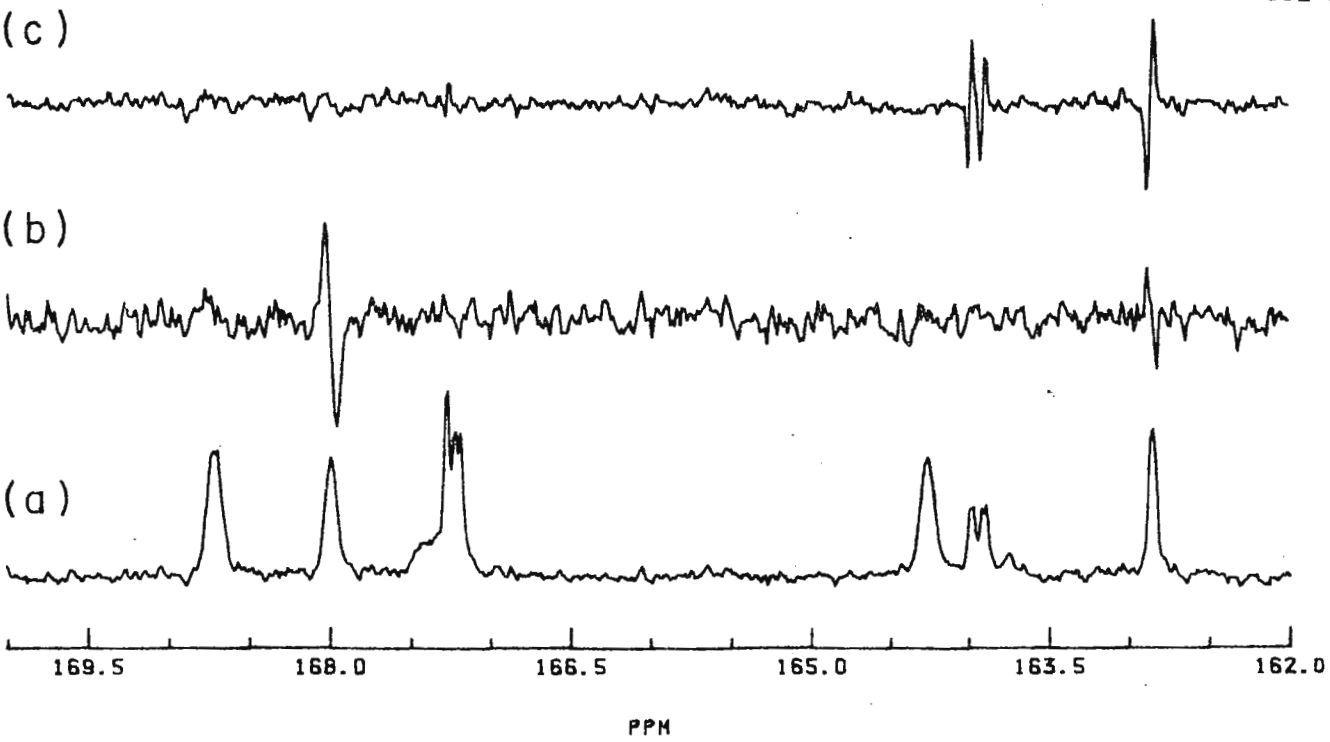


Figure 1 : The low field part of the 125 MHz ^{13}C N.m.r. spectrum of phomopsin A.

(a) Single frequency n.O.e. spectrum.

(b) After a selective π-pulse was applied to a low-field transition of the proton at δ_H 9.59 ($\not\pi H_2$ = 5 Hz)

(c) After a selective π-pulse was applied to a high-field transition of the proton at δ_H 9.32 ($\not\pi H_2$ = 5 Hz)

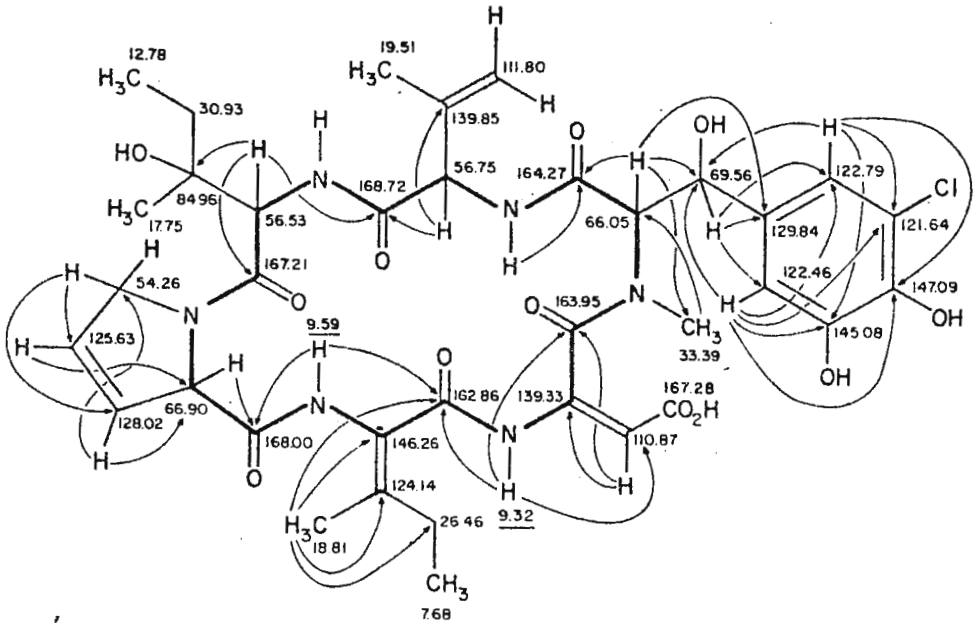


Figure 2 : The structure and ^{13}C N.m.r. data for phomopsin A. The (^{13}C, ^{1}H) connectivity pattern as indicated by arrows was determined by ^{13}C-{^{1}H} SPI experiments

302-15 **CSIRO**

Division of Applied Organic Chemistry
506 Lorimer Street, Fishermens Bend, Victoria.

A Division of the Institute of Industrial Technology

G.P.O. Box 4331, Melbourne, Vic. 3001, Australia.
Telephone (03) 64 0251
Cables and Telex AA 33951

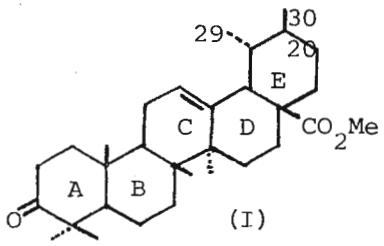
7th October, 1983.

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

SIMPLIFICATION OF ^{1}H SECOND-ORDER NMR SIGNALS
BY ^{13}C-^{1}H CHEMICAL SHIFT CORRELATED 2-D SPECTRA

Dear Professor Shapiro,

We have recently used ^{1}H nmr to assign the structure of a new triterpene from Lantana tiliaefolia. The signals from secondary methyl groups on ring E provide a most useful indicator of the presence of an urs-12-ene skeleton (I). In earlier studies at 60MHz the distorted appearence of both the 29Me and 30Me signals was ascribed to "second-order perturbation effects".



(I)

In the 250MHz spectrum of methyl ursonate (I) it can be seen, Fig.1a, that the signal from 29Me is an uncomplicated doublet (δ 0.86, J 7.3Hz) while the signal from 30Me is more complex. This complexity stems from the close proximity in proton chemical shift of the 30Me group and the C20 proton to which it is strongly coupled. The chemical shifts of 30Me(0.94) and C20-H(1.01) have been obtained from a ^{13}C-^{1}H chemical shift correlated 2-D spectrum (Fig,2) from the known ^{13}C chemical shifts of C30(21.2) and C20(38.9). The computer simulated ^{1}H spectrum in Fig.1b confirms this assignment.

More interestingly, however, the cross-sectional plot in the 2-D spectrum through C30 shows a first-order proton-proton coupling (7.2Hz) for the 30Me proton signal similar in size and resolution to that in the cross-sectional plot through C29 (Fig.3). Whereas overlap of the C20$\underline{H}$,30 $^{12}C\underline{H}_3$ multiplets in the 1-D spectrum leads to a highly second-order spectrum, the large ^{13}C-^{1}H coupling of 130Hz separates the C20$\underline{H}$,30 $^{13}C\underline{H}_3$ signals in the correlated 2-D spectrum and gives the first-order splitting. Of course, the converse effect could be observed in the spectra of other coupled systems.

Please credit this contribution to the account of Dr. D.P. Kelly, University of Melbourne.

Yours sincerely,

S.R. Johns R.I. Willing

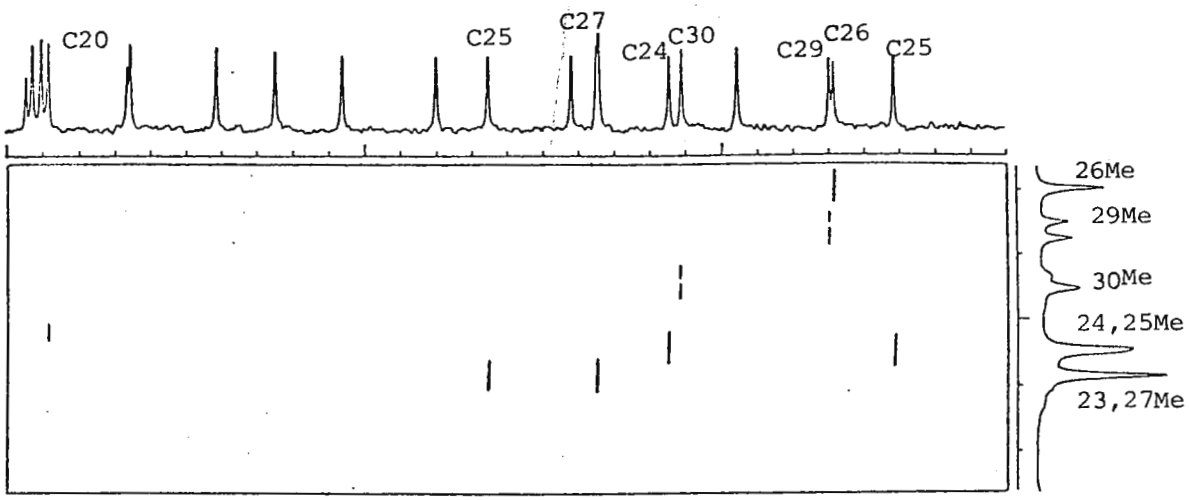


Fig.2: Contour Plot of ^{13}C-^{1}H Chemical Shift Correlated 2-D nmr of (I) showing ^{13}C range 12-40 ppm and ^{1}H range 0.8-1.2 ppm.

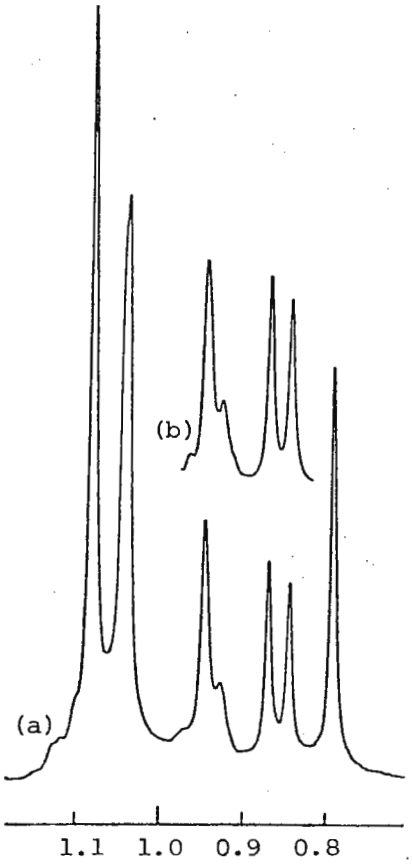


Fig.1a; Methyl region of 250MHz ^{1}H nmr spectrum of (I)
b: Computer simulated spectrum of 30Me and 29Me signals ($\Delta\nu_{20,30}$ 15Hz)

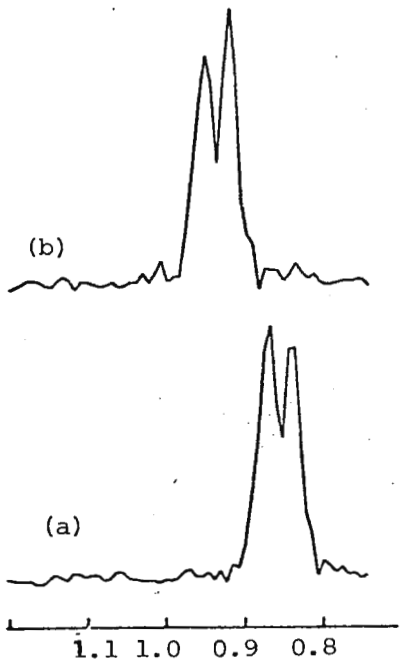


Fig.3: Cross-sectional Plots of correlated spectrum through (a) C29 (b) C30.

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Department of
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St. Catharines,
Ontario L2S 3A1
Canada

October 4, 1983.

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

Fe^{2+} Effects in ^{29}Si Magic Angle Spinning NMR

Dear Barry,

Magic-angle-spinning ^{29}Si nmr[1] has been applied to various silicate minerals, and very high magnetic fields greatly increase the sensitivity and make possible the rapid and routine collection of ^{29}Si MAS nmr data.[2] This technique may, therefore, have the potential for becoming a standard analytical method for the mineralogist. However, a major problem with natural minerals is the widespread occurrence of paramagnetic impurities, Fe^{2+} and Fe^{3+} being the most common.

We have been using our limited instrument time on the South Western Ontario NMR Centre's Bruker WH-400 to carry out ^{29}Si MAS nmr studies on various natural minerals, in order to explore how helpful the technique is likely to be to geologists. We quickly found that samples with high iron content give no detectable signal, and that samples with lower iron content give large spinning sidebands; typical spectra are shown. Similar results have been reported by Oldfield and co-workers[3] and by Grimmer.[4]

In collaboration with Mike Bancroft of the University of Western Ontario, we have studied pyroxene samples for which Fe^{2+} and Fe^{3+} concentrations have been determined by Mössbauer spectroscopy: the best technique for distinguishing the iron

oxidation states in minerals. Pyroxenes are chain silicates in which a variety of cations bond the chains of SiO_4 tetrahedra together. While a plot of total iron content against peak width gives a very poor correlation, a plot of Fe^{2+} content alone against peak width gives a straight line with a correlation coefficient of 0.98 for a series of omphacite and diopside pyroxenes. Fe^{2+} gives enormous line broadening, and the effects of Fe^{3+} are negligible in comparison. These results seem consistent with some of our results on feldspars where resolution seemed unaffected by traces of Fe^{3+}. There is no inherent reason why Fe^{2+} and Fe^{3+} (d^6 and d^5 ions, respectively) should have similar effects.

Brock University's chemistry department has at last, after 18 years, abandoned "temporary" quarters. Perhaps the move to our new building can serve as an excuse for not replying before now to your multicoloured reminders. Last week our two nmr instruments (Bruker WP-60, 1974 vintage, and recent Bruker WP-80CW) were moved, with some fear and trepidation. Within a day of the move the WP-80 was operating and up to spec, but a pump in the distilled water circulation unit of the WP-60 did not survive. This seems to be the only damage (we hope!).

With best wishes,

Yours sincerely,

Steve Hartman Barbara L. Williams

J. S. Hartman,
Professor of Chemistry,

Barbara L. Williams,
Graduate Student,
Department of Geological Sciences.

References

1. E. Lippmaa, M. Mägi, A. Samoson, G. Engelhardt and A.-R. Grimmer, J. Am. Chem. Soc. 102, 4889 (1980).

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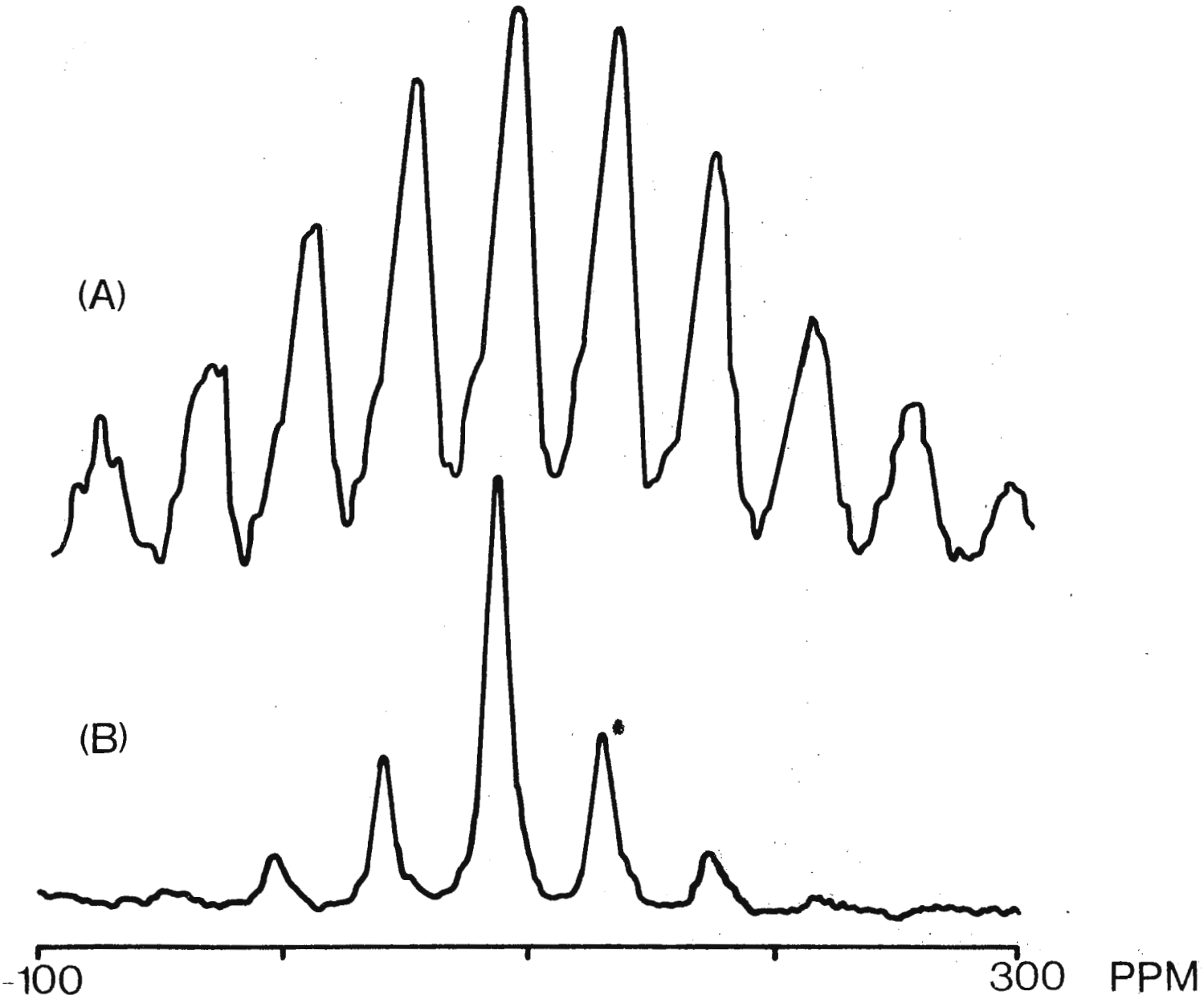
3. E. Oldfield, R. A. Kinsey, K. A. Smith, J. A. Nichols and R. J. Kirkpatrick, J. Mag. Res. 51, 325 (1983).

4. A.-R. Grimmer, private communication.



79.46 MHz ^{29}Si MAS nmr spectra of diopsides with (A) 0.08 and (B) 0.012 Fe^{2+} atomic proportions to six oxygens in $Ca(Mg,Fe^{2+})(Si_2O_6)$.

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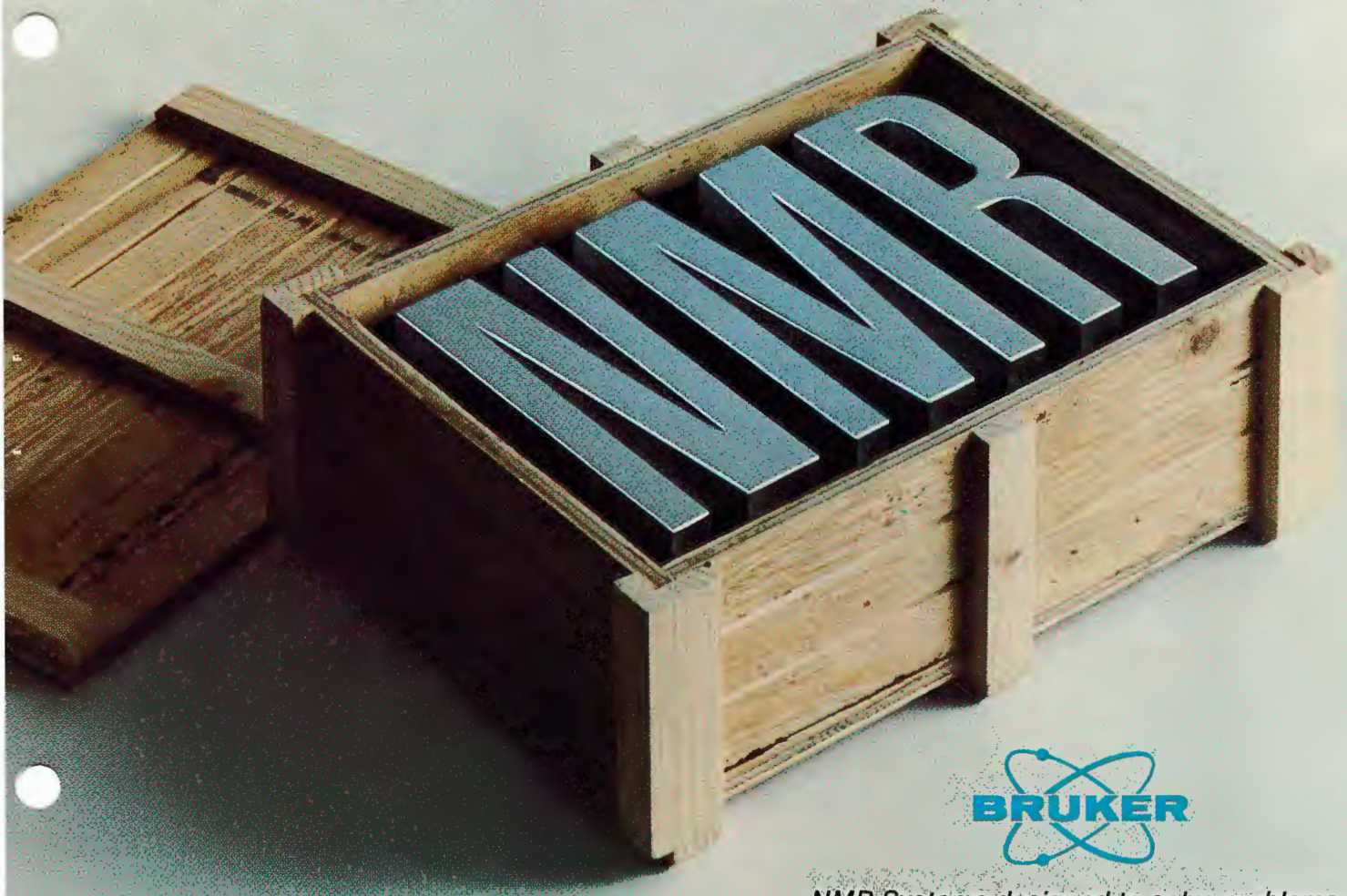

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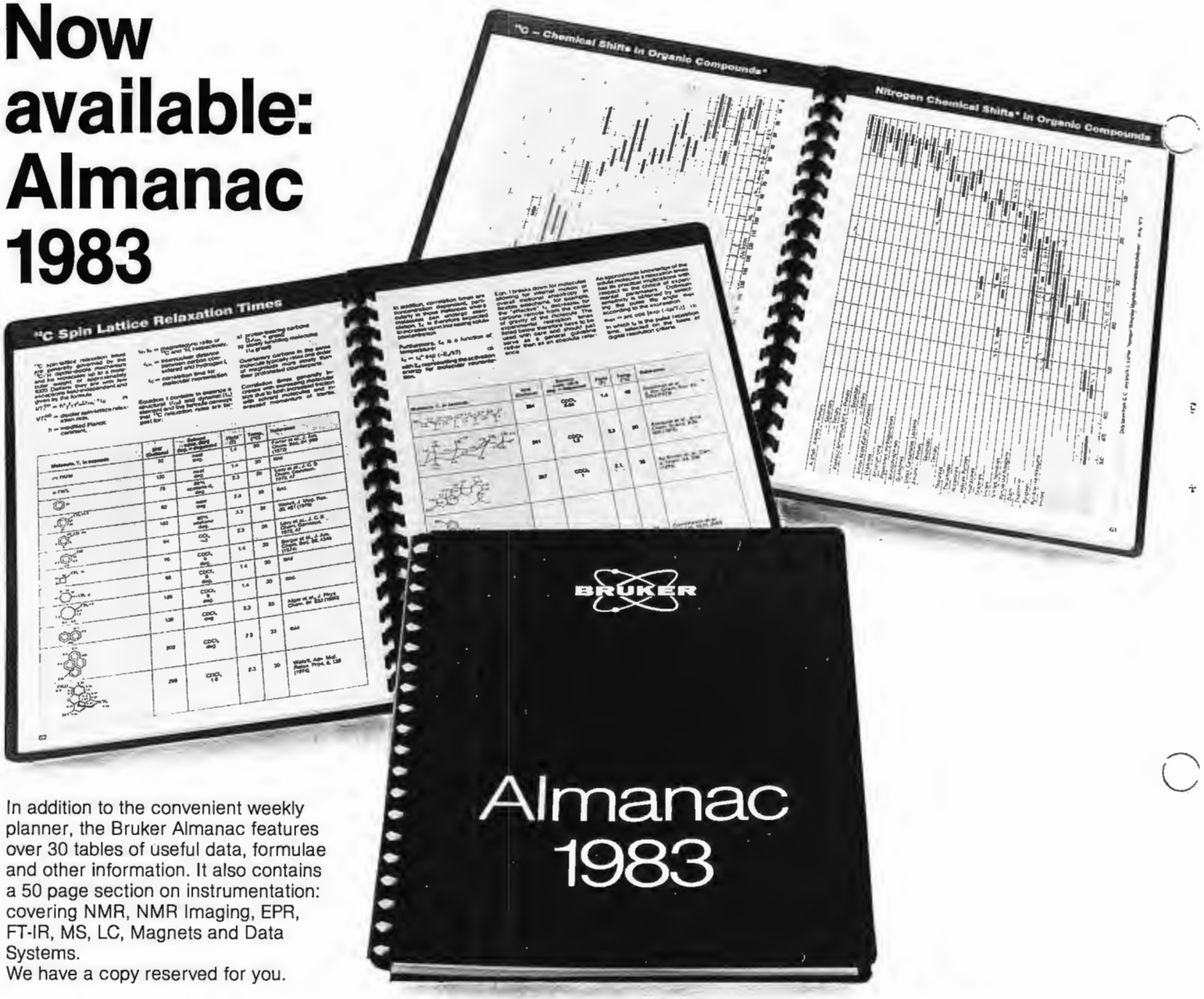

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CHAIRMAN OF DEPARTMENT PROFESSOR R.D. BROWN
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ORGANIC CHEMISTRY PROFESSOR W.R. JACKSON

Wednesday 5 October, 1983

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

$^4J_{FF}$ in o-fluorobenzyl fluorides

Dear Barry

We have been interested for some time in $^4J_{FF}$ in what used to be called o-fluorobenzyl fluorides. The original work with CF_3 groups was done by Gutowsky and Jonas who showed that this coupling died away quickly as the dihedral angle went from zero to 180°, i.e. as the distance between the two fluorines increased.

We find the same kind of dependence of the fragment coupling upon geometry but the absolute magnitude of J is smaller when the sp^3 carbon has fewer fluorines on it. Unfortunately we could not measure signs. The curves below show the scale of things. The value for the etheno-naphthalene was important in fixing the position of the lowest curve.

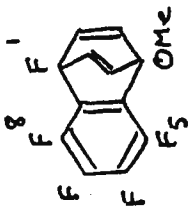
Our new Bruker AM300 arrives next month and should be settled down in time for a multinuclear Christmas.

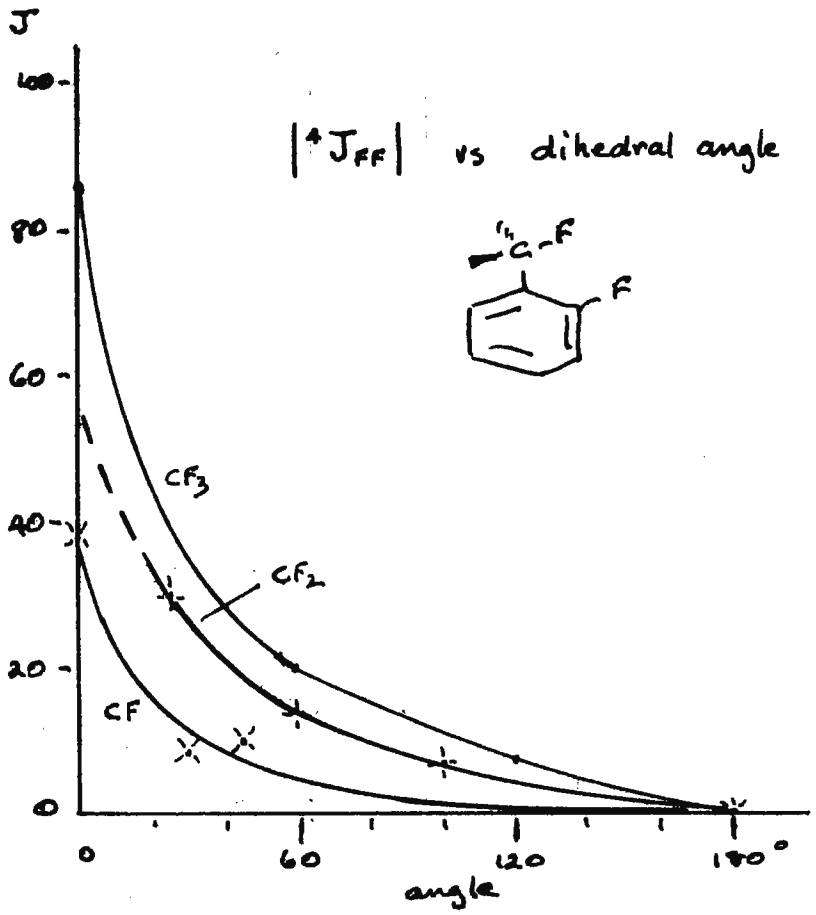
Kind regards

Ian

Ian D. Rae

$J_{1,8}$ = 37.7 Hz $J_{1,5}$ = 4.6 Hz





UNIVERSITÉ RENÉ DESCARTES (PARIS V)

U E R DES SCIENCES PHARMACEUTIQUES ET BIOLOGIQUES

DÉPARTEMENT DE CHIMIE ORGANIQUE
ERA 613 DU CNRS
SCN 21 DE L'INSERM
PROFESSEUR B. P. ROQUES

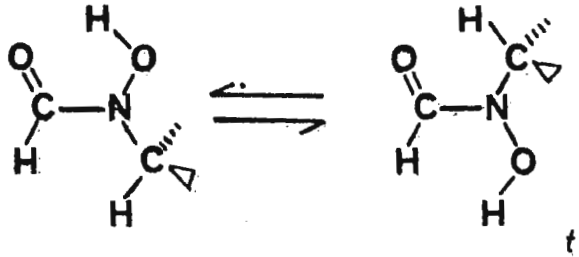
PARIS, LE October 11th, 1983.

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

Dear Professor Shapiro,

Unambiguous assignment of Z and E configurations in hydroxamic acid group.

A partial carbon nitrogen double bond character occurs in hydroxamic acid group as in amide. Rotation about this N-hydroxyamide bond is restricted ($\Delta G^{\neq} \sim$ 16 kcal mole^{-1}). At room temperature ^{1}H NMR spectra of N-formyl, N-hydroxyaminoacid (1) or related peptide (figure 1) show double signals for formyl and H_α protons.



cis (Z) *trans* (E)

Assignment of these signals to isomers with *cis* (Z) and *trans* (E) configurations was proposed using aromatic solvent induced shift (2) or carbonyl anisotropic effects (1). However neither of these technics was unambiguous. Indeed, anisotropic effects of an amide carbonyl group may be, in some cases, opposite to that observed for formyl of ketone groups (3).

Therefore, in order to propose an unambiguous interpretation of this equilibrium we performed a $\{^1H\text{-}^1H\}$ NOE experiment on N-formyl-N-hydroxy-phenylalanylglycine, a compound synthetized in our laboratory.

In *cis* (Z) conformation the spatial proximity between CHO and H_α is expected to produce a NOE enhancement, while in the *trans* (E) form these protons are too far from each others to lead such an effect.

The peptide was dissolved in $(CD_3)_2CO$ and the NOE's measured at 223°K since at room temperature, complete saturation transfert occured.

An enhancement (10%) was obtained on H_{2A} by irradiation of H_{1A}. Conversely, irradiation of H_{2A} led to 13% NOE on H_{1A}. No effect was observed by irradiation of H_{1B} nor H_{2B} (Figure 2).

The unambiguous assignment of Z and E forms in the studied compound agrees with previous studies (1,2), but it can be observed that in the present case the anisotropic effect of the CO group, at the level of the H_α proton, is inverse to that observed in N-alkyl formamid.

Yours sincerely.

B.P. Roques J. Belleney M.C. Fournie-Zaluski

1. T. Kolasa, Tetrahedron 39, 1753-1759 (1983).
2. W. Walter and E. Schaumann, Liebigs Ann. Chem. 743, 154-166 (1971).
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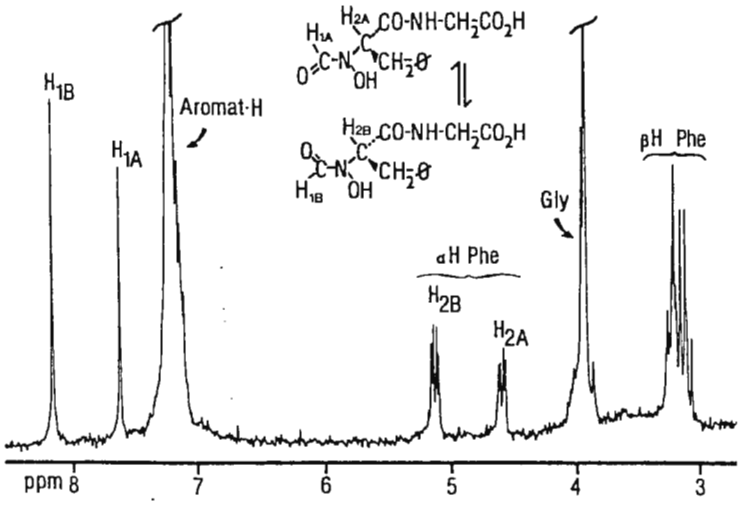


Figure 1. 270 MHz ^{1}H NMR spectrum of N-formyl-N-hydroxy-phenyl-alanyl glycine in $(CD_3)_2CO$ at room temperature.

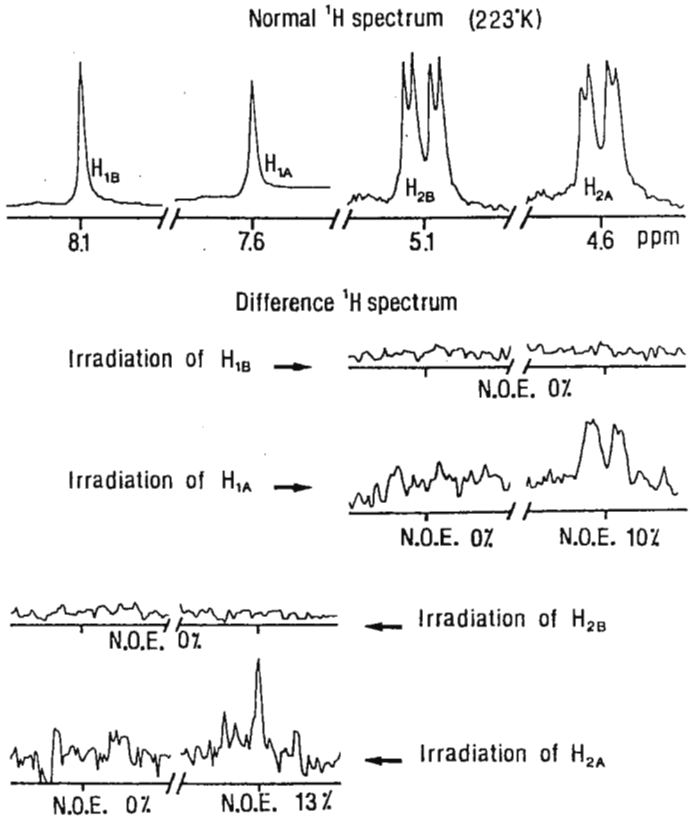


Figure 2. ^{1}H NMR spectrum of N-formyl N-hydroxyphenylalanyl glycine at 223°K and NOE experiments.

University of Cincinnati

Cincinnati, Ohio 45221
(513) 475-2263

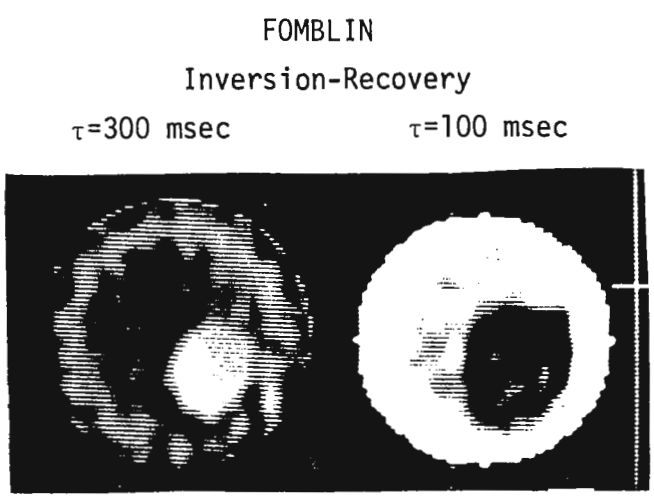
DEPARTMENT OF CHEMISTRY

October 12, 1983

Postdoctoral Position: Fluorochemical NMR Imaging

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

Dear Barry:



The image at the left illustrates (to the extent it survived the reproduction process) an example of the neat things one can do with fluorocarbons. The entire field of view is a T_1-weighted image obtained on one of the ^{19}F resonances in Fomblin-YO1, a complex perfluorinated polyether. The small round object in the lower right differs from the rest in having a higher oxygen partial pressure than that of the surroundings. Because we observe fluorine, the method has high intrinsic NMR sensitivity. The high solubility of O_2 (a paramagnetic molecule) in the fluorocarbon gives rise to excellent image contrast to noise ratio for pO_2's in the physiological range.

We have an immediate opening for a postdoctoral student to work on this NIH-funded project devoted to the development and applications of ^{19}F NMR imaging of fluorochemical emulsion blood substitutes. Fluorine imaging of these materials introduces complications when compared to the conventional proton modality, but also opens up numerous exciting possibilities in medical diagnosis not easily achieved with proton-based techniques.

In addition to myself, there are three other co-principal investigators: Leland C. Clark, Jr., (P.I.; Professor Clark performed the first liquid breathing experiments, and is one of the pioneers of fluorochemical blood substitute science), Children's Hospital Research Foundation; Ronald W. Millard, Pharmacology and Cell Biophysics, University of Cincinnati College of Medicine; and Stephen R. Thomas, Radiology, UCCM.

The responsibilities of this postdoctoral person will include a mix of gathering conventional spectra on Chemistry's NMR's, obtaining images on our small scale imaging system (which generated the image above), and participating in the completion and use of our whole body imager. He/she will work primarily with Professor Thomas and myself. The whole body spectrometer will have a nearly dedicated large scale computational facility in place of the usual NMR minicomputer.

Interested parties should submit their vita and arrange for two letters of recommendation to be sent to me at the above address.

The University of Cincinnati is an equal opportunity employer, and especially encourages applications from female and minority candidates.

Regards,

Jerry

Jerome L. Ackerman
Associate Professor of Chemistry

js

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Telephone (06) 12 46 33

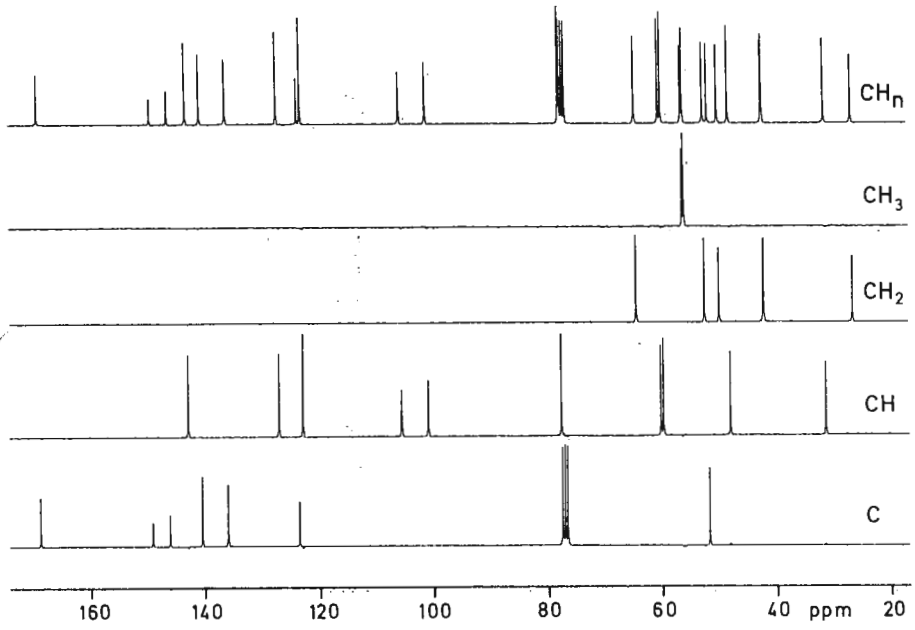
Oct. 6, 1983
HJJ/EL

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

^{13}C Subspectral Editing Using the SEMUT Method on the Varian XL-300

Dear Barry,

Since our last contribution to the TAMU NMR Newsletters we had our new Varian XL-300 spectrometer installed at the NMR laboratory in Aarhus. We have been very pleased by its performance. One of the first projects on the new system involved the incorporation of the SEMUT pulse sequence (1) for decomposing a ^{13}C NMR spectrum into four subspectra (CH_3, CH_2, CH, and C), a demand put forward by the user's group. Our version of the SEMUT method on the XL-300 includes a fully automated subspectral editing procedure and several improvements of the experimental technique used in spectral editing. The figure illustrates the XL-300 edited ^{13}C subspectra obtained for a sample (mixture of brucine and 2-bromothiazole) which has a spread in J couplings from ca. 125 to 192 Hz.



Sincerely yours,

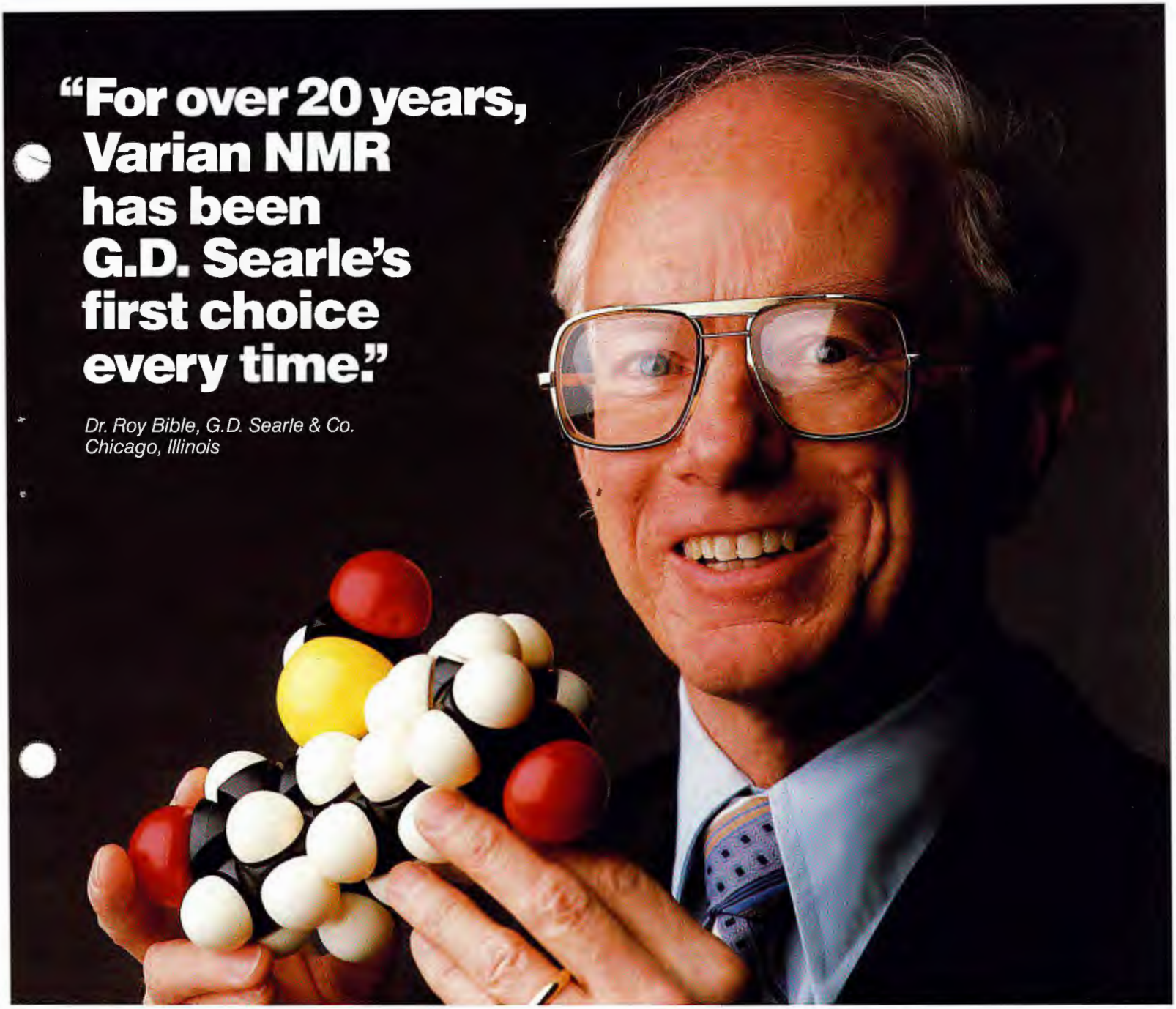
Hans H.Bildsøe

H.J.Jakobsen H.Bildsøe S.Dønstrup O.W.Sørensen (ETH,Zürich)

(1) H.Bildsøe, S.Dønstrup, H.J.Jakobsen, and O.W.Sørensen, J.Magn. Reson. 53, 154 (1983).

"For over 20 years, Varian NMR has been G.D. Searle's first choice every time."

Dr. Roy Bible, G.D. Searle & Co.
Chicago, Illinois



Dr. Bible, Research Fellow and Manager of Searle's Physical Methodology Department, has published two books on nuclear magnetic resonance and is the co-author of an ACS audiovisual course on the interpretation of NMR spectra. He is shown here with a molecular model of Searle's aldosterone antagonist, spironolactone.

Here's why Dr. Roy Bible has depended on Varian NMR to solve G.D. Searle's chemical structure problems. "Our task in the Physical Methodology Lab," says Dr. Bible, "is to produce accurate information on an uninterrupted basis for Searle R&D scientists. We need reliable, yet sophisticated instruments to meet that responsibility. In NMR, the record speaks for itself: we've purchased nine Varian instruments since 1961."

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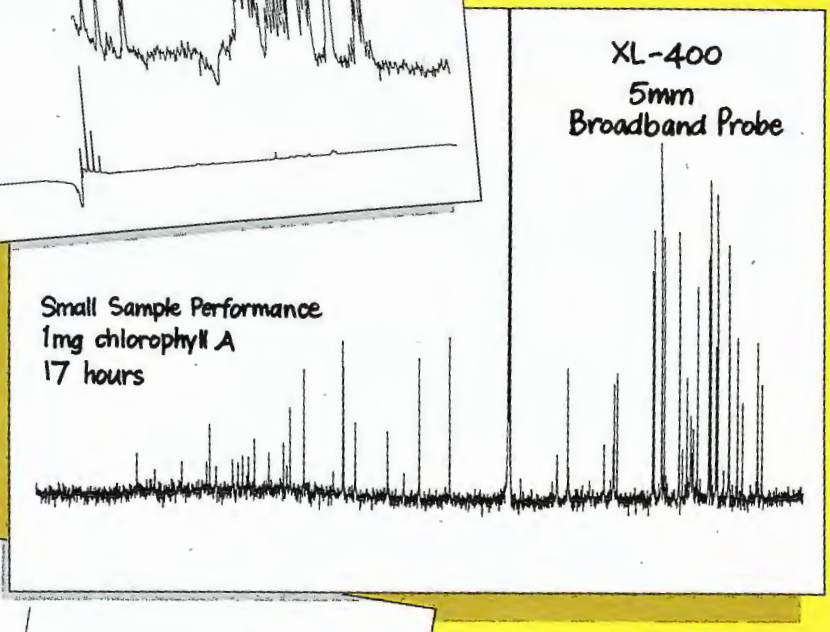

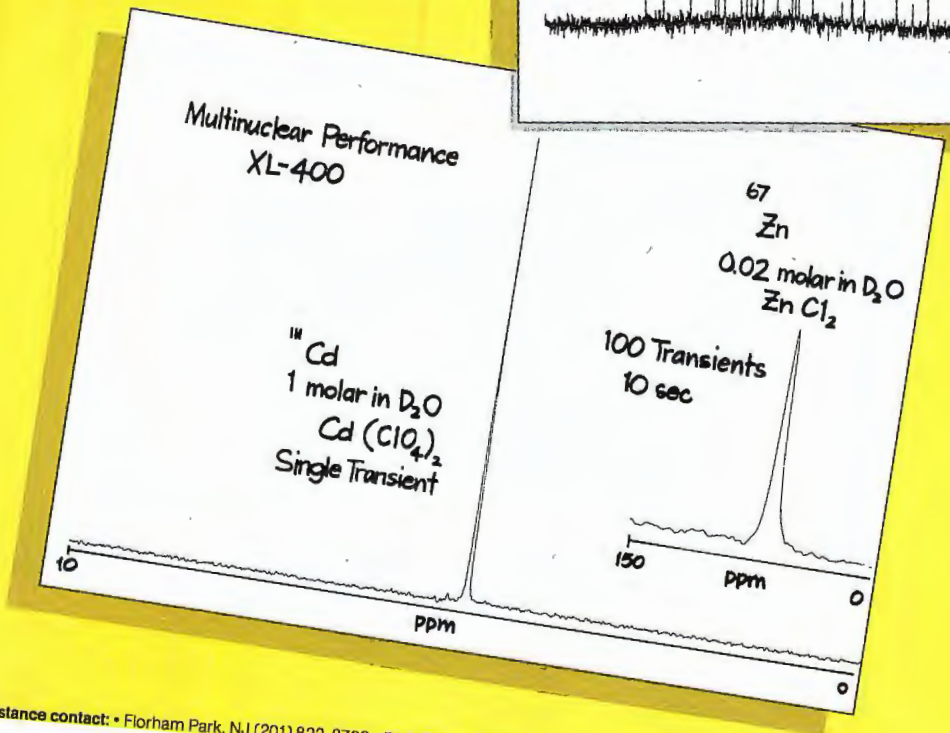

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DEPARTMENT OF HEALTH & HUMAN SERVICES

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October 12, 1983

Dr. Barry Shapiro
NMR. Newsletter
Dept. of Chemistry
Texas A & M University
College Station, TX 77843

Title: Positions Available

Dear Barry:

I have two openings in my new laboratory, one a research position and one for an electronics technician.

A Varian XL-400 spectrometer is on order and I expect to be able to purchase a wide-bore magnet spectrometer for small-scale imaging and in vivo NMR work in the coming year. In addition, at N.I.H. we have access to 100, 200, 270, 300, 400, and 500 MHz spectrometers, as well as a new whole-body NMR imager. Thus, the persons who obtain these positions will be part of an active NMR community.

The research-level position is for someone preferably with experience in experimental NMR imaging. This person will be expected to carry out biomedical research applications relevant to the mission of the laboratory as well as interact with the Radiology Department, where the whole-body imager is located. The electronics technician will be expected primarily to maintain, trouble-shoot and improve the 2 spectrometers, as well as being involved in research activities. The levels and salaries of both positions will depend on the experience of the individuals selected.

Yours sincerely,

Jack Cohen

Jack Cohen, Ph. D.
Clinical Pharmacology Branch
Clinical Oncology Program
National Cancer Institute

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Professor Bernard L. Shapiro
Texas A&M University

October 19, 1983

re: use of model compounds to faciliate assignment of homonuclear shift correlated 2D NMR spectra

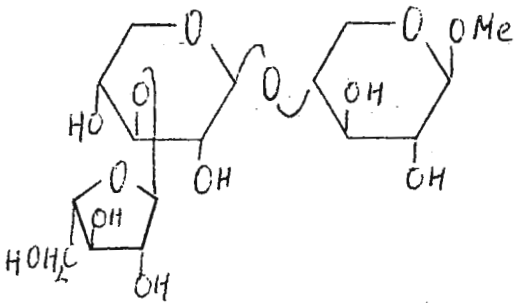
Dear Barry

If Archimedes had a point to stand upon he could move the world. Similarly, we can assign all the lines in a complex NMR spectrum of a molecule if we know the assignment of one line only. All we need is ample measuring time on a modern spectrometer and a sufficient amount of the compound. When this is not the case we must supplement additional information. In 2D NMR spectroscopy the latter approach results in considerable savings of spectrometer and researcher time and yet not reduces the exactness of the assignment which can be checked for self-consistency. Homonuclear shift correlated spectra of trisaccharides A and B illustrate this point.

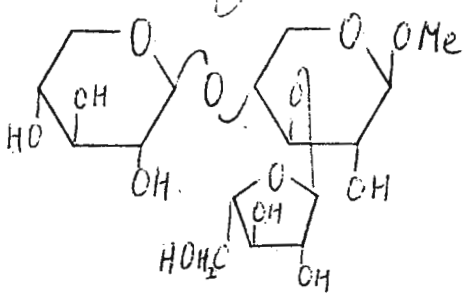
Finding the correct assignment of heavily overlapped spectrum of A by trials and errors might take several hours, assigning the spectrum of B is a matter of a few minutes and it greatly simplifies the problems with A. For example, the cross-peak pattern at 260 Hz in A is easily visualized as a superposition of cross-peaks at 260 Hz (H_{arab}-2) and at 280 Hz (H_{arab}-4) in B. The cross-peak pattern can be utilized in other spectra as it changes only little.

Sincerely yours,

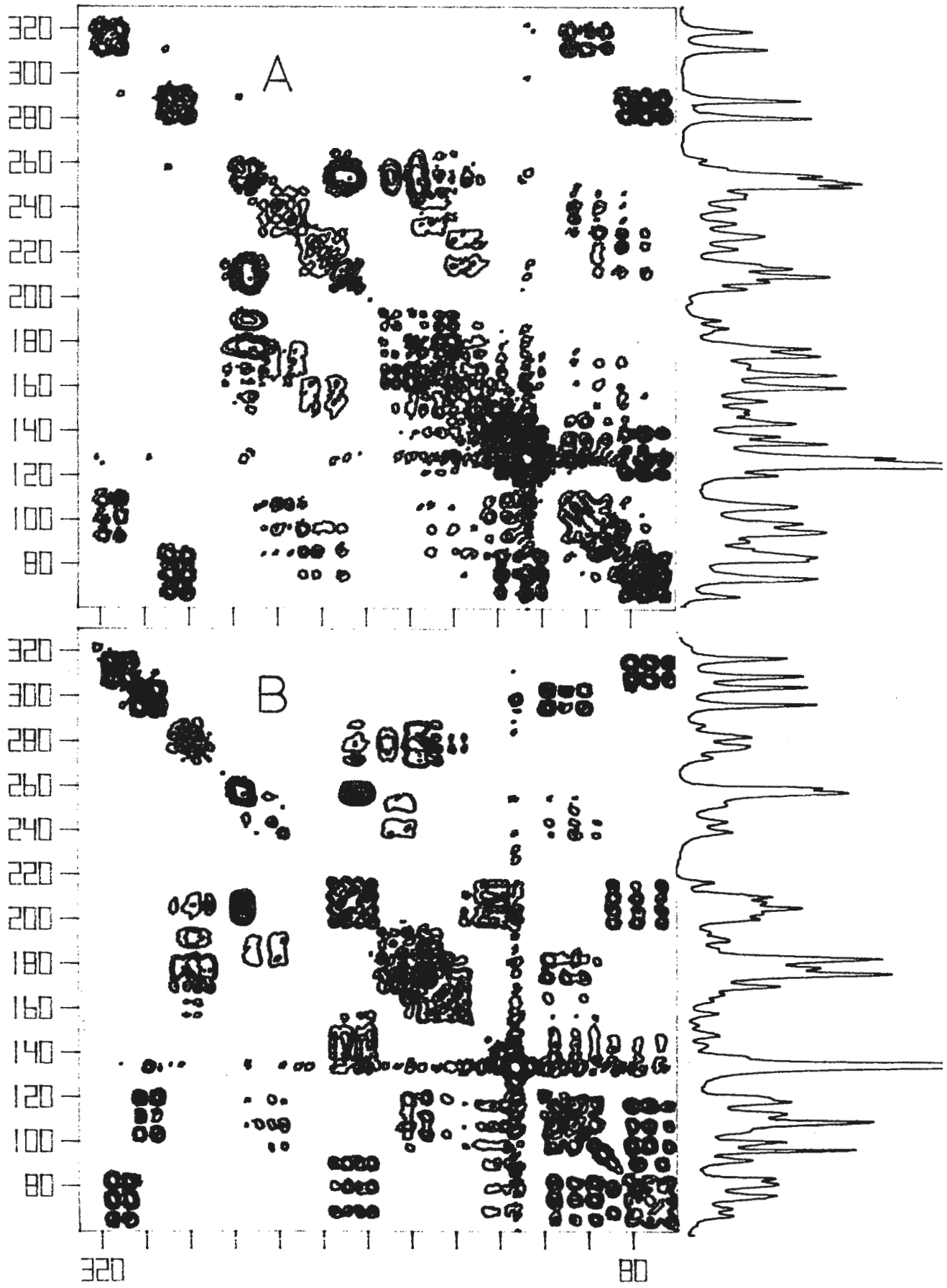
Jan Schraml



A



B


A
B
320
300
280
260
240
220
200
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160
140
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100
80
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80

Prof. Dr. GERHARD HÄGELE
Institut für Anorganische Chemie
und Strukturchemie I
der Universität Düsseldorf
M. Engelhardt

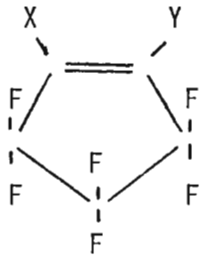
4000 Düsseldorf, den 13.10.1983
Universitätsstr. 1/26.42.U1.32
Telefon 0211 - 311-2288/2287
Telex 8 587 348 uni d

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

Title : Perfluorocyclopentene

Dear Professor Shapiro,

fluorinated cyclopentenes 1-7 gave rise to quite a number of preparative and some ^{19}F-NMR-studies :



N°	1	2	3	4	5	6	7
X	F	F	F	Cl	Cl	Cl	J
Y	F	Cl	J	H	Cl	J	J

Cavalli and Harris [1] reported on a full subspectral analysis of compounds 3, 5, 6 and 7, while Feeney, Sutcliffe and Walker [2] obtained some of the NMR-parameters from 1, 2 and 4 using certain restrictions concerning the symmetry of coupling parameters.
We wish to inform about our results from 84.665 MHz ^{19}F-NMR-work on perfluorocyclopentene 1 based on spectra given in figures 1-3 using subspectral approaches $[A[M]_2X]_2$ [3] and iterative treatment $[A[B]_2C]_2$ with LACX [4].
Resonance frequencies and coupling constants are listed in table 1.

This piece of work was rather laborious, so our next report in TAMU NMR NEWSLETTERS will deal with "Automated Analysis and Simulation of NMR-Spectra" .

We hope, this letter erases one of those "reminders" we received before holidays started.

Sincerely yours

G. Hägele M. Engelhardt

(Professor G. Hägele) (M. Engelhardt)

1) L. Cavalli and R.K. Harris, J. Magn. Res. 10, 355 (1973)

2) J. Feeney, L.H. Sutcliffe and S. M. Walker, Trans. Faraday Soc. 62, 2969 (1966)

3) M. Engelhardt, Diplomarbeit, University of Duesseldorf, 1983

4) C.W. Haigh in "Annual Reports on NMR-Spectroscopie" 4, 311, Academic Press, New York 1971

Parameters	
ν_1, δ_1	2769.733 Hz , 15.029 ppm
ν_2,ν_3,δ_2,δ_3	5517.98 Hz , 45.489 ppm
ν_4, δ_4	4502.853 Hz , 33.499 ppm
J_{11}	0.843 Hz
$J_{22} = J_{33}$	2.643 Hz
J_{44}	240.0 Hz
$J_{12} = J_{13}$	-12.713 Hz
$J_{21} = J_{31}$	10.417 Hz
$J_{14} = J_{41}$	4.023 Hz
J_{23}	260.0 Hz
J_{32}	1.705 Hz
$J_{24} = J_{43}$	0.516 Hz
$J_{42} = J_{34}$	-2.770 Hz

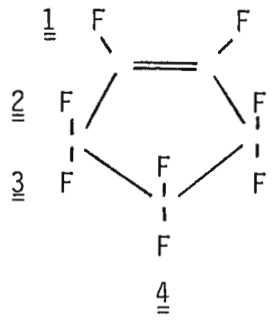


Table 1 : Resonance frequencies and coupling constants of perfluorocyclopentene
Solvent : C_6D_6 50% v/v , Reference : C_6F_6

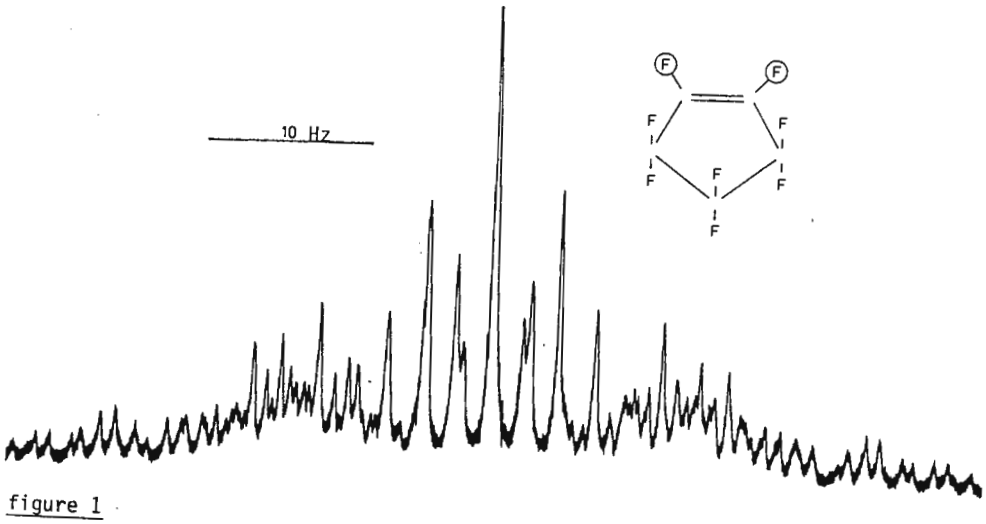


figure 1

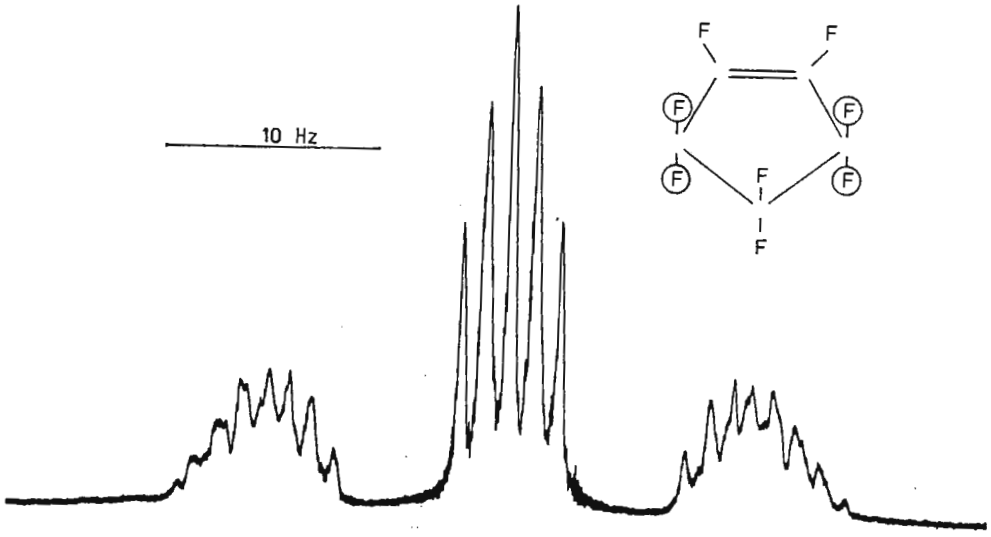


figure 2

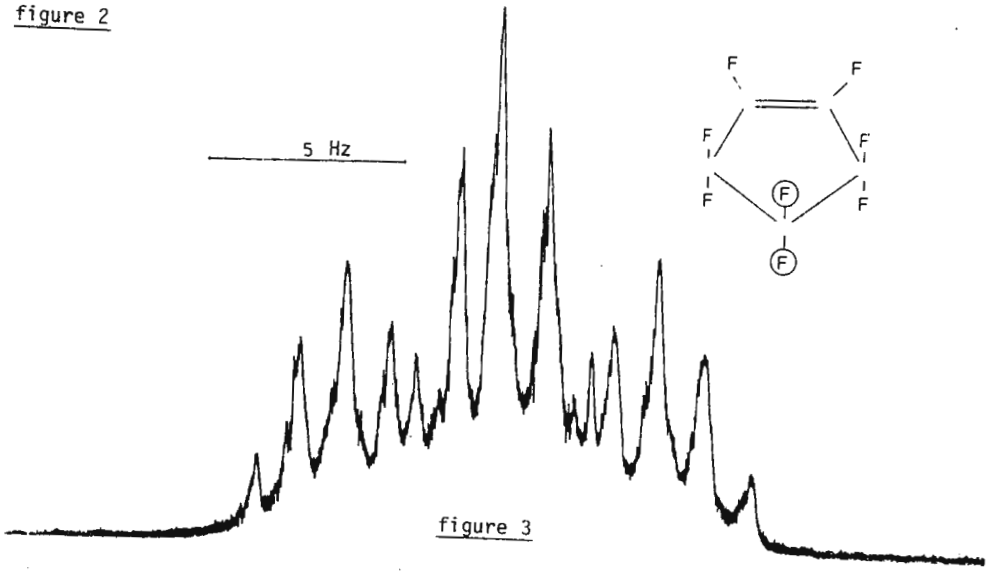


figure 3

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DEPARTMENT OF HEALTH & HUMAN SERVICES

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Research Triangle Park, N.C. 27709

October 24, 1983

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77483

Dear Professor Shapiro,

I have recently joined the Laboratory of Molecular Biophysics at the NIEHS, and your dreaded yellow note finds me in a period of transition, with the NMR effort at planning and refurbishing stages.

I can offer a tidbit on an effort which Michael Brown (U of Virginia) and I began a while back and is now bearing some fruit. Early models had suggested that the bulk acyl methylenes of phosholipid bilayers should obey a relaxation law with $T_1^{-1} \alpha \omega_c^{-2}$. In contrast, ^{2}D NMR data at three field strengths suggested a relaxation law of the form $T_1^{-1} = A\tau_f + BS^2\omega_o^{-\frac{1}{2}}$. We therefore measured the ^{13}C relaxation of lipid bilayers at <u>seven</u> field strengths (15 - 126 MHz). The ^{13}C NMR data yield straight lines when T_1^{-1} is plotted vs $\omega_c^{-\frac{1}{2}}$, and curved lines when T_1^{-1} is plotted vs ω_c^{-2}. The increased number of data points in the ^{13}C data relative to the ^{2}D NMR clearly allows this distinction, and the relaxation law dependent on $\omega_c^{-\frac{1}{2}}$ can be viewed with some confidence at present.

Sincerely yours,

Anthony Ribeiro

Anthony Ribeiro

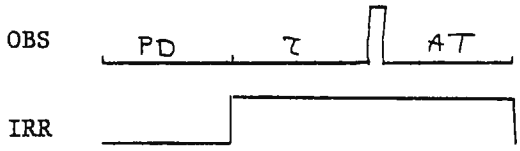
UNIVERSITY OF STOCKHOLM
Physical Chemistry

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

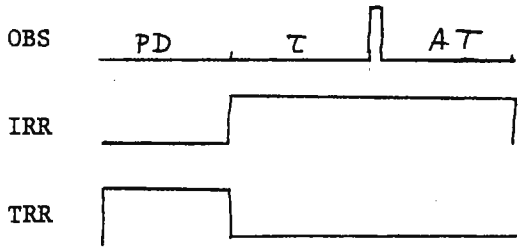
Stockholm, October 24, 1983

Dear Prof. Shapiro,

For many years, our group has been a warm proponent of using dynamic NOE (DNOE) technique for measuring NOE and, under certain circumstances, also T_1 [1]. On our new GX400, however, the usual sequence



did not seem to work very well. Being the lucky owners of a triple resonance oscillator, we have been able to modify the sequence to



Setting the levels in IRR and TRR channels to give a constant proton power to the probe and offsetting TRR by about 50 kHz from resonance produced nice result for both ^{13}C and ^{29}Si experiments. I would be delighted to illustrate this point with spectra, but we have changed to the RSX 11M operating system last week and all the old data on disks are gone.

Best regards,

Jozef Kowalewski

[1] J. Kowalewski, A. Ericsson, and R. Vestin, J. Magn. Res. 31, 165 (1978).

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DEPARTMENT OF CHEMISTRY

October 26, 1983

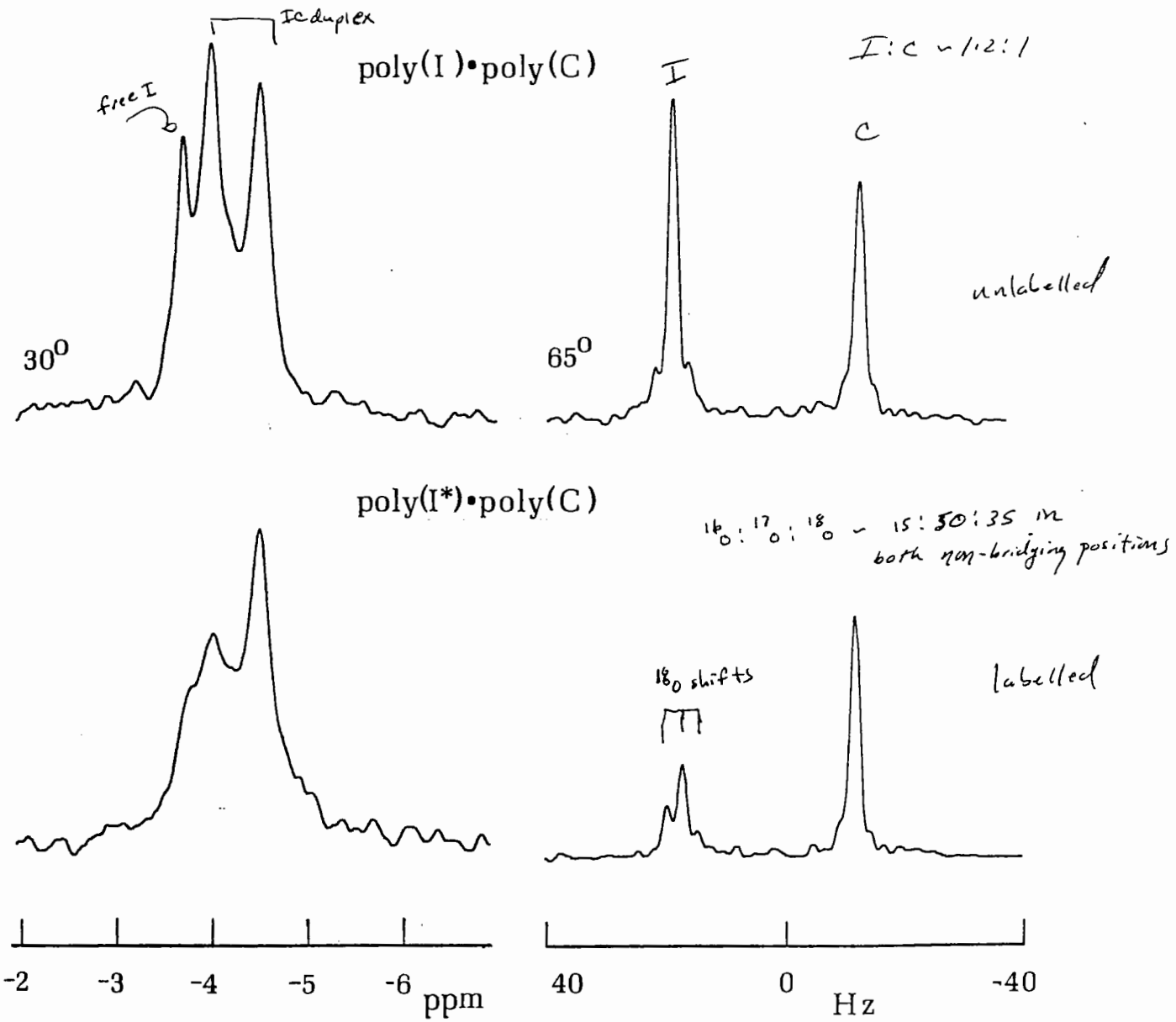
"How to Assign the ^{31}P Spectra of Polynucleotides"

Dear Barry:

Many dim years ago when I was at UCSD with David Kearns we ran a ^{31}P spectrum of poly(I)-poly(C) with Tom Early. The result was that there are two signals of equal intensity. This observation has since been made by others and it seems to be a general feature of the ^{31}P spectra of polynucleotides that multiple peaks are present. Since the differences in chemical shifts may have something to do with conformation there is interest in such chemical shift dispersion. However, before the chemical shift information can be interpreted some way of assigning the ^{31}P spectra is needed. Examination of the spectra as a function of temperature is not helpful since there is too much funny business. However, the incorporation of ^{17}O into the non-bridging positions of one of the two polynucleotides will allow unambiguous assignment. The ^{17}O induces broadening of the ^{31}P lines primarily through a dipolar mechanism. For the sample used here the ratio of proton dipolar to chemical shift anisotropy relaxation in T_2 is about 2:1 at 81 MHz as deduced from experiments at 81 and 202 MHz. The ^{17}O dipolar relaxation is significant since the ^{17}O is close to the ^{31}P and has spin 5/2. The results in the figure allow unambiguous assignment of the two signals of poly(I)-poly(C). More examples are in progress.

Sincerely,

Philip Bolton


Ic duplex
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unlabelled
poly(I*)•poly(C)
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18O shifts
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-40
Hz

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMISTRY
CAMBRIDGE, MASSACHUSETTS 02139

October 28, 1983

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

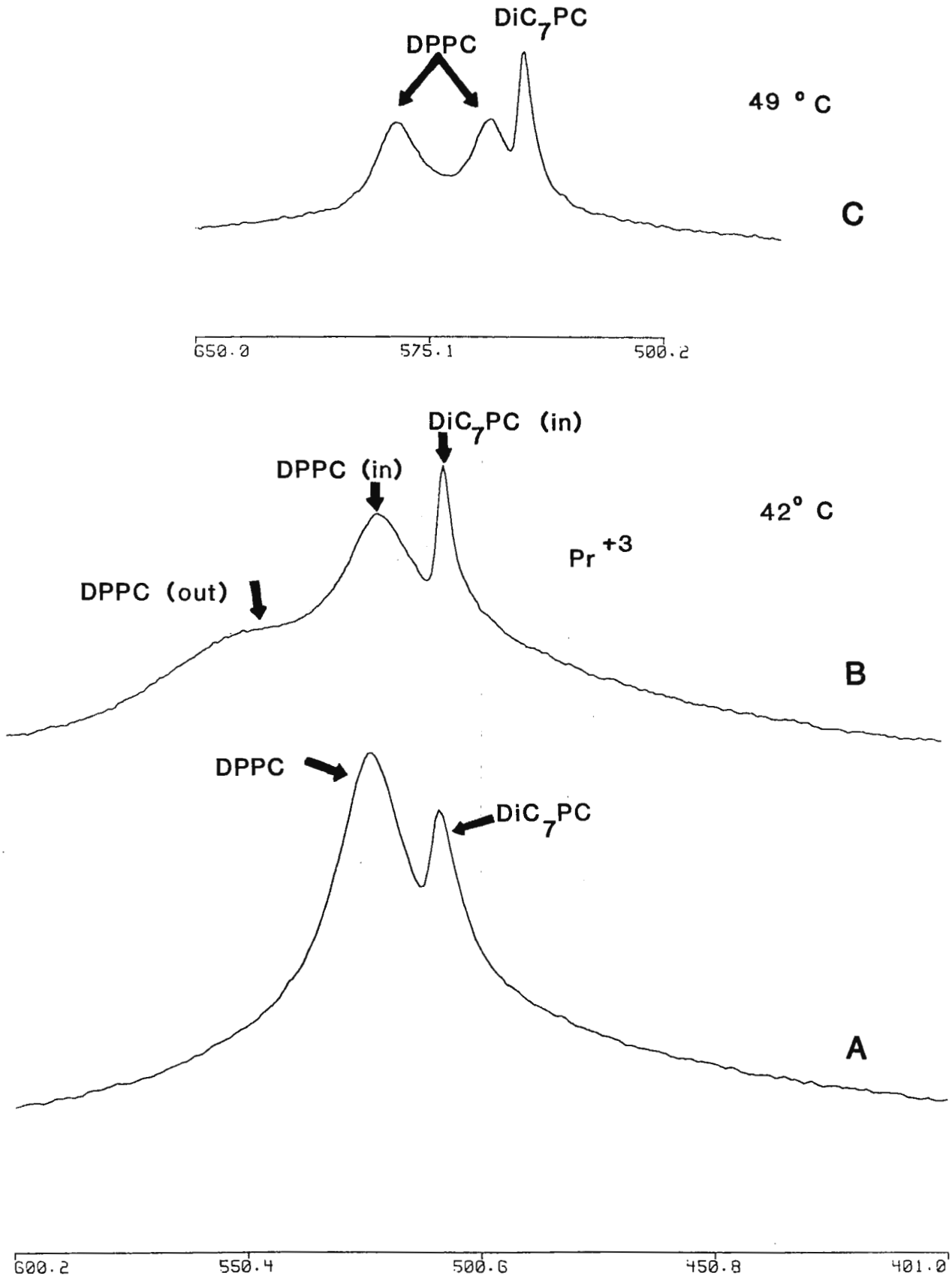
Dear Prof. Shapiro:

"Novel Stable Moderate-Sized Unilamellar Vesicles"

We wish to alert those interested in bilayer membrane models to novel, stable unilamellar vesicles spontaneously formed by mixing long-chain lecithins with small amounts of micellar short-chain lecithins. Dipalmitoyl-PC (20 mM) and diheptanoyl-PC (5 mM) spontaneously form vesicles (verified by ^{31}P-NMR/Pr^{3+} experiments) of about 800 Å in aqueous solution (determined by EM studies). These vesicles are impermeable to Pr^{3+}. An examination of the 500 MHz ^{1}H NMR spectrum of these aggregates shows two $N(CH_3)_3$ peaks visible without added lanthanide ions (Fig. 1a). Rather than reflecting inside/outside lecithin molecules, these peaks are attributed to diheptanoyl-PC (narrower resonance) and the separate dipalmitoyl-PC molecules by examining the ^{1}H NMR spectrum of vesicles formed with $N(CD_3)_3$-dipalmitoylPC and short-chain lecithin. What is most interesting to us is the observation that nearly all of the diheptanoyl-PC appears on the <u>inside</u> of these vesicles. Fig. 1b shows that when Pr^{3+} is added to the exterior buffer, three $N(CH_3)_3$ resonances are observed: two relatively invariant peaks (a narrow one from diheptanoyl-PC, a broad one from dipalmitoyl-PC on the interior layer) and a downfield shifted component (due to the exterior monolayer of dipalmitoyl-PC and any diheptanoyl-PC). Sharper resolution of these three $N(CH_3)_3$ resonances is obtained at 49°C (Fig. 1c). If Pr^{3+} is encapsulated in the vesicles and EDTA added to the exterior, then virtually all of the sharp diheptanyol-PC signal shifts downfield. Thus, most of the short-chain species is on the inner monolayer. Such an asymmetric distribution of acyl chain lengths in particles with little curvature is interesting ...

Sincerely,

Mary F. Roberts N. Elise Gabriel


DiC7PC
DPPC
49 °C
C
650.0
575.1
500.2
DiC7PC (in)
DPPC (in)
42° C
Pr +3
DPPC (out)
B
DPPC
DiC7PC
A
600.2
550.4
500.6
450.8
401.0
Frequency (Hz)

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DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

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October 28, 1983

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

Slowed NH Proton Exchange of Carboxy-terminal Amino Acids in Peptides.

Dear Barry:

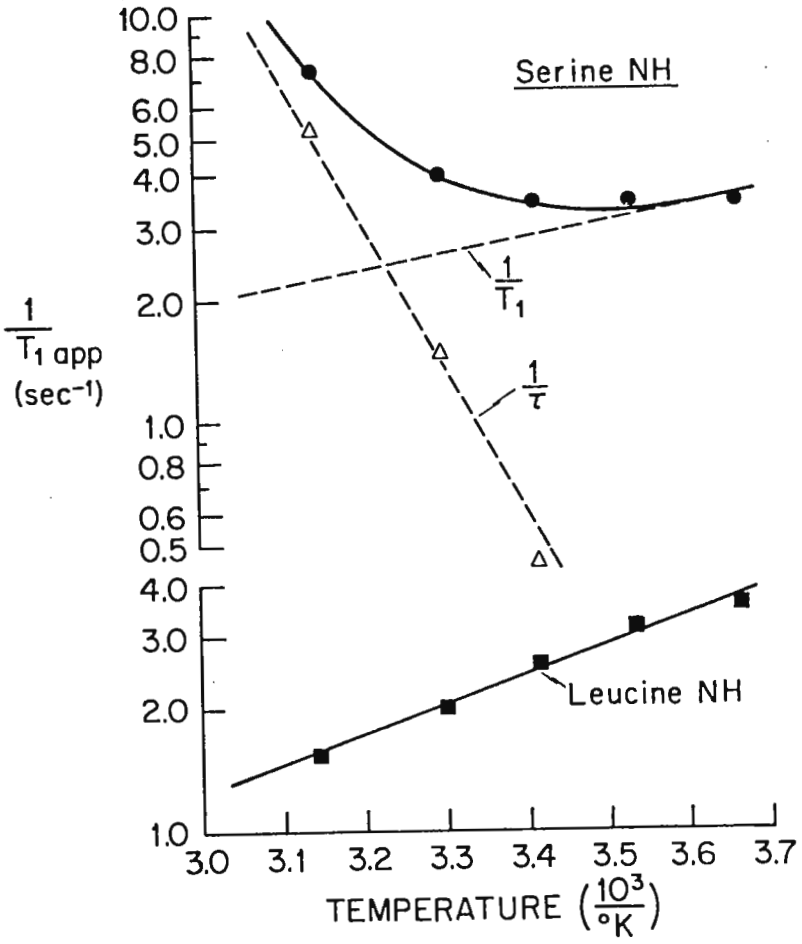
We have recently been studying the conformation of a pentapeptide substrate (Arg-Arg-Ala-Ser-Leu) bound to cAMP dependent protein kinase. This work involved observation of the exchangeable amide (NH) protons of the substrate, to which distances from a paramagnetic metal-binding site on the enzyme were ultimately determined. During a preliminary study of the pentapeptide alone, the $1/T_1$ values of these amide protons were found to respond in a non-uniform manner to variations in temperature. The NH of the carboxy terminal leucine exhibited a decrease in its apparent $1/T_1$ with increasing temperature, while the amide protons of the internal residues, arginine, alanine, and serine showed the opposite effect. In an attempt to explain this anomaly, the exchange rates of the amide protons with water were measured at various temperatures. This was accomplished by saturating the water resonance and determining the consequent loss of magnetization by each of the NH resonances, quantitated by comparing peak heights after saturation (M) to peak heights in the absence of any saturating pre-irradiation (Mo). Using the equation $1/\tau = 1/T_{1\ \text{apparent}} (1-\frac{M}{Mo})$, the exchange rate ($1/\tau$) of each amide proton with water was determined. It was discovered that only the leucine NH showed no measurable exchange with water over the range of temperatures studied (0°-45°C). The observation of increasing exchange rates at higher temperatures for the remaining amide protons provided a likely explanation for the temperature dependence of their $1/T_{1\ \text{app}}$ values. When the $1/T_{1\ \text{app}}$ at each temperature was considered as the sum of an exchange rate and an "actual" $1/T_1$ value (exemplified by serine NH in Figure 1), the $1/\tau$ vs temperature function agreed well with that observed, and the $1/T_1$ vs temperature function approximated that of leucine NH.

To learn the basis of the non-exchangeability of the leucine NH proton, two model compounds, N-acetyl-serine and N-acetyl-serine amide, were utilized in temperature experiments analogous to those performed with the pentapeptide. The amide proton of N-acetyl-serine amide behaved exactly as had the amide proton of the internal serine residue of the pentapeptide. However, the NH of N-acetyl-serine showed a lack of exchange and $1/T_1$ behavior similar to the NH of leucine, the carboxy-terminus of the pentapeptide. Therefore, it was clear that the presence of a free carboxyl group, not a hydrogen bond or a specific effect of the leucine

side-chain, was slowing the exchange of the amide proton. This characteristic may be useful during assignment of unknown NH resonances in a polypeptide.

Sincerely,

David C. Fry Paul R. Rosevear Albert S. Mildvan



Temperature dependence of the longitudinal relaxation rates of the Serine NH (upper) and the leucine NH (lower) in the pentapeptide Arg-Arg-Ala-Ser-Leu. The $1/T_{1\ app}$ for Serine has been fitted by a $1/\tau_M$ and $1/T_1$ contribution as indicated. The data points along the $1/\tau_M$ line were independently measured by saturation transfer from H_2O. (Other components present were 5 mM MES buffer, pH 5.8; 150 mM KCl; 0.1 mM DTT; 10% ^2H_2O).

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CHIMIE ORGANIQUE PHYSIQUE
E.R.A. nº 315 - C.N.R.S.

Dear Professor shapiro,

SPINACH AGAINST VERMIFUGE !

Levamisole is an organic compound whose biological effects are well known (vermifuge ...). First used as an anthelmintic drug in animal and human subjects, it has been increasingly developed as an immuno-stimulant. It reacts slowly with water (1) but the action with $NaNO_2$ is fast and the resulting compound has been studied by NMR.

The ^{1}H spectrum does not evidence a thiol function (absence of triplet at ≈ 1,3 ppm) (2). However, the absence of a thionitrite S-N=O function is ascribed to its fast degradation into the disulphide and the triplet at 3,1 ppm (J = 6,5 Hz) is attributed to the CH_2-S in the disulphide. The two protons of the CH_2 adjacent to the CH_2-S are magnetically non-equivalent due to the chirality of the molecule.

In ^{13}C, the chemical shift of the carbonyl carbon (153,6 ppm) corresponds better with a nitroso-urea (3) than with the imidazolone formed by hydrolysis (162,4 ppm).

Finally, the formation of N-nitroso-imidazolone is confirmed by ^{15}N NMR (4).

$\delta^{15}N/CH_3NO_2$	+ 184,1 and - 110,6 ppm	N- nitroso
	- 287,0 ppm	Amide

Sincerely yours,

J.P. GOUESNARD

(1) N.A. DICKINSON, R.E. HUDSON and P.J. TAYLOR, Analyst, 96, 235, 1971.

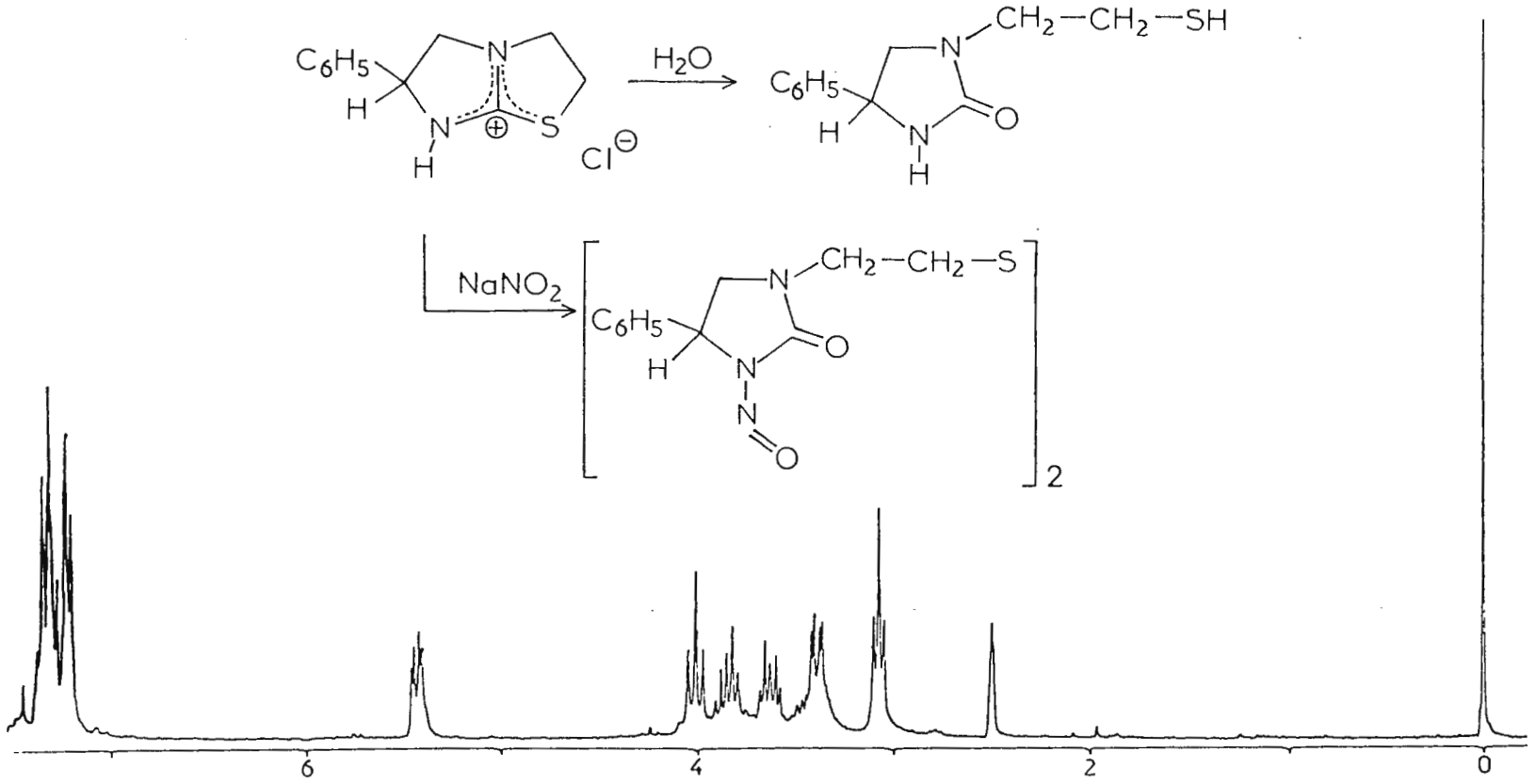
(2) D.C.H. BIGG, A.W. FAULL and S.R. PURVIS, J. Heterocyclic Chem., 14, 989, 1977.

(3) J.P. GOUESNARD, J. Mol. Struct., 96, 101, 1982.

(4) G.J. MARTIN, M.L. MARTIN and J.P. GOUESNARD, ^{15}N-NMR Spectroscopy, Springer-Verlag, Berlin, 1981.

P.S. - Please credit this contribution to Prof. G. MARTIN account.

Téléphone (40) 74.50.70 - 2, rue de la Houssinière - 44072 NANTES-CEDEX (FRANCE)



^1H spectrum (250 MHz) of disulphide in DMSO-d_6

302-47

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Telex 348476

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October 12, 1983

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

POSITIONS AVAILABLE

Over the last several months, we have enjoyed considerable growth in our NMR business. As a result, we are increasing our staff in both Research and Development and in Marketing. I would like to alert your readers to several openings in our Palo Alto, California facility. Immediate openings include:

Software engineers:	Activities include creating applications software, generation of new software techniques, networking, etc. taking advantage of the most sophisticated computer hardware.
Computer hardware engineers:	Design the next generation of NMR computer systems, including multi-user computer environments, networks, and the most up-to-date computer architectures.
Product marketing:	Define and implement marketing plans for major new product introductions, with responsibility for market evaluation and research, product definition, pricing, promotion activities, etc.
Manufacturing engineering mgr:	Responsible for improving manufacturing techniques in all areas of production, including electronic test, magnet production, etc.

Please send resumes, indicating the particular opportunity of interest to:

Neil Selvin
Varian Associates
611 Hansen Way
Palo Alto, CA 94303

Varian is an equal opportunity employer.

Sincerely,

Neil Selvin
Marketing Manager

/sc

Position Available - Switzerland

I am pleased to say that we are planning to increase our staff in our NMR application laboratory in Zug, Switzerland and are advertising for suitable applicants. We are looking for chemists with an NMR background who would like to practise their craft in the commercial environment of a manufacturer's application laboratory.

The duties are varied and include working with customers' application problems, training customers in the optimal operation of NMR spectrometers, lecturing at scientific meetings, producing new ideas for the use of NMR and NMR instruments, evaluating new products and providing the scientific support for the technical sales team in Europe. English is essential and other languages will help with the communications part of the job. A reasonable amount of travel is involved which adds to the variety of th job.

Any applicant should write to Tony Luechinger, Personnel Manager at Varian AG, Steinhauserstrasse, CH-6300 Zug, Switzerland, giving details of career to date. (Varian is an equal opportunity employer, of course.)

Yours sincerely,
Varian AG

A.R.J. Arthur
Manager
Magnetic Spectroscopy Operations
Europe

TENURE-TRACK FACULTY POSITION IN ORGANIC CHEMISTRY, UNIVERSITY OF GEORGIA

An opening is anticipate for September, 1984. Potential candidates should have a solid record of research accomplishment and show promise of developing a vigorous, independent program of scholarly research. Candidates must demonstrate interest and aptitude for teaching undergraduate and graduate courses. Applicants with specific expertise in NMR spectroscopy or other research areas which complement those of the present faculty may be given preference. To apply, send biographical resume, outline of research plans, and names and addresses of three or more references, by January 2, 1984, to Dr. R. K. Hill, Department of Chemistry, University of Georgia, Athens, GA 30602. The University is an Equal Opportunity/ Affirmative Action employer.

Sincerely,

Richard K. Hill

Richard K. Hill
Professor of Chemistry
Organic Division Coordinator

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA 93106

October 14, 1983

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

Re: Positions Available

Dear Barry:

Permit me to add to the flurry of "positions available" notices which have adorned recent pages of the Newsletter.

(1) There is a post-doctoral opening in my group available immediately for someone interested in high field fluorine and proton nmr studies of various calcium-binding proteins. Experience with protein isolation and characterization including hplc techniques would be an asset but the primary qualifications, as always, are interest and enthusiasm. Salary commensurate with experience.

(2) The department will shortly start recruiting a staff person to be responsible for the day-to-day operation of its nmr spectrometers. The exact duties to be assigned to this person, and the salary, will be dependent on the interests and background of the individual but could include a significant fraction of time being made available for personal research.

Persons interested in either of these openings should write or phone me (805/961-2113).

Sincerely,

J. T. Gerig
Professor of Chemistry

C S I R

Council for Scientific and Industrial Research

National Chemical Research Laboratory

P O Box 395 Pretoria 0001 South Africa
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Tel.: National (012) 86-9211
International + 27 12 86-9211

Our file 600/1/4/7-Shapiro Your file

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

Dear Professor Shapiro

POST-DOCTORAL POSITION AVAILABLE

We currently have a position available within the National Chemical Research Laboratory of the CSIR for a post-doctoral research scientist in the field of NMR spectroscopy.

We are the main centre for NMR spectroscopy in the Republic of South Africa and are in addition to our own research activities also obliged to supply a service to other research organizations in the country. The NMR instrumentation available within our group are a Bruker WM500 NMR spectrometer and Varian XL100, CFT20 and EM390 NMR spectrometers.

The applicant should have a Ph.D. in chemistry, biochemistry or other related field. Experience in the application of NMR spectroscopy to biochemical problems will be a distinct advantage.

We would be glad to hear from any interested applicants. They should submit a letter detailing their background and interests along with a curriculum vitae and two letters of professional recommendation to the Chief Director at the above address.

Salary is negotiable according to experience. This will also include partial support toward travel expenses.

Yours sincerely

P.L. WESSELS
SENIOR CHIEF RESEARCH OFFICER

302-51

National Research Council Canada
Conseil national de recherches Canada

Division of Biological Sciences
Division des sciences biologiques

Ottawa, Canada
K1A 0R6

21 October 1983

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 Barry:

STAFF NMR POSITION
IN MOLECULAR BIOPHYSICS

We have a tenure track position available for an NMR spectroscopist in our Molecular Biophysics section. The spectroscopist would have responsibility for two high power instruments (Bruker CXP 300 plus home built 200), including their maintenance and modification, as well as access to our divisional Bruker AM 500. The research would be in collaboration with a group of specialists in membrane structure and metabolism of microorganisms and mammals. A good knowledge of contemporary NMR techniques and hardware is essential.

We have no preset limits on the level of this appointment, but postdoctoral experience and familiarity with NMR of the solid state are distinct advantages. The disposition to work in a large interdisciplinary group is indispensible. The salary, dependent on qualifications, would range from $30,000 to $50,000 per annum, plus extensive fringe benefits.

Interested persons should write to me directly, and request that references from at least two senior scientists familiar with their abilities be sent to me as well. The position is available as of December, 1983.

Yours sincerely,

Ian

ICPS:cg

Ian C.P. Smith

Canada

You never had NMR like this before.

NMR is the most powerful structural analysis technique available to the organic chemist today. It lets you determine molecular structure, investigate kinetic phenomena, and perform quantitative analysis of organic compounds in complex mixtures.

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The QE-300 makes it possible for virtually anyone to get high quality NMR spectra—quickly and easily—without previous training or NMR experience.

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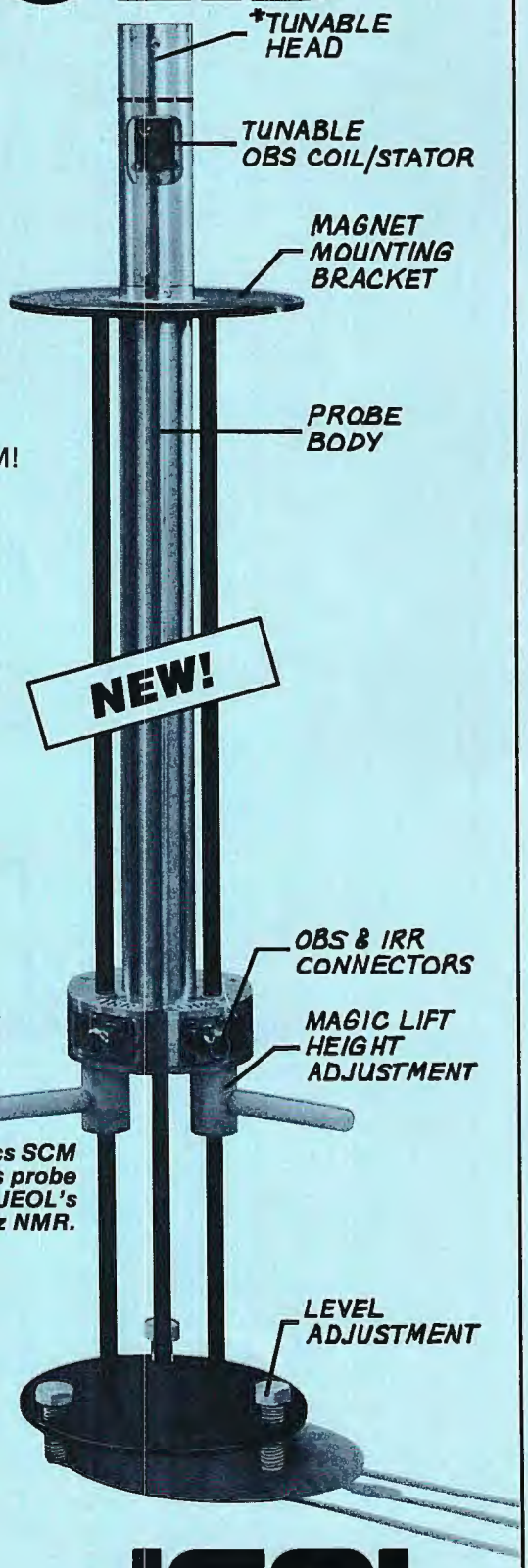

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