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NMR NEWSLETTER

NO. 303

DECEMBER 1983

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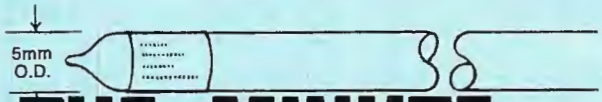

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	WGH-24	20% Acetaldehyde + 2% TMS in Acetone-d$_6$	Resolution	33.00
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Chemagnetics, Inc.

All Newsletter Correspondence
Should be Addressed to:

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

AUTHOR INDEX ------ TAMU NMR NEWSLETTER NO. 303, DECEMBER 1983

DEADLINE DATES

No. 304 ------ 2 January 1984

No. 305 ----- 6 February 1984

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October 13, 1983

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

Heteronuclear NOE Difference Spectroscopy

Dear Barry:

We have been involved with developing experiments which perturb NMR signal intensities in a predictive manner such that these changes can be used in structure determination. One such method which appears to be very successful is a heteronuclear difference NOE experiment. This experiement can be performed quite easily on our JEOL FX 200 or 90Q by making use of the bit register in the decoupler mode settings. Simply by putting the decoupler mode on EXT and setting this = 229, selecting the proper irradiation power and offset and using the standard difference NOE program provided with the spectrometer one can, for example, distinguish a hydrogen bound from non-hydrogen bound carbonyl group. See enclosed figure.

Details concerning this work can be provided upon request.

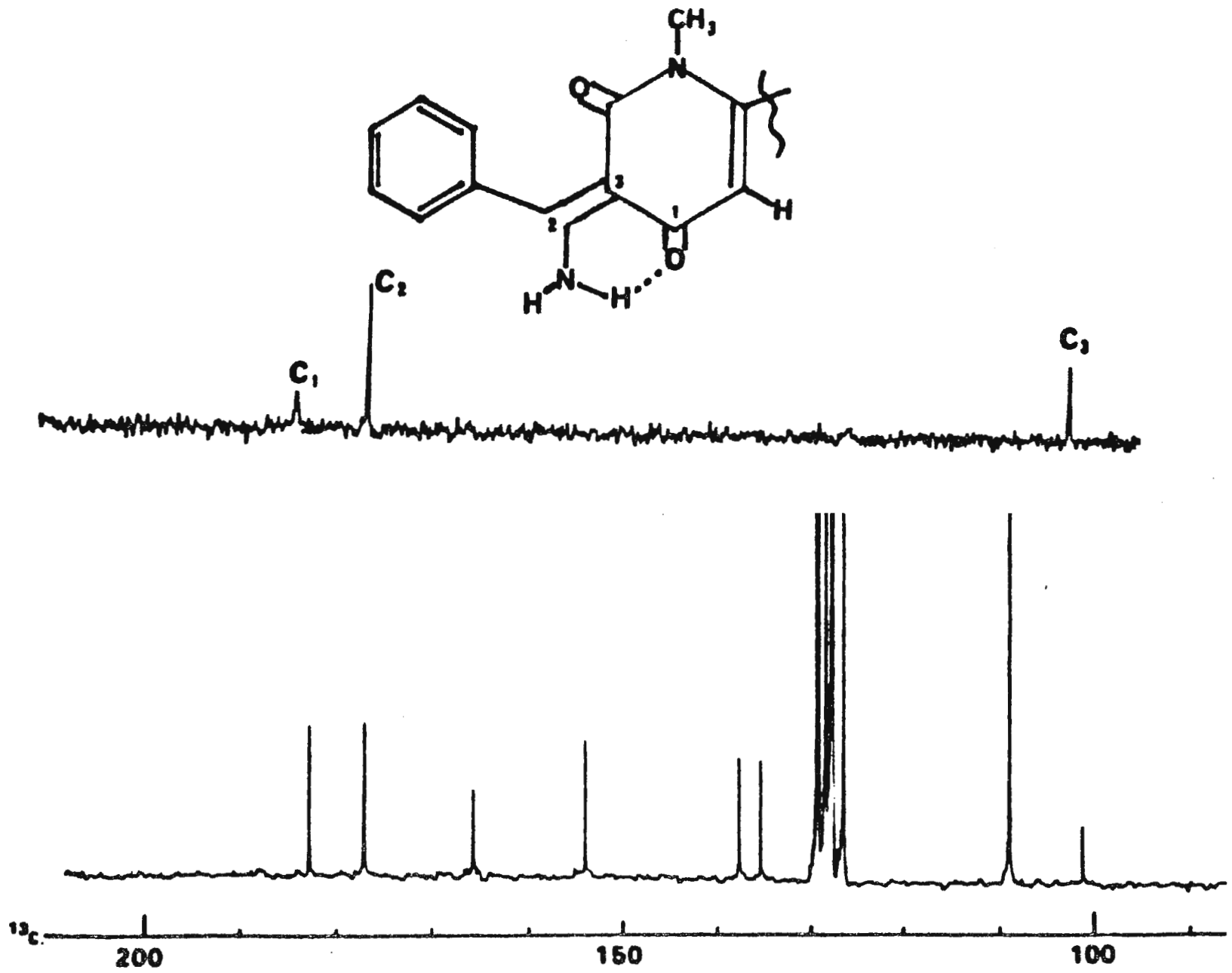
Sincerely,

Michael J. Shapiro, Ph.D.
Head, NMR Laboratory

MJS:epb

1a. J.J. Ford, W.A. Gibbons, N. Niccolai, JMR, 47, 522 (1982).
b. M.A. Khaled and C.L. Watkins, JACS, 105, 3363 (1983).
c. M.J. Shapiro, et al., to be published.

Please credit the account of Sandor Barcza.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University of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building,
295 Cathedral Street, Glasgow G1 1XL Tel: 041-552 4400
29th November, 1983.

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

Pentaerythritol Sulphite Spectra

Dear Barry,

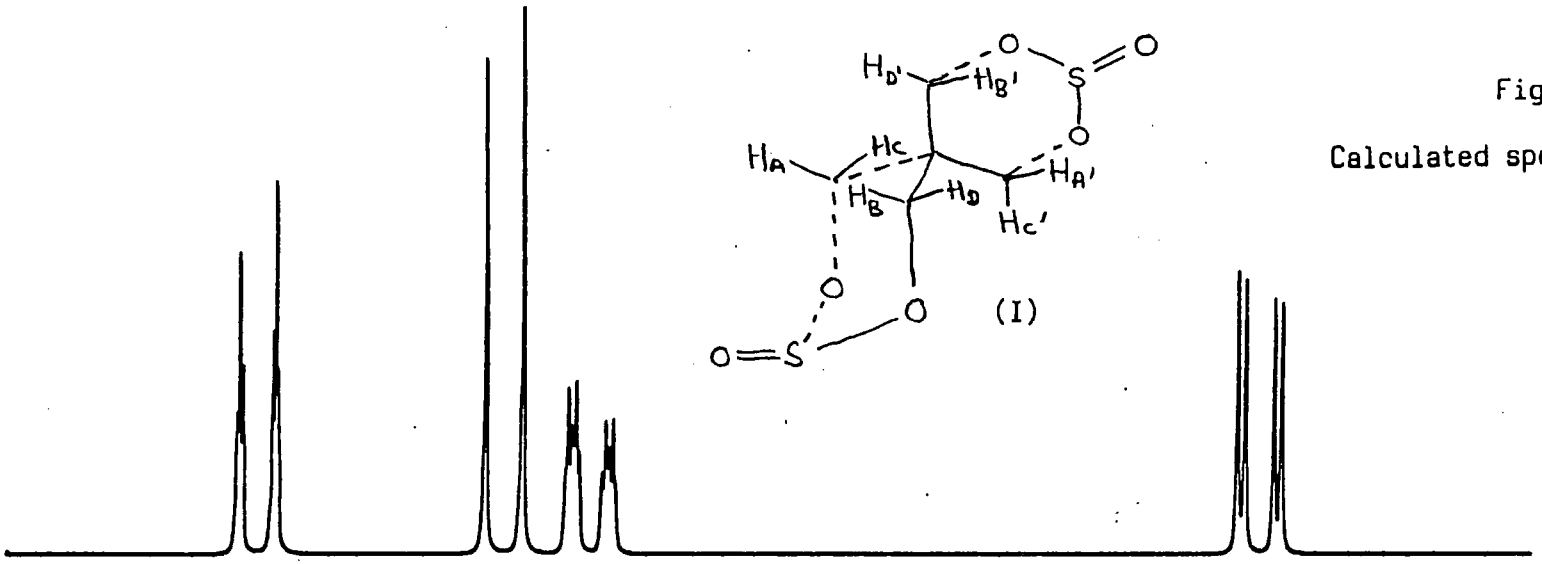
The proton n.m.r. spectrum of the bis-sulphite of pentaerythritol has intrigued me for some time, and with every (in our case belated) improvement in instrumentation, I have taken the opportunity to rerun the spectra to see if the assignments can be improved. The molecule, at first sight quite simple consists of two rigid spiro joined rings and has symmetry C_2 (it is in principle resolvable). It has four pairs of chemically equivalent but magnetically non-equivalent protons. The proton spectrum (Figure 1) run in $CDCl_3$ at 250.13 MHz (WM-250) consists of four multiplets at δ 4.85 (A), 4.53 (B), 4.43 (C), and 3.54 (D) p.p.m. The assignments as shown in the structure (I) are based on the presence of 'W' arrangements of the proton pairs CD (& C'D') and AA' giving rise to 4-bond couplings. The calculated spectrum (figure 2) using the PANIC program involved the couplings: J_{AC}-11.81, J_{BD}-11.91, J_{AA} 2.03, and $J_{CD'}$ 2.54. There is evidence of at least one further long-range coupling since the C multiplet shows a further splitting (~0.8 Hz).

In contrast to the large chemical shift differences in the proton spectrum, the ^{13}C-spectrum shows a small difference for the shifts of the methylene carbons (δ 58.77 and 58.94). The central carbon has δ 34.68 ppm. Attempts at correlating the proton and carbon spectra have been so far frustrated by this small shift difference.

Yours sincerely,

Peter Bladon

Dr. Peter Bladon



(I)

Figure 2

Calculated spectrum

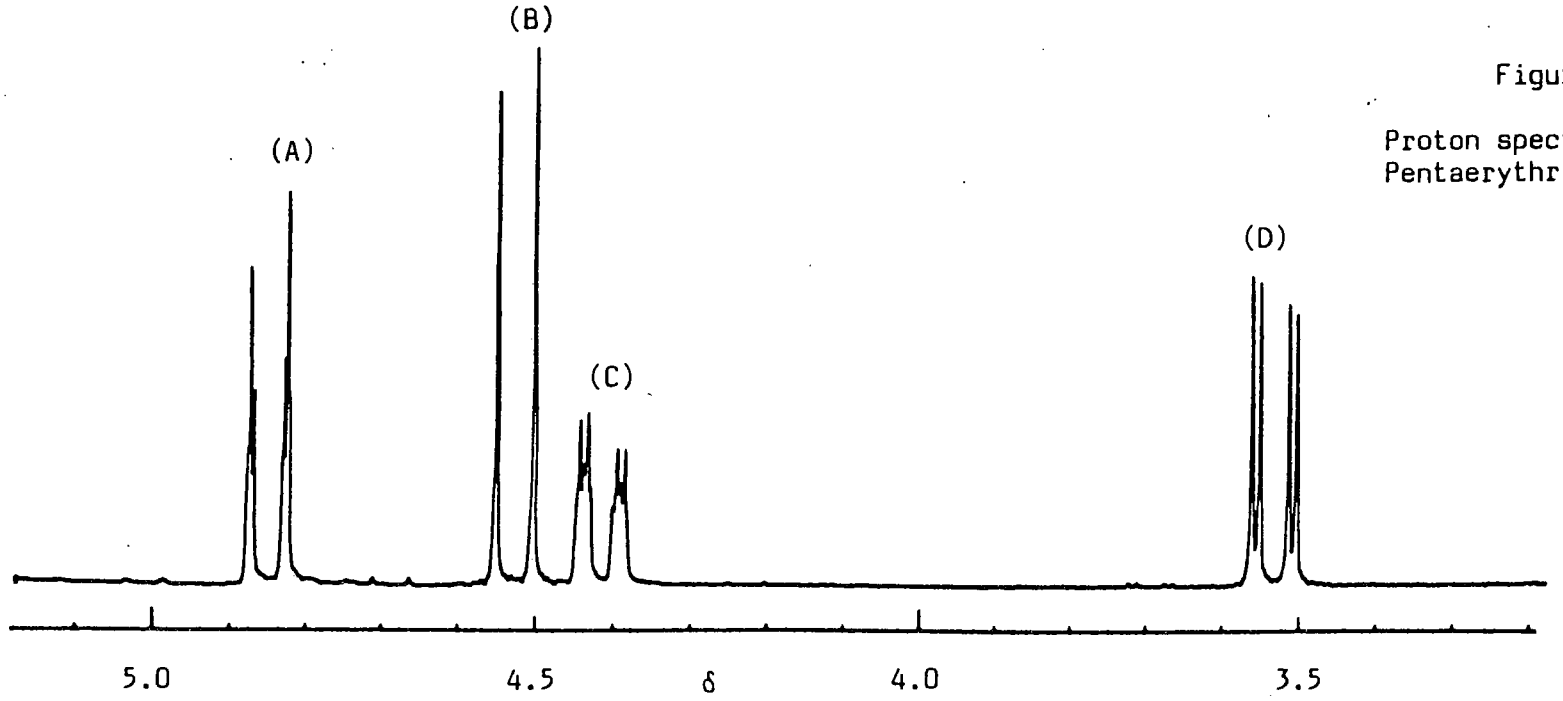


Figure 1

Proton spectrum
Pentaerythritol sulphite.

PROFESSOR V.F.BYSTROV

USSR Academy of Sciences

Shemyakin Institute of Bioorganic Chemistry

UI. Vavilova, 32
117988 Moscow, B-334
USSR

September 30, 1983

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

Title: Solution Structure of Insectotoxin I_5A

Dear Barry,

The three-dimensional structure of the *Buthus eupeus* scorpion insectotoxin I_5A (35 amino acid residues, four disulfide bonds) in aqueous solution has been established by 2D proton NMR spectroscopy at 500 MHz (Bruker WM-500). The signals were assigned by COSY and NOESY spectra analysis according to the corrected primary structure [A.S.Arseniev, *et al.*, *Bioorg. Khim.*(USSR) *9*, 768 (1983)]. From the NOE connectivities, vicinal proton coupling constants and NH deuterium exchange rates the local conformation of the amino acid residues and of the secondary structure domains were deduced. All three X^i - Pro^{i+1} peptide bonds have *trans*-configuration as follows from the NOE between H^{α}_i and H^{δ}_{i+1} protons [TAMU NMR Newsletters, 294/3]. Antiparallel β-structure was revealed in the fragment Asn^{23}-Asn^{34} and right hand α-helix - in Asn^{11}-Cys^{19}. Analysing the full set of the NOE connectivities by distance geometry algorithm [W.Braun, *et al.*, *BBA*, *667*, 377 (1981)] in preudoatomic approximation the overall spatial structure was established as shown in the Figure and the most plausible set of disulfide bridges was proposed (2-19, 5-31, 16-26 and 20-33 shown by dashed lines). The details will be published soon in "Bioorg. Khim." (USSR).

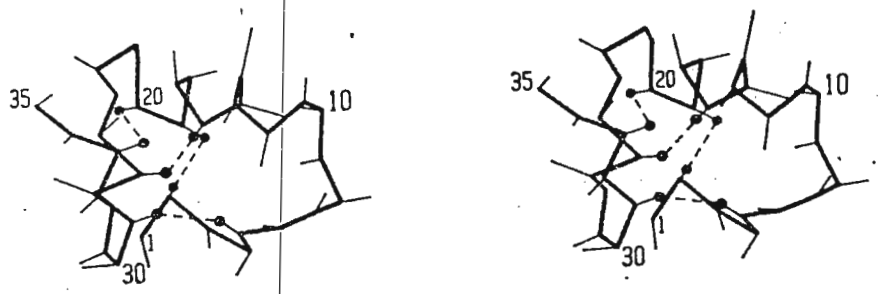


Figure. Stereoscopic view of the *Buthus eupeus* insectotoxin I_5A solution structure.

V.Bystrov A.Arseniev V.Kondakov V.Maiorov

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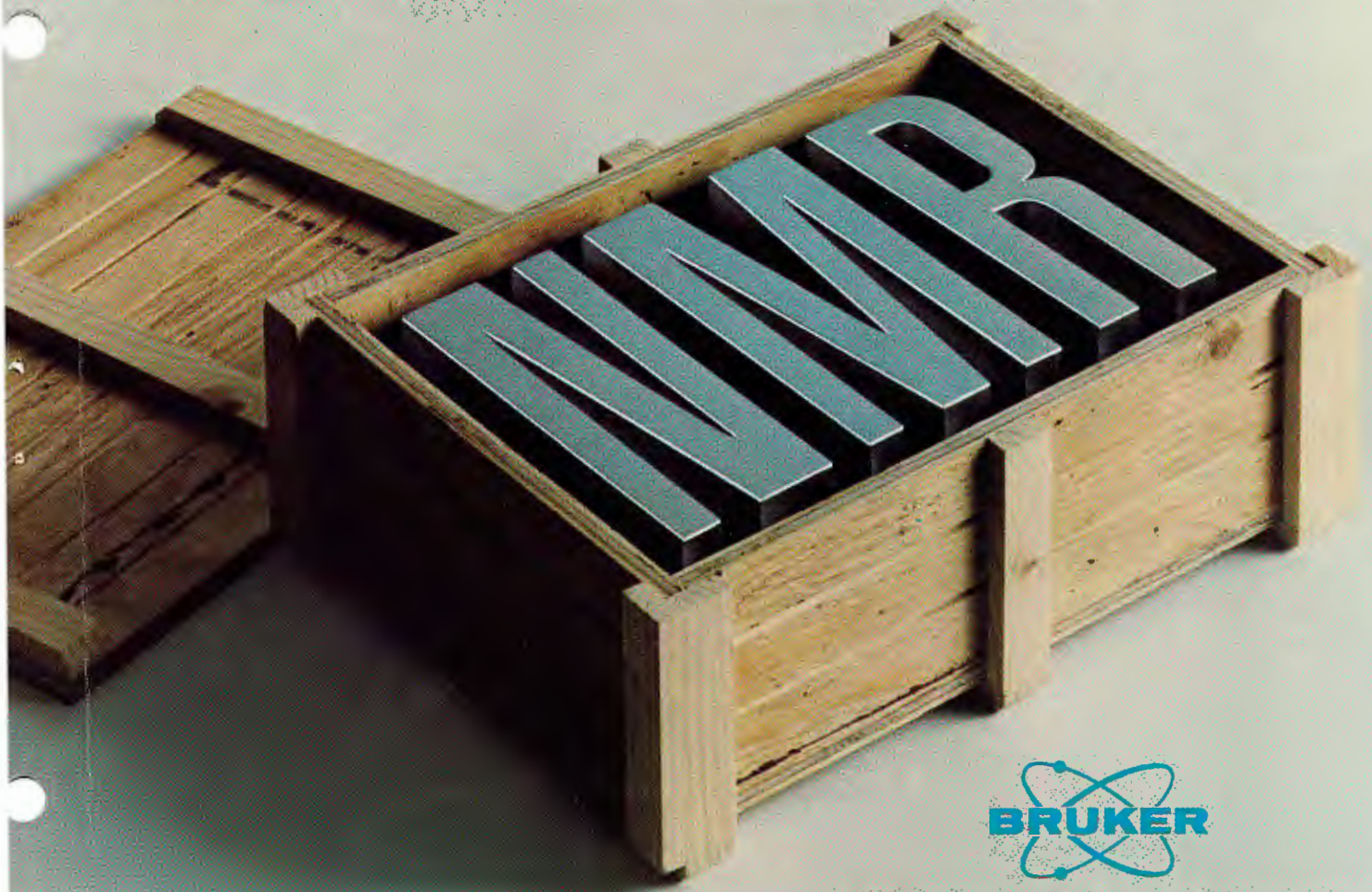

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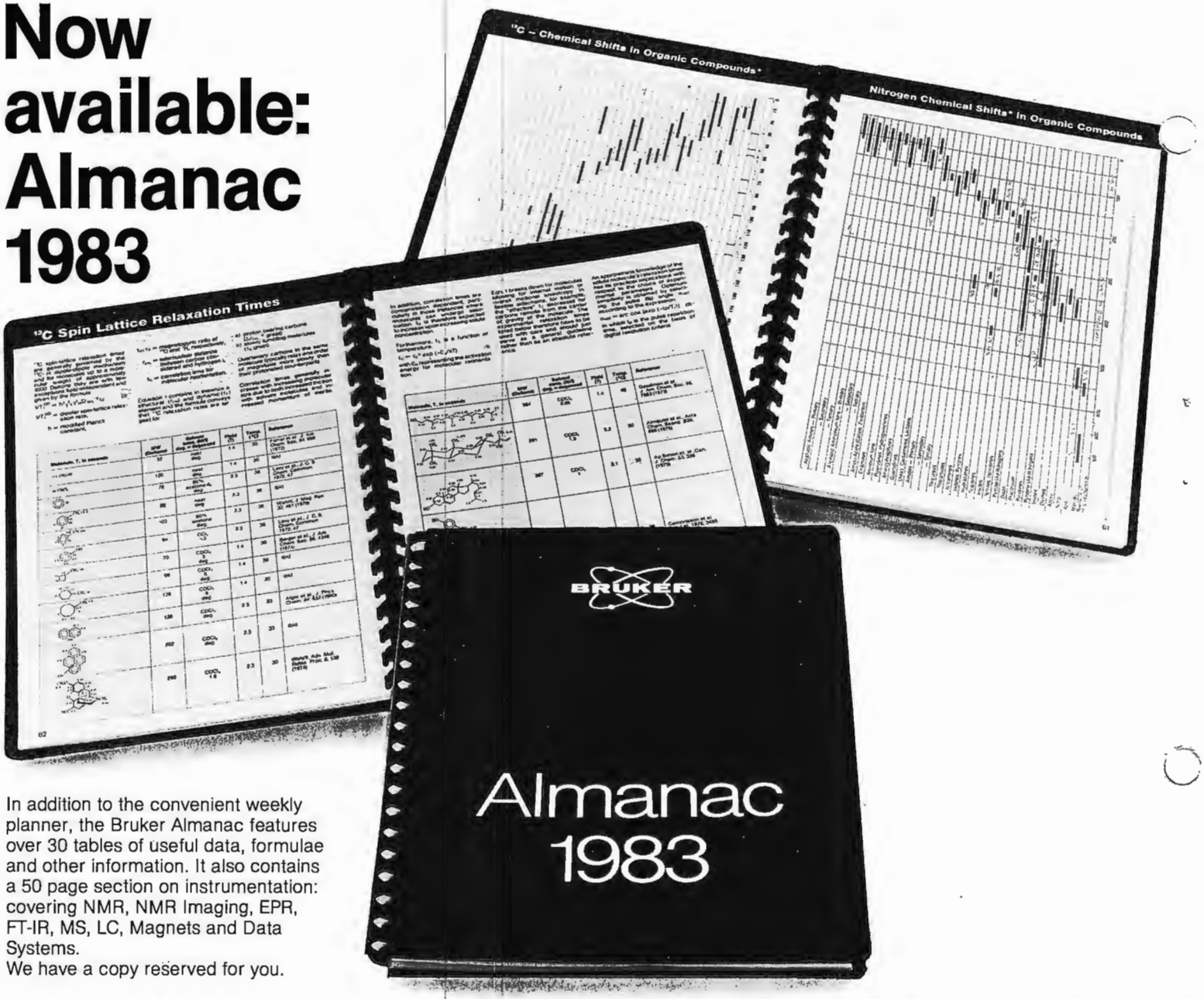

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Prof. B. L. Shapiro
Editor and Publisher
TAMU NMR Newsletter
Texas A&M University
Dept. of Chemistry

College Station, Texas 77843

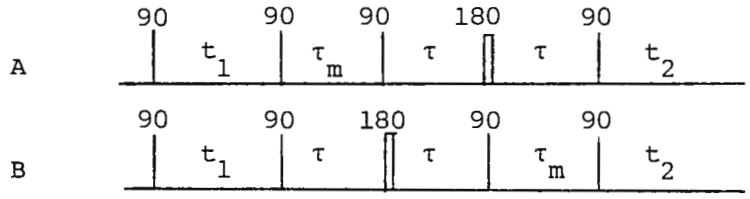
USA

Zürich, November 23, 1983

2D Relayed NOESY Spectra of Proteins

Dear Dr. Shapiro,

I have used a combination of coherence transfer with incoherent magnetization transfer by NOE to solve ambiguities in the identification of NOESY cross peaks in protein spectra(1). With this technique NOESY cross peaks can be transferred from crowded to empty spectral regions. This enables us to identify such NOE connectivities that would otherwise be ambiguous because of degeneracy of resonances. Two different pulse sequences were used:



The magnetization pathway for sequence A can be described with

$$H_k(\omega_1) \xrightarrow{NOE} H_\ell \xrightarrow{J} H_m(\omega_2)$$

The magnetization of spin H_k is frequency labelled during t_1, turned into longitudinal magnetization, and transferred by NOE to the intermediate spin H_ℓ. Then the magnetization is turned again into transverse magnetization and transferred to a J coupled spin H_m which is finally detected during t_2 with ω_2. With pulse sequence B first a coherence transfer is performed wich is followed by an incoherent magnetization transfer via NOE. This pathway can be described as:

$$H_m(\omega_1) \xrightarrow{J} H_\ell \xrightarrow{NOE} H_k(\omega_2)$$

Thus both experiments are symmetry related. The spectrum obtained with sequence A is essentially a mirror image, with respect to the diagonal, of the one obtained with sequence B. The individual experiments, however, are asymmetric with respect to the diagonal. Fig.1A shows a small section of a relayed NOESY spectrum of the basic pancreatic trypsin inhibitor (BPTI), recorded with sequence A. For comparison, Fig.1B shows the same sections of a normal NOESY spectrum. Phase sensitive Fourier transformations were used.

The relayed NOESY spectrum contains four types of peaks:

1. Relayed NOESY cross peaks are identified wit "rN" and the residue numbers. The cross peak at ω_1 = 9.36 ppm and ω_2 = 9.05 ppm, for example, represents the magnetization pathway

$$\text{NH F33}(\omega_1) \xrightarrow{\text{NOE}} \alpha\text{T32} \xrightarrow{J} \text{NH T32}(\omega_2)$$

These connectivities are not present in the normal NOESY spectrum of Fig.1B.

2. Direct COSY cross peaks are identified with "C", and with type and number of the residue. In the part of the spectrum that is shown they represent connectivities between NH and α protons within a residue.

3. Direct NOE cross peaks are identified with "N". They are strongly reduced compared with the NOESY of Fig.1B.

4. Diagonal peaks are supressed in a similar way as the direct NOE cross peaks.

Relayed NOESY and direct COSY cross peaks are in pure 2D absorption, direct NOE cross peaks and diagonal peaks are absorptive along ω_1 and dispersive along ω_2.

Sincerely yours

Gerhard Wagner

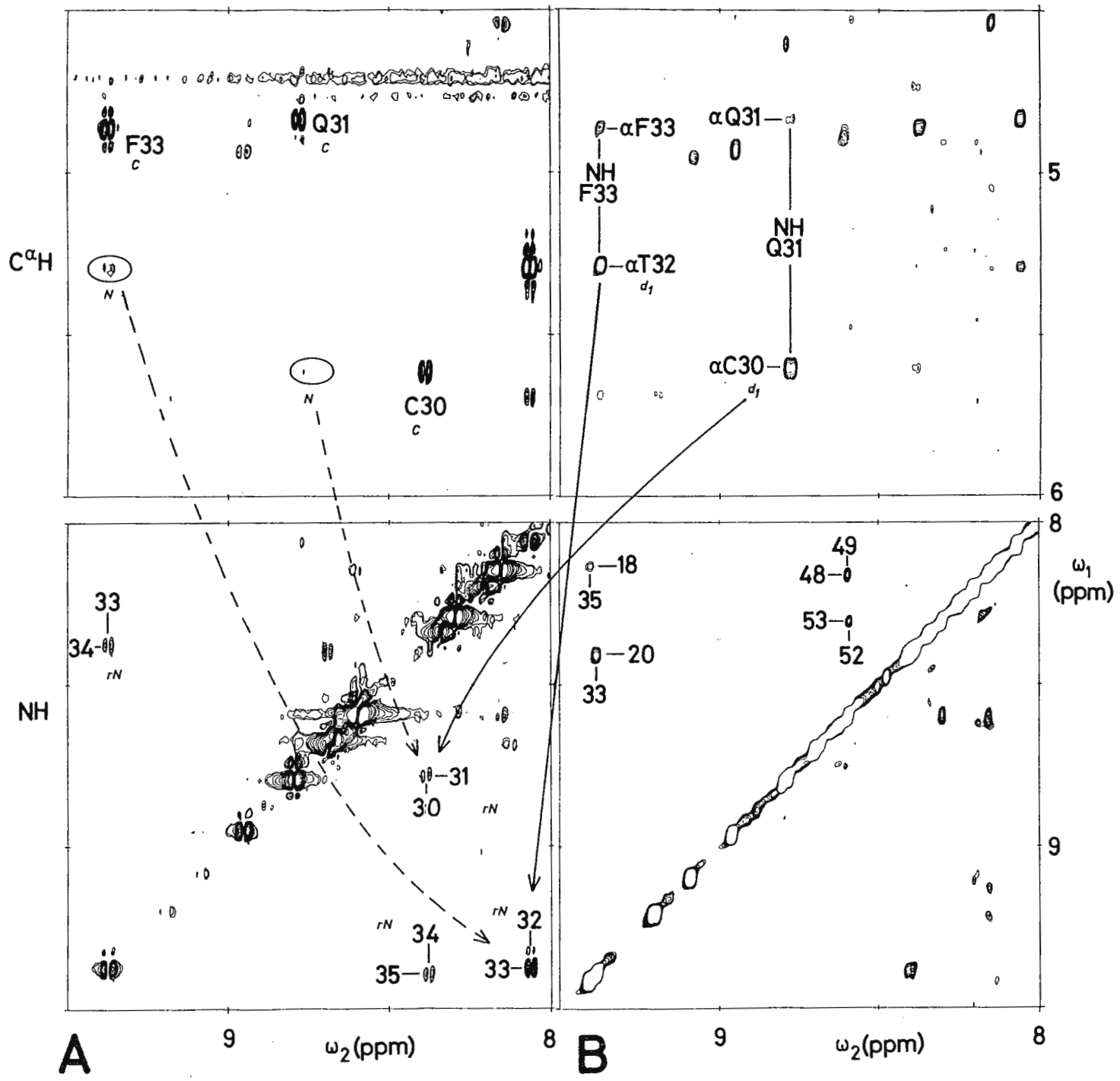
Gerhard Wagner

1. G. Wagner, J. Magn. Reson., submitted.

Figure Caption

Comparison of a relayed NOESY spectrum (A) with a normal NOESY spectrum (B) of BPTI. The spectra were recorded on a Bruker WM 500 spectrometer. Only two small sections are shown containing NH-NH and NH-$C^{\alpha}H$ cross peaks in the lower and the upper sections, respectively. Phase sensitive spectra are shown. Relayed NOE, direct NOE and direct COSY cross peaks are identified with "rN", "N", and "C", respectively. Some of the cross peaks are further identified with residue number and residue type. "d_1" in the NOESY spectrum means a connectivity between the NH of residue i+1 to the α proton of residue i. The solid arrows indicate to which positions cross peaks of the NOESY spectrum have been transferred by the relayed NOESY technique. Broken arrows show the same transfer within Fig. A.

"please credit this contribution to the subscription of Kurt Wüthrich".


F33
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26 October 1983

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

RE: ^{13}C NMR of Deoxy-Oligonucleotide Duplexes

Dear Barry:

The figure shows a $^{13}C\{^{1}H\}$-nmr spectrum of duplexed d(CpGpC-pGpCpG) at 11 mM in single strands and 0.1 M NaCl obtained in a standard 10 mm nmr tube. The lower panel shows the signals from the base carbons, of which GuaC8, CytC5, and CytC6 have covalently attached protons. The sugar resonances are displayed in the upper panel, C5' and C2' are doubly protonated, the rest are singly protonated. All of the sugar carbons except C1' are coupled by two or three bonds to ^{31}P, but the lines are probably too broad to measure the coupling constants. There are six of each class of sugar carbon and three of each class of base carbon. Many single carbon lines are resolved, and comparison with spectra of the $d(CG)_4$ duplex (not shown) allows us to assign eight of these to individual monomer units at the duplex termini. Upon increasing the temperature, most of the signals undergo a rather sharp transition in chemical shift centered about 70°C. The changes in chemical shift cover a range from -1.6 to +1.6 ppm.

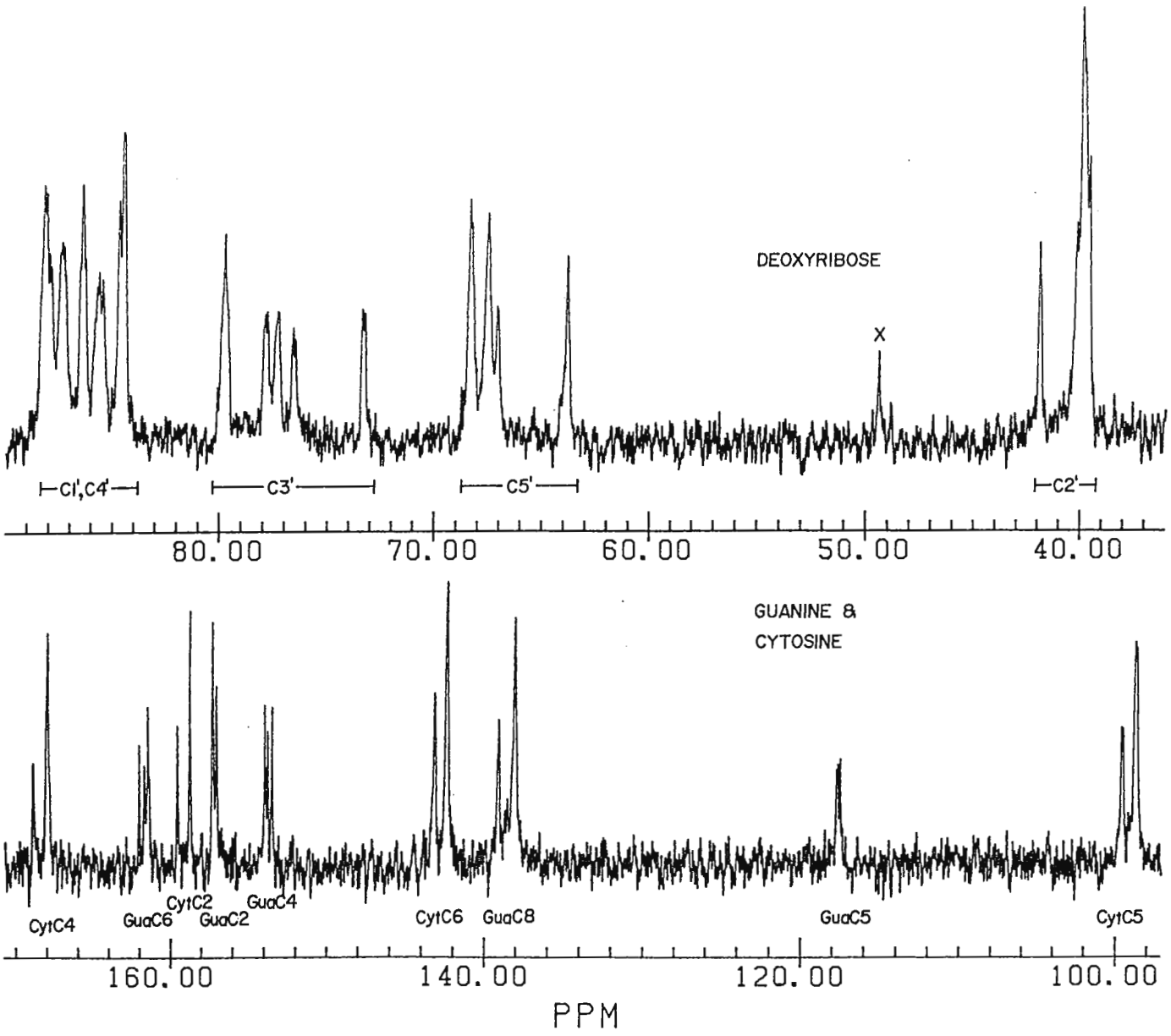
We have measured T_1 and NOE values for both the hexamer and octamer duplexes at low salt and the octamer duplex in 6M LiCl where it should adopt the left-handed Z-form. T_1 values are typically less than 0.2 sec and NOEF values up to 0.6 for the protonated base carbons; T_1's up to 0.8 sec and NOEF's < 0.2 for the non-protonated ones. T_1's from 0.1 to 0.4 sec and NOEF's from 0.3 to 0.8 characterize the sugar carbons. (T_1 and NOEF data for the octamer duplex in low salt.) Preliminary analysis of this data indicates that the ends of the helix move more freely than internal residues, and that there is significantly more motion at C2' than at other positions. Isotropic tumbling closely models the overall motion with a correlation time near 5 ns.

Sincerely,

George C. Levy
Professor

and

Philip N. Borer
Research Associate Professor



SU NMR LABORATORY

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DATE: 8 -19 -83
TIME: 0 : 0 : 0

d(CG)9 11 mM, low salt, 28C
If you read this far, you will KNOW that we had to respond to a dreadad PINK!

SPECTROMETER:	NM-360
OBS. FREQ:	90.559998 MHZ
DECP. FREQ:	360.000000 MHZ
LOCK FREQ:	55.000000 MHZ
EXPERIMENT:	1pls
QUADRATURE PHASE	
ACQUISITION TIME	.26 SEC
SCAN INTERVAL	.86 SEC
TOTAL TIME	7 HRS
	90.28 MIN
SCANS	91415
SPECTRUM WIDTH	15625 HZ
NO. REAL DATA POINTS	8 K
DATA SCALING FACTOR	0
DISPLAY SCALING FACTOR	-22

APODIZATION:
3.00 HZ LINE BROADENING

DECOUPLING:
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Lund, October 27, 1983

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

Potassium Binding by
^{39}K NMR

Dear Barry,

Despite the intrinsic interest in K^+ as the predominant intracellular cation, the applicaton of ^{39}K NMR has lagged far behind that of ^{23}Na NMR, in particular with respect to biological systems. The reason is simple: in contrast to ^{23}Na, ^{39}K is one of the worst of all NMR nuclei [1]. Nonetheless, with the advent of higher magnetic fields and the use of sideways solenoid coils [2] we are now able to routinely obtain good signal/noise for $^{39}K^+$ signals at concentrations as low as a few mM [3].

We have recently completed ^{39}K NMR studies of potassium binding to (1) double helical DNA and (2) the highly charged egg-yolk protein phosvitin. The DNA work was carried out in collaboration with Dr. Lars Nordenskiöld from the Arrhenius laboratory in Stockholm, with help and encouragement from Professor Tom Record of the University of Wisconsin-Madison.

For both DNA and phosvitin, the picture obtained from our measurements is of relatively weak, non-specific interactions of K^+, characterized by narrow linewidths (on the order of 50 Hz), fast exchange and only small (if observable) deviations from extreme narrowing. For DNA, our $^{39}K^+$ results are in complete agreement with previous measurements of $^{23}Na^+$ binding to DNA. Thus, we have not observed any evidence of ion-specificity. In contrast, for phosvitin, we observed some differences between K^+ and Na^+ binding. In the accompanying figure we present an illustrative example of the quality of the data we have been able to obtain for these systems.

We think that our results clearly demonstrate the potential of ^{39}K NMR for exploring ionic interactions in other biological systems. Detailed descriptions of this work can be found in manuscripts that we have recently submitted for publication.

Sincerely

William Braunlin Torbjörn Drakenberg Hans Vogel Sture Forsén

Hans Lilja

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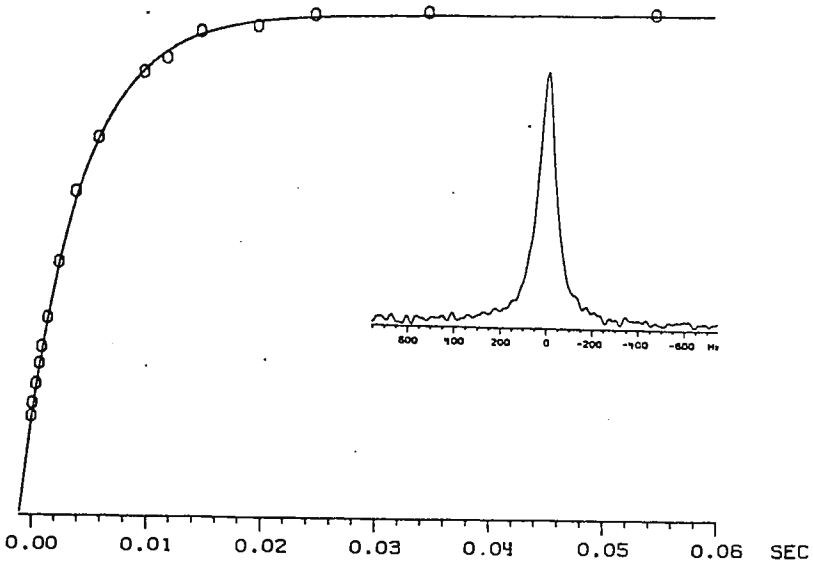


Potassium-39 inversion-recovery data obtained at 24°C for a sample containing 16.6 mM K^+, 12.3 mM DNA phosphate, 2.8 x 10^3 transients were collected to obtain each experimental point. The total time of the experiment was 7.9 hrs. The solid curve shows a 3-parameter fit of the data, giving T_1 = 5.1 msec. The inset shows the spectrum corresponding to the point at the largest delay time (τ = 55 msec).

1. Lindman, B. and Forsén, S. (1978) in "NMR and the Periodic Table" (R. Harris and B. Mann, eds.) Academic Press, New York.

2. Drakenberg, T., Forsén, S. and Lilja, H. (1983). J. Magn. Reson. 53, 412-422.

3. Neurohr, K.J., Drakenberg, T., Forsén, S. and Lilja, H. (1983). J. Magn. Reson. 51, 460-469.

303-15

Columbia University in the City of New York | *New York, N.Y. 10027*

DEPARTMENT OF CHEMISTRY

Havemeyer Hall

5 November 1983

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

Dear Professor Shapiro,

^{31}P Spin-Spin Coupling Constants of Cardiac ATP

Continuing our NMR studies of perfused rat hearts, we decided to try to measure the phosphorus coupling constants of ATP in the heart. The top part of the figure shows a typical P-31 NMR spectrum of a perfused rat heart.We have been unable to reveal any multiplet structure in the ATP peaks by digital resolution enhancement.However, the use of 2D J-spectroscopy enables the gamma and alfa peaks to be resolved into doublets, as shown in the lower part of the figure.

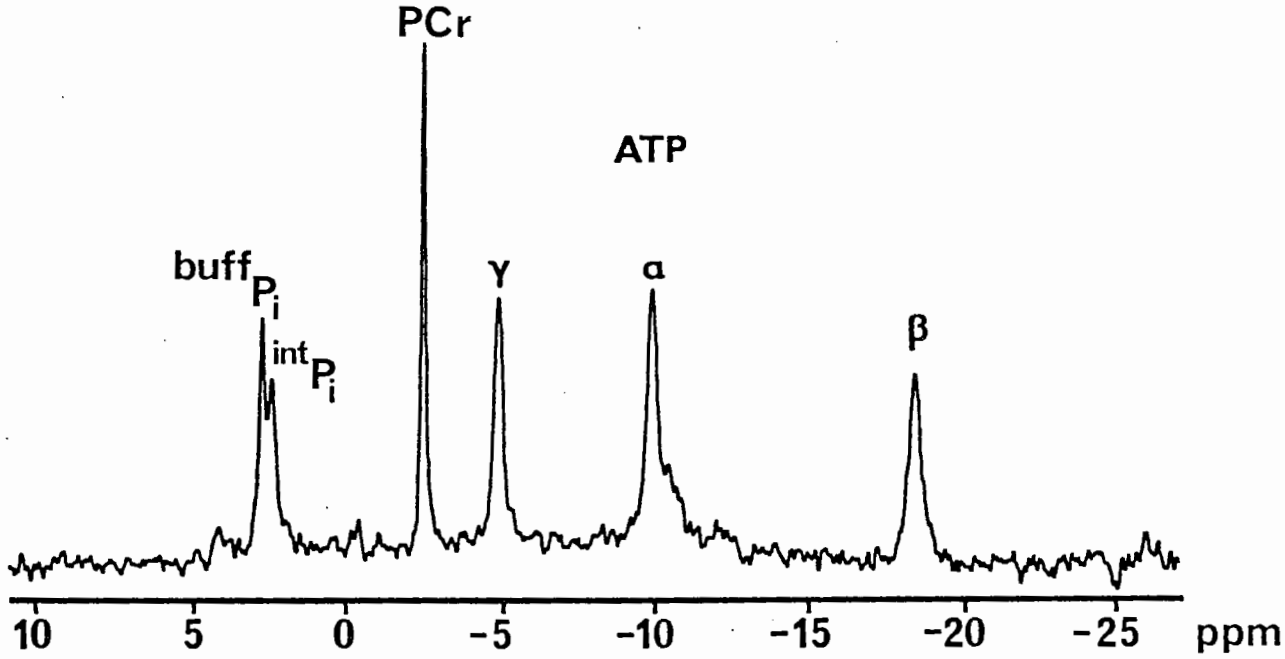
The coupling constants can be measured from the phase sensitive displays and are found to be equal (within experimental error) to the values measured in solution for Mg^{++}-ATP.One-dimensional spectral editing by J-modulated spin echoes also reveals these coupling constants.

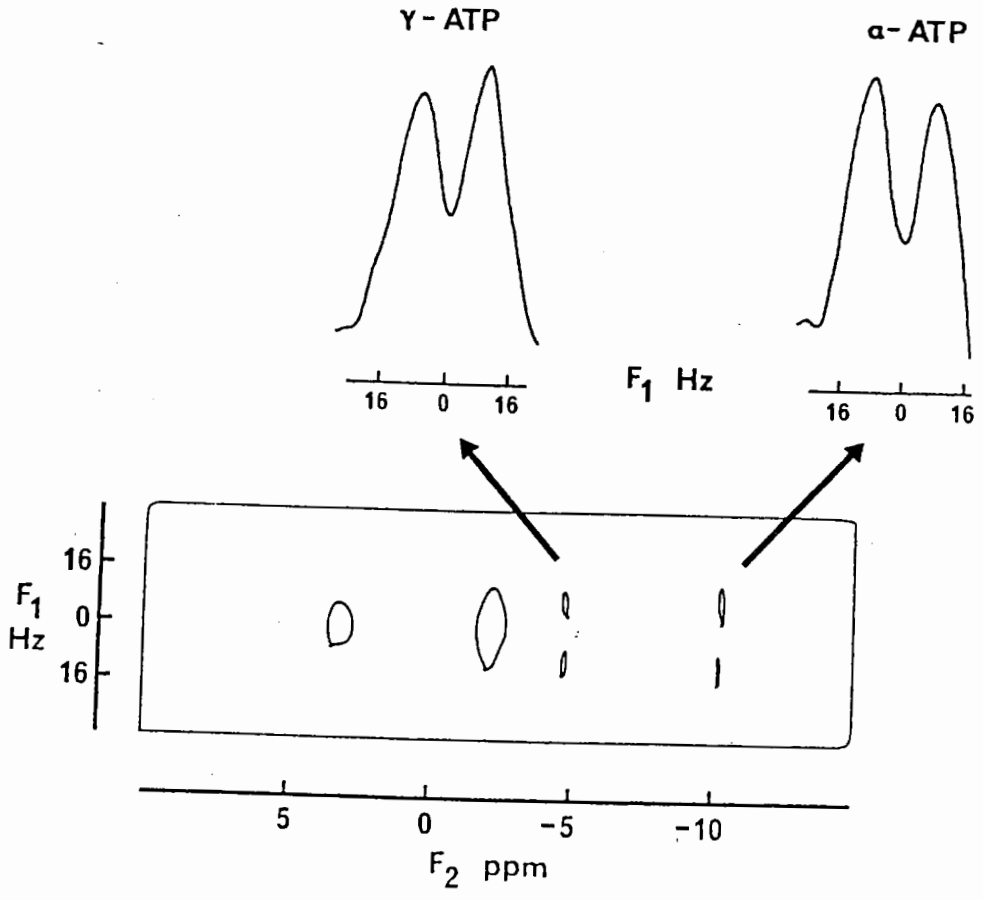
Thus, we might conjecture that the molecular conformation of the cardiac ATP polyphosphate chain appears to be quite similar to that in solution, assuming that phosphorus coupling constants are a sufficiently sensitive probe to measure this parameter.

Yours Sincerely

C. J. Turner
Department of
Chemistry

P. B. Garlick
Department of
Pharmacology


PCr
ATP
buff Pi
int Pi
γ
α
β
10
5
0
-5
-10
-15
-20
-25
ppm


γ - ATP
α - ATP
16
0
16
F1 Hz
16
0
16
F1 Hz
5
0
-5
-10
F2 ppm

303-17

מכון ויצמן למדע
THE WEIZMANN INSTITUTE OF SCIENCE
76100 REHOVOT · ISRAEL ישראל · 76100 רחובות

ISOTOPE DEPARTMENT
Direct phone: (054) 8

מחלקת איזוטופים
טלפון ישיר : (054) 8

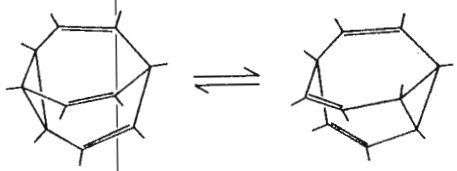
7 November, 1983

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

Re: The Cope Rearrangement in Bullvalene by Deuterium NMR in Liquid Crystalline Solvents

Dear Barry,

Fast dynamic processes of molecules dissolved in normal liquids have been extensively studied by ^{1}H and ^{13}C NMR. Recently we have shown that the method can be extended to liquid crystalline solvents and in certain cases the method may have considerable advantages over the use of isotropic solvents. In particular, by using deuterium NMR of deuterated compounds, simple dynamic spectra can be obtained which cover very wide dynamic ranges.[1-2] As an example consider the Cope rearrangement of bullvalene.



Its high temperature ^{1}H NMR spectrum in liquid crystalline solvent consists of a binomial decaplet due to fast averaging of all sites by the Cope rearrangement process.[3] Upon cooling, the line broadens and eventually gives a very complicated exchange broadened ten spin spectrum. The dynamic deuterium spectrum in liquid crystals is considerably simpler and is easily interpretable. Experimental spectra in phase V are shown on the left hand side of the enclosed figure. At -13°C when the dynamic process is slow, four quadrupole doublets corresponding to the four inequivalent sets of deuterons with relative intensities 1:3:3:3 may be observed. Their assignment and the relative signs of the corresponding quadrupole interactions can readily be made from the known molecular structure of bullvalene. In heating, the lines broaden and eventually coalesce to a single doublet representing the average quadrupole interaction. At 49°C this coalescence is not complete and further heating is necessary for complete coalescence. The computation of the dynamic lineshapes is straightforward and examples which approximately match the experimental spectra are shown on the right hand side of the figure.

We hope that this example demonstrates the power of the proposed method i.e. dynamic deuterium NMR in liquid crystalline solvents.

Yours sincerely,

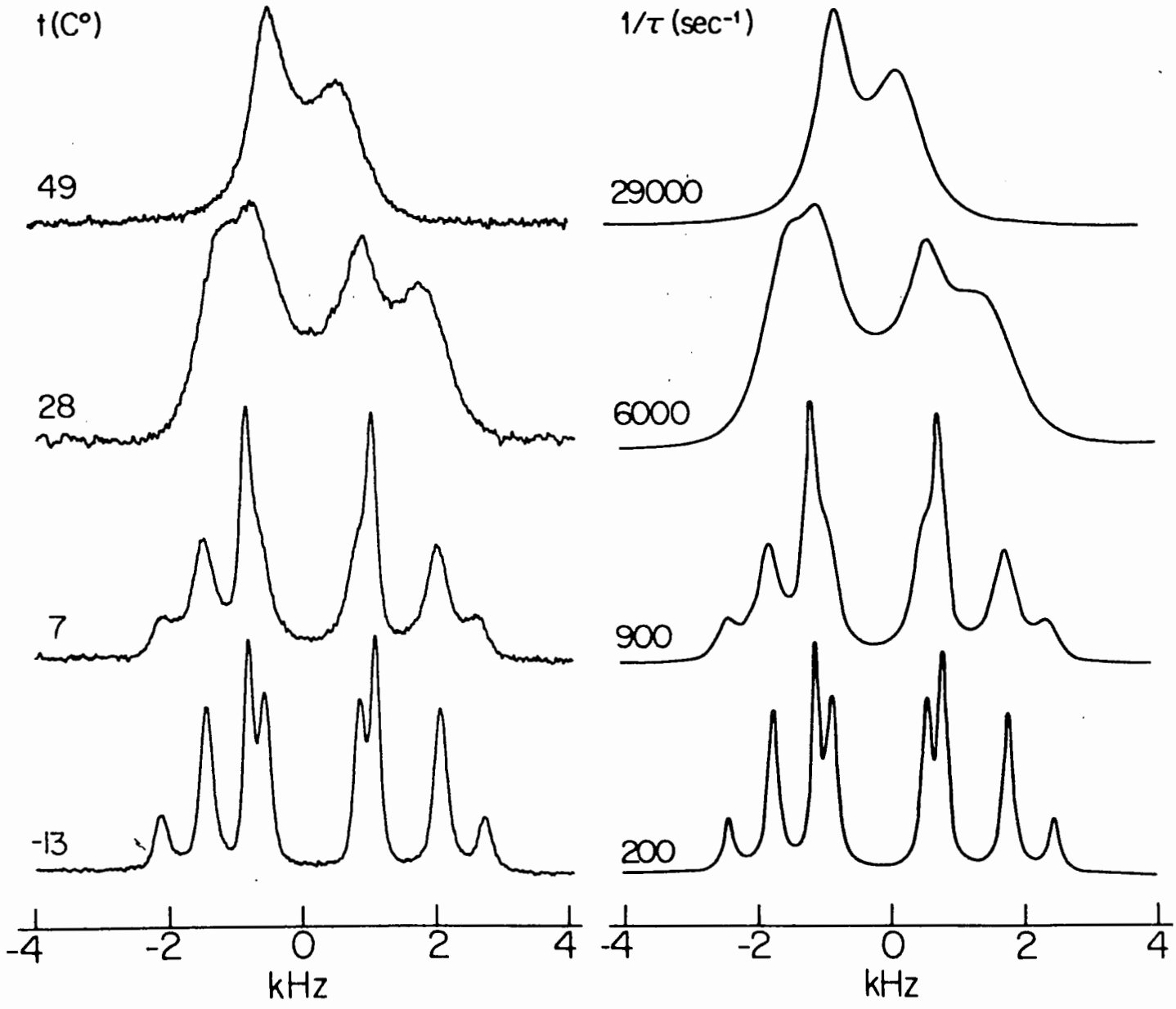
Z. Luz R. Poupko H. Zimmermann

CABLE ADDRESS: WEIZINST Israel מען למברקים: PHONE: (054) 82111-83111 טלפון: TELEX: 31 900 טלקס:

References:

1. R. Poupko and Z. Luz, J. Chem. Phys. 75, 1675 (1981).
2. M.E. Moseley, R. Poupko and Z. Luz, J. Mag. Res. 48, 354 (1982).
3. C.S. Yannoni, J. Am. Chem. Soc. 92, 5237 (1970).

^{2}D NMR Spectra of Bullvalene-d_{10} in Phase V



303-19

University of Nottingham

Department of Chemistry

UNIVERSITY PARK NOTTINGHAM NG7 2RD
TEL NOTTINGHAM 56101

HB/JL

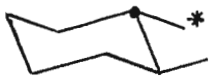
11th November 1983

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

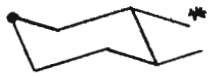
$^{13}C - {}^{13}C$ Coupling Constants

Dear Professor Shapiro,

During a recent low temperature ^{13}C study of trans-[1-methyl-^{13}C]-1,2-dimethylcyclohexane,[1] we recorded the following $^{13}C - {}^{13}C$ coupling constants (measured using 32 K data over 4000 Hz):-



^{1}J 35.2 ($\pm$ 0.13) Hz at 233 K

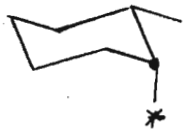


^{3}J 4.2 ($\pm$ 0.13) Hz at 243 K

The following are less accurate, unfortunately (16 K data over 10,000 Hz):-

cis 

^{1}J 35.2 ($\pm$ 0.63) Hz at 169 K.

cis 

^{1}J 35.7 ($\pm$ 0.63) Hz at 169 K.

Happy New Year !!

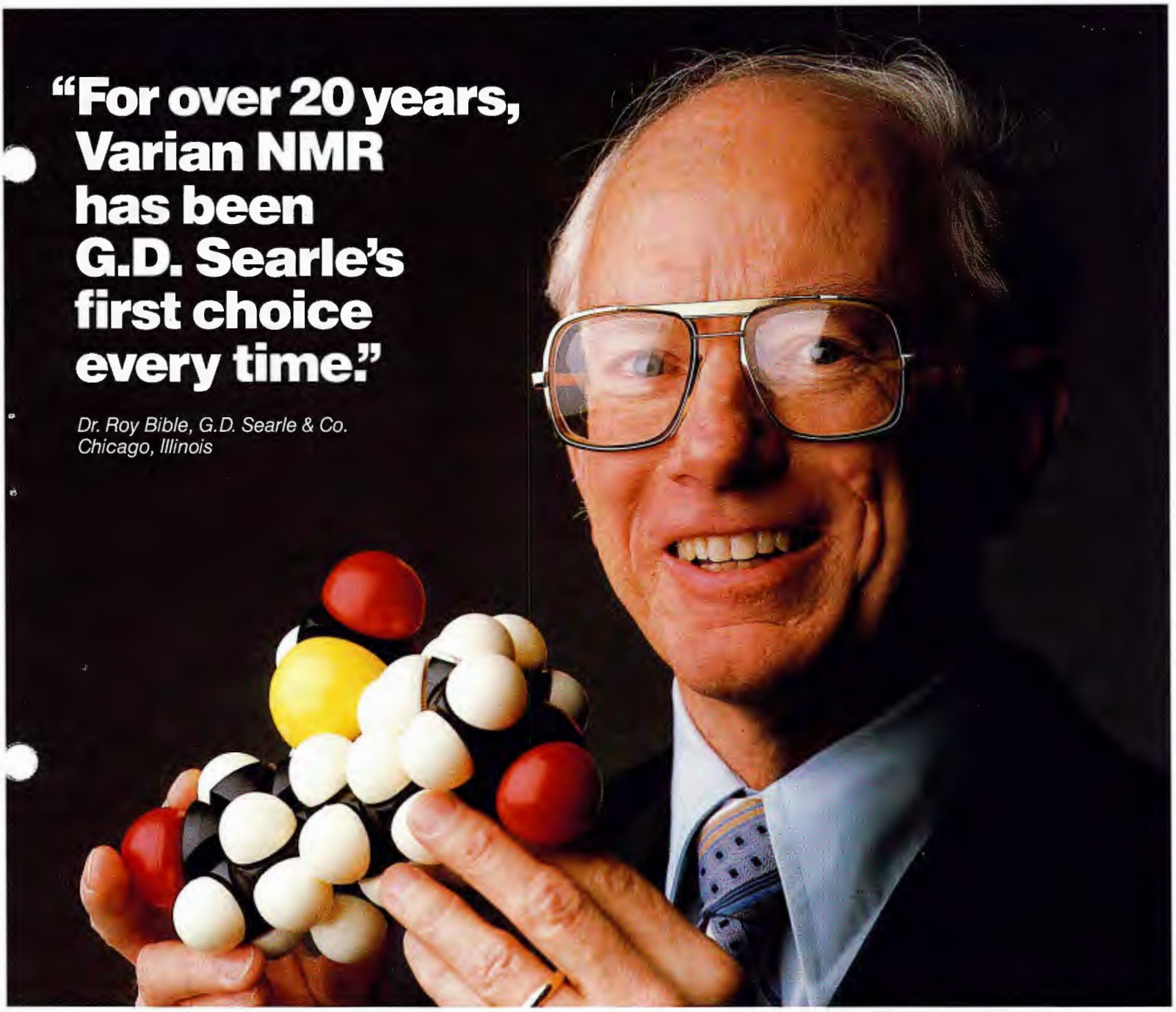
Harold Booth.

Dr. H. Booth.

1. H. Booth and T.B. Grindley, J.Chem.Soc., Chem.Comm., 1983, 1013.

"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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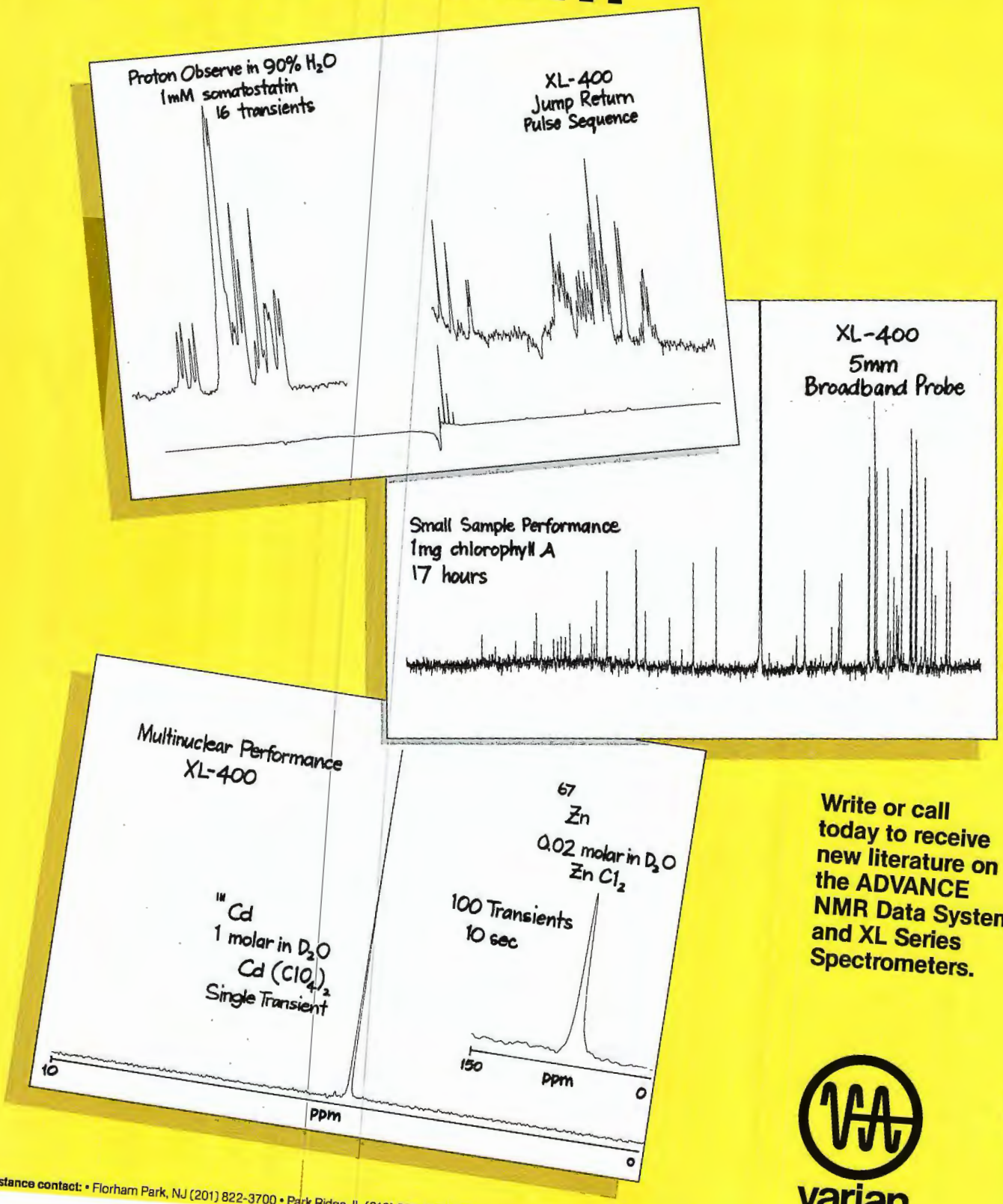

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Professor B L Shapiro
Department of Chemistry
Texas A & M University
College Station
Texas, U S A

10 November 1983

Dear Barry

OBSERVING "PROTONS" IN BIOLOGICAL SAMPLES BY ^2H AND 2D NMR:

INFINITE WATER SUPPRESSION

We have been using in vivo NMR to look at formaldehyde metabolism in the bacterium E.coli. With carbon-labelled formaldehyde it is easy (once you know how!) to see metabolism to a whole set of metabolites including methanol, formate and some mysterious XCH_2Y compounds in the 60 - 70 ppm region. Two questions which the carbon results did not resolve were

(1) Are the methanol and formate made independently or by a single "Cannizzarase" enzyme in this way:

$$2CH_2(OH)_2 \longrightarrow CH_3OH + HCO_2H + H_2O$$

(2) What are the proton chemical shifts in our mystery compounds?

We solved (1) by in vivo deuterium NMR. Feeding 10 mM $CD_2(OH)_2$ to bugs in deuterium depleted water gave the spectra shown in Figure 1. The methanol signal is split into a 1.7 Hz doublet by coupling to proton (confirmed by decoupling). Therefore the product is CD_2HOH, and the formaldehyde has been reduced by effectively H^-; had the Cannizzarase been operating, it would have made CD_3OH. These spectra, which took about 20 minutes to acquire, are the first in vivo deuterium spectra of which we are aware.

The second problem was solved by ^1H-^{13}C 2D chemical shift correlation experiments on the supernatant from bugs which had metabolised ^{13}C-formaldehyde. The contour plot (Figure 2) clearly shows formaldehyde at 83δ, methanol at 50δ and the unknowns at 60, 64 and 68δ. The f_1 cross section (Figure 3) give us the spectra only of those protons attached to carbon-label. Note how clean the formaldehyde signal is - less than 0.2 ppm from the invisible water! So we now have a water suppression ratio of infinity. Clearly the XCH_2Y groups at 64 and 68 ppm have diastereotopic protons, so taken together with other evidence, they appear to be *C-CH_2OH, where *C is chiral.

All this work together with its microbiological implications, is being published in Biochemistry quite soon.

With best wishes

Brian K Hunter | Kathryn M Nicholls | Jeremy K M Sanders

Fig 1: Lower spectrum was acquired at the beginnning of a metabolic experiment. and the upper one after about three hours.

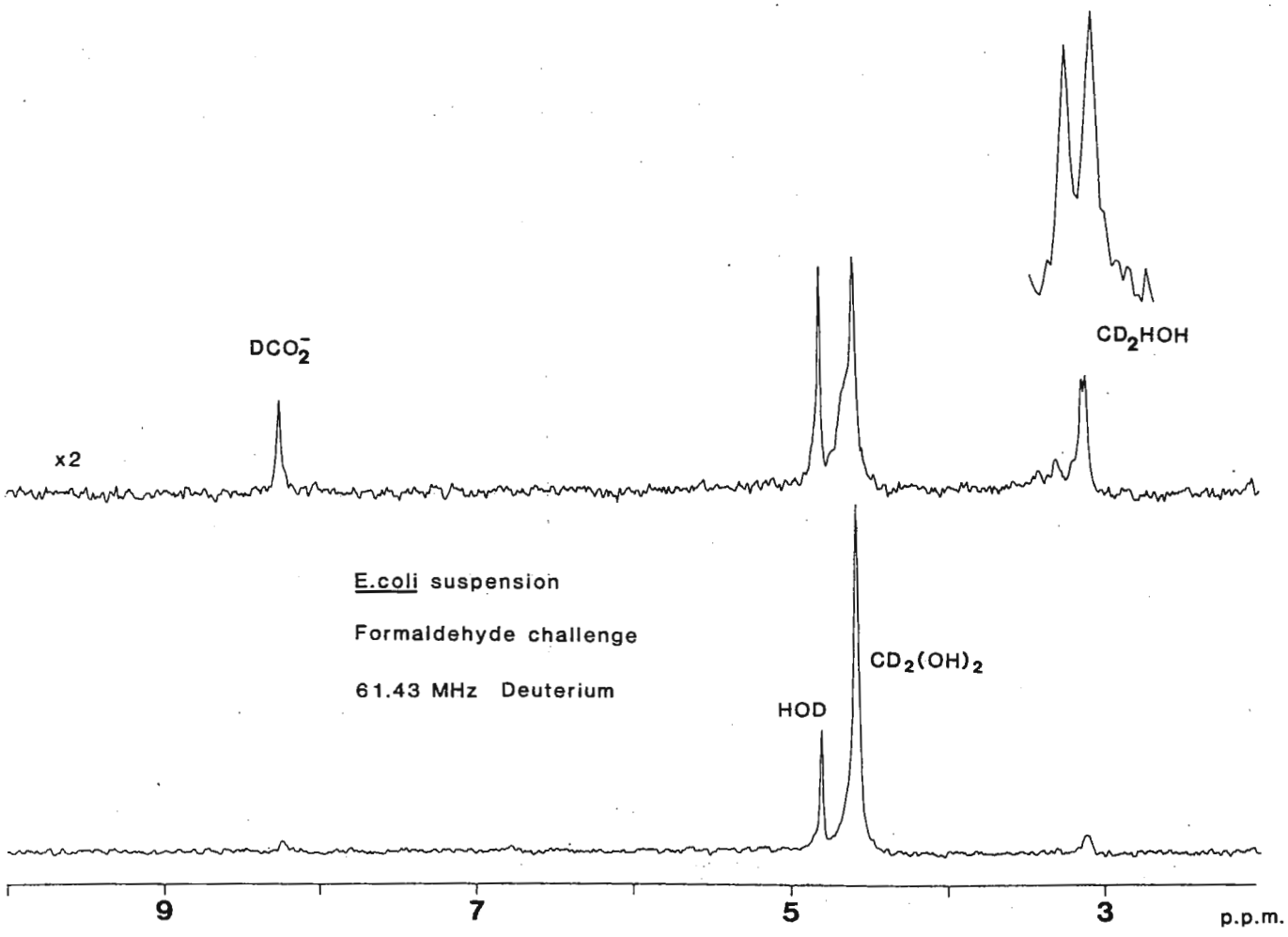


Fig.2

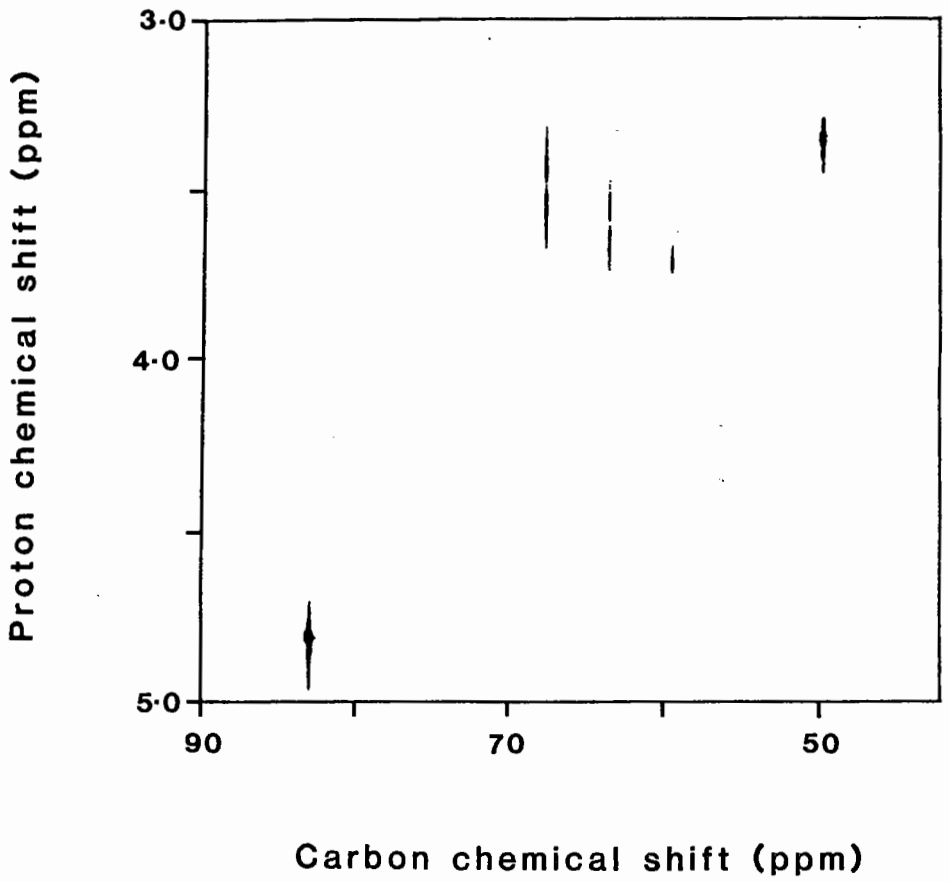
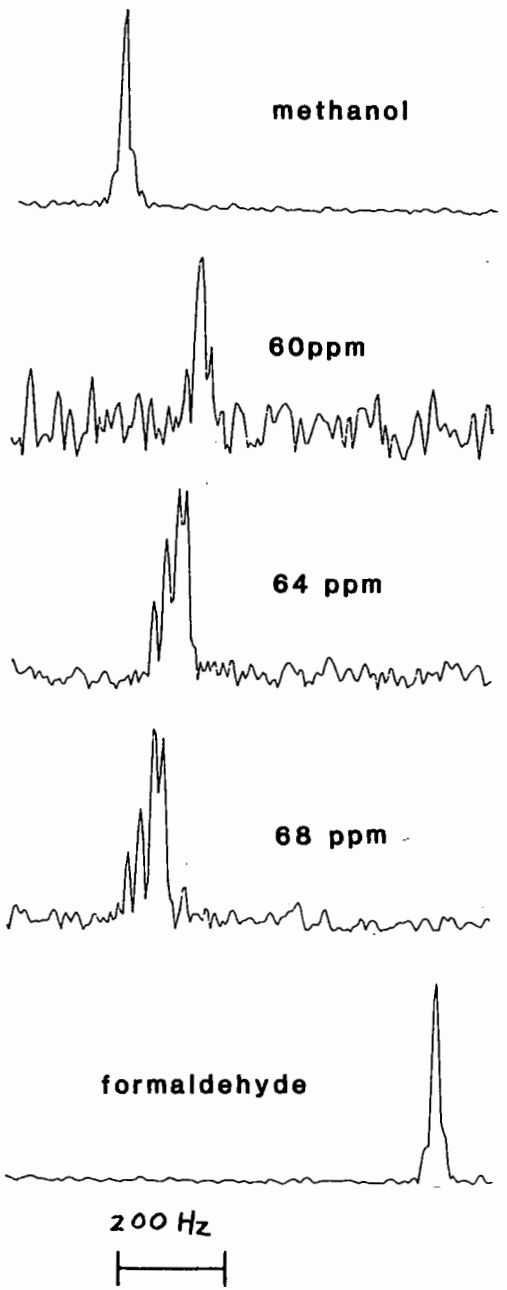

3·0
4·0
5·0
90
70
50
Proton chemical shift (ppm)
Carbon chemical shift (ppm)

Fig.3 →


methanol
60ppm
64 ppm
68 ppm
formaldehyde
200 Hz

Mobil Research and Development Corporation

November 9, 1983

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EUGENE L. JONES
MANAGER

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

Low Power MAS Signals from
Quadrupolar Nuclei in Solids

Dear Barry:

I have become interested in making magic angle spinning measurements on quadrupolar nuclei such as aluminum-27 using a JEOL FX-270 spectrometer with the Chemagnetics solids accessory. The natural mineral low albite is a useful reference mineral for many experiments. It is perfectly ordered, with all of the aluminum in one crystallographic site of tetrahedral coordination and quadrupole coupling constant of 3.3 MHz. The asymmetry parameter of 0.64 causes the observable -1/2 to +1/2 transition to have a complex MAS NMR line shape. This enables the Al-27 NMR spectrum to exhibit effects which are not so apparent in the synthetic zeolites which have received so much attention.

In the accompanying figure are spectra from 90° pulses of varying pulse amplitudes obtained by using a calibrated attenuator. The spinning speed was approximately 4.5 kHz. Note that there is a gradual change in line shape as longer pulses are employed. The spectrum at the shortest pulse length is closest to the "true" shape, as is proved by calculations of simulated spectra. The visual changes in NMR line shape are much more spectacular than the numerical changes in positions of maxima, shoulders, etc. I do not attempt to explain these changes; I leave that to the theoreticians who have more time than I have. However, it seems reasonable that the quadrupole coupling constant, the asymmetry parameter, the spinning speed, the pulse duration, and the NMR frequency should be pertinent parameters.

These results show that spectra of quadrupolar nuclei can be obtained with reasonably low pulse power levels. However, the line shapes may be distorted. This observation is especially pertinent to those who use low-power spectometers to obtain spectra which are to be analyzed by comparison with spectra computed under the assumption of infinitely short 90° pulses.

Sincerely,

Don

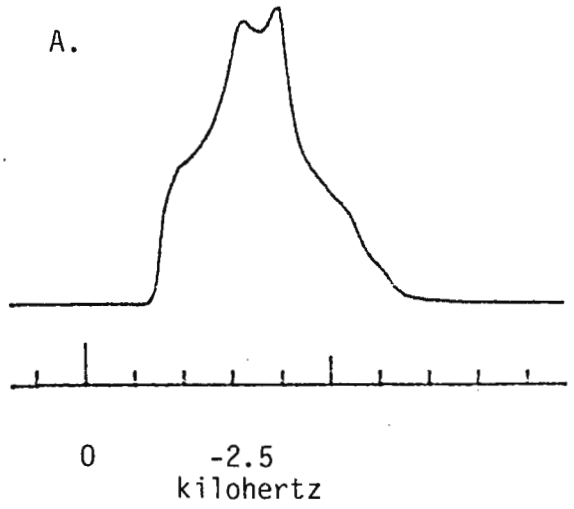
D. E. Woessner

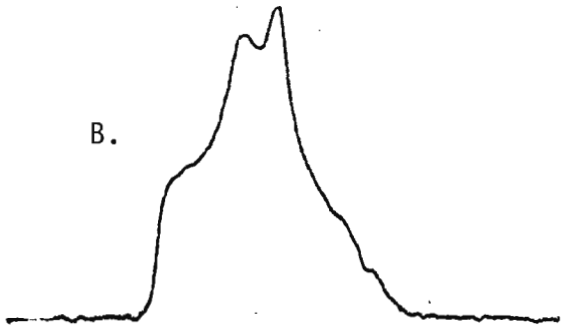
DEW:ms
Attachment

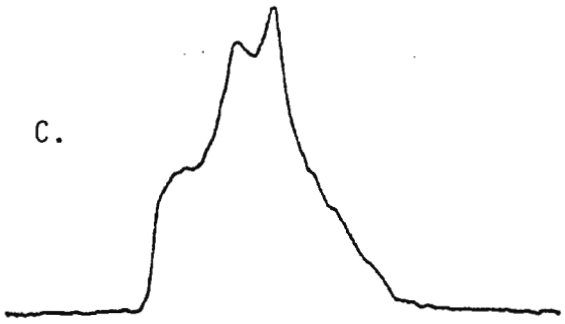
cc: E. L. Jones
J. T. Nipper
A. G. Ostroff

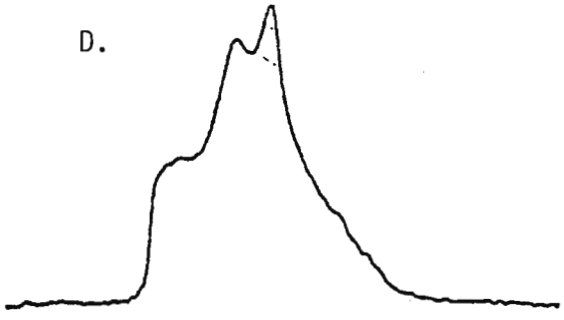
^{27}Aℓ MAS NMR spectra of low low albite at various 90° pulse lengths:

A. 2.6 microseconds
B. 8.0 microseconds
C. 17.0 microseconds
D. 28.0 microseconds
E. 53.0 microseconds









ETH EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE ZÜRICH

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November 10, 1983

Professor Bernard L. SHAPIRO
Texas A&M University
College of Science
COLLEGE STATION, Texas 77843
U.S.A.

Suggested Title. $^{1}J(^{13}C,^{13}C)$ Values in a Pd(II) Quinoline Complex.

Dear Professor Shapiro,

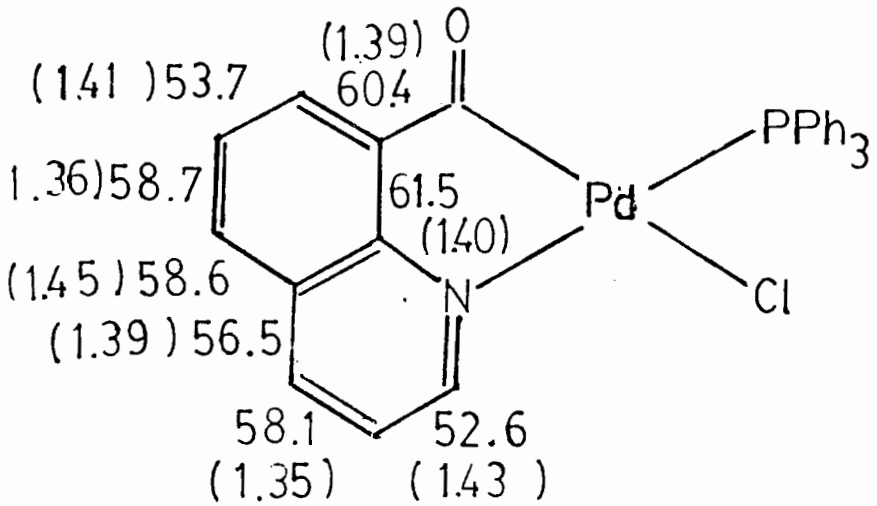
Our synthetic studies have recently produced the acyl palladium complex $PdCl(C_{10}H_6NO)(PPh_3)$, see figure, whose X-ray structure reveals alternately longer and shorter C-C distances in the quinoline ring. If indeed the double bonds are localised, then it is conceivable that the $^{1}J(^{13}C,^{13}C)$ values will reflect this electronic structure. The ^{13}C spectrum of this complex (usual INADEQUATE sequence) is shown in the upper trace, along with a conventional spectrum, below. Allthough the correlation between <C - C> and $^{1}J(^{13}C,^{13}C)$ is not perfect, the shorter distances are, in general, associated with the larger one-bond coupling constants. The most obvious deviation occurs at the remote carbon atoms separated by 145 Å. We are currently investigating some closely related systems in the hopes of expanding on this general theme.

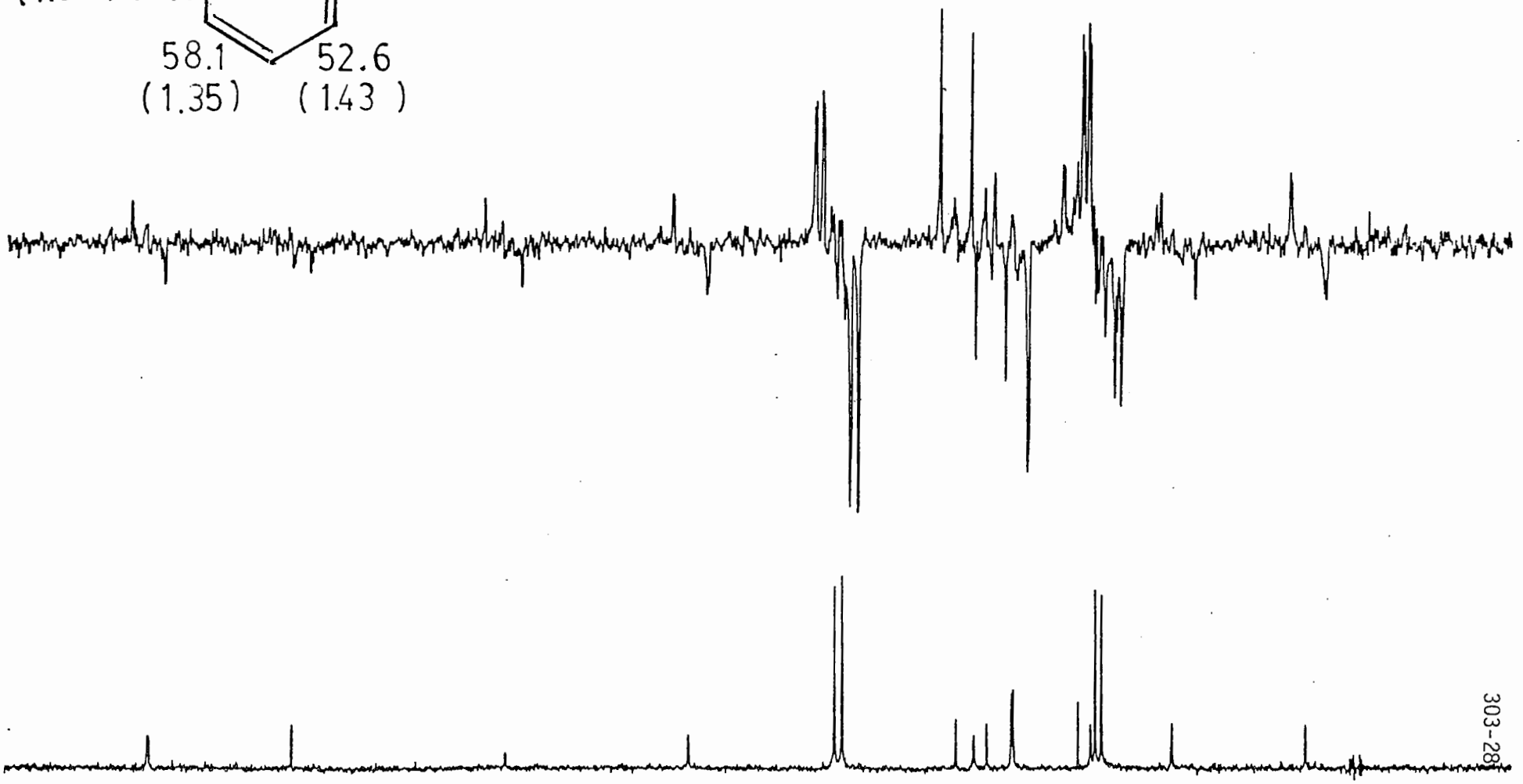
Sincerely

C. Anklin P.S. Pregosin

P.S. Please credit this contribution to the account of L. M. Venanzi.

^{13}C - INADEQUATE - NMR





Rijksuniversiteit Utrecht

Organisch chemisch laboratorium

Croesestraat 79
3522 AD Utrecht The Netherlands
Telefoon 030 - 882311

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

Datum
Uw kenmerk
Ons kenmerk
Onderwerp

Solvent dependency of direct proton-carbon coupling constants

Dear professor Shapiro,

Investigations on the solvent dependency of spin-spin coupling constants fall broadly into two different categories[1]:

- the change in the measured coupling constant may be attributed to solvent induced changes in the relative populations of the rotamers or conformers of the molecule being studied.
- the relative spatial locations of the coupled nuclei, as well as the relative positions of substituents with respect to the coupling pathway, are constrained; in this case the medium effects arise from electronic changes in the solute molecule induced by the solvent.

The last category is the least studied. The aim of our studies is to obtain a model description for some of these latter effects, excluding effects arising from direct intermolecular interactions such as complex formation or solvation effects.

Models generally employed to describe the solvent effect on NMR-parameters use the electric field dependency of these parameters. A solvent may induce an electric field at the site of the solute by means of the so-called *reaction field effect* and/or the *solvent stark effect*.

The reaction field R, arising when the point dipole moment μ of a solute (with polarizability α and refractive index n) polarizes the surrounding solution (with dielectric constant ε) is, for a spherical solute cavity, given by[2]:

$$R = \frac{n^2-1}{3\alpha} \cdot \frac{\varepsilon-1}{\varepsilon+n^2/2} \cdot \mu = \frac{n^2-1}{3\alpha} \cdot \mu \cdot R(\varepsilon) \qquad \text{eq. 1.}$$

We postulate, on the basis of a simple perturbation theory treatment of the electric field effect on a direct carbon-proton coupling:

$$^1J(CH) = J_o + j_r \cdot \frac{n^2-1}{3\alpha} \cdot \mu \cdot R(\varepsilon) \qquad \text{eq. 2.}$$

Experimentally we found, that indeed the measured coupling constants $^1J(^{13}C^1H)$ correlate linearly with the dielectric function $R(\varepsilon)$ in the cases of:

- $^{13}C^1HCl_3$ in CCl_4 in varying concentrations (fig. 1);
- $^{13}C^1H_2Cl_2$ in cyclohexane/cyclohexanone mixtures (fig. 2);
- the methine CH-coupling of paraldehyde in a number of selected solvents (fig. 3).

j_r was found to be 75 ± 4, a constant indeed.

However, similar experiments on acetonitrile, which is very polarizable and has a large dipole moment, were disappointing, as j_r for the methyl group was found to be very small. The same was the case for the coupling $^1J(C-H)$ in the methyl group of paraldehyde. Therefore it seems that the carbon atom, in the carbon-proton coupling studied, has to be the center of polarizability as well as the main center of the molecular dipole moment. We are still testing this hypothesis.

The story is not yet complete. In solutions with high dielectric constants the linear correlation (depicted in fig. 3) for the paraldehyde methine CH-coupling breaks down. It turns out that one has to take into account the root mean square electric field arising from the spherical shell of solvent molecules (each of which has a large dipole moment!) surrounding the solute cavity. This contribution, the solvent stark effect S, is given by[3]:

$$S = C \cdot \frac{(\varepsilon-1)(2\varepsilon+1)}{\varepsilon}^{\frac{1}{2}} = C \cdot S(\varepsilon)^{\frac{1}{2}} \qquad \text{eq. 3.}$$

The constant C contains terms arising from the geometry of the solvent shell, and possibly the dipole moment of the solute.

In fig. 4, the correlation between the methine CH-coupling in paraldehyde and a linear combination, determined by multiple linear regression analysis, of $R(\varepsilon)$ and $S(\varepsilon)^{\frac{1}{2}}$ is given. At the moment, we are still trying to calculate the factor C of equation 3.

References

1. M. Barfield and M.D. Johnston, Jr., *Chem. Rev.*, 73, 53 (1972).
2. L. Onsager, *J. Amer. Chem. Soc.*, 58, 1486 (1936).
3. M.E. Bauer and M. Nicol, *J. Chem. Phys.*, 44, 3337 (1966).

Yours Sincerely

M.J.A. de Bie
H.W.A. Biessels
J.C. Roos-Venekamp

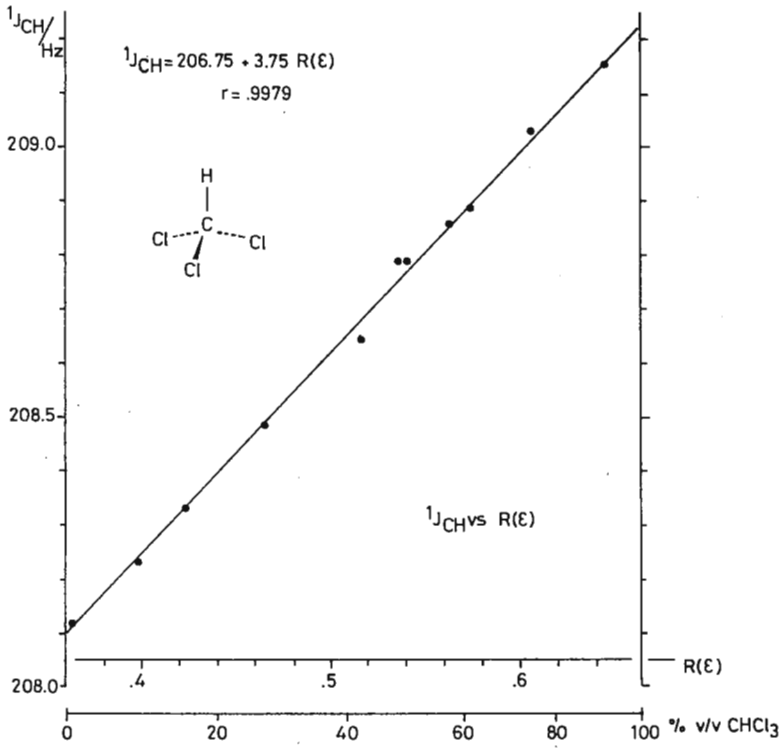


Fig. 1

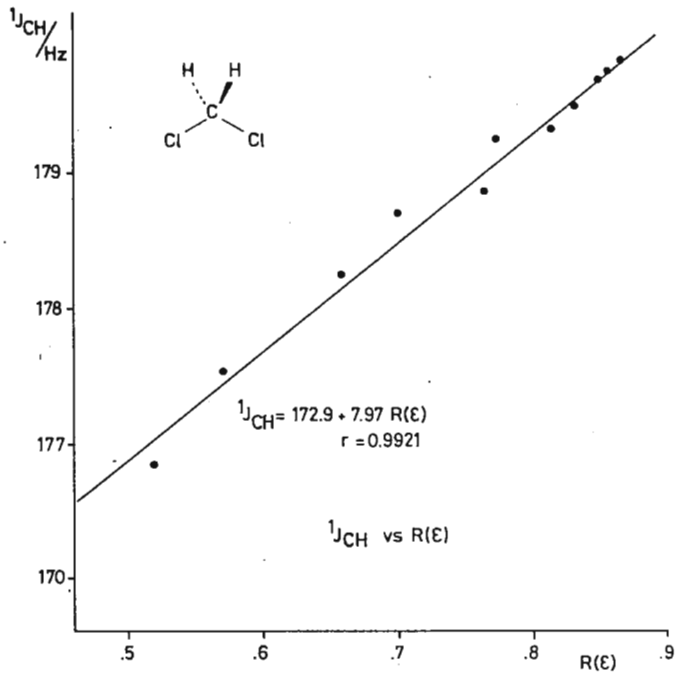


Fig. 2

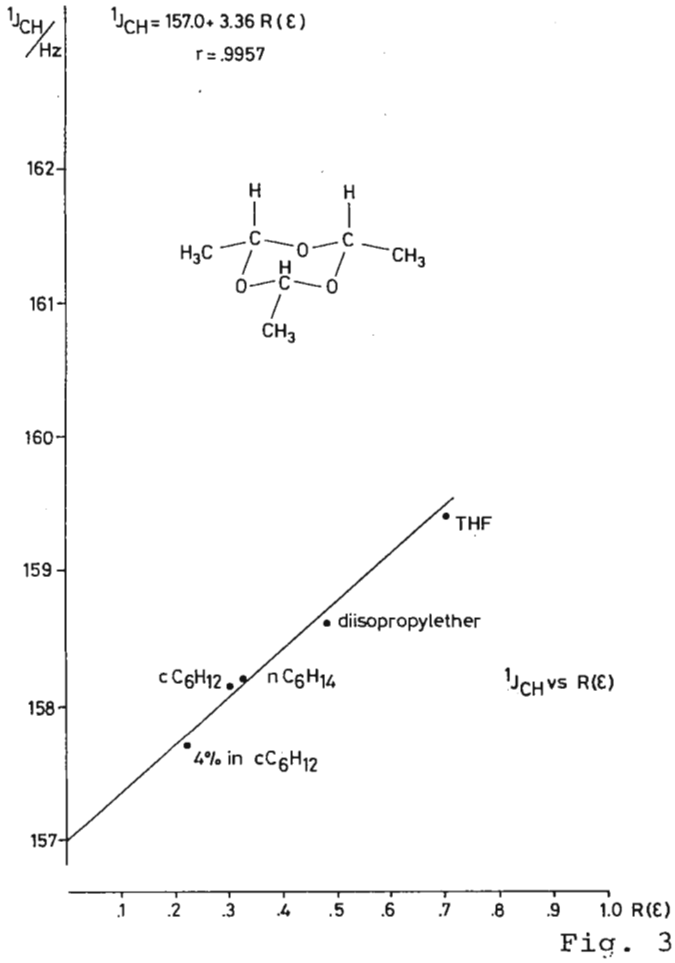


Fig. 3

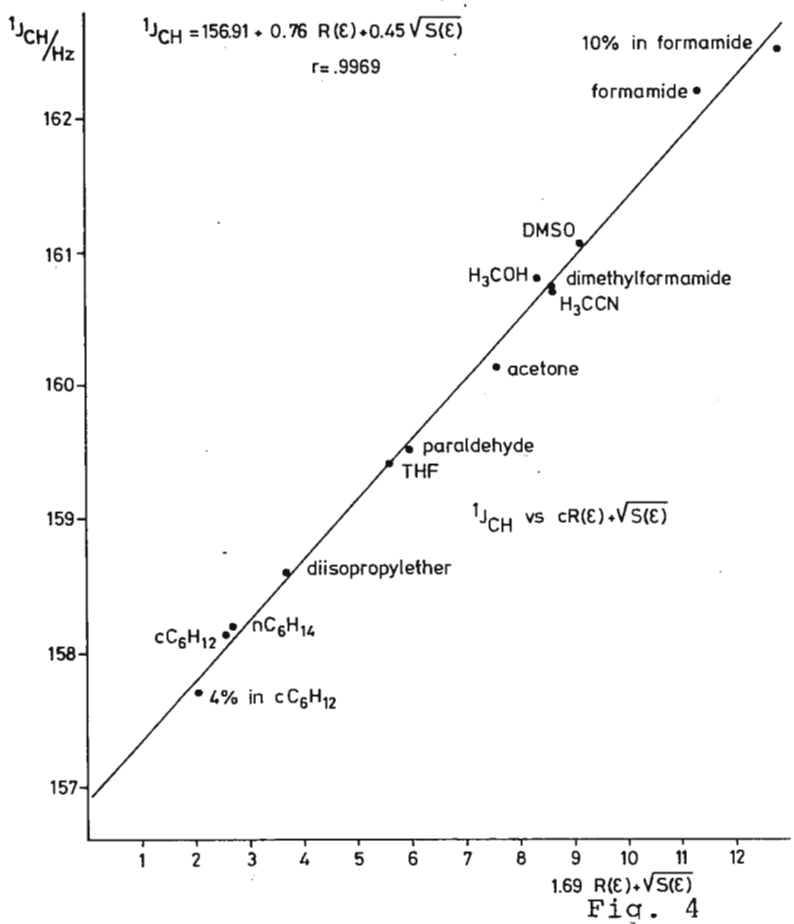


Fig. 4

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Laboratorium voor Technische Natuurkunde

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Professor B.L.Shapiro
Department of Chemistry
Texas A & M University
COLLEGE STATION TX 77843
USA

Uw kenmerk	Uw brief van	Ons kenmerk	Datum
		JT/MM/273	4 November 1983

Delft, Lorentzweg 1
Doorkiesnummer (015) 78

Onderwerp

Dear professor Shapiro,

Improved probe for DNP experiments

In our group we apply DNP (dynamic nuclear polarization) as a method to increase the NMR sensiitivity. The experiments are performed at an ESR frequency of 39.4 GHz, which corresponds to a proton frequency of about 60 MHz. The construction of a probe for this type of experiments is a difficult problem, especially if one intends to employ samples of a reasonable size (about 4 mm inner diameter in our case). In principle the required strong H_1 field for the microwaves can be obtained with the help of a cavity. However, because of the short wave length such a cavity must be strongly oversized compared to a standard ESR cavity. We had many difficulties with these oversized cavities. This was mainly due to the appearance of wrong modes in the cavity, which were difficult to suppress. Therefore we decided to employ a very simple system for our Q-band DNP probe, consisting of a horn antenna and a movable reflector. The sample is placed between the antenna and the reflector, whilst the reflector is positioned in such a way that the H_1-field has a maximum at the site of the sample. Attractive results ware obtained with this system, as can be found in the literature.[1,2]

Recently we spent much time in improving our DNP system, in particular with respect to the amplitude of the microwave field. This was done because the strength of the H_1 field was not large enough in many DNP experiments. Finally, we obtained the best results with a cylindrical cavity of a somewhat special design. The wall of the cavity, namely, does not consist of massive metal, but, using an old trick, is constructed with the help of tightly wound copper wire (diameter of the wire is about .25 mm). This implies that only circular wall currents are possible in the wall of the cavity. These circular wall currents only belong to modes which can be very

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BRIEF No. 273 d.d. 4 november 1983

useful for DNP experiments. Hence, this is a very effective way to suppress the unwanted modes mentioned above.

The cavity system was constructed in three parts: the top plate assembly containing the waveguide to cavity coupling system (in our case a Gordon coupler), the wire-wound body and the bottom plunger. The cavity is shown schematically in the attached figure. The properties of the cavity system including the NMR coil are as follows:

a. The cavity resonates in the TE_{02n} mode with n between 3 and 6 in practice.

b. The NMR coil does not disturb the field pattern in the cavity very strongly. The coil consists of about 10 turns.

c. The Q_L of the cavi ty amounts to about 180, which is certainly not bad for an oversized Q-band cavity containing an NMR coil.

d. The value of H_1 (rotating component) is about 1 Oe in case of a klystron power of about 13 W.

The usefulness of our new DNP system can be clearly demonstrated by mentioning a few results. For one of our samples (coal) we obtained a proton enhancement of about 32 with the horn antenna. With the new cavity system we found an enhancement of 53, which is certainly a real improvement. The gain in enhancement is even much better in case of the polymer polystyrene doped with BDPA free radicals (BDPA = 1,3 - bisdiphenylene-2-phenyl allyl). A proton enhancement of 36 was observed with the old system, whilst the cavity produced an enhancement of 170.

1. R.A.Wind, F.E.Anthonio, M.J.Duijvestijn, J.Smidt, J.Trommel, and G.H.C. de Vette, J.Magn.Res. 52, 424 (1983)

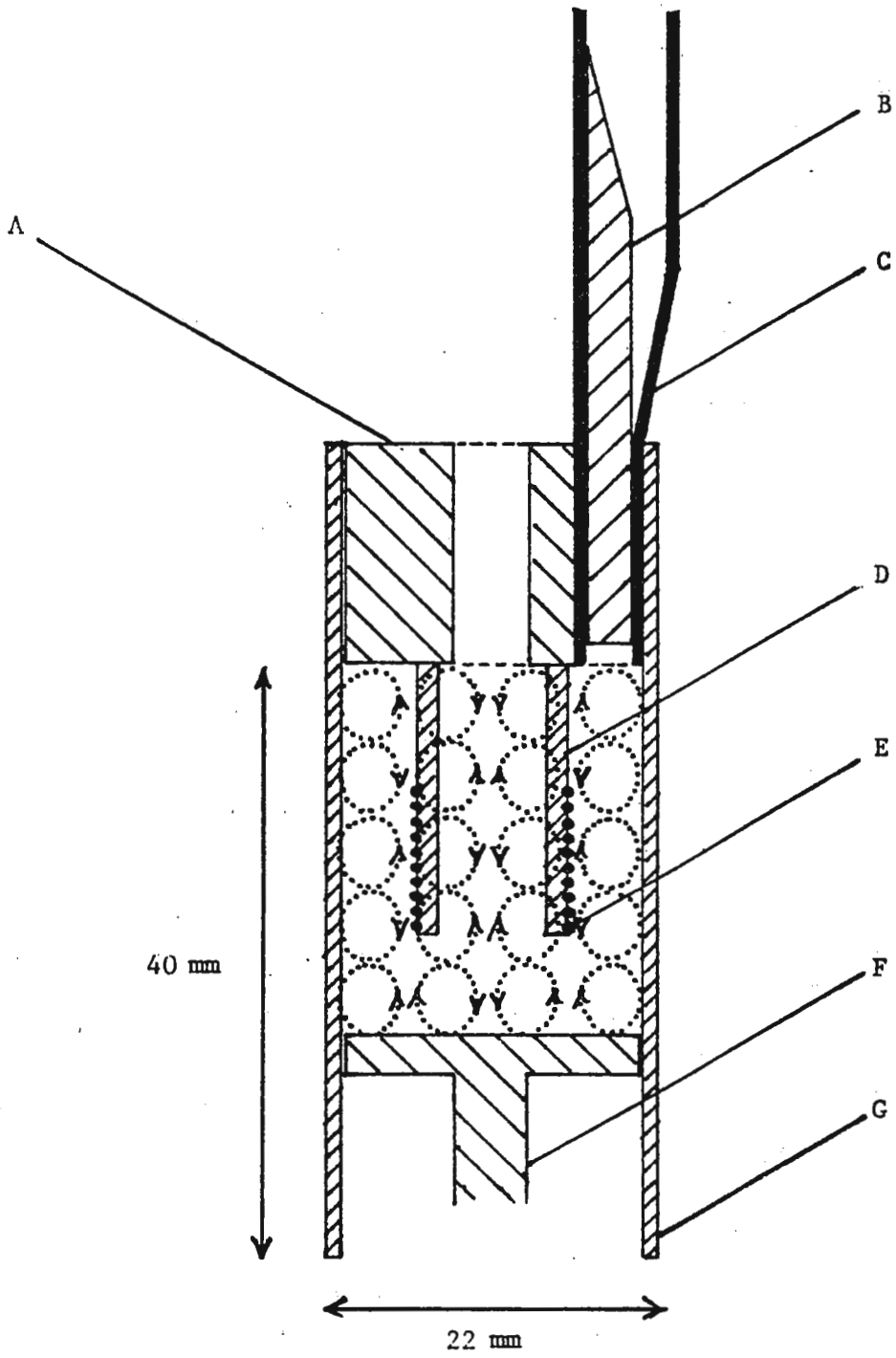
2. J.Trommel, thesis, Delft, Univ. of Technology, Delft, 1978.

Sincerely yours,

H.Lock

Dr.Ir.J.Trommel

P.S. Please credit this contribution to the subscription of Prof. Smidt.



A = top plate

B = teflon wig (part of Gordon coupler)

C = Gordon coupler

D = holder for NMR coil

E = NMR coil

F = tuning plunger

G = teflon holder for the wire-wound cavity wall.

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Klingelbergstrasse 82, Telefon 061 - 44 22 80
CH - 4056 Basel (Schweiz)

Nov. 9, 1983

Prof. Dr. P. Diehl

Prof. B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843
USA

Approximate vibration corrections for NMR parameters of oriented molecules

Dear Barry

Vibration corrections have been successfully applied for many years to the direct couplings observed in NMR spectra of the oriented molecules. On the contrary, chemical shifts, indirect couplings and quadrupole couplings have generally been left uncorrected. The reason is, that the functional dependence of the relevant tensors on the nuclear positions is much more complex. Some time ago, we noticed, that in many cases an approximate correction is possible in terms of few primary parameters :

We assume the parameters to be approximately determined by axially symmetric bonds. These contribute to the tensor $T_{\alpha\beta}$:

$$T_{\alpha\beta} = \Delta T \ell_\alpha \ell_\beta + T_\perp \delta_{\alpha\beta} \qquad (1)$$

where $\Delta T = T_\parallel - T_\perp$, and $T_\parallel$, $T_\perp$ are principal values of the tensor in the bond axis system. ℓ_α are direction cosines for the bonds with respect to the molecular coordinate frame. We also assume the bond to be insensitive to the displacement of nuclei other than those belonging to the bond and that bond bending does not affect the principal values $T_\parallel$ and $T_\perp$. On this basis we derive the vibrational average for $T_{\alpha\beta}$:

$$\langle \Delta T \ell_\alpha \ell_\beta \rangle \equiv \phi_{\alpha\beta} = \phi^e_{\alpha\beta} + \phi^a_{\alpha\beta} + \phi^h_{\alpha\beta} + \ldots \qquad (2)$$

where

$$\phi^{e}_{\alpha\beta} = \Delta T^{e} \ell_{\alpha} \ell_{\beta} \tag{3}$$

$$\phi^{a}_{\alpha\beta} = \frac{\Delta T^{e}}{r} \left(\ell_{\alpha} \langle \Delta_{\beta} \rangle + \ell_{\beta} \langle \Delta_{\alpha} \rangle + a \ell_{\alpha} \ell_{\beta} \sum_{\mu} \ell_{\mu} \langle \Delta_{\mu} \rangle \right) \tag{4}$$

$$\phi^{h}_{\alpha\beta} = \frac{\Delta T^{e}}{r^{2}} \left[C_{\alpha\beta} + a \left(\frac{1}{2} \ell_{\alpha} \ell_{\beta} \sum_{\mu} C_{\mu\mu} + \ell_{\alpha} \sum_{\mu} \ell_{\mu} C_{\mu\beta} + \right. \right.$$

$$\left. \left. + \ell_{\beta} \sum_{\mu} \ell_{\mu} C_{\mu\alpha} \right) + b \ell_{\alpha} \ell_{\beta} \sum_{\mu,\nu} \ell_{\mu} \ell_{\nu} C_{\mu\nu} \right] \tag{5}$$

Here the ℓ_{α}'s and r (bond length) denote the values in equilibrium geometry, $C_{\alpha\beta} = \langle \Delta_{\alpha} \Delta_{\beta} \rangle$, $\underset{\sim}{\Delta}$ is the change of the vector connecting the bonded nuclei from its equilibrium value and

$$a = \frac{r}{\Delta T^{e}} \Delta T' - 2 \tag{6}$$

$$b = \frac{r^{2}}{2\Delta T^{e}} \Delta T'' - \frac{5r}{2\Delta T^{e}} \Delta T' + 4 \tag{7}$$

where $\Delta T'$ and $\Delta T''$ are the first and second derivatives of the ΔT with respect to r, respectively (at equilibrium bond length).

For partially oriented molecules we are interested in

$$T_{aniso} = \frac{2}{3} \sum_{\alpha,\beta} \langle T_{\alpha\beta} \rangle S_{\alpha\beta} = \frac{2}{3} \sum_{\alpha,\beta} \phi_{\alpha\beta} S_{\alpha\beta} \tag{8}$$

In the harmonic approximation only $\phi^{h}_{\alpha\beta}$ survives.
It can be easily be calculated, if the derivatives of $T_{\parallel}$ and $T_{\perp}$ with respect to the bond length are known. The covariance matrix $C_{\alpha\beta}$ is available from the computer program VIBR [1]. In fact the above results are <u>exactly</u> valid for the case of direct dipolar coupling between arbitrary (not necessarily bonded) nuclei.
Here $T_{\parallel} = -2T_{\perp} = K/r^{3}$ where K is a constant; thus a = -5, b =35/2, and equations (3) - (5) reduce to the known special forms [1].

In case of the indirect coupling, chemical shift or quadrupolar coupling the derivatives of the parameters $T_{\parallel}$ and $T_{\perp}$ must be evaluated by approximate electronic structure calculations.

As an example we have used data by Caves and Karplus [2] on CH_3D to show that the vibration correction to the measured quadrupole coupling constant of the oriented molecule CD_3I is of the order of +3%.

With best regards
Sincerely yours

J. Lounila P. Diehl

References

[1] S. Sýkora, J. Vogt, H. Bösiger and P. Diehl
J. Magn. Reson. 36 (1979) 53.

[2] T. Caves and M. Karplus, J. Chem. Phys. 45 (1966) 1670.

WASHINGTON UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY

November 11, 1983

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

POSTDOCTORAL POSITION AVAILABLE AND IN VIVO
TISSUE HIGH FIELD C-13 SURFACE COIL STUDIES

Dear Barry:

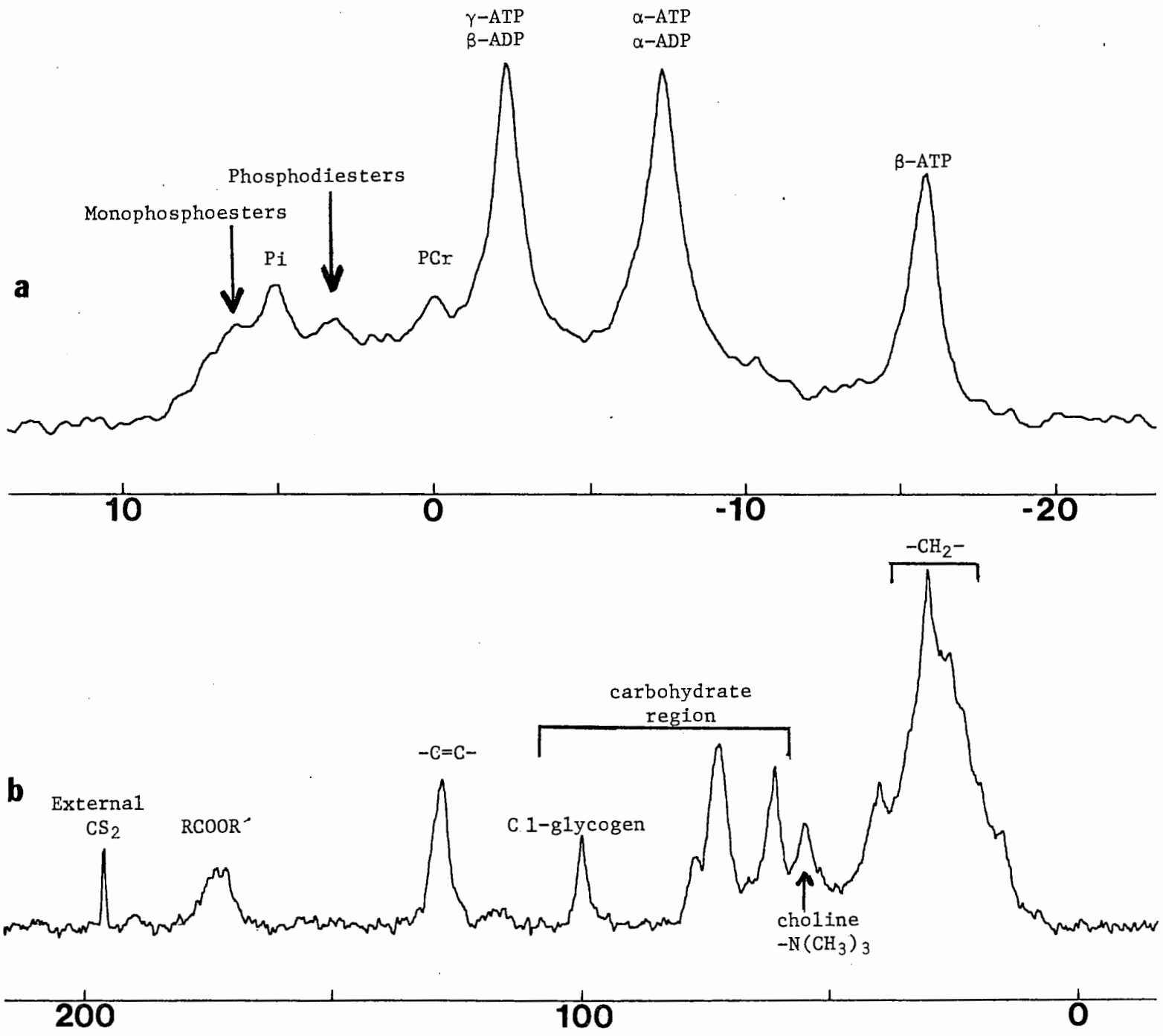
We currently have a position available for a postdoctoral research associate in the field of intact tissue NMR. The applicant should have a Ph.D. in Chemistry, Physics, Biochemistry or other related field with extensive hands-on experience in magnetic resonance. Interested candidates should write for more detailed information concerning this position.

On another related matter, we have been pursuing some high field (8.5 tesla) C-13 surface coil experiments with small laboratory animals. These experiments are motivated, in part, by much of the work coming out of Robert Shulman's laboratory [see for example: Biochem., 22, 4974-4980 (1983)] where C-13 NMR has been shown to provide an elegant probe of carbon metabolism in in vitro and in vivo intact biological systems. Thus, the C-13 experiment provides an important complement to P-13 studies of "high energy" phosphorus metabolism. Our animal studies at high field are restricted by a relatively narrow magnet bore diameter(98 mm) but are sensitivity-enhanced by the strong static field. We thought your readers might be interested in a rough sensitivity comparison between natural abundance C-13 (1.1%) and P-31 (100%) surface coil (10 mm dia.) NMR in vivo rat liver spectra at 8.5 tesla. These are shown in the accompanying figure: (a) a P-31 spectrum (24 hour fasted rat) with one minute total data acquisition time, (b) a C-13 spectrum (ad lib fed rat) with a ten minute total data acquisition time.

Sincerely,

Joseph J.H. Ackerman Nicholas V. Reo Coleen S. Ewy

Barry A. Siegfried


γ-ATP
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Phosphodiesters
Monophosphoesters
Pi
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a
10
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region
-C=C-
b
External
CS2
RCOOR´
C 1-glycogen
choline
-N(CH3)3
200
100
0

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DEPARTMENT OF CHEMISTRY
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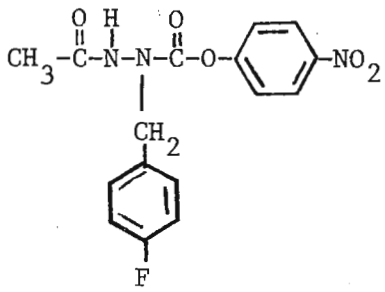
11 November 1983

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

"Structural Heterogeneity in an Acyl Chymotrypsin"

Dear Barry,

In 1977 Orr and Elmore reported that compound I reacts stoichiometrically with the enzyme α-chymotrypsin to produce a reasonably stable, catalytically inactive protein (1). The structure generated likely resembles the acylenzyme



I

intermediate formed during action of the enzyme on phenylalanine-containing substrates. We have been undertaking a number of nmr experiments aimed at elucidating the dynamics of rotation of the fluorophenyl ring in this structure and have determined, at several field strengths, the fluorine T_1 relaxation time and the linewidth of the signal observed. The latter is presumably related to T_2. Fluorine-proton Overhauser effects have also been examined. Attempts to fit the data to theoretical models for the dynamical situation at the active site of the enzyme were frustrating in that we found that T_2 values expected theoretically were always several times larger than those anticipated from the observed linewidths. When T_2 was determined by spin echo methods there was much better agreement, leading to the conclusion that the broad, apparently Lorentzian line observed is, in reality, due to a collection of several sharper lines.

The Figures illustrate some of the results. In Figure 1 is shown the fluorine signal for chymotrypsin inactivated with I, observed at 282 MHz. After correcting for the broadening introduced by exponential multiplication of the fid, the line is about 65 Hz wide, corresponding to $T_2 \sim 4.8$ ms. A spin echo experiment (Figure 2) gives T_2=13.5 ms, corresponding to a line about 24 Hz wide. Lineshape simulations suggest that at least three species with chemical shifts clustered about the observed value are needed to account for the experimental lineshape. These species likely represent different conformational forms of the acylchymotrypsin that are in slow exchange at 25°, for

attempts to "burn a hole" in the observed line by the DANTE sequence (2) lead to saturation of the entire band, a result that is consistent with the presence of several species that have similar chemical shifts but are interconvertible.

A more complete analysis incorporating deuterium relaxation data is now underway.

Sincerely,

Steve Hammond Tom

S.J. Hammond
Postgraduate Research Chemist

J.T. Gerig
Professor of Chemistry

1. Orr, G.A., and Elmore, D.T. Biochem. Biophys. Res. Commun. 74 755 (1977).
2. Morris, G.A., and Freeman, R. J. Magn. Reson. 29 433 (1978).

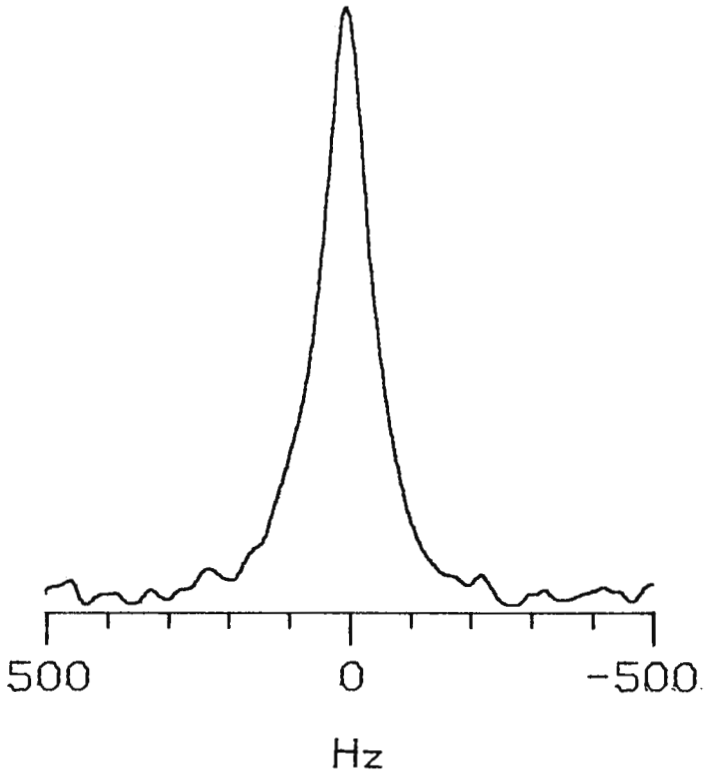


Figure 1. ^{19}F Spectrum of chymotrypsin modified with I, 282 MHz, 25°.

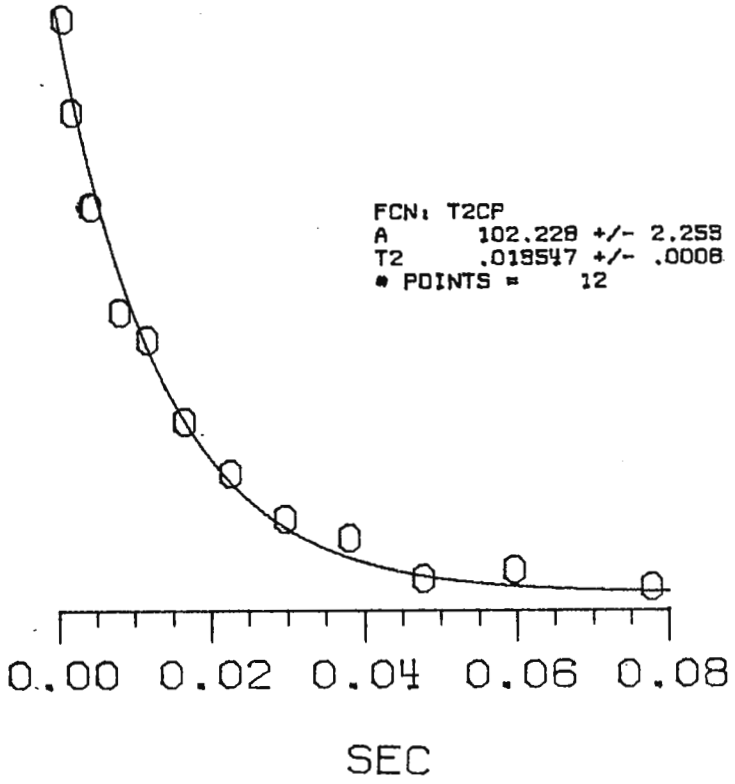


Figure 2. Carr-Purcell spin echo determination of T_2 for the same signal.

303-43

THE UNIVERSITY OF MANITOBA DEPARTMENT OF CHEMISTRY Winnipeg, Manitoba
Canada R3T 2N2

November 28, 1983.

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

Dear Dr. Shapiro:

Re: Double Decoupling Re-visited

During our study of long-range coupling in methyl-^{13}C enriched methoxybenzenes and ^{15}N enriched N-methylanilines it was necessary to simplify the spectra by decoupling the methyl protons from the ring protons. This required 2 decoupling frequencies separated by $^{1}J_{CH}$ or $^{2}J_{N-CH}$. These frequencies were produced by modulating the decoupler of our WH90 as described by Miller et al (1) and detailed in Fig. 1. The decoupler synthesizer was set at the chemical shift of the methyl group and the modulating frequency was set at 1/2 the coupling constant. Results with this technique, in general, have been quite good. However, harmonic sidebands do occur and can approach 10% of the amplitude of the main peaks. Carrier (centreband) suppression is much better. Unwanted double resonance effects can occur if the frequency of one of these signals coincides with a peak in the spectrum. These spurious signals are probably generated by the non-linear character of the diodes in the mixer, but may be generated by any non-linear device following the mixer. Beware of class C decoupler amplifiers! The unwanted harmonics may be minimized by proper adjustment of the amplitude of the modulating signal. This is easily done by monitoring the decoupler signal (suitably attenuated!) with the spectrometer receiver. The signal is recorded as a normal single scan FID, Fourier transformed and displayed in absolute value mode. A typical decoupler "spectrum" is shown in figure 2. For best performance the incident power applied to an SRA1(2) should be less than 0dBm. Higher-power mixers are available. Mixer-loss, when modulated for least spurious signal production, is 6 to 10 dB.

Combining the output from 2RF synthesizers is, no doubt, the best way of generating 2 decoupling frequencies. For those not blessed with a suitable spare synthesizer "kicking around" in the laboratory this method offers an attractive low-cost alternative.

Please credit this letter to Ted Schaefer's account. He's still around here on occasion.

Sincerely,

Kirk Marat.

KM:dmh

1. I.D Brindle. T.R.B. Jones and J.M. Miller. TAMU NMR Newsletter, 209, 26 (1976).
2. Mini Circuits Laboratory. Brooklyn, N.Y.

Fig. 1

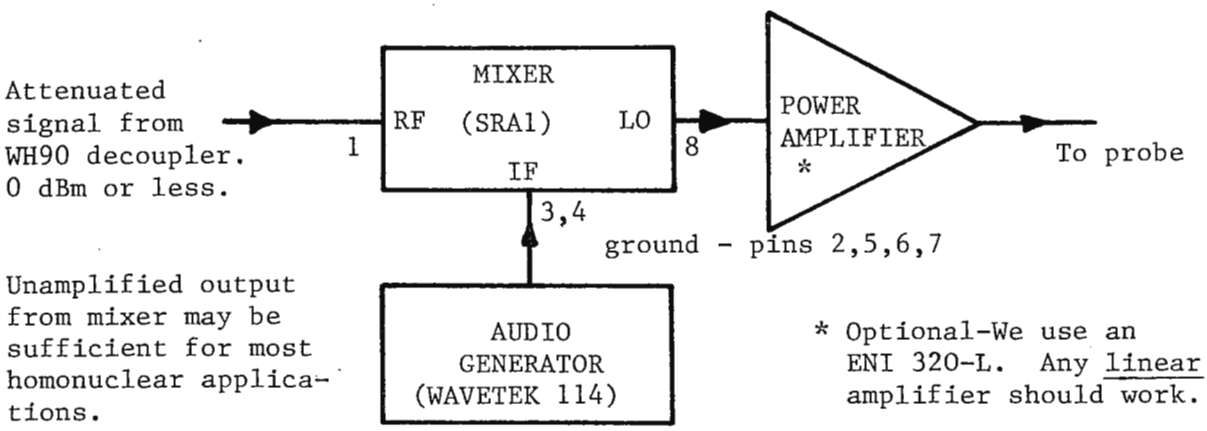
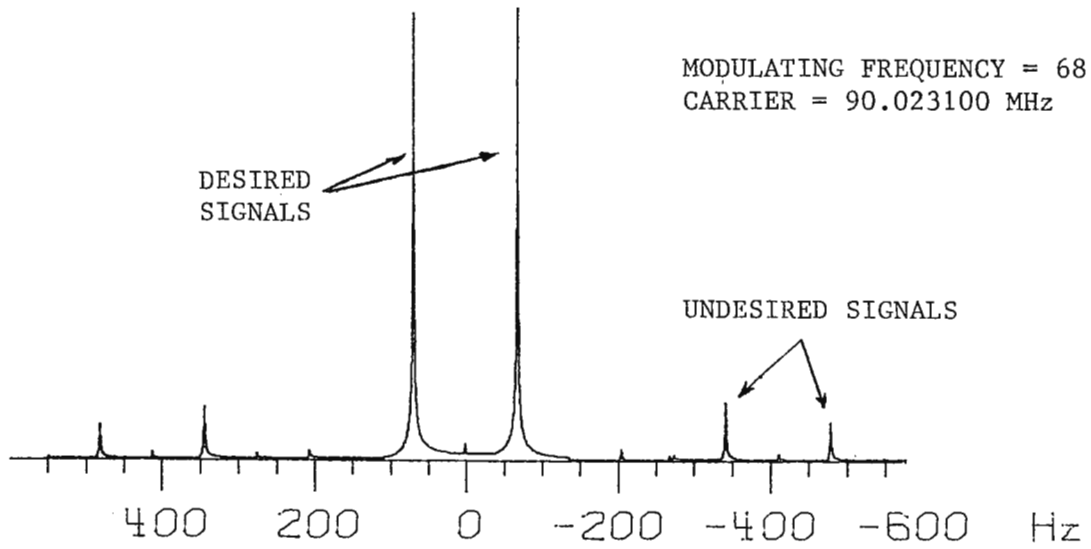

Attenuated signal from WH90 decoupler. 0 dBm or less.
MIXER
RF (SRA1) LO
IF
1
8
3,4
POWER AMPLIFIER *
To probe
ground - pins 2,5,6,7
Unamplified output from mixer may be sufficient for most homonuclear applications.
AUDIO GENERATOR (WAVETEK 114)
* Optional-We use an ENI 320-L. Any linear amplifier should work.

Fig. 2


MODULATING FREQUENCY = 68.5 Hz
CARRIER = 90.023100 MHz
DESIRED SIGNALS
UNDESIRED SIGNALS
400
200
0
-200
-400
-600
Hz

TOWSON STATE UNIVERSITY
TOWSON, MARYLAND, 21204

Department of Chemistry (301) 321-3058

November 28, 1983

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

Dear Barry:

Title: "Some Observations on Dipolar and Spin-rotation Relaxation of Alcohols"

As my first contribution to the TAMU NMR Newsletter, I would like to respond to Joe Lambert's request for help in understanding the difference in spin rotation relaxation for CF_3CH_2OH and CH_3CH_2OH. In collaboration with Ted Becker, I have been studying the association of $(CH_3)_3COH$ in $C_{16}D_{34}$ by measuring the relaxation time of the quaternary carbon as a function of concentration (this carbon is 90% C-13 labeled). Part of the relaxation of the carbon is by a mechanism which is concentration and field independent. Although the system did not permit a thorough study of T_1 as a function of temperature, I measured the relaxation rate for 0.0867 M at 301 and 333°K and found to my dismay that the values for the rates were 0.0202 and 0.0132 sec^{-1}, not what you would expect if spin rotation contributes significantly. When I measured the NOE's, I found to my amazement they were 1.13 and 0.34! The dipolar rate dropped from 0.0115 to 0.0023 sec^{-1} with a 10% increase in temperature, swamping the slight increase in the spin rotation rate (from 0.0087 to 0.0110 sec^{-1}). This enormous change in the dipolar rate can be accounted for by the change in the position of equilibrium (changing the effective size of the molecule, whose equilibrium constants are known[1]), the change in viscosity and the expected dependence of the dipolar rate on 1/T. Thus for molecules whose effective molecular size may change with temperature, it is not surprising that the dipolar relaxation dominates and prevents the expected temperature effect from spin rotation from being observed.

The spin rotation relaxation in aggregated molecules may well be due to methyl rotation rather than rotation of the whole molecule. Methyl spin rotation relaxation is much less sensitive to temperature than overall molecular spin rotation relaxation since it is rather oblivious to viscosity changes[2]. For appreciation of

why CF_3 groups exhibit more spin-rotation relaxation than CH_3, I recommend papers by Chan[2] and Flygare[3]. If I understand it correctly, the relaxation is caused by interruptions in the rotation generating magnetic field fluctuations which are roughly proportional to the size of the magnetic field produced by the rotating CX_3. Fluorines generate larger magnetic fields because of the larger electron density that is rotating, in spite of the expected lower rotation rate, and thus generate larger magnetic field fluctuations. In the case of CH_3CH_2OH, spin-rotation of the methyl group may never become important enough to dominate the relaxation as it does for CF_3CH_2OH, and thus the usual reversal in the temperature effect on the relaxation time is not observed.

Our work on t-butyl alcohol has recently been submitted for publication.

Yours sincerely,

Linda

Linda M. Sweeting
Associate Professor

LMS:tcg

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2. T. E. Burke; S. I. Chan. J. Magn. Reson., 1970, 2, 120-40.

3. W. H. Flygare. J. Chem. Phys., 1964, 41, 793-800.

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Directeur : Professeur J. REISSE

B-1050 Bruxelles, le October 24, 1983.

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

Measurement of diffusion coefficient

Dear Prof. Shapiro,

Several probes have been developed in our laboratory to measure diffusion coefficient by the well-known spin-echo technique with pulsed field gradients. Provided that the residual static gradient is negligible compared with the pulsed field gradient, the echo amplitude A(g) is given by

$$A(g) = A(o) \exp - \gamma^2 g^2 \delta^2 (\Delta - \frac{\delta}{3}) D \qquad (1)$$

where A(o) is the amplitude of the echo without pulsed gradient, Δ is the separation between the two gradient pulses, δ is the length of the gradient pulse, and g its amplitude.
It has been shown[1,2,3] that it is somewhat difficult to achieve a high level of accuracy using this method. In order to attenuate the effects of the instrumental artefacts, we tried to optimise the treatment of experimental data by non-linear fit.
Two methods were compared :

1. A(g) and A(o) were successively measured. D was directly computed from equation (1)
2. A(g) was measured under variable g. D was obtained from equation (1) using a Newton Raphson computation with two adjustable parameters A(o) and D.

Whereas computer-simulated experiments (with a reasonable level of noise) could not orient our choice clearly, a statistical analysis of our experimental results showed that the measurement which is by far the most exposed to errors is A(o).

Method 2 therefore seems to be the most suitable in our case. The current control unit which feeds the quadrupolar gradient coils was equipped with a device scanning ten predetermined field gradient values under computer control.

Yours sincerely,

M. Claessens O. Fabre D. Zimmermann

(1) P.T. Callaghan, K.W Jolley, C.M. Trotter, J. Magn. Res. 39, 525 (1980)

(2) K.R. Harris, R. Mills, P.J. Back, S. Webster, J. Magn. Res. 29, 473 (1978)

(3) M. Hrovat, C. Wade, J. Magn. Res. 44, 62 (1981)

id. 45, 67 (1981)

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BECKENHM 23937

9th November 1983.

Dear Dr. Shapiro,

^{31}P PERFUSION EXPERIMENTS IN A NARROW BORE WM-360

We have recently been using our conventional narrow-bore magnet, Bruker WM-360 system to study the ^{31}P spectra of perfused beating guineapig hearts. A special probe was constructed for us to our design by Spectrospin in Zurich which gives a clear i.d. of 17 mm. No sample tube is used and the glass r.f. coil support itself provides the sample holder and is capable of being maintained full of perfusate. Perfusing solutions are fed in through tubes fixed into holes drilled in the ceramic base of the insert and waste liquid is sucked away in a similar manner. The receiver coil is double tuned for ^{31}P and ^{2}H but there are no ^{1}H decoupling coils. Non spinning resolution on 15 mm 1% TMP is a few Hz and we obtain good spectra in 2-4 minutes thus having a reasonable time resolution for evaluating our interest in the effects of drugs on nucleotide and other phosphate levels.

We can supply details of the probe if anyone is interested.

Yours sincerely,

DR. J. C. LINDON
Department of Physical Chemistry

Book Reviews

Editor: W. B. Smith
Texas Christian University
Fort Worth, Texas

The Multinuclear Approach to NMR Spectroscopy
edited by Joseph B. Lambert (Department of Chemistry, Northwestern University, Evanston, Illinois)
and Frank G. Riddell (Department of Chemistry, University of Stirling, Stirling, Scotland)

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190 Old Derby St.
Hingham, Massachusetts 02043, U.S.A.

1983, 548 pages, $72.00

This volume is the product of a NATO Advanced Study Institute held at Stirling in Scotland in August of 1982. The audience consisted of active NMR practitioners, and the speakers were all recognized leaders in their respective fields. Their efforts were collected and edited by Joe Lambert and Frank Riddell to produce a most useful account of multinuclear NMR.

The scope of the volume is best presented by the table of contents (with authors): 1. High Resolution Multinuclear Magnetic Resonance: Instrumentation Requirements and Detection Procedures (C. Brevard); 2. The Calculation and Some Applications of Nulcear Magnetic Shielding (G.A. Webb); 3. Calculations of Spin-Spin Couplings (G.A. Webb); 4. Relaxation Processes in Nuclear Magnetic Resonance (J. Reisse); 5. Dynamic NMR Processes (J.B. Lambert); 6. Nuclear Magnetic Resonance in Solids (K.J. Packer); 7. Applications of High Resolution Deuterium Magnetic Resonance (H.C. Jarrell and I.C.P. Smith); 8. Deuterium NMR of Anisotropic Systems (H.C. Jarrell and I.C.P. Smith); 9. Tritium Nuclear Magnetic Resonance Spectroscopy (J.A. Elvidge); 10. Nitrogen Nuclear Magnetic Resonance Spectroscopy (R.L. Lichter); 11. Application of ^{17}O NMR Spectroscopy to Structural Problems (W.C. Klemperer); 12. The Alkali Metals (P. Laszlo); 13. Alkaline Earth Metals (O. Lutz); 14. The Alkaline Earth Metals--Biological Applicaltions (T. Drakenbert and S. Forsen); 15. Group III Atom NMR Spectroscopy (R.G. Kidd); 16. Solution-State NMR Studies of Group IV Elements (Other than Carbon) (R.K. Harris); 17. High Resolution Solid-State NMR Studies of Group IV Elements (R.K. Harris). 18. Group V Atom NMR Spectroscopy Other than Nitrogen (R.G. Kidd); 19. Group VI Elements Other than Oxygen (O. Lutz); 20. The Halogens--Chlorine, Bromine, and Iodine (T. Drakenberg and S. Forsen); 21. Transition Metal NMR Spectroscopy (R.G. Kidd); 22. Cadmium-113 Nuclear Magnetic Resonance Spectroscopy in Bioinorganic Chemistry. A Representative Spin 1/2 Metal Nuclide (P.D. Ellis).

The introductory chapters provide a nice bridge for those of us who routinely run ^{1}H and ^{13}C FTNMR spectra, but who have yet to jump into highfield/or multinuclear instruments. We are brought up to date on sensitivity enhancement methods, and the difficulties posed by nucleii of low receptivity and quadrupole moments which impose practical limitations of sample size and observation times.

The program at Stirling was billed as an Advanced Institute, and the program reflected in the text supports the fact that this is not an introductory work. However, the presentations all give enough introductory material to provide easy entre' into the meat of the subject. Frequently, such multiauthored works are subject to much repetition and presentations are nonuniform in quality. I found the writing styles here to be remarkably consistent and informative; surely a compliment to editors as well as authors.

I've arrived at that point in life were texts prepared from typed camera-ready copy pose a problem in the smallness of the printing. One gets a lot of words for the money per page here, and the figures virge on being too small. This can all be justified by the enormous content packed into 548 pages. For a happy change, I found the index to be adequate.

W.B.S.

303-51

DEPARTMENT OF THE NAVY
NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555

IN REPLY REFER TO:
3851/EDE:bh
Reg 385-693-83
18 November 1983

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

Dear Dr. Shapiro:

I would appreciate your assistance in locating a recent Ph.D. or post-doctoral associate to fill a position in my division. The individual we are seeking will have a strong demonstrated expertise in interpretive and practical nuclear magnetic resonance spectroscopy. He or she should be able to conduct his or her own research program as well as collaborate with other chemists with their research efforts. Equipment in this facility includes a new Nicolet NT200WB spectrometer with the CP/MAS accessories and multinuclear probes, as well as Varian XL-100 and EM-360 spectrometers. The starting salary for this position will be about $30,000 depending on training and experience.

The Chemistry Division has a staff of approximately 50 including 34 professionals. This position is in the Instrumental Chemical Analysis Branch. It is the largest branch in the division and consists of three permanent Ph.D. chemists, one part-time Ph.D. chemist, two B.S. chemists, two technicians, and one technician trainee. Current research in this branch is directed toward structural analysis of new compounds, the development of new detectors, pollution abatement, surface analysis, and the development of chemiluminescent materials. Members of the branch frequently collaborate with other chemists in the division, as well as other scientists and engineers at the Naval Weapons Center, to solve a wide variety of analytical problems. In addition, the branch is responsible for the operation and maintenance of facilities for NMR, GC/MS, chromatography, FTIR, laser analysis, general spectroscopy, electroanalytical chemistry, and glassblowing. Other analytical facilities at the Naval Weapons Center include those for EPR, X-ray diffraction and fluorescence, SEM, SAM, GPC, atomic absorption, and thermal analysis.

Living in China Lake, or the adjacent town of Ridgecrest, is not for everyone. However, it is one of the few places I know where one can combine living in a small town community with a stimulating intellectual environment, both on and off the job. The area is high desert (elevation 2,500 feet) and is surrounded by mountains. Within a 3-hour drive one can be in Los Angeles, at Mount Whitney, in Death Valley, or almost any type of environment in between.

Anyone interested in this position should send a resume, including the names of three references by 15 January 1984, to:

Personnel Division (Code 09201)
Naval Weapons Center
China Lake, CA 93555

They should mention they are interested in the position in Code 3851. If there are any questions or you desire further information please call our current NMR specialist, Mr. Don Moore, collect, at (619) 939-2852. The Naval Weapons Center is an Equal Opportunity Employer. Applicants must be U.S. citizens and must be able to obtain a security clearance.

Thank you for your help in this matter.

Sincerely,

Adolph B. Amster

ADOLPH B. AMSTER, Head
Chemistry Division

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For additional information call Everett Santee, (216) 375-7537 at the University of Akron, Akron, Ohio.

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of Bioorganic Chemistry

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117988 Moscow, B-334
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Prof. Bernard L.Shapiro
Department of Chemistry
College of Sciences
Texas A & M University
College Station, Texas 77843
USA

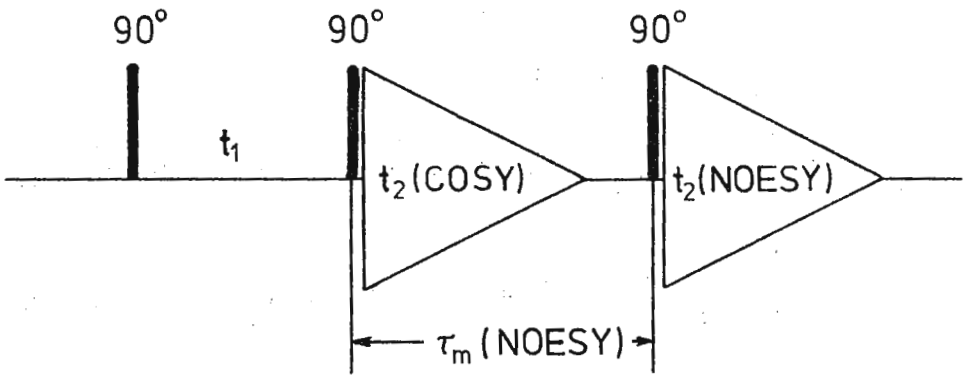
November 1, 1983

Title: One experiment instead of two in 2-D NMR Spectroscopy

Dear Barry,

We permanently employ the two-dimensional proton NMR spectroscopy on our Bruker WM 500 in the course of conformational analysis of peptides and proteins in solution. For this sort of study essential data are provided, in particular, by ^{1}H COSY (correlated spectroscopy) and ^{1}H NOESY (nuclear Overhauser effect spectroscopy) spectra obtained at identical experimental conditions. Conventionally, they are recorded by two separate experiments. Figure shows that the two experiments can be combined, if τ_m(NOESY) > t_2(COSY), and COSY and NOESY spectra sequentially accumulated in two

Pulse Diagram of a Combined COSY-NOESY Experiment



different parts of computer memory. For this purpose we modified: a) the standard Bruker FP810515.DISK program so that the start address of computer memory intended for the spectrum is rised by the block size after t_2(COSY) and is returned back after t_2(NOESY), and b) corresponding phase cycling program for COSY-NOESY experiment. The time saving factor of discribed modification is close to 2, which is fairly important for peptide and protein spectra accumulated during 10-40 hours.

Sincerely yours,

A.Z.Gurevich I.L.Barsukov A.S.Arseniev V.F.Bystrov

P.S. Please credit this to prof. V.F.Bystrov's subscription.

You never had NMR like this before.

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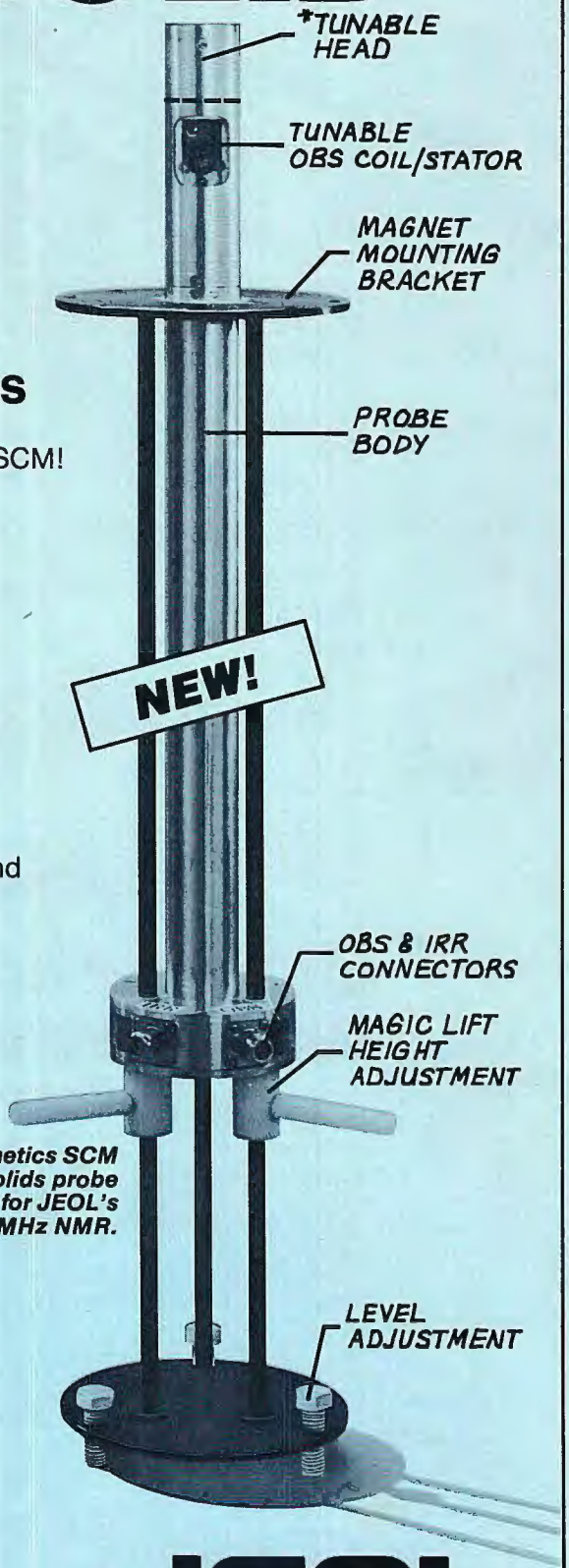

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