TEXAS A&M UNIVERSITY

NMR

NEWSLETTER

No. 296

May, 1983

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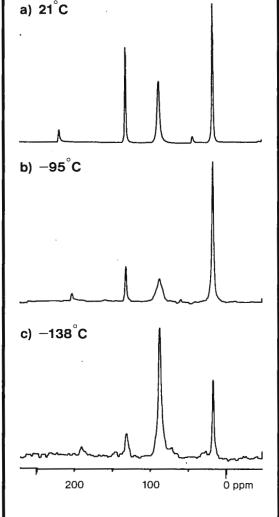
DEADLINE DATES: No. 297   6 June 1983
                 No. 298   4 July 1983

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

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

New England Nuclear®

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

March 28, 1983

Sub: 45.05 MHz ^{99}Tc and 81.016 MHz ^{31}P nmr spectroscopy of a cationic
technetium complex for myocardial imaging
. . .

Dear Prof. Shapiro:

^{99m}Technetium is the most desired isotope for nuclear medicine procedures.
Until now there has been no Tc-99m agent available for determining myocardial
perfusion function. Recently, we have prepared a cationic technetium
complex that has been successfully used for myocardial imaging in a variety
of animals including rabbits, dogs and baboons. The diamagnetic complex
formulated $[Tc(dmpe)_3]^+$ has Tc in +1 oxidation state octahedrally co-ordinated
by six phosphorus atoms; it is prepared by refluxing an aqueous ethanolic
solution of NH_4TcO_4 with 5-molar excess of the ligand for 3 hours. The pale
yellow complex is isolated as the chloride salt. Elemental analysis, FABMS
and X-ray crystallographic studies confirm the structure(figure 1).

Following a report nearly two years ago on ^{99}Tc nmr of NH_4TcO_4(1), we were
interested in looking at the ^{99}Tc and ^{31}P nmr of the above complex on our
multinuclear Bruker WP-200. With a sensitivity of 0.376 relative to ^{1}H=1.0,
we were able to establish quickly the observation parameters employing a
D_2O solution of NH_4TcO_4. Because of the 30 KHz sweep-width limitation on
our WP-200, we had to play with the synthesizer [setting=(200.133-X)/2] in
order to observe the ^{99}Tc resonance of the Tc(dmpe)$_3$ complex(0.1 M in dmso-d$_6$);
the septet (figure 2), resulting from coupling to six equivalent ^{31}P atoms,
was observed in a short time. We back-calculated the chemical shift of the
(center of the) ^{99}Tc resonance of the complex to be -1891 ppm w.r.t. $NH_4^{99}TcO_4$.

Observing the ^{31}P spectrum of the complex was straightforward; the ten-line
pattern resulting from coupling to ^{99}Tc (I=9/2) and centered at 39.5 ppm w.r.t.
external 85% H_3PO_4 was observed in a matter of minutes(Figure 3).

In all the above cases, proton noise-decoupling was employed to reduce line-
widths and eliminate further splittings due to ^{1}H-X couplings which caused
considerable broadening of the lines with fine structure at the top. With
proton-decoupling, the line-widths at half-heights were about 25 Hz for the
^{99}Tc spectrum and 37.5 and 45 Hz, respectively, for the two outer lines and the
eight inner lines of the ^{31}P spectrum.

With best regards,

Sincerely yours,
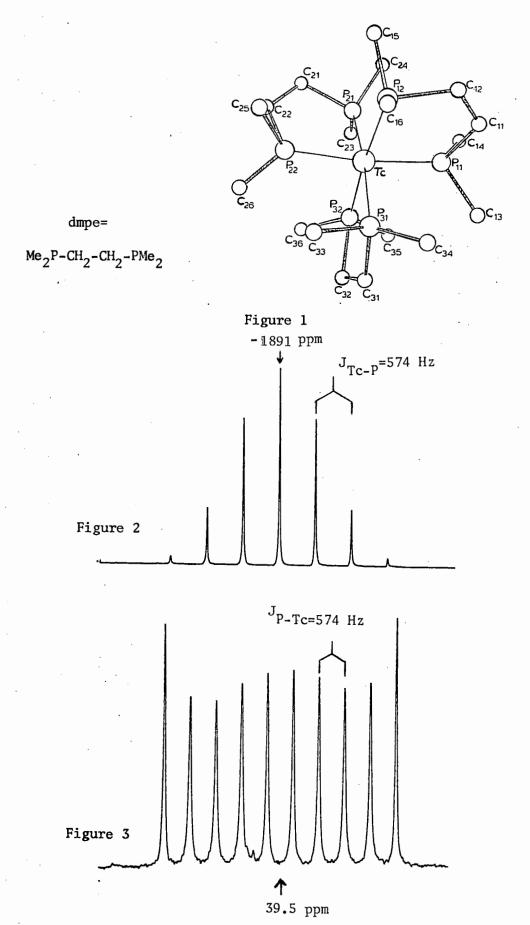
V. Subramanyam   Karen Linder   P. R. Srinivasan

dmpe=

$Me_2P-CH_2-CH_2-PMe_2$

Figure 1

−1891 ppm

$J_{Tc-P}=574$ Hz

Figure 2

$J_{P-Tc}=574$ Hz

Figure 3

39.5 ppm

Ref: 1. M. J. Buckingham, G. E. Hawkes and J. R. Thornback, Inorganica Chimica Acta , 56, L41-L42(1981)

OSU

The Ohio State University

Department of Chemistry

140 West 18th Avenue
Columbus, Ohio 43210

Phone 614 422-2251

March 31, 1983

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

Alkynyllithium, rotational barriers in acyl dihydropyridines

Dear Barry:

In response to your dire notes I belatedly report the following news.

Alkynyllithium: We teach undergraduates that alkynylmetal compounds are salts containing alkynyl anions. The latter are stabilized thanks to the 50% plus "s" character associated with the sigma orbital on carbon. This idea, at least for lithium compounds is now thoroughly debunked by the results of an NMR experiment. Carbon-13 NMR of C_1 of 3,3-dimethyl-1-lithiobutyne in THF at $-50°$ consists, for the ^6Li enriched (96%) species, of a 7 line multiplet, closely, 1:3:6:7:6:3:1, and for the ^7Li (normal) material 10 lines, 1:3:6:10:12:12:10:6:3:1 indicating three lithiums symmetrically coupled to each α-carbon. The coupling constants are $J(^{13}C,^7Li)=16Hz$ and $J(^{13}C,^6Li)=6Hz$ which is the expected ratio and confirms where the splittings are coming from. Altogether these results mean that this typical alkynyllithium compound exists as a cubic tetramer, where each lithium

is coordinated to one THF molecule. This is just what has been found for most simple organolithium etherates (methyl, vinyl, aryl). Further the ^{13}C, lithium coupling constants are also very similar to the reported ones for other lithium compounds.

The alkynyllithium in THF is not any more ionic than the other RLi etherates and should not be described as a salt.

Dihydropyridines-barriers to rotation: Recently we became interested in using rotational barriers to assess the effect on bonding of inserting a heteroatom across the termini of a π-electron loop, viz 3-aza-1,4-dienyl, so we have barriers for the N-acetyl dihydropyridine, I, and its sulfone analog II. We think the

Professor B. L. Shapiro   March 31, 1983

twisted state of II is stabilized (relative to twisted I) because the nitrogen lone pair and the double bonds we provide 6 π electrons and there is p,p over-lap between carbon and sulfur, i.e. have an "aromatic" transition state for rotation.

I am interested in the comments of theoretically inclined readers.

Best wishes.

Yours sincerely,

Gideon Fraenkel
Professor of Chemistry

Post-Doctoral Position

There is now a Post-doctoral position open in my group for someone who will work on structure and dynamic behavior of organolithium compounds. This involves synthesis of isotopically enriched, ^{6}Li and ^{13}C, organolithium compounds and their study using ^{13}C, ^{6}Li and ^{1}H NMR line-shape analysis. A high field multinuclear instrument is used in this work as well as an electromagnet system assembled in this department. The person we appoint will also help in maintaining the electromagnet NMR.

Address inquiries to:

Professor Gideon Fraenkel
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GENERAL ELECTRIC COMPANY ● RESEARCH AND DEVELOPMENT CENTER ● P.O. BOX 8 ● SCHENECTADY, NEW YORK 12301 ● (518) 385-2211

April 4, 1983

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

Carbon-13 NMR of PPO Copolymers

Dear Barry,

We have recently been examining some PPO copolymers in which the comonomer with 2,6-xylenol is 2-methyl-6-isopropylphenol. Variations in the polymerization conditions can produce polymers which range from fully random to highly blocked copolymers. Carbon-13 NMR is a very useful way of determining the structure of the final copolymer.

As shown in the expansion in the figure, the C-4 carbon of each ring resolves into two peaks as a result of sequencing. In the case of a random 50:50 copolymer (A=B) the spectrum shown is obtained in which each resonance is of the same intensity. In a more blocked copolymer, the intensities of BB and AA increase at the expense of the interblock units BA and AB.

We have examined polymers of different composition and with other alkyl groups in B and have found similar results. A full paper on these copolymers will be submitted soon.

Sincerely,

E. A. Williams   P. E. Donahue

Materials Characterization Operation
R&D Applications Operation

/ldr
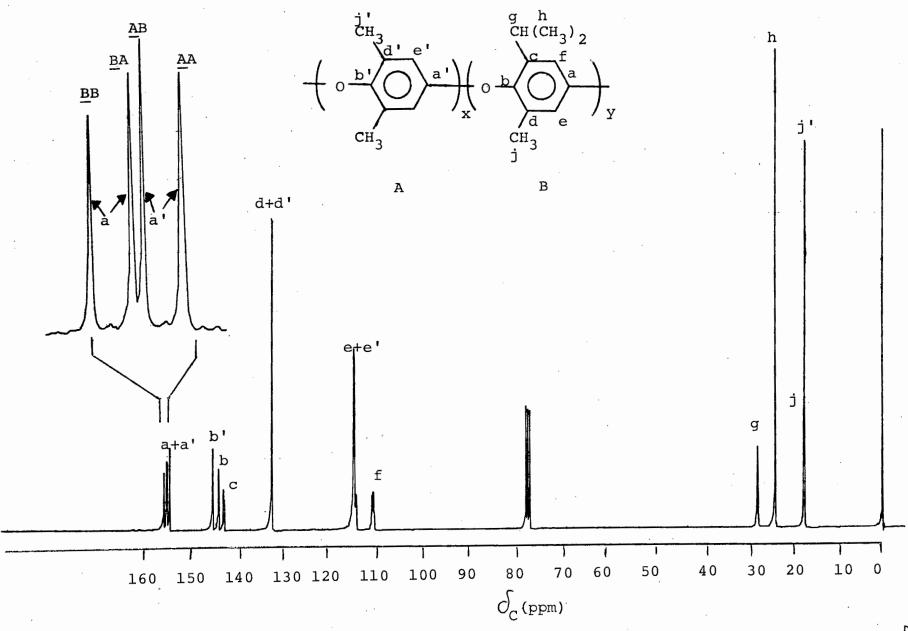
Figure. Carbon-13 nmr spectrum of PPO-Me$_2$/PPO-Me,$\underline{i}$-Pr copolymer at 75.4MHz.

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Prof. Barry Shapiro
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Texas A&M University
College Station, Texas 77843
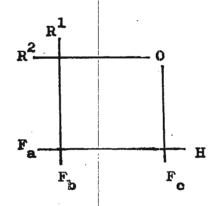
Praha, 6.4.1983
č.j. 1157/83

Title:

"Configuration and Conformation of 2-Alkyl-3,3,4-Trifluoroxetanes"

Dear Prof. Shapiro,

In 1976 we started together with Dr. Hrušovský who died accidently in summer of the 1980 year, a study of group of 2-alkyl-3,3,4-trifluoroxetanes. This type of compounds is similar to the cyclobutane system previously studied by Ernst[2,3] and Roberts[4,5].

$$R^1 = H, CH_3$$
$$R^2 = CH_3, C_2H_5, (CH_3)_3C, C_6H_5$$

Now we have performed a detailed analysis of 2-alkyl-3,3,4-trifluoroxetanes to determine the relative configuration of fluorine atom on carbon atoms 2 and 4 and to obtain the approximate conformation of the oxetane ring. The chemical shifts and the coupling constants were calculated from the experimental data by means of the iterative LAOCN3 procedure. Relative signs of the coupling constants were determined by INDOR and DQT experiments (the sign of $^2J_{CF_2}$ we supposed to be positive). From solvent effects, temperature dependences, LSR experiments (with $Yb(FOD)_3$) and a comparison of experimental data with the theoretical geometry of oxetane ring calculated

by EHT method, we obtained following conclusions:

1) Conformation of oxetane ring is nonplanar.

2) Vicinal spin-spin coupling constant $^3J_{FF}$ lies in the range from 8 to 12 Hz for trans configuration and from -4 to -11 Hz for cis configuration (of both fluorine atoms).

3) Fluorine atom in the CF_2 group which is in pseudoequatorial position is deshielded in comparison with the pseudoaxial one.

4) If substituent $R^1=R^2$, the F_c atom in the dominant ring conformation is pseudoaxial. If $R^1 \neq R^2$, the conformation of the ring depends on the more bulky substituent, which occupies predominantly the pseudoequatorial position.

5) Fluorine atom F_c decreases the shielding of the gauche fluorine atom in the CF_2 group (probably due to an interaction with the electrical dipole of the CHF_c group).

We hope you will receive our contribution before writing us the second warning.

    With best regards, yours sincerely

Petr Trška   Milan Hájek

    Prague Institute of Chemical Technology

1. I.Hrušovský: Thesis, SVŠT Bratislava, 1977
2. R.R.Ernst: Mol.Phys.16,241(1969)
3. R.R.Ernst: J.Chem.Phys.45,345(1966)
4. J.B.Lambert,J.D.Roberts: J.Amer.Chem.Soc.87,3884(1965)
5. M.Takamashi,D.R.Davis,J.D.Roberts: J.Amer.Chem.Soc.84,2935(1962)

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FACHBEREICH 8
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Organische Chemie II
Prof. Dr. H. Günther

Prof. Bernard L. Shapiro
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5900 Siegen, April 6, 1983
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Durchwahl 740–4390/4400

TANDEM-SEFT

Dear Barry,

having a lot of deuterated systems at hand – a consequence of our studies on ^{2}H/^{13}C isotope effects – we thought it would be fun to join the pulse game (1). Spin echo modulation by ^{13}C,^{2}H coupling was a promising first try and the rules in one and two dimensions were quickly worked out (2). For practical applications, ^{2}H-SEFT is of interest for the analysis of deuterated compounds and we have developed, in combination with difference spectroscopy, a strategy for this purpose (3). The latest hit is, however, TANDEM-SEFT, where we pulse the ^{1}H and the ^{2}H decoupler independently:

Minor instrumental modifications were necessary to perform this experiment on our WH 400 spectrometer. They are available on request. TANDEM-SEFT offers four unique possibilities for signal editing of partially deuterated systems not easily available otherwise:

(1) Suppression of all proton- and/or deuterium-bearing carbons with sole detection of quarternary carbons [$(\tau_1 = 1/2J(C,H)$; $\tau_2 = 1/3J(C,D)$];

(2) Suppression of all deuterium-bound carbons [$(\tau_1 = 1/J(C,H)$; $\tau_2 = 1/3J(C,D)$] and phase selection for CH_n groups;

(3) Suppression of all proton-bound carbons [$(\tau_1 = 1/2J(C,H)$; $\tau_2 = 1/2J(C,D)$] and phase selection for CD_n groups;

(4) Combined selection of deuteron and proton multiplicity [$(\tau_1 = 1/J(C,H)$; $\tau_2 = 1/2J(C,D)$].

The details will be submitted to JACS.

Hope to see you in Chicago! Best regards,
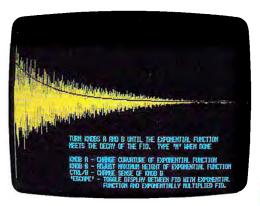
P. Schmitt   J. R. Wesener   H. Günther

(1) For a review see R. Benn and H. Günther, Angew. Chem., May or June '83.
(2) P. Schmitt, J.R. Wesener, and H. Günther, J. Magn. Reson. <u>52</u>, Nr. 3 (1983).
(3) J.R. Wesener and H. Günther, Org. Magn. Reson., in press.

cSU

(303)491-6480

Colorado State University
Fort Collins, Colorado
80523

Department of Chemistry

April 11, 1983

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

Note of Caution in Using Br-79 to Set the Magic Angle for C-13 MAS
Experiments.

Dear Barry:

We have been using $K^{79}Br$ to set the magic angle for ^{13}C CP/MAS spectra for the past year (TAMU 279, 42, December 1981). The proximity of the resonance frequencies of ^{79}Br and ^{13}C is a great advantage in that the probe and power amplifier do not need to be retuned. In some ^{13}C gated-decoupled MAS spectra, however, we see a sharp signal that arises from ^{79}Br aliased into the ^{13}C region. At 3.5 T the resonances are only 140 kHz apart, and a 5 μs pulse excites both nuclides. The aliased ^{79}Br peak can be identified by opening the input filters or expanding the sweep width and noting the great increase in intensity.

The ^1H spin-temperature alternation feature of the cross polarization experiment effectively removes this FT signal, for we have not observed it even in long CP runs. Please credit this contribution to Gary Maciel's "account".

Sincerely,

James S. Frye

James S. Frye

JSF:lb

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FACULTEIT DER WISKUNDE
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Uw kenmerk	Uw brief van	Ons kenmerk
		U5259/AK,FS,WS/DvdW Datum

April 19, 1983

Onderwerp
—

Dear Professor Shapiro,

^{27}Al magic angle spinning NMR of zeolites

Crystalline alumino silicates like zeolites can absorb relatively small molecules like for instance water. Most of the water molecules are physisorbed in the pores of the material but some are chemisorbed at Si-O-Al and Si-OH sites. With ^{1}H MAS NMR, water molecules at these two adsorption sites can be distinguished [1]. The Si-O-Al sites (Brønsted sites) play an important role in the catalytic activity of the zeolites and therefore the interaction between adsorbed molecules and these sites is of interest.

It is believed that water molecules adsorbed at Brønsted sites form clusters with the acidic proton: $H^+(H_2O)_n$ where n is of the order of two [2]. Therefore, hydration and dehydration of zeolites is expected to alter the position of the H^+ proton and consequently change the configuration of and charge distribution around the aluminum-oxygen tetrahedron. In a perfect tetrahedron the ^{27}Al quadrupole interaction is zero and the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ ^{27}Al transition narrow. For a perturbed tetrahedron this NMR transition should broaden due to the quadrupole interaction, a broadening which is not eliminated by magic angle spinning [3]. A broadening by quadrupole interaction of the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition is characterized by its field dependence, the larger the Zeeman interaction relative to the quadrupole interaction, the smaller the broadening.

Fig. 1 shows ^{27}Al MAS spectra of H-ZSM-5 at three different frequencies for the hydrated and dehydrated form. Clearly, on dehydration the ^{27}Al $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ NMR

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Geadresseerde	Ons kenmerk	Datum	Blad No
Prof. B.L. Shapiro	U5259/AK,FS,WS/DvdW	19-4-'83	- 2 -

line broadens. The field dependence of the broadening establishes the quadrupole origin (at 15.6 MHz the line of the dehydrated sample is too broad to be detected). Clearly, removing the chemisorbed water changes the charge distribution around aluminum.

Fig. 2 shows ^{27}Al MAS spectra at 78.2 MHz for Na-ZSM-5 as a function of hydration. These spectra show not only a line from four-coordinated Al at 53 ppm, the genuine ZSM-5 aluminum, but in addition lines at 65 ppm and around 0 ppm. The lines around 0 ppm originate from six-coordinated Al $(Al(H_2O)_6^{3+}$ in the pores and Al_2O_3 impurities). On dehydration the line from the four-coordinated Al of the catalytic active sites of Na-ZSM-5 broadens so much that it is practically unobservable. On rehydration it slowly reappears again. Apparently, the counter ion Na^+ on dehydration perturbs the electric field gradient at Al more than H^+ in H-ZSM-5. This makes it plausible that the increase of the electric field gradient at Al on dehydration is not only due to a change in the location of the counter ion H^+ or Na^+ but also due to a distortion of the aluminum-oxygen tetrahedra.
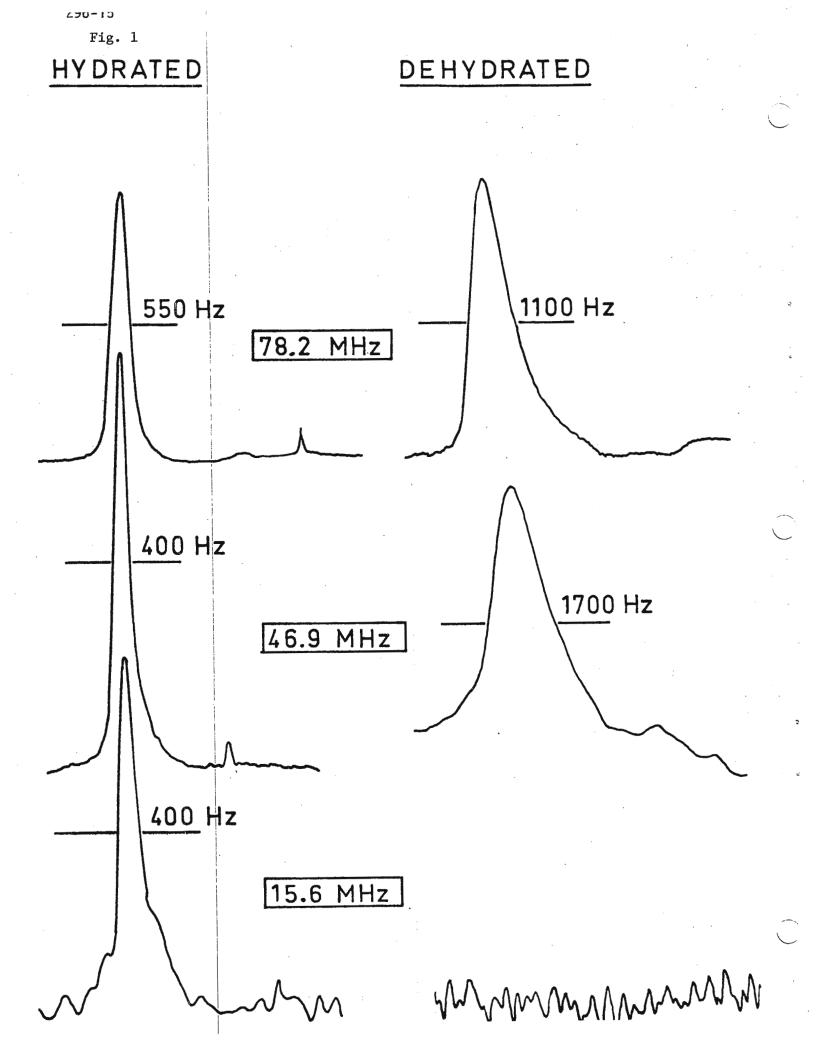
[1] K.F.M.G.J. Scholle, W.S. Veeman, J.G. Post and J.H.C. van Hooff, Zeolites, in press.

[2] H. Nakamoto and H. Takahashi, Zeolites, 2 (1982) 67.

[3] E. Kundla, A. Samoson and E. Lippmaa, Chem. Phys. Letters, 83 (1981) 229.
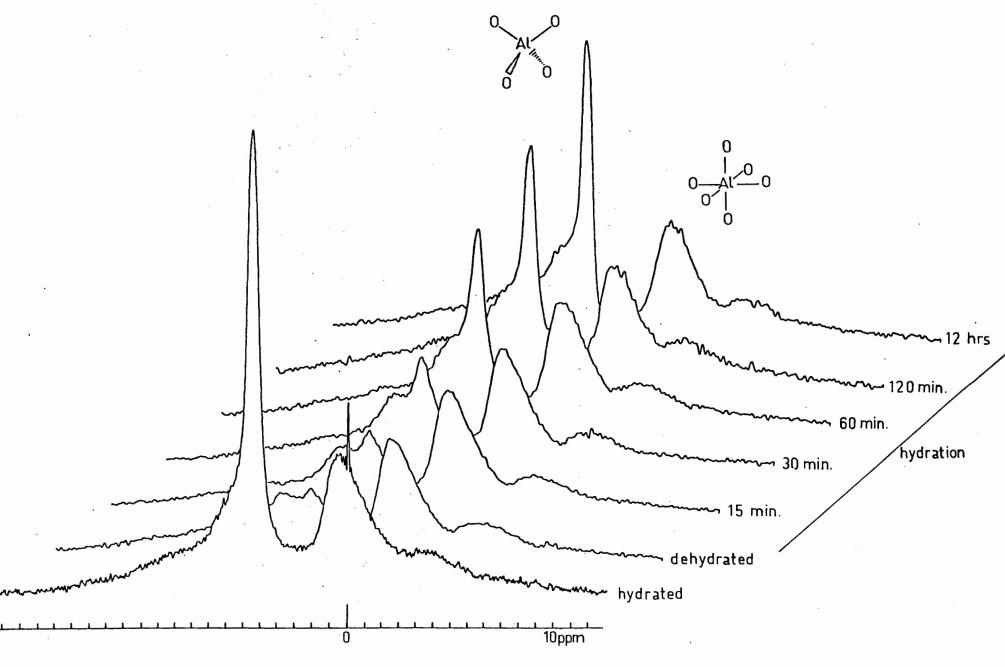
Best regards,

A.P.M. Kentgens   K.F.M.G.J. Scholle   W.S. Veeman

P.S. Please credit this contribution to the subscription of Prof. E. de Boer.

Fig. 1

HYDRATED

DEHYDRATED

550 Hz

1100 Hz

78.2 MHz

400 Hz

1700 Hz

46.9 MHz

400 Hz

15.6 MHz

Fig. 2

12 hrs

120 min.

60 min.

hydration

30 min.

15 min.

dehydrated

hydrated

0   10ppm

IBM Instruments Inc.

Orchard Park
PO Box 332 Danbury CT 06810

Telephone: 203 796 2500

April 7, 1983

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

2D Magnetization Transfer in the Rotating Frame

Dear Barry:

We have for some time been interested in investigating chemical exchange
in small peptides. The problem often encountered is that the resonances of
interest are close together (<25 Hz) and the use of the more common techniques
(transfer of saturation and selective inversion) becomes impractical. One
instance of this is the cis-trans resonances of the C-4H histidine resonances
in TRH (p-glu-his-pro-NH$_2$) where the separation for the two conformations is
about 22 Hz (using an IBM Instruments WP270SY spectrometer).

Using the Hennig and Limbach technique of magnetization transfer in the
rotating frame (J. Magn. Resn. <u>49</u>, 322-28 (1982)) we measured the T$_{1\rho}$ of the
two resonances using the fixed delays $\tau = \frac{1}{\Delta f}$ and $\tau = \frac{1}{2\Delta f}$ with a frequency
offset of Δf (22.06 Hz) downfield from the trans resonance. Since spin-
locking effectively narrows the lines in the rotating frame the technique is
potentially useful in cases where the resonances under investigation have only
a small chemical shift difference.

After completing the one dimensional experiments we decided to extend the
experiment to two dimensions (J. Jeener et. al., J. Chem. Phys. <u>71</u>(1), 4546
(1979)). The fixed delay τ in the one dimensional experiment becomes the
incremented delay D0 (and the F1 frequency domain after Fourier transformation).
The initial value of D0 was 1 msec and was incremented by 2.5 msec 63 times.
The 90° (P1) pulse was 9 μsec and the spin locking (P2) pulse was 200 msec.
This pulse (P2) corresponds to the mixing time in 2DNOE experiments. The two
pulses had a relative phase shift of 90°. Sixteen transients were acquired
in each of the 64 files.

The contour plot shown opposite reveals the results of the experiment.
The 'wings' at the bottom of the plot are present because constant phase was
used in the F1 dimension and only the region from 0 to -90 Hz is plotted. We
performed the 2DNOE experiment on this molecule at 60°C and saw cross peaks.
However, for the two dimensional Hennig and Limbach experiment it was necessary
to raise the temperature to 75°C to see the cross peaks. This is probably due
to the fact that the T$_{1\rho}$ is shortened by coupling to N-14 which is modulated
by quadrupolar relaxation (Bleich and Glasel, Biopolymers, <u>17</u>, 2445 (1978)).
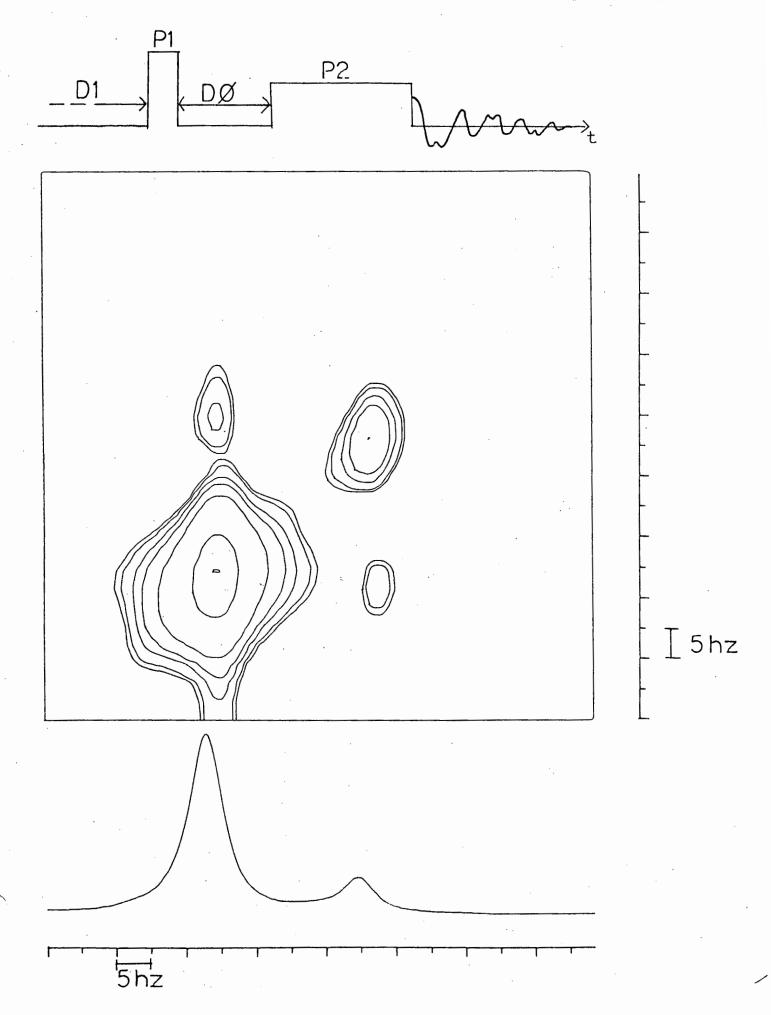
Sincerely,

Joyce A. Wilde   Hermann E. Bleich   Richard E. Schwemm

/lw
Enc.

P1

D1   DØ   P2

t

5 hz

5 hz

University of East Anglia

Professor R.K. Harris

School of Chemical Sciences
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Norwich NR4 7TJ, England

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April 13 1983

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

Dear Barry,

2-D Silicon-29 Spectra

Your green letter arrived on my desk at the same time as some splendid
2-D spectra obtained using the Bruker 400 MHz spectrometer (ca.80 MHz for
^{29}Si) at the University of Warwick, so we are able to respond to your prodding
quickly. The chemical problem, which has been fascinating us for some time,
is that of establishing the structures of the complex mixture of anionic
species which are in equilibrium in alkaline silicate solutions. We have
made extensive use[1,2] of enrichment with ^{29}Si, in combination with tedious
point-by-point homonuclear decoupling experiments. The full spectra are
complicated, so 2-D work offers elegant alternatives. The attached partial
J-resolved spectrum shows the power of these techniques. We also have
useful COSY spectra of these systems. We believe these are the first 2-D
homonuclear ^{29}Si spectra in existence. The notation for the structures given
on the figures is such that Q^1, Q^2 and Q^3 represent silicate units with one,
two and three siloxane bridges respectively. So far, unfortunately, although
we've nicely confirmed some previous deductions, no really new information has
emerged - but we're still hoping.

Best wishes,

Yours sincerely,

Robin

ROBIN HARRIS

Max
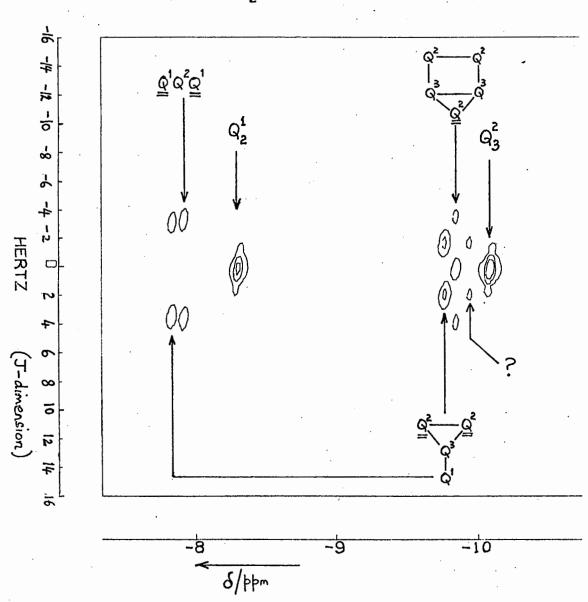
MAX O'CONNOR[*]

1. R.K. Harris, C.T.G. Knight & W. Hull, J. Amer. Chem. Soc. <u>103</u>, 1577 (1981)
2. R.K. Harris, C.T.G. Knight & W.Hull, ACS Symp. <u>194</u>, 79 (1982)

* On leave from La Trobe University, Melbourne.

PARTIAL 2-D J-RESOLVED ^{29}Si NMR SPECTRUM
of an alkaline potassium silicate solution
~ 1.41 M in SiO_2 K:Si = 1:1   278 K

LABORATOIRES DE CHIMIE

Département de Recherche Fondamentale de Grenoble

N/référence DRF/CH/83-134/AP
Y/réf. : BLS/lmk March 9th, 1983

Grenoble, le April 5, 1983

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

NMR Investigation of the cellulose conformation in an aprotic solvent solution

Dear Professor Shapiro,

The recent discovery of new organic solvents (1) for cellulose, allows to investigate the conformation of this natural macromolecule in solution, by using ^{1}H NMR. Among these solvents NN-dimethylacetamide containing 5 to 10 % lithium chloride, is of particular interest, due to its aprotic character. As shown by Figure 1, it is possible to observe the hydroxyl proton signals of cellulose in this solvent. The low signal resolution of this spectrum is due to the high viscosity of the solution.

Figure 2 shows the temperature effect on the hydroxyl proton signals. The chemical shift increment with temperature are :

$\frac{\Delta\delta}{\Delta T}$ 10^{-3} ppm/°C	1.9	2.5	1.	6.75
Proton	H-1	OH-2	OH-3	OH-6

It is known that the   effect of temperature on proton NMR signals is mainly governed by a change in intermolecular and intramolecular association. The lower value of $\Delta\delta/\Delta T$ for OH-3 observed here has also been found for cellobiose, the cellulose dimer, in a serie of aprotic solvents (2). Generally, hydroxyl group involved in intramolecular hydrogen found are less affected by temperature variation. To explain the particular behaviour of OH-3 we propose an intramolecular hydrogen bond between OH-3 and the ring oxygen atom 0-5' of the next D glucopyranosyle unit of the chain, as it has been found in the solid state.

Sincerely yours,

Dr Marc VINCENDON
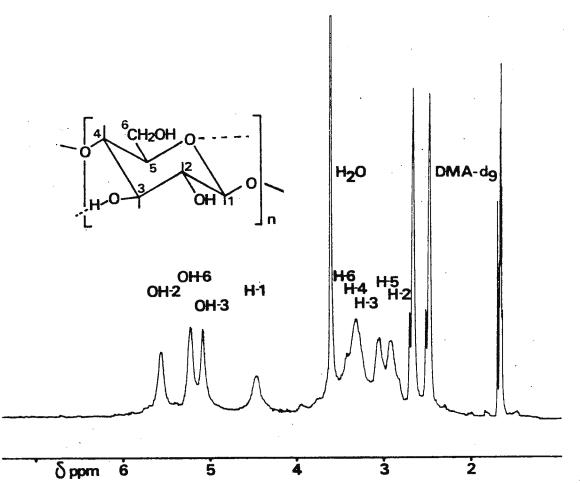
Figure 1 : ^{1}H NMR spectrum (250 MHz) of cellulose in N,N-dimethylacetamide-LiCl solution at 60°C.
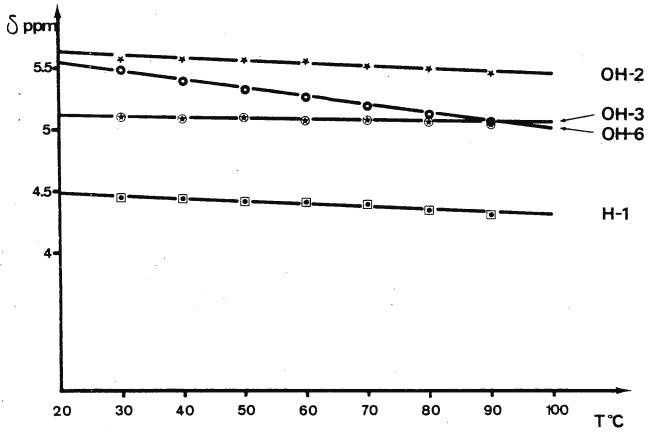
Figure 2 : Temperature variation of cellulose hydroxyl protons with temperature.

References :

1) A.F. TURBAK, A. EL KAFRAWY, F.W. SNYDER and A.B. AUERBACH
French Patent 2, 466, 473 (1981)

2) D. GAGNAIRE, J. SAINT GERMAIN and M. VINCENDON
J. Appl. Polymer Sci in Press

P.S. : Please credit this contribution to Dr Roselyne BRIERE account.

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April 6, 1983

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

Dear Dr. Shapiro:

Recent months have been exciting. The University of Illinois at the Medical Center (UIMC) and the University of Illinois Circle Campus (UICC) have been consolidated since September 1, 1982 into one entity called the University of Illinois at Chicago. This new institution has two campuses referred to as the UIC Health Sciences Center (HSC) and UIC University Center (UC), respectively.

The Research Resources Center of the HSC has recently purchased two (2) Nicolet broadbanded NMR spectrometers--a 360 NB and a 200 WB. These instruments are positioned in the basement of our building to avoid the vibration problems experienced by some instruments on upper floors of a building. Of course, during the installation it was discovered that we had a floor vibration problem. Vibrations above 20 Hz were not too troublesome but vibrations below 10 Hz made shimming for line shape very difficult. The troublesome side bands looked like spinning side bands except that they would vary in frequency and were not related to spinning rate.

To prove that these artifacts were caused by just floor vibrations, we measured just floor vibrations using a blood pressure transducer with its diaphragm resting on a metal washer set on the base plate of the magnet. Only floor vibrations caused the diaphragm to oscillate which was observed using a carrier preamplifier with an oscilloscope or strip chart recorder. The frequency offset of the troublesome side bands correlated very well with the frequency of the floor vibrations.

To reduce the problem, the energized magnet was lifted off its base plate, four (4) rubber air cushions were installed under the base plate, and the magnet was lowered and reconnected to the base plate. The total cost in dollars was $350. The total cost in aggrevation is not printable. The problem was reduced by about a factor of 100.

Michael Mutaw
Biomedical Engineer

Sincerely,

Robert A. Kleps, Ph.D.
Senior Spectroscopist

RAK:ac

PHYSICAL CHEMISTRY LABORATORY

OXFORD UNIVERSITY

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SOUTH PARKS ROAD
OXFORD
OX1 3QZ

31st March, 1983

RF/ml

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

Dear Barry,

Practical tips for Broadband Decoupling

Most readers will be aware of the recent new methods of heteronuclear broadband decoupling using "supercycles" (1) built up from magic cycles (2) of composite spin inversion pulses (3). Some results were reported in this Newsletter about a year ago (TAMUNMR 284 May, 1982). The purpose of this note is to point out some of the experimental precautions needed to obtain the very best decoupling performance and to advocate a more recent scheme called WALTZ-16 (4,5). We emphasize that for many routine carbon-13 applications (e.g. where very high resolution is not important) these adjustments may well be superfluous.

1.   Inaccurate radiofrequency phase shifts.

When observing carbon-13 line widths of the order of 0.1 – 0.2 Hz, sequences which use 90° radiofrequency phase shifts are quite sensitive to the accuracy of the three phase shifts involved. A simple solution to this problem is to use the spin inversion element (4)

$$R = 90°(x)\ 180°(-x)\ 270°(+x) \equiv 1\ \overline{2}\ 3$$

All sequences which employ only 180° radiofrequency phase shifts can be shown to be insensitive to errors in the phase shift (5). This element is therefore superior to earlier composite inversion pulses, simpler to implement, and covers a rather wider proton bandwidth. We have gone over completely to the WALTZ-16 sequence. With $\gamma B_2/2\pi$ = 2kHz (about 0.5 watts of power supplied to the Varian XL-200 probe) it covers a proton range of approximately 4 kHz. Incidentally, at these low power levels, we have noticed that shimming the B_o field is a much easier operation.

2.   Amplitude Imbalance between Channels

With the WALTZ-16 scheme there are only two decoupler channels (0° and 180°). Computer simulations and experiments suggest that the B_2 level in each channel should be equal within better than 0.5% for optimum decoupling. If the phase shift is generated at an early stage of the amplifier chain (as in Varian XL-200) good amplitude balance is achieved automatically. However if the decoupler phase shift is accomplished by way of a double-balanced mixer,

there could be difficulties, either because the balance is insufficiently precise or because the rise and fall times of the driving pulse amplifiers are too slow. The cure is to use a current amplifier (for example National Semiconductors LH0002C) to drive the double-balanced mixer. No decoupling capacitor is used on the output since this would slow down the switching. A suitable circuit is shown in Figure 1. Setting up the amplitude balance is first done roughly by observation on an oscilloscope. Then the decoupled peak height is monitored for a very narrow line (few tenths of 1 Hz) for an offset $\Delta B = 0.25\ B_2$ (chosen because it is relatively sensitive), carefully adjusting the 10-turn balance potentiometer for optimum peak height. This is a once-and-for all adjustment.

3. Cycling Sidebands

The cycling rate of the decoupler is much slower than the carbon-13 sampling rate, and this introduces very weak "cycling sidebands" into the decoupled spectrum. Many of these have random phases if the proton pulsing and carbon sampling processes are desynchronized. The cycling sidebands can be considerably attenuated by using a "blackbox" hardware decoupler instead of computer-controlled decoupler pulsing. A suitable circuit (5) is shown in Figure 2.

Kindest regards,

James Keeler
A. J. Shaka
Ray Freeman

1. Levitt, Freeman and Frenkiel, J. Mag. Reson., 50, 157 (1982).
2. Levitt and Freeman, J. Magn. Reson. 43, 502 (1981).
3. Levitt and Freeman, J. Magn. Reson. 33, 473 (1979).
4. Shaka, Keeler, Frenkiel and Freeman, J. Magn. Reson. 52, 335 (1983).
5. Shaka, Keeler and Freeman, J. Magn. Reson., to be published.

Keeler et al.

Figure 1

WALTZ-16 input   1K

+5V   .01

RF. in

Double-balanced mixer

MD108
SRA-1
SBL-1
etc.

100Ω

3 1 2 8

4 5

-5V   100Ω

10 Turn 500Ω   1K

.01

100Ω

-5V

RF out

National LH0002C

Figure 2

Frequency adjust

22K

+5   1K   1K   0.1

NE555

8

1

6800 pF

14 7493 +5

14 7492 +5

+5   1K   100pF

14 74121

½ 7486   TP $4\left(\frac{\gamma B_2}{2\pi}\right)$ Hz

½ 7486

+5

Output to phase shifter
$Q = \overline{3}2\overline{4}2\overline{1}3\overline{2}4\overline{3}$

+5   +5   +5   +5   +5   +5

16 74165   16 74165   16 74165

1   1   1

+5   +5 +5   +5

Reset and load

100 nanosecs

Papanicolaou Cancer Research Institute at Miami, Inc.

1155 Northwest 14th Street • Miami, Florida • Telephone (305) 324-5572

Mailing Address: Box 016188 • Miami, Florida 33101

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

April 14, 1983

Dear Prof. Shapiro:

In-Vivo ^{31}P NMR Spectrum of a Rat Tumor
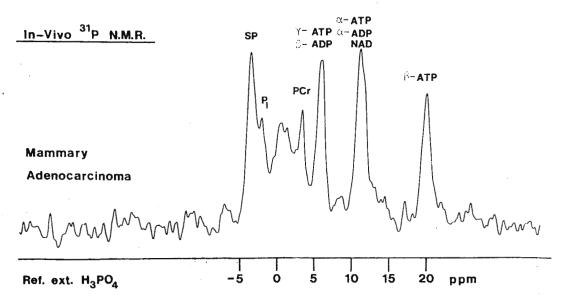
I wish to report that we have entered a phase of our work which involves obtaining ^{31}P NMR spectra from tumors in live animals. The spectrum shown here was obtained at 36.2 MHz from a rat mammary adenocarcinoma using a 10 mm coil on the tumor and 1600 54° pulses. Convolution difference was carried out with 15 Hz and 400 Hz line broadening factors. Preliminary spectral assignments are shown where SP = sugar phosphates, P_i = inorganic phosphate, PCr = phosphocreatine, NAD = reduced nicotinamide adenine dinucleotide, ATP and ADP = adenosine tri- and di-phosphate respectively.

I would appreciate it if you would reinstate our subscription to the Texas A & M NMR Newsletter. Thank you very much.

Sincerely yours,

Ronald E. Block, Ph.D.
Associate Scientist

In-Vivo ^{31}P N.M.R.

Mammary Adenocarcinoma

Ref. ext. H_3PO_4

StonyBrook

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794
telephone: (516) 246-5050

April 14, 1983

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

FACTS ABOUT AQUEOUS SHIFT REAGENTS
FOR HIGH RESOLUTION CATIONIC NMR

Dear Barry:

We have continued our work (J. Mag. Res., 46, 348 (1982)) on the above named shift reagents (SR). The accompanying Figure shows the isotropic hyperfine shifts, Δ, induced in several nuclei by $Ln(CA)_3^{6-}$ SR (CA^{3-} is chelidamate, 4-hydroxypyridine-2, 6-dicarboxylate). The Δ values were calculated as the differences in observed reasonant frequencies in the presence and absence of SR. The spectrometers were locked on the ^2H_2O resonance of the solvent.

The ratios of the shifts induced in the $^{23}Na^+$ resonance by $Dy(CA)_3^{6-}$ over those induced by $Tm(CA)_3^{6-}$ (bottom two curves) are quite close to the value of -1.9 expected for a pure dipolar (pseudocontact) mechanism. This is strong evidence that this mechanism dominates, as expected, and that field-frequency locking eliminates most of the bulk-susceptibility contributions. We have observed similar results with the $Dy(TTHA)^{3-}/Tm(TTHA)^{3-}$ ($TTHA^{6-}$ is triethylenetetraminehexaacetate) and $Dy(PPP)_2^{7-}/Tm(PPP)_2^{7-}$ (PPP^{5-} is tripolyphosphate) pairs.

The facts that the $^{25}Mg^{2+}$ and $^{39}K^+$ shifts induced by $Dy(CA)_6^{3-}$ are significantly greater than that of $^{23}Na^+$ mean that the binding of the former ions is greater and/or that the spatial coordinates of the binding sites are different. The ^{23}Na curve can be fitted quite well with the 1:1 thermodynamic binding constants $K_{Na} = 1579\ M^{-1}$ and $K_{Li} = 61.5\ M^{-1}$ and a limiting shift $\Delta_{Na} = +11.9$ ppm. The fact that observed shifts of $^{25}Mg^{2+}$ and $^{39}K^+$ rise significantly above +12 ppm is strong evidence that the binding sites are different. (The field-independence of some ^{23}Na shifts has been established.) Limiting dipolar shifts (in ppm) for identical binding sites would be independent of the nucleus observed. We observe similar behavior for the $^{39}K^+/^{23}Na^+$ pair with $Dy(TTHA)^{3-}$ and $Tm(TTHA)^{3-}$. We find an extreme example of binding site difference in that $Dy(NTA)_2^{3-}$ (NTA^{3-} is nitrilotriacetate) shifts the $^{43}Ca^{2+}$ resonance upfield but the $^{113}Cd^{2+}$ resonance downfield. There are, of course, also differences in binding. The binding constants for Na^+ and Li^+ to $Dy(CA)_3^{6-}$ reported above show this. We have also found that K^+ out-competes Na^+ for binding to $Dy(PPP)_2^{7-}$ (the Guptas' SR).

In these kinds of experiments, there are three essential components: a) the Ln ion, b) the metal cation observed, and c) the chelate ligand. Examples of individual variation of a) and b) are given above. As an example of the variation of c), we report that while $Dy(CA)_3^{6-}$ shifts the $^{23}Na^+$ resonance upfield (Figure), $Dy(TTHA)^{3-}$ shifts it downfield. More details of much of this work will be appearing soon (July) in Inorganic Chemistry.

Please credit this contribution to the Stony Brook subscription (c/o Paul Lauterbur).

Best regards,

Charlie
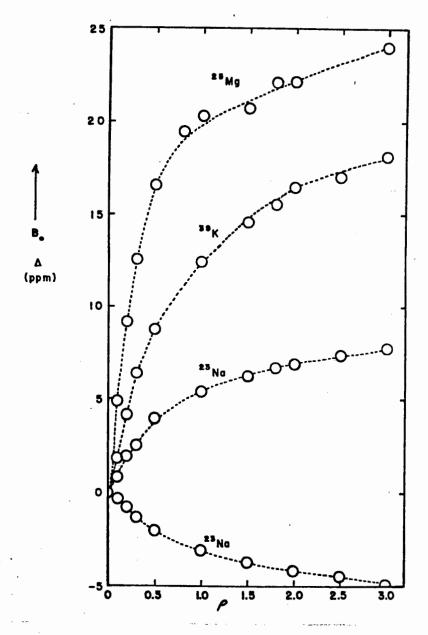
Charles S. Springer, Jr.
Assoc. Prof. of Chem.

James a Balschi
Research Assist.

Dave Yarmush

David M. Yarmush
Postdoctoral Assoc.
Mass. Inst. of Tech.

Simon C. Chu
Research Assist.

(Also contributing to this work were Marty Pike, Dave Hillman, Bob Lenkinski, Jean DeLayre, Eric Fossel, and Tom Smith).

The isotropic hyperfine shift, Δ, of various metal cationic resonances versus the stoichiometric mol ratio of shift reagent to cation, ρ. In all cases, the metal chloride ($MgCl_2$, KCl, $NaCl$) concentration is held constant at 50 mM. The magnetic isotope observed is present at natural abundance. In all cases, tris (tris(hydroxymethyl)aminomethane) buffer was present at a total tris concentration of 10 mM. The dashed curves are intended merely to guide the eye. For the upper three curves, the shift reagent was $Li_6Dy(CA)_3 \cdot 3LiCl$. In the $MgCl_2$ case ([25]Mg NMR, 24.5 MHz, 9.40T), the pH varied smoothly from 8.4 in the solution with no shift reagent to 7.8 in the solution with 150 mM SR. The temperature was ca.297°K. In the KCl case ([39]K NMR, 14.0 MHz, 7.05T), the pH varied from 8.7 to 7.7. The temperature was ca. 297°K. In the NaCl case (^{23}Na NMR, 26.5 MHz, 2.35T), the pH varied from 8.6 to 7.9. The temperature was ca. 301°K. For the lower curve, (^{23}Na NMR, 26.5 MHz, 2.35T), the shift reagent was $Li_6Tm(CA)_3 \cdot 3LiCl$. The pH varied from 8.9 to 7.9. The temperature was ca. 301°K.

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April 15, 1983

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

Title: NMR studies of perfused cells; Mag.
Res. Biol. Vol. 2.

Dear Barry:

I would like to briefly describe a novel technique which we have developed for the perfusion of cells. The advantages of our technique are that it is applicable to any cells grown in culture and can be used with any standard NMR spectrometer. The method involves embedding the cells in an agarose gel matrix[1] extruded in the form of a fine thread. This allows rapid diffusion (ca. 1 min) of metabolites, or drugs, into the cells. We are not aware of any other method which has these advantages. We have published a preliminary description of the method[2] and applications to mammalian cells using ^{31}P and ^{1}H NMR are in progress (Figure).[3]

I also take this opportunity to inform you about the publication of Vol. 2 of Magnetic Resonance in Biology.[4] This contains excellent chapters by: Debrosse & Villafranca, on "Isotope effects on phosphorus chemical shifts: applications to enzyme mechanisms;" Makinen & Kuo, on "Spin label probes of enzyme action" and Shindo, on "DNA backbone conformation and dynamics." We have also written a chapter (Lou Hughes, Jan Wooten and myself), entitled "Observations of amino acid side chains in proteins by NMR methods," which focusses on individual side chain types (His, Met, Tyr, etc.) and contains ca. 350 references. For those who are interested in water in tissue, and its potential relevance to NMR imaging there is a chapter by Lynch, on "Water relaxation in heterogeneous and biological systems." Altogether a varied yet in-depth collection. Additionally I draw your attention to two other reviews on different topics that we have written this year (a busy one), namely on "^{31}P NMR studies of DNA and RNA",[5] and a general review entitled "NMR in Biology and Medicine" being published as a single tract.[6]

In further news from our laboratory I should emphasize we are still very active in ^{31}P NMR studies of DNA conformation, particularly in relation to the B to Z transition.[7] And lastly I confirm that I will be transferring to the National Cancer Institute and setting up a new laboratory there devoted to the multivariate uses of our favorite technique.

Yours sincerely,

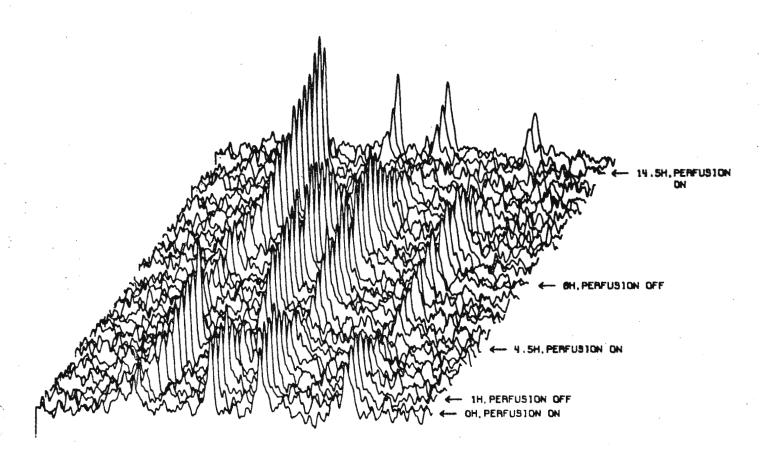Jack S. Cohen
Laboratory of Theoretical and
 Physical Biology
National Institute of Child
 Health and Human Development

JSC:ell

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1. L. Jacobson and J. S. Cohen Biosci. Reports 1 141 (1981).
2. D. Foxall and J. S. Cohen J. Mag. Res. 51 346 (1983).
3. R. Knop, C. Chen, D. Foxall, J. S. Cohen, J. Mitchell and A. Russo, submitted.
4. J. S. Cohen (ed) Magnetic Resonance in Biology, Vol. 2, Wiley-Interscience, 1983.
5. C. Chen and J. S. Cohen, to appear in "Phosphorus-31 NMR: Principles and Applications," D. Gorenstein (ed), Academic Press, in press.
6. J. S. Cohen, R. Knop, G. Navon and D. Foxall, Life Chemistry Reports, Harwood Academic Press, in press.
7. C. Chen, J. S. Cohen and M. Behe, Biochemistry, in press.

Figure Legend: A stacked plot of ^{31}P NMR spectra at 109 MHz of Chinese hamster lung fibroblasts (ca. 108 cells) perfused in agarose gel threads at a flow rate of 2.7 ml/min with F12 medium (plus 10% FCS, 20mM Hepes, pH 7.35) in a Wilmad 10 mm screw cap tube. Each accumulation took 22 min (77° pulse, 220 msec delay) at 25°C. On stopping perfusion, the ATP signals decrease while the P_i signal concomitantly increases. On reperfusing the reverse occurs and the original levels are attained. This indicates that the cells can be kept metabolically active under the conditions of the experiment over a period of many hours. Microscopic examination, plating and other criteria indicate the cells remain morphologically normal.

DIVISION OF PHYSICAL CHEMISTRY
THE ROYAL INSTITUTE OF TECHNOLOGY   Stockholm, April 19, 1983
S-100 44   STOCKHOLM 70
SWEDEN
Cable address: Technology

Professor B L Shapiro
Texas A&M University
College Station
TX 77843   U S A

Dear Professor Shapiro,

SIMULTANEOUS MEASUREMENTS OF SELF-DIFFUSION COEFFICIENTS AND SPIN-LATTICE
RELAXATION TIMES

Measurements of self diffusion coefficients with the FT-NMR pulsed-gradient
spin-echo method (1) have proved to be a valuable tool for elucidating struc-
tures of complex liquid systems, *e.g.* microemulsions and micellar solutions
(2). The pulse sequence used is shown in Fig. 1a.

By combining the inversion recovery-method for measuring T_1 with the pulsed
gradient spin-echo method, as shown in Fig. 1b, we have found it possible to
simultaneously measure T_1 as well as the self-diffusion coefficients. The
attenuation is in this case given by

$$\frac{A}{A_0} = (1-be^{-\tau/T_1}) \, e^{-\gamma^2 g^2 D\delta^2(\Delta-1/3\delta)} \qquad [1]$$

where A_0 is the amplitude of a line in the Fourier transformed spin-echo
without field gradient and A the corresponding amplitude with gradient pulses
present, g is the magnitude of the field-gradient, D is the self-diffusion
coefficient and τ, Δ, δ are time-parameters defined in Fig. 1b.

Fig. 2 shows the results from a typical ^{1}H measurement. The sample used was
an un-degasser 1:1 by weight mixture of C_6H_6 (Merck, p.a.) and $(CH_3)_2CO$
(Merck, p.a.).

The measurements were performed at 27^0C with a Bruker CXP-100 spectrometer
operating at 90 MHz, using quadrupolar gradient coils (3). The field gra-
dient was determined by calibration with a H_2O-sample; the calibration
yielded a value of g = 1.30±0.01 G/cm. T_1 and D were evaluated by a non-
linear curve-fitting of the parameters in Eq. [1] to the data. The values
are consistent with those obtained in separate measurements, with comparable
accuracy for the self-diffusion coefficients and somewhat lower for T_1. The
idea behind this method can, of course, also be applied to simultaneous measu-
rements of T_1 and T_2 by combining the "inversion recovery" experiments with
a CPMG-sequence.

Sincerely yours,

Ulf Henriksson   Torbjörn Wärnheim

References:

1.   P Stilbs and M E Moseley, Chem. Scr. 15, 176 (1980).
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3.a H Breuer, Rev. Sci. Instr. 36, 1666 (1965);
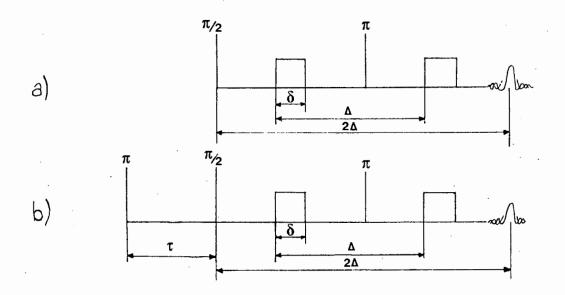 b G Ödberg and L Ödberg, J. Magn. Reson. 16, 342 (1974).

Fig. 1 a) Pulse sequence used in the pulsed-gradient spin-echo experiment.

b) Pulse sequence for simultaneous measurements of self-diffusion coefficients and spin-lattice relaxation times.
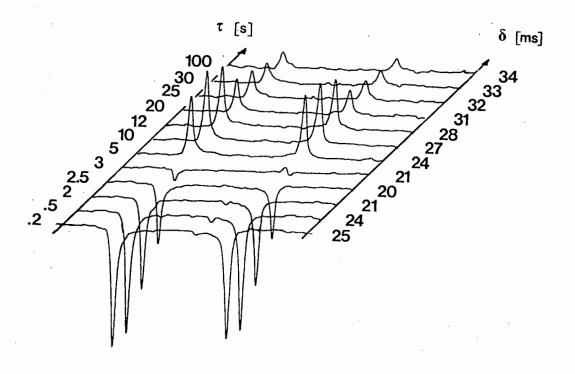

Fig.2 Spectra for 1:1 benzene-acetone mixture at different values of τ and δ. The time interval $\Delta=0.140$ s in all experiments.

STATE UNIVERSITY LEIDEN - THE NETHERLANDS
GORLAEUS LABORATORIES - DEPARTMENT OF CHEMISTRY

P.O. Box 9502, 2300 RA Leiden   Phone: 71-148333, extension: 3921

Your letter:
Your ref.:
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Subject:

Dr. J. Lugtenburg

LEIDEN, April 20, 1983.

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

Dear Professor Shapiro,

^{1}H- and ^{13}C-NMR spectra of 11 ^{13}C all-trans-retinal (1).

For our studies in the rhodopsin and bacteriorhodopsin field we prepared all-trans-retinal with 92% ^{13}C incorporation on carbon position 11. The source of ^{13}C label was 1 ^{13}C acetonitrile (M.S.D. 92%).
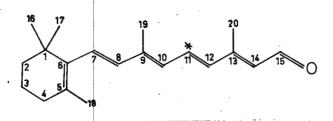

fig. 1 11-^{13}C-all-trans-retinal (1)

In figure 2(A) the 300 MHz ^{1}H-NMR spectrum of 1 is depicted.
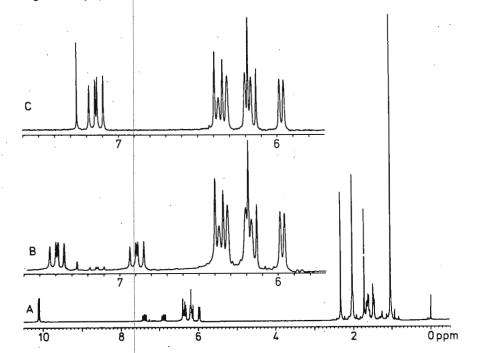

fig. 2 300 MHz
^{1}H-NMR spectrum of 1

In 2(B) the vinylic region is expanded and in 2(C) the same region of all-trans-
-retinal is recorded. From the spectrum the value for $J_{C_{11}-H_{11}}=150.4$ Hz is
obtained and the signals at 7.14 ppm show the presence of 8% unlabeled and 92%
^{13}C labeling at C_{11}. All other signals are essentially unchanged.[1]
In figure 3A the ^1H noise decoupled ^{13}C-NMR(75.5 MHz) spectrum is shown.[2]
In 3B the strong singlet of 1 at 132.5 ppm corresponding to the 92% incorporation
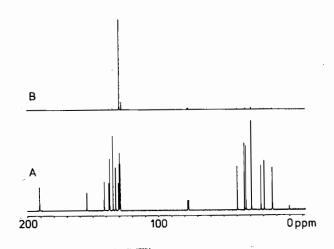at C_{11} is clearly visable.

fig. 3

From the natural abundance ^{13}C NMR spectrum of 1 the following $^{13}C-^{13}C$
coupling constants could be obtained.

$C_{10}-C_{11}=58.7$ Hz	$C_9-C_{11}=0$	$C_{11}-C_{14}=8.2$Hz	$C_{11}-C_{20}=3.3$Hz
$C_{11}-C_{12}=69.8$ Hz	$C_{11}-C_{13}=0$	$C_{11}-C_{19}=4.3$Hz	

Up to now in the hydrocarbon field only the ^1J $^{13}C-^{13}C$ values of a few simple
molecules are known. This is the first case where a larger polyene chain has
been studied. The values for the various types of bonds agree very well with
those known for small systems. We hope to prepare via 1 rhodopsin and bacterio-
rhodopsin with 92%. ^{13}C on position 11 in their chromophoric part. Magic Angle
Spinning ^{13}C NMR spectroscopy of these molecules is expected to give novel
essential information about the interaction of chromophore and apoprotein in
these systems.

Sincerely yours,

(P.P.J. Mulder)   (J.A. Pardoen)   (C. Erkelens)   (J. Lugtenburg)

1) For the ^1H-NMR values of all-trans-retinal, D.J. Patel, Nature 221, 825-828 (1969).
2) For the ^{13}C-NMR values of all-trans-retinal, G. Engbert, Helv. Chim. Acta, 58,
   2367-2390 (1975).

University of Bristol   School of Chemistry

Cantock's Close
Bristol
England BS8 ITS
19th April 1983

Telephone: Bristol 24161 Ext.

Dear Professor Shapiro,

We do a lot of work with diphosphorus compounds, so come across AA'X spectra (A = ^{31}P, X = ^{13}C) quite often. They are also common in coupled ^{13}C spectra where A = ^{1}H.

The typical symmetrical 5-line spectrum (see figure) is often simplified to 4 lines (if $J_{AA'} \ll L$, $I_{mid} \approx 0$) or 3 lines (if $J_{AA'} \gg L$, $I_{out} \approx 0$). The first case occurs frequently when A = ^{1}H and the carbon is bonded to one of the protons; the second is common when A = ^{31}P.

When the 5-line pattern is observed it is obviously impossible to extract the three coupling constants from the two line separations involved, although in many P-P cases one of the coupling constants can be assumed to be zero. We have therefore investigated the use of line intensities to provide further information. The following simple relationships are used:

$$J_{AA'} = 2D \sqrt{I_{mid}/2} = 2D \sqrt{1 - I_{out}}$$

This technique has been tested for a number of cases where A = ^{1}H, and compared with the results obtained by the use of ^{13}C satellites (see Table). The carbons that give five-line spectra are not those bonded to the two protons, but those for which $L \approx J_{AA'}$.

For diethylmethylenemalonate the satellite method is unusable, but the 5-line spectrum of the carbonyl carbons (see Figure) gives a value of 0.88 ± 0.05 Hz for the geminal H-H coupling constant. The alternative method of determining this coupling constant, deuterium exchange, would probably fail with such small couplings, quite apart from the synthetic difficulties of preparing the labelled compound.

A problem that can arise when $J_{AA'} < L$ is that the N doublet and the combination lines are of such similar intensity that they cannot be assigned. In this case the off-resonance technique of Fritz and Sauter (J. Mag. Res. 1974, 15, 177) can be used.

Please credit this contribution to Robin Goodfellow's subscription.

Yours sincerely,

Martin Murray   Kevin Higgins

Figure: ^{13}C Spectrum of Diethylmethylenemalonate
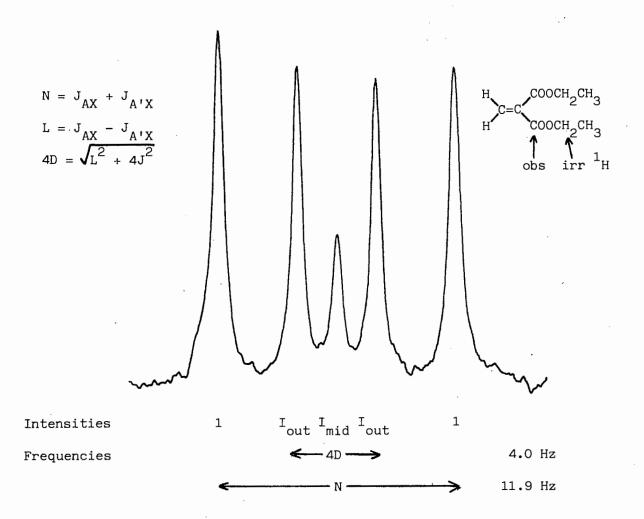
$$N = J_{AX} + J_{A'X}$$

$$L = J_{AX} - J_{A'X}$$

$$4D = \sqrt{L^2 + 4J^2}$$

Intensities	1	I_{out} I_{mid} I_{out}	1	
Frequencies		$\longleftarrow$ 4D $\longrightarrow$		4.0 Hz
	$\longleftarrow$ N $\longrightarrow$			11.9 Hz

Table: Values of J_{H-H} for Symmetrical Molecules

	from ^{13}C of $\underline{C}$	from ^{13}C satellites of $\underline{H}$
	3.39 $\pm$ 0.07	3.5 $\pm$ 0.2
	5.74 $\pm$ 0.07	5.7 $\pm$ 0.1
	12.16 $\pm$ 0.08	12.0 $\pm$ 0.2
	11.74 $\pm$ 0.18	11.8 $\pm$ 0.2

TCU

TEXAS CHRISTIAN UNIVERSITY
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4/8/83

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

Dear Barry:

It is now clear that twenty years of contributions to the
Newsletter does not absolve one from your dunning letters.
I am thus reassured that nine months after I ultimately depart
this earth someone will remember me.

We have been studying the electrophilic additions of
several types of reagents to the benzobicyclo[2.2.2]octadienes
below for the past several months. Depending on the nature
of the reagent and of the R groups one can get either <u>syn</u> or

R = CH₃ or Ac

<u>anti</u> addition of the reagent in either a <u>syn</u> or <u>anti</u> sense
with reference to the aromatic ring side of the double bond.
Often one gets rearrangements. Given the complexities of the
situation, the use of NMR for structure assignment would be
helpful. Even though carbon assignments can often be made
by conventional means, it is not always evident whether rearrange-
ment has occurred or not.

Aromatic methoxy or acetoxy groups bind Yb(FOD)₃ very
weakly when compared with hydroxy, epoxy or even keto groups
on the bicyclic ring. An exception is the rearranged iodohydrin
below where the geometry allows the molecule to serve as
a strong bidentate ligand. The values in () are the relative
LIS. It would be interesting to do a Wilcott-Davis fit to see
where the lanthanide is located here, but that takes us away
from our main interest.

Dunning may also be defined
as the act of making something
dun colored–rather like this
brief report.

Wishing you a better spring,

Bill

William B. Smith

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DEPARTAMENTO DE QUIMICA

April 20, 1983.

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

Fluorine-19 nmr measurements of steroidal drugs.

Dear Professor Shapiro:

The low solubility of many fluorinated corticosteroids in conventional nmr solvents has in general precluded systematic measurements of both their proton and fluorine spectra, although some isolated cases can be found in the literature (1).

Although the use of trichloroacetyl isocyanate reaction (2) of some corticosteroids allowed analyses of the derived carbamates, in particular for fluorine containing molecules a much more specific spectral determination is provided by F-19 nmr of the underivatized compounds.

Pulse-FT determinations could solve the sensitivity problem for these substances, although the very large spectral width required particularly for fluorine measurements preclude its application in a practical way.

In order to solve these problems spectra were measured using 12 mm sample tubes in which it was possible to dissolve some 5 mg of the individual steroids in approximately 4 ml of either deuterochloroform or hexadeuteroacetone. This concentration is still low for obtaining good fluorine spectra and therefore the measurements were performed by continuous wave time averaging using a Varian XL-100A spectrometer in combination with the 620L-100 computer. In general 10 to 25 scans were accumulated thus providing a 3 to 5 fold increase in sensitivity. The deuterium of the solvent was used to lock the spectrometer. The data show that there is a $\Delta\delta \approx$ 20 ppm between the 6α and the 9α fluorines in accordance with the known shielding of an axial as compared to an equatorial fluorine (3). Moreover, observation of the $^{19}F-^{1}H$ vicinal coupling constants evidences the potential of this technique for the conformational analysis of this type of molecules.

1.- A. D. Cross and P. W. Landis, J. Am. Chem. Soc., 86, 4005 (1964).

2.- M. Lanouette, D. Legault and B. A. Lodge, J. Pharm. Sci., 65, 8, 1214 (1976).

3.- H. J. Schneider, W. Gschwendtner, D. Heiske, V. Hoppen and F. Thomas, Tetrahedron, 33, 1769 (1977).

I: R_1 = F; R_2 = F; R_3 = H.
II: R_1 = F; R_2 = F; R_3 = Ac.
III: R_1 = F; R_2 = H; R_3 = H.
IV: R_1 = H; R_2 = F; R_3 = Ac.

V: R_1 = F; R_2 = F; R_3 = H.
VI: R_1 = H; R_2 = F; R_3 = Ac.

VII: R = H.
VIII: R = Ac.

IX

X

XI

^{19}F CHEMICAL SHIFTS (in ppm)* AND HETERONUCLEAR ^{19}F-^{1}H COUPLING CONSTANTS (in Hz)** IN FLUORINATED CORTICOSTEROIDS

Compound	Solvent	$F_{6\alpha}$				$F_{9\alpha}$		
		δ	$J_{6\alpha,6\beta}$	$J_{6\alpha,7\alpha}$	$J_{6\alpha,7\beta}$	δ	$J_{9\alpha,8\beta}$	$J_{9\alpha,11\alpha}$
I	C_2D_6CO	186.8	48.5	14.5		165.5	28.0	9.0
	$CDCl_3$	188.1	49.0	13.5		166.7	27.0	8.3
II	C_2D_6CO	187.1	49.0	14.5		165.5	28.0	8.5
	$CDCl_3$	187.9	49.0	14.0		167.0	27.0	8.0
III	C_2D_6CO					165.9	29.0	10.0
	$CDCl_3$					167.6	28.0	9.0
IV	C_2D_6CO	183.9	49.0	11.5	3.2			
	$CDCl_3$	185.0	49.0	11.7	3.5			
V°	C_2D_6CO	186.8	48.5	14.5		164.2	28.0	9.5
VI	C_2D_6CO	185.8	50.0	13.5				
	$CDCl_3$	187.0	49.5	13.0				
VII°	C_2D_6CO					165.4	29.0	9.7
VIII	C_2D_6CO					165.4	29.7	10.0
	$CDCl_3$					167.0	29.0	9.0
IX	C_2D_6CO	186.9	49.0	14.8		164.4	29.0	10.0
	$CDCl_3$	187.5	48.8	13.6		164.6	28.0	8.2
X	C_2D_6CO	184.0	48.8	11.0	3.0			
	$CDCl_3$	184.9	49.0	12.0	3.5			
XI	C_2D_6CO	184.0	49.7	14.5	9.0			
	$CDCl_3$	185.2	49.7	14.5	9.5			

*From $CFCl_3$ as internal standard (δ=0 ppm).

**Additional couplings are evident from signal broadening.

°Insoluble in $CDCl_3$ for measurement.

Sincerely yours,

P. Joseph-Nathan
Professor of Chemistry

R.L. Santillán

J. Espiñeira

TEXAS A&M UNIVERSITY

DEPARTMENT OF CHEMISTRY
COLLEGE STATION, TEXAS 77843

1983-84 Newsletter Subscriptions and Related Matters

It will soon be time for the execution of subscription renewals for the 1983-84 year of the TAMU NMR Newsletter – our 26th year of continuous operation! (I suppose that we will soon have to begin offering "Senior Citizen" discounts.) The mails being what they are, especially overseas postings, many of you will receive your subscription renewal notices and invoices about the same time, or even before, this May 1983 issue. In any event, permit me to make a special plea that subscription renewal handling be done expeditiously, for it really does add significantly to our cost of operation when we must do extra book-keeping, send reminders, etc. If you do not receive a subscription renewal notice and invoice by, say, July 18, please inform us immediately by airmail, and we will provide replacement copies. The subscription renewal notices will go into the mail on July 1 (airmail for overseas recipients).

I know it will not escape your attention that there is a small increase in the subscription fee for the Newsletter subscriptions, beginning with the 1983-84 year. The small increase only partially looks after the increased costs since the current rate went into effect in 1981.

The entirely self-supporting TAMU NMR Newsletter continues to exist, then, not solely by funds raised by the subscription fees we charge. Rather we continue to be dependent strongly on the generosity of our Contributors and Sponsors, and on the equally reliable and supportive role played by our Advertisers, most especially those who advertise every month. All of us in the NMR community owe these Advertisers a debt of gratitude for keeping this apparently useful Newsletter alive. Thus please permit me to ask that you provide suitable feed-back to our Advertisers to the effect that the Newsletter is indeed worthy of their continued and generous financial support. We continue to need additional support in all categories, especially Sponsors, Contributors, and Advertisers.
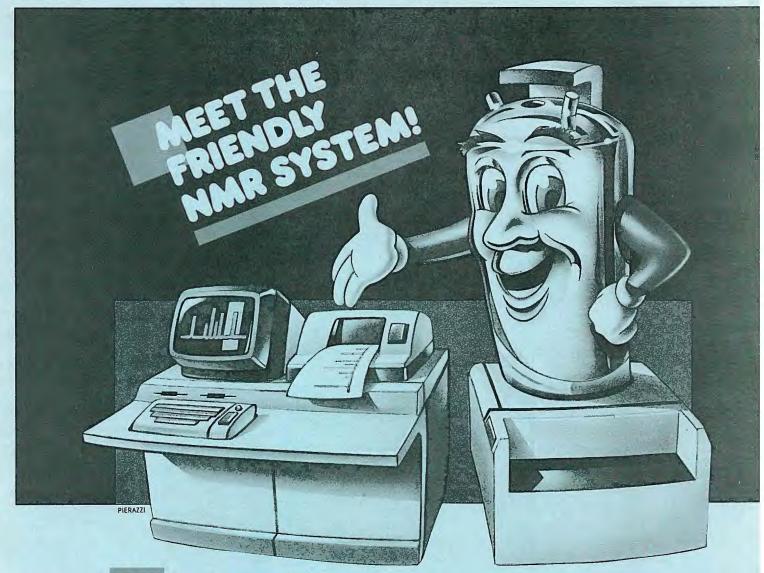
I have in mind certain changes in the Newsletter – primarily additions – and will of course welcome suggestions for improving any aspect of the Newsletter operation. Please don't be shy! The first change which will occur will be the occasional, irregular appearance of a "Book Review" section. I have volunteered my good friend and colleague, Professor William B. Smith of Texas Christian University, to do the book reviews. Bill's breadth of interest and well-known fairness will make the book reviews useful; his incisiveness and wit guarantee that the reviews will also be a pleasure to read and occasionally amusing. (If the latter aspect begins to fail, we will apprentice him to Ray Freeman for a few months.)

Again, if you do not have a Newsletter subscription renewal notice and invoice in your hands by Monday, July 18, 1983, please let us know immediately. The Newsletter continues to thrive technically, but we must unfortunately keep its finances healthy as well...

B. L. Shapiro
2 May 1983