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M &
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Newsletter

No. 132
SEPTEMBER, 1969

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Deadline Dates:   No. 133:   6 October 1969
                  No. 134:   3 November 1969
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All Newsletter correspondence, etc., should be addressed to:

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EURATOM

C C R

Magnetic Resonance

ISPRA
(ITALIA)

Ispra, 28 July 1969
HS/mg
79/69

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

RE: Sign of J_{PH} in phosphine

Dear Barry:

I'm afraid that this will be one of the "cooling coil" type of contributions, but the last couple of months were a kind of agitated for certain Europeans envolved in nuclear energy research.

Some years ago Ferretti and Paolillo[1] drew the conclusion that due to the trend of substituent effects on H-C-X coupling constants the sign of the directly bonded H-P coupling constant should be negative.

If, however, one determines the bond angle of phosphine from its spectrum in a nematic solvent one finds a meaningful value (94° $5'$ $\pm$ $3'$) only if one used a positive sign for J_{PH} in $|2B_{PH} + J_{PH}|$. A negative sign yields a value larger than 115° for the HPH bond angle.

1) J.A. Ferretti, L. Paolillo, Ricerc. Scien. A36, 1008 (1966)

Yours,

Oregon Graduate Center
/for Study and Research

July 30, 1969

Professor Barry Shapiro
Chemistry Department
Texas A & M University
College Station, Texas

$^{13}C\equiv^{15}N$ Couplings and ^{15}N Shifts in Alkyl Nitriles

Dear Barry:

While we are still in the process of getting our spectrometer in shape, I'll report some of the data obtained at Davis in my thesis work. One phase of the work involved determination of $^{13}C\equiv^{15}N$ coupling constants in certain alkyl nitriles ($^{13}C-^{13}C$ couplings and ^{13}C shifts are reported in J. Magnetic Res., 1, 407 (1969)). These couplings are listed below for acetonitrile, ethyl-, isopropyl-, and t-butyl cyanides. Also listed are the ^{15}N shifts for these, referenced to a capillary containing aqueous saturated solution of $KC^{15}N$, which also served as a lock signal for the HA-100 operating at 10·1 MHz. The $^{13}C\equiv^{15}N$ couplings were determined using neat ^{15}N-enriched liquids and observing the natural abundance ^{13}C operating in frequency-sweep mode locked on a $^{13}CS_2$ capillary with time-averaging.

Gary Maciel has applied Pople's finite perturbation technique to the data and this work will be published in the near future.

Sincerely,

George

George Gray
Assistant Professor of Chemistry

GG/sh
Encl.

Compound	$J^{13}C^{15}N(Hz)$	$\delta^{15}N(ppm)$ [b]
CH_3CN [a]	-17.5 ± 0.2	$+38.20 \pm 0.01$
CH_3CH_2CN	$(-)16.4 \pm 0.1$	$+35.88 \pm 0.01$
$(CH_3)_2CHCN$	$(-)15.4 \pm 0.1$	$+36.02 \pm 0.01$
$(CH_3)_3CCN$	$(-)15.0 \pm 0.1$	$+35.81 \pm 0.1$

a. G. Binsch, J.B. Lambert, B.W. Roberts and J.D. Roberts, J. Am. Chem. Soc., 86, 5564 (1964).
b. In ppm from saturated aqueous $KC^{15}N$ capillary. Positive sign indicates increased shielding.

A. Time-averaged spectrum of propionitrile-^{15}N at 10·1MHz. 218 scans were accumulated at 0.3 Hz/sec locked on $KC^{15}N$ (aq.).

B. Time-averaged spectrum of t-butyl cyanide at 10·1 MHz. 19 scans were accumulated at 0.4 Hz/sec locked on $KC^{15}N$ (aq.).

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8001 Zürich, Rämistrasse 76
Telefon 34 24 50
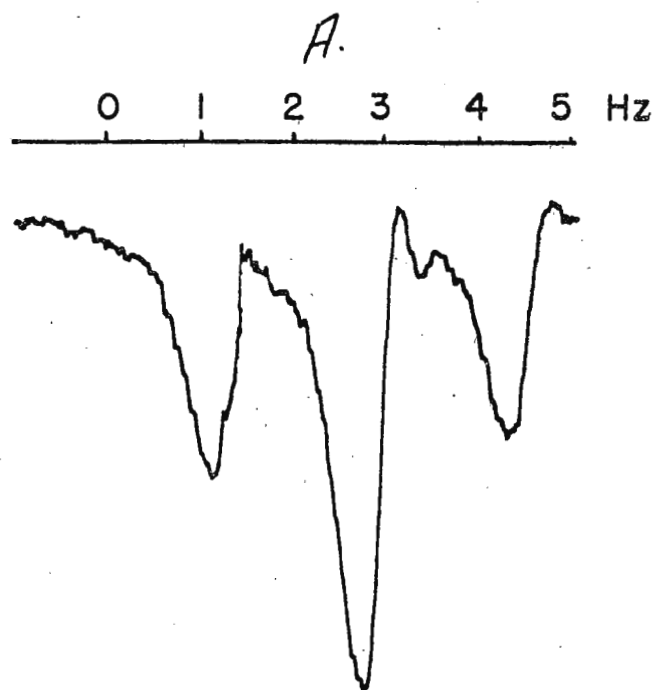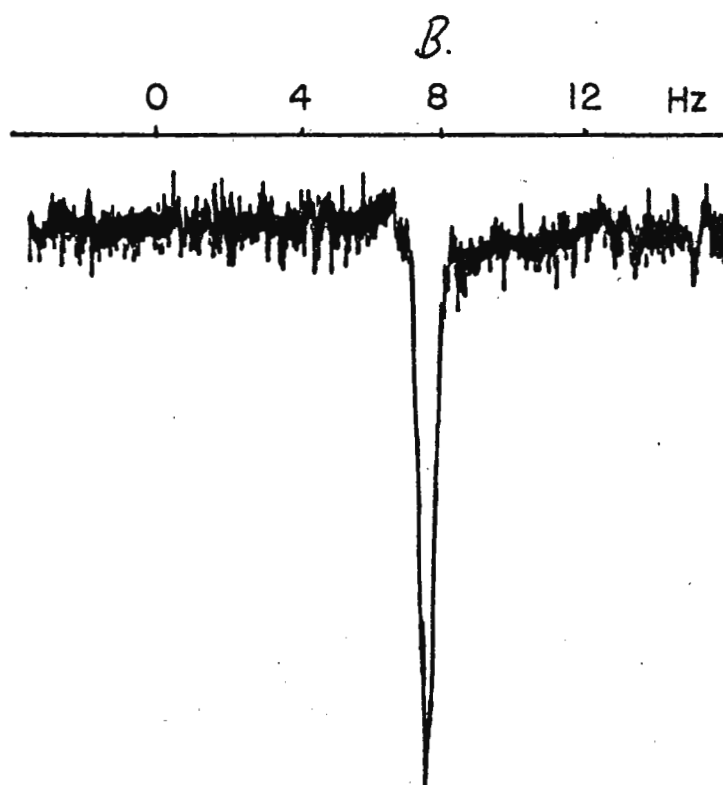
July 31, 1969

Prof. B.L. Shapiro
Department of Chemistry
Texas A. & M. University

College Station, Texas 77843
USA

"Homoallylic Coupling in Fivemembered Heterocycles"

Dear Barry :

Although long-range proton-proton coupling is not as exciting
anymore as it has been a number of years ago, there are still
some puzzling phenomena lacking satisfactory interpretation.
Recently, Dr.K.G.R. Pachler has pointed out in this Newsletter
[1] that the problem of unusually large homoallylic coupling in
certain fivemembered heterocyclic systems is not yet solved.
Such systems can be described by the general formula I.

I, X = O, NR
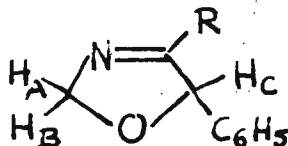
IIa, R = $-C_6H_5$
IIb, R = $-C_6H_4CH_3$

For the two protons indicated in I coupling constants as high
as 7 Hz have been observed [2] with typical values between
3 and 5 Hz. Because of their magnitude these coupling constants
may easily be taken for vicinal interactions and hence it is
important to know when such abnormal homoallylic coupling con-
stants can be expected. More data has to be collected.

Recently, we have observed a very clear example of this pheno-
menon with IIa and IIb which have been obtained in the course
of photochemical studies [3].

The 100 MHz spectrum of the three protons on the fivemembered ring in IIa is illustrated in the figure.
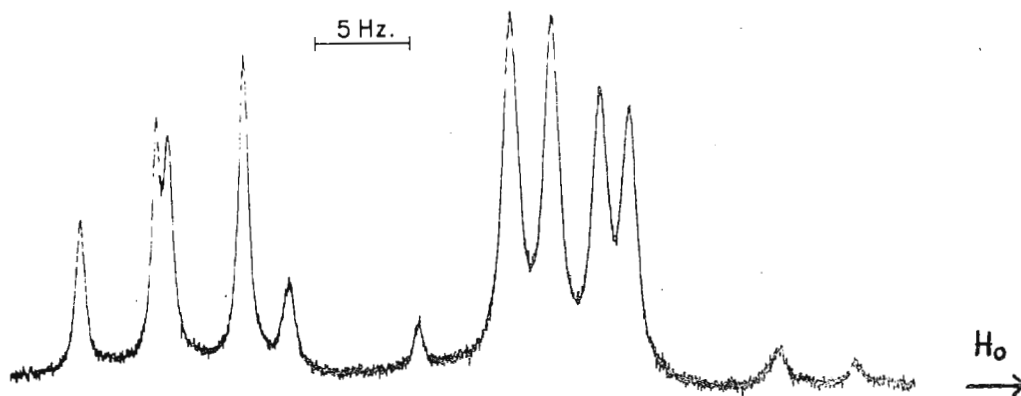
100 MHz Proton Spectrum of IIa in CDCl₃
(5.6-6.2 ppm region)

An ABC analysis together with double resonance experiments gives the following sets of parameters :

IIa		IIb	
δ_A = 5.812 ppm	J_{AB} =-11.9 Hz	δ_A = 5.805 ppm	J_{AB} =-12.0 Hz
δ_B = 5.875 ppm	J_{AC} = +3.2 Hz	δ_B = 5.859 ppm	J_{AC} = +3.1 Hz
δ_C = 6.050 ppm	J_{BC} = +5.6 Hz	δ_C = 6.035 ppm	J_{BC} = +5.6 Hz

Since it is not possible from this spectrum to distinguish H_A and H_B with respect to their stereochemistry it cannot be decided at present whether the larger long-range coupling must be assigned to the trans- or to the cis-interaction. Such an assignment has been possible in the cases of 2,5-disubstituted 2,5-dihydro-derivatives of furans (I, X =O) [4] and pyrroles (I, X = NR) [5]. It was found that J_{trans} > J_{cis} with the following range of values, J_{trans} 3.5-7.2 Hz, J_{cis} 0-3.2 Hz. In one case the reverse assignment has been claimed [6]. We intend to establish an unambigous assignment of the two long-range coupling constants in II by suitable chemical substitution.

To rationalize the unusually large coupling constants in these systems additivity of the interactions via the two possible pathways (four and five bonds) has been considered. However, substantial arguments have been presented [1][4] showing that ^4J across the heteroatom cannot be expected to give a significant contribution.

We hope that you will accept this letter as a renewed subscription by an old and faithful customer of your Newsletter.

Best wishes,

W. von Philipsborn   T. Winkler

References :

[1]   P.L. Wessels, J.P. Tollenaere and K.G.R. Pachler, this Letter No. 126-8 (1969).

[2]   S. Sternhell, Quart.Rev. 23, 236 (1969).

[3]   H. Giezendanner, H.-J. Rosenkranz and H. Schmid, Zürich, unpublished results.

[4]   C. Barbier, D.Gagnaire and P. Vottero, Bull.Soc. chim.France, 1968, 2330.

[5]   T.J. Batterham, N.V. Riggs, A.V. Robertson and W.R.J. Simpson, Australian J.Chem. 22, 725 (1969).

[6]   K. Katagiri, K. Tori, Y. Kimura, T. Yoshida, T. Nagasaki and H. Minato, J.Medicinal Chem. 10, 1149 (1967).

TITLE – "MAGNETIC RESONANCE FOR BIOLOGISTS" AND
WHEN DOES AA' MM' X_3 equal $A_2 M_2 X_3$?

Your Reference:

Our Reference:

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

9th July, 1969

Dear Dr. Shapiro,

Thank you for your 'pink prod' reminding me of the price of your news letter.

I am at the moment organizing a Workshop, designed to give Biologists a 'complete' guide to N.M.R. and E.S.R. in a week, starting from scratch. The course is entitled "Magnetic Resonance for Biologists" and will take place 15–19th September at the Royal Holloway College not far from here. If anyone is interested in attending etc., I will be pleased to supply further details.

The general activities here have been based round installing our HA100-15. I have some interesting ^{27} Al spectra but as yet am not quite sure what they mean; work is proceeding.
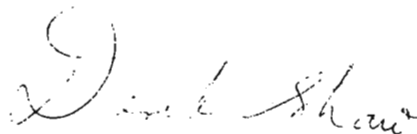
The main topic I would like to raise is illustrated by the enclosed spectrum of trans $Os Cl_4$ (As ^{n} Prop$_3$)$_2$. The complex is a d^4 system showing Van Fleck paramagnetism hence the crazy shifts. The Knight shift is irrelevant except to permit analysis on a first order basis. The spectrum is clearly AA' MM' X_3; why isn't it $A_2 M_2 X_3$ or AB MN X_3? Propyl groups are normally the special case of AA' MM' X_3; where J (AM) = J (A M'), by rotation. In this compound J (AM) ≠ J (AM'), values are in fact compatible with a rigid eclipsed chain. The chemical equivalence is easily explained as the AS-C bond has a plane of symmetry. The magnetic inequivalence has two possible explanations, i.e.

i)   The propyl group is in a fixed trans conformer (about the CH_2-CH_2 bond).

ii)   The values of J (AM) and J (AM') do not have the same average value over all conformers. Normally J (AM) and J (AM') do have the same average value but it is possible to conceive a set of values where average J (AM) ≠ J (AM') even for 'free rotation', either by having very unequal populations in the possible conformers and/or by allowing the position of the Os to affect the value of J H-H (trans) in conformer.

I think this molecule is case i) especially as the spectrum shows no effect of temperature, apart from the expected affect on the Knight shift, over the range ± 80°.   Case ii) interests me and I am investigating the limiting conditions etc., further.

Any comments very welcome.

Yours sincerely,

(Dr)   Derek Shaw

P.S.   I use the term Knight shift as the terms contact and pseudocontact imply mechanisms which arn't applicable here.   These molecules have no unpaired electrons!

100 Mc/s p.m.r. spectrum of $OsCl_4(AsProp_3)_2$
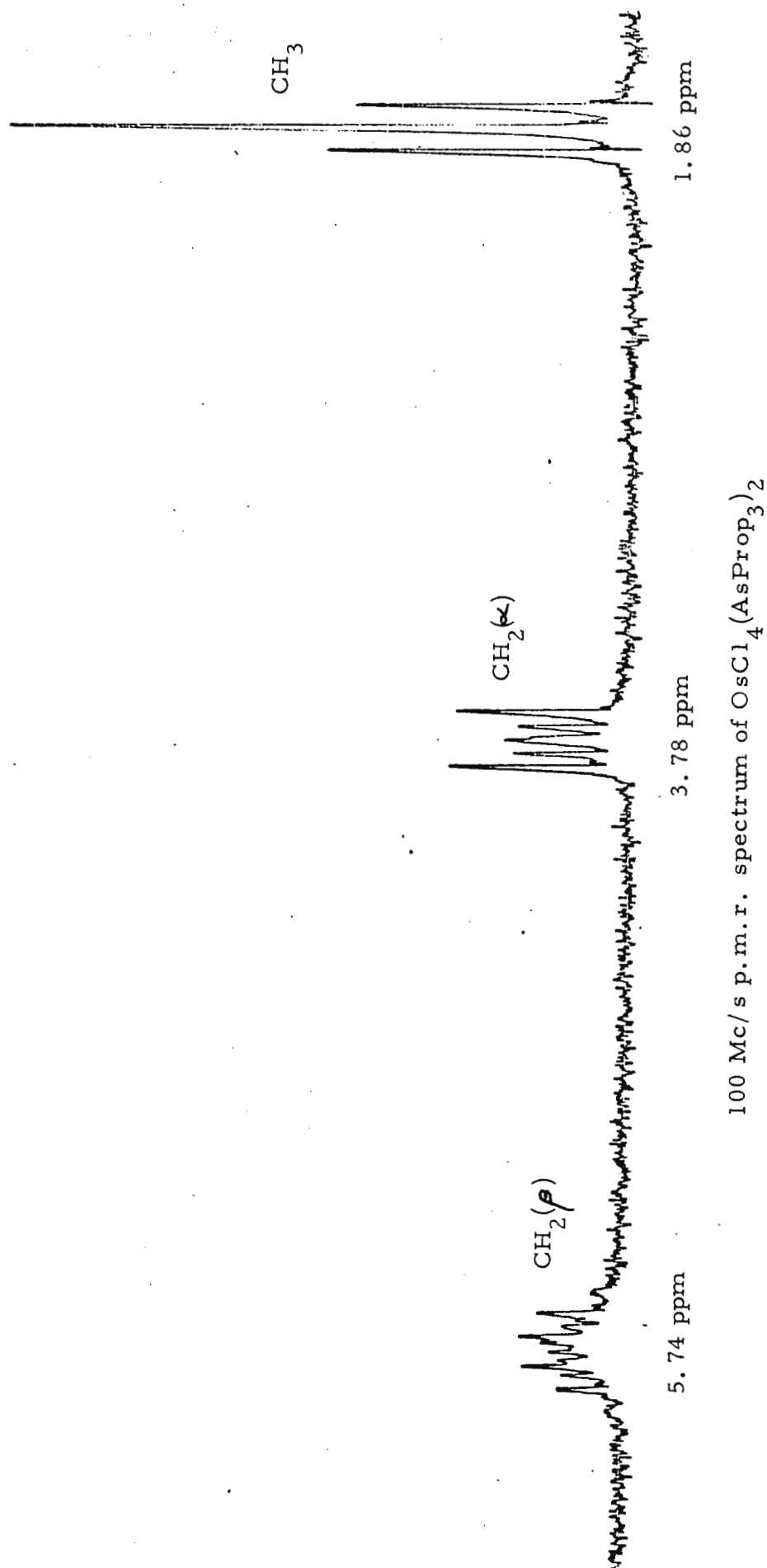
THE CHEMICAL LABORATORY UNIVERSITY

OF COIMBRA – PORTUGAL

31st July, 1969

Professor B.L. Shapiro

Department of Chemistry

Texas A & M University

College Station

Texas,

U.S.A.

Dear Professor Shapiro,

ABSTRACTS OF THE 1968 NATO SUMMER SCHOOL ON N.M.R.

(COIMBRA, PORTUGAL)

May I use the N.M.R. Newsletter to tell those interested
that we still have copies of the printed Abstracts of the NATO meeting
on N.M.R. for distribution free of charge.

Yours sincerely,

Victor Gil

Victor M.S. Gil

Gerhard Englert

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DEPARTMENT
Phy. A.   5th August, 1969.
Eng/hb

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

Oriented 2-Spin System

Dear Barry:

As usual, I have to apologize for needing to be reminded by your terrifying red letter. Since my last work on oriented mercury dimethyl will appear very soon in Z.f.Naturf.(a), I tried my best to find something else being worthwile to be included in your most interesting NMR-Newsletter.

Although extremely simple to treat, PMR-spectra of molecules with only 2 protons and chemical shift $\delta \neq 0$ oriented in a nematic liquid crystal have - to my knowledge - not yet been published. Therefore, I should like to present (see figure) as an example the spectrum of 2,4,5-trichloro-nitrobenzene at 27°C recorded on a HA-100 spectrometer (frequency sweep, internal TMS for lock). It is interesting to note that in the oriented AB-case the outer lines can be more intense than the inner ones. This behaviour is opposite to the well known AB-case in isotropic solution.

The 2-spin system has been theoretically treated by Buckingham and Pople (Trans. Farad.Soc. 59, 2421 (1963)) and Diehl and coworkers (Mol.Physics 14, 465 (1968)) have demonstrated that two sets of solutions (indirect and direct couplings J and D, chemical shift difference $\nu_A - \nu_B$) are obtained even if intensity information is used. The correct solution may be depicted in suitable cases by tickling experiments (Diehl and Khetrapal, to be published in: NMR, Basic Principles and Progress, Vol. 1, Springer Verlag 1969) or by the observation that one solution leads to an unrealistic value of the calculated J.

In the example discussed here the indirect coupling is small ($J \sim 1$ Hz) compared to the direct coupling and will therefore be neglected. Consideration of the calculated intensities therefore leads to only one set of parameters.

The frequencies (referred to $\frac{1}{2}(\nu_A + \nu_B) = 0$) and intensities of the oriented 2-spin system are given by:

./.

Transition	Frequency	Intensity	
(1)	$\frac{1}{2} J + D + C$	$1 - \sin 2\theta$	$\left.\right\} H_A$
(2)	$-\frac{1}{2} J - D + C$	$1 + \sin 2\theta$	
(3)	$+\frac{1}{2} J + D - C$	$1 + \sin 2\theta$	$\left.\right\} H_B$
(4)	$-\frac{1}{2} J - D - C$	$1 - \sin 2\theta$	

The following abbreviations are being used:

Direct H,H-coupling: $D = -\dfrac{\gamma^2 H}{4\pi^2 r^3} S_{H,H}$ ($r_{H,H}$ = proton-proton distance)

Degree of order: $S_{H,H} = \frac{1}{2} \langle 3 \cos^2 \alpha - 1 \rangle$ (α = angle of H,H-axis and magnetic field)

$$C = \frac{1}{2} \sqrt{(\nu_A - \nu_B)^2 + (J - D)^2}$$

$$\sin 2\theta = \frac{J - D}{2 C}$$

The repeated spacings in the spectrum are:

$\Delta(1,2) = \Delta(3,4) = |J + 2D| \sim |2D|$

$\Delta(1,3) = \Delta(2,4) = 2C$

The spectrum is independent of the sign of D, we therefore use a positive one. Two assignments and two sets of parameters are possible from the experimental data:

I: $2D = 123$ Hz
      $2C = 92$ Hz
      $\nu_A - \nu_B = 68.4$ Hz

II: $2D = 92$ Hz
       $2C = 123$ Hz
       $\nu_A - \nu_B = 114.1$ Hz

	Freq.	Int.
(1)	107.5	1.67
(2)	- 15.5	0.33
(3)	15.5	0.33
(4)	-107.5	1.67

	Freq.	Int.
(1)	107.5	1.37
(2)	15.5	0.63
(3)	- 15.5	0.63
(4)	-107.5	1.37

From the intensity ratio of the outer and inner transitions it is immediately seen that assignment I (shown in the figure) must be correct. This is in agreement with the observation that the first and third line possess a considerable larger line width due to quadrupole effects of the nitrogen nucleus. These two lines have to be assigned therefore to proton A in position 6.

Sincerely yours,

f. Englert

(Gerhard Englert)

100 MHz ^{1}H-spectrum of oriented 2,4,5-trichloro-
nitrobenzene at 27°C. Nematic solvent: 1:1 mixture of
$H_3CO-C_6H_4-N=N-C_6H_4OCO(CH_2)_4CH_3$ and
$H_3CO-C_6H_4CH=N-C_6H_4CH=CCH_3-CO-O(CH_2)_2CH_3$

ANORGANISCH-CHEMISCHES LABORATORIUM
DER
TECHNISCHEN HOCHSCHULE MUNCHEN

VORSTAND: O. PROF. DR. E. O. FISCHER
O. PROF. DR. H. P. FRITZ

8 MUNCHEN 2, den   7.8.1969
Arcisstraße 21
Ruf-Nr. (0811) 5592/330/331/332
Telex Nr. 05/22854

Herrn

Professor Bernard L. Shapiro

Department of Chemistry,
Texas A u. M University,
College Station,

Texas 77843

   U.S.A.

[14]N Resonances of Metal Complexes, Spectra Accumulation in the HR Mode of HA-100

Sehr geehrter Herr Shapiro !

Das Speichern von Heterokernresonanzen (z.B. [14]N) in paramagneti-
schen Komplexlösungen an unserem HA-100-Spektrometer der Firma
Varian stellte bislang ein Problem dar, weil sowohl interne als
auch externe (in Kapillare) "trigger"-Signale durch die magneti-
schen Momente der Übergangsmetalle zu sehr verbreitert werden.
Der Einbau eines Relais, das den Schreiberschalter mit dem
"decrease/increase"-Schalter der "slow sweep"-Einheit (V-3507)
verbindet [1] erlaubt Speichern im HR-Modus. Bei geeigneter
Einstellung des "drift"-Potentiometers konnte z.B. bei 50
Speichergängen (sweep time 5o sec) eine Feldkonstanz von $\pm$ 3 ppm
("sweep"-Bereich 15o ppm) erhalten werden. Da bei den von uns
untersuchten Komplexen die Halbwertbreiten der Signale in der
Größenordnung von 2o - 1oo ppm liegen, spielt die Feldänderung
während des Speicherns nur eine untergeordnete Rolle für die
Genauigkeit.

Uns interessierten vor allem die Verschiebungen von direkt an ein
Übergangsmetall gebundenen ^{14}N-Kernen, und zwar in den 2:1-Pyri-
dinaddukten der Eisen(II), Kobalt(II)- und Nickel(II)-bis(salicyl-
aldehyd)-Komplexen [2], deren [1]H-KMR-Spektren bereits ausführlich
diskutiert wurden [3].

Aus der Abhängigkeit der Verschiebung des Lösungsmittels Pyridin
von der zugegebenen Komplexmenge, aus dem Vergleich mit den Ver-
schiebungen von Bis(acetylacetonat)komplexen des Kobalt(II) und
Nickel(II) [4] und unter Berücksichtigung einer Mitteilung über
die ^{14}N-Verschiebung von Nickel(II)-Acetylacetonat in Pyridin

bei erhöhter Temperatur [5] ergab sich, daß bei 32°C für FeSal$_2$.2Py, CoSal$_2$.2Py und Co(acac)$_2$.2Py die Bedingungen des "schnellen Austauschs", für NiSal$_2$.2Py und Ni(acac)$_2$.2Py diejenigen des "langsamen Austauschs" erfüllt sind, so daß aus der Verschiebung und Linienbreite des Lösungsmittelsignals in der Komplexlösung entweder die Verschiebung des direkt an das Metall gebundenen Liganden oder die Austauschgeschwindigkeit berechnet werden kann [6]. Die Ergebnisse für den Austausch des koordinierten Pyridins mit dem Lösungsmittel Pyridin bei 32°C sind in der folgenden Tabelle zusammengefaßt, wobei k$_1$ die Geschwindigkeitskonstante pseudo-1.Ordnung für den Pyridinaustausch und ν_c/ν die Kontaktverschiebung des an das Metall gebundenen ^{14}N-Kernes bedeutet.

	k$_1$(Hz)	ν_c/ν (ppm)
FeSal$_2$.2Py	$\geq 2,0 \cdot 10^5$	$- 7\ 800 \pm 400$
CoSal$_2$.2Py	$\geq 1,8 \cdot 10^5$	$- 5\ 400 \pm 300$
NiSal$_2$.2Py	$2,3 \cdot 10^4$	
Co(acac)$_2$.2Py	$\geq 1,5 \cdot 10^5$	$- 15\ 000 \pm 500$
Ni(acac)$_2$.2Py	$6,5 \cdot 10^4$	$- 15\ 400 \pm 300$ [5]

1) D.Shaw, Varian Associates, persönl. Mitteilung
2) abgekürzt MSal$_2$.2Py   M = Fe, Co, Ni
3) H.P.Fritz, W.C.Gretner, H.J.Keller, K.E.Schwarzhans, Z.Naturforschg. 23b, 906 (1968)
4) abgekürzt M(acac)$_2$.2Py   M = Co, Ni
5) Yu.Molin, TAMU NMR Newsletter 127-18 (1969)
6) T.J.Swift, R.E.Connick, J.Chem.Phys. 37, 3o7 (1962)

Mit freundlichen Grüßen

H.P.Fritz   W.Gretner

BRYN MAWR COLLEGE
BRYN MAWR, PENNSYLVANIA 19010, USA

DEPARTMENT OF CHEMISTRY   TEL: (215) LA 5-1000

8 August 1969

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

Dear Barry:

One note on instrumentation and one on gadgetry comprise
this belated contribution to the TAMU NMR Newsletter.

Decoupling on the A-56/60A

Don Vickers at NMR Specialties agreed with some trepidation
to install an HD-60 on our A-56/60A. We have begun to do
experiments with the result (diagram below).

We have used the HD-60 in both straight carrier and SSB
modes. Sideband operation seems preferable, although tuning
the frequency of irradiation is most convenient using the
decade switches and interpolation oscillator on the Schomandl
ND-30M. Contemplated additions are a field:frequency:frequency
lock and frequency sweep. The $H_0:\nu_1:\nu_2$ lock can be established
by extracting a 2 MHz signal from the A-56/60A transmitter,
dividing by two (details in a later letter) and using the
resulting 1 MHz to replace the crystal oscillator in the Scho-
mandl ND-30M. The A-56/60A locks H_0 to ν_1; the divider and
external source locks ν_2 in as well. A linear sweep voltage
applied to the VCG which provides audio modulation to the HD-60
will enable us to simulate frequency-sweep spectra. H_0 and
ν_2 will be swept simultaneously at the appropriate ratio of
sweep rates, while ν_1 remains constant. INDOR is also a possibility.

Irradiation at 60 MHz on the A-56/60A failed; any rf
power at 60 MHz swamped the control channel and lock was lost.
In spite of not achieving the $^{19}F-\{^1H\}$ experiment at first
try, BMC thanks Don Vickers and Tom Hill of NMRS for their
patient work. We understand we are operating the first A-56/60A--
HD-60 system; it works.

A Flair for Spectra

Parker "Flair" fibre-tip pens can be used on a chart
recorder, allowing cheap and reliable writing in black and
at least a half dozen mod colors. A plexiglass bracket was
machined (sketch below) and cemented to a steel plate which

B. L. Shapiro--TAMU NMR
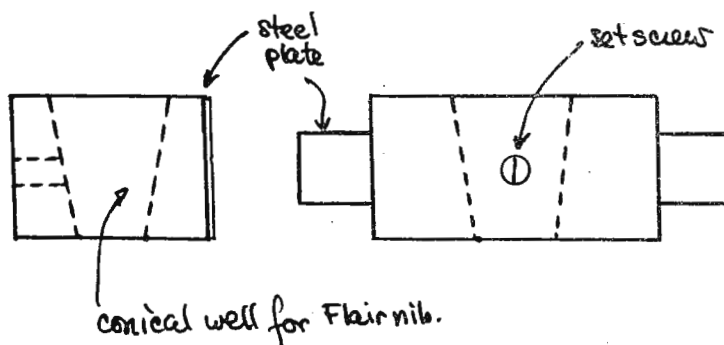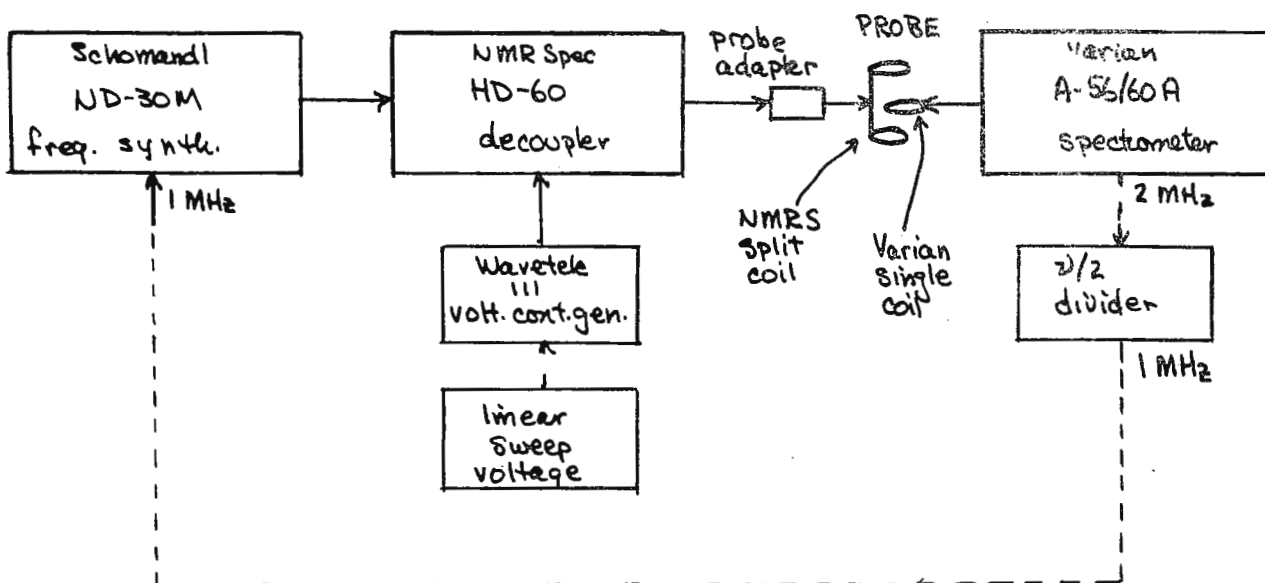8 August 1969
Page 2

fits onto the magnetic pen holder of the A-56/60A (and other)
flatbed recorder; a set-screw grips the nib of the Flair.

    With the gadgetry under control, I hope we can send some
chemistry for our next contribution!

                    Sincerely yours,

                    Jay Martin Anderson
                    Associate Professor

Dartmouth College HANOVER · NEW HAMPSHIRE · 03755

Department of Chemistry · TEL. (603) 646-2501

August 12, 1969

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

Dear Professor Shapiro:

A Temperature Controlled Pulsed NMR Probe

We have thermostated an NMR pulse probe to +0,005°C using
a closed loop thermostat with water as the heat exchange medium.
We had decided to undertake an NMR study of the liquid-liquid
critical point which demanded a level of temperature control
not available using a gas thermostat. We found that by insulating
a single coil probe from direct contact with the water we could
still obtain an NMR signal, The signal from the protons in the
thermostat was eliminated by shortening the relaxation time with
a sufficient amount of $MnCl_2$ dissolved in the water,

The probe body is a rectangular plexiglas box which serves
as a water jacket as well as supporting the coils and the coil
support, Two "twin" single coils are used in order to follow
signals from both phases of a binary liquid mixture. To insure
complete insulation from the bath water, the coils are wound on
a 3/4" plexiglas coil form in 1/8" deep grooves, These grooves
were later filled in with Duco cement, Five coils were wound
and the best two chosen,

In an earlier attempt to build a plexiglas probe it was
found that if two pulses were brought closer together than 100 m
sec, the free induction decay of the second pulse was unstable
in regards to amplitude and phase, At pulse spacings larger than
100 m sec the effect was absent. The problem seemed to be
connected to the coil-sample support (they were both supported
by the same plexiglas tube), The sample support and coil support
were separated and improved in the present version of the probe
and the 100 m sec effect disappeared,
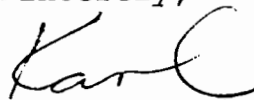
The coils are supported on one side by a plexiglas tube
containing the coil leads and extending through the front wall of
the box, A rod attached to the rear wall of the box completes
the coil support, The sample support is held in like manner, by
two rods, attached to the front and rear of the probe body, The
sample support is a nylon collet (similar to that which holds the
mill in a milling machine) and works very well,

page 2
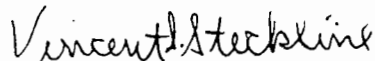
The thermostating is of the simple circulating loop design so that bulky thermostat parts could be placed outside of the volume between the pole caps. In the loop a pump forces the water past a controlled heater through a cooling condensor and back to the pump. Temperature is controlled by a thermistor and proportional temperature controller (Sargent "thermoneter") in a feedback loop with the controlled heater which is a coil of nichrome wire wound tightly around a glass tube. Small temperature changes are monitored by a second thermistor, connected in a simple Wheatestone bridge. The output of the bridge is displayed on milivolt recorder. A thermometer is also placed in the sample chamber for an accurate absolute temperature reading.

The temperature control and probe have been tested in a narrow range of temperatures around 20°C (The aim was to achieve close control in a narrow range.) But we feel that there is no reason why the probe cannot be used within the temperature limits of the proportional temperature controller and plexiglas probe body.

Sincerely,

Karl F. Kuhlmann
Assistant Professor
of Chemistry

Vincent S. Steckline

/w

P.S. Please credit this to Professor P. R. Shafer's account.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA   93106

August 12, 1969

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

Title: On-Line Computation of N.M.R. Lineshapes

Dear Barry:

Last spring we programmed our local on-line computer system
to generate theoretical n.m.r. lineshapes in a real-time mode.
The on-line system includes about 50 local consoles and is
serviced by an IBM 360/75. The primary output device is a Tektronix
storage scope. The enclosed series of photographs will, perhaps,
give you some idea of how the system and the n.m.r. programs
operate. Plate a shows the sign-on prologue for the system.
Here billing information for user 118 (That's me) and a
identification code are recorded by the system. With the
appearance of that comforting message USER SYSTEM LOADED, one
is ready to generate lineshapes.

The program asks questions to get the information it needs. The
frequency assigned to the left side of the scope face, to the right
side of the scope face and the number of data points to be computed
are first supplied in reply to appropriate questions (b, c). Chemical
shifts, linewidths and tau values are next asked for and, upon
receipt, the computer draws the absorption spectrum. (f) [The dispersion
mode curve is available to those who know the boss.] A series of
decremented tau values produce the curves superimposed in g and,
finally, a singlet appears at a small enough value of tau. Each piece
of information requested by the computer can be changed at will and
independently of the others by pressing an appropriate key on the
control console. Additional buttons provide for other display modes
and for a summary of input data (i). The system can handle the
familiar Gutowsky-Holm two-site type of lineshape as well as the AB →
A_2 collapse. As the last picture suggests, it can also draw nice
designs. The maximum number of data points that can be computed is,
at present, limited to 124 in order that the response time of the on-
line system can be as rapid as possible.

Best wishes,

J. T. Gerig
Department of Chemistry

a

USER SYSTEM 15 JULY 69
FOR IMPORTANT MESSAGES
PRESS SYST LOG
USER NO=
USER SYSTEM 15 JULY 69
FOR IMPORTANT MESSAGES
PRESS SYST LOG
USER NO=118
ID NO=
SYSTEM NAME=NMRSYS1
NOW LOADING
USER SYSTEM LOADED

TWO-SITE NMR EXCHANGE.
WHAT IS LEFT FREQ.?
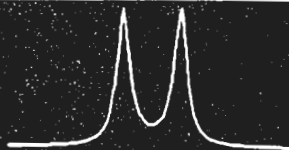
f

b

TWO-SITE NMR EXCHANGE.
WHAT IS LEFT FREQ.?
0
WHAT IS RIGHT FREQ.?
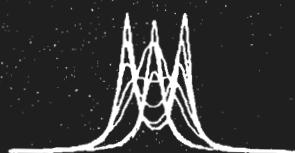
g

c

TWO-SITE NMR EXCHANGE.
WHAT IS LEFT FREQ.?
0
WHAT IS RIGHT FREQ.?
2.5   +1
HOW MANY POINTS?
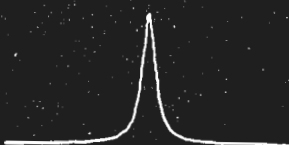
h

d

POPULATION AT SITE 1?
5   -1
LINE WIDTH AT SITE 1?

TWO-SITE NMR EXCHANGE.
WHAT IS LEFT FREQ.?
0
WHAT IS RIGHT FREQ.?
2.5   +1
HOW MANY POINTS?
100
FREQ. AXIS COMPLETED.
CHEM. SHIFT AT SITE 1?
1   +1
CHEM. SHIFT AT SITE 2?
1.5   +1

SUMMARY OF INPUT DATA.
CHEMICAL SHIFTS
1   +1
1.5   +1
POPULATIONS
5   -1
5   -1
LINE WIDTHS
1
1
TAU VALUES
7.8125   -3
7.8125   -3

i

e

LINE WIDTH AT SITE 2?
1
TAU AT SITE 1?
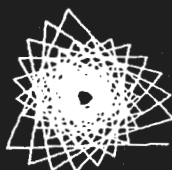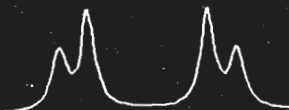
**ABORATORIUM VOOR ORGANISCHE
CHEIKUNDE DER UNIVERSITEIT VAN
AMSTERDAM**
NIEUWE ACHTERGRACHT 129
TELEFOON 9471 74 (5 LIJNEN)

AMSTERDAM, August 12, 1969

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

Solid State Linear Sweep
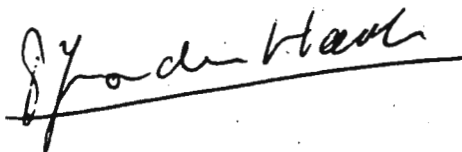
Dear Professor Shapiro,

We constructed a solid state linear sweep to replace our
Varian V-4352. It consists of a saw-tooth generator, a scope
amplifier and a booster amplifier (fig. 1). When switch SW1
is in the "stand-by" position, a reed-relay (mounted in the
oscilloscope) is actuated. This relay blanks the scope, so we
don't have to fumble with the scope's intensity control every
time we switch from "scope" to "recorder" and vice versa.

Schematic diagrams are given in fig. 2.
We made the frequency range of the generator smaller than that
of the V-4352, since we never use extreme values. The ampli-
tude control is a 10-turn potentiometer which we find easier
to operate then the original coarse- and fine-controls.
The advantages of this linear sweep are: no maintenance, better
linearity and no carrier-wave ripple on the output.

Sincerely yours,

P.J. van der Haak

B. Maris
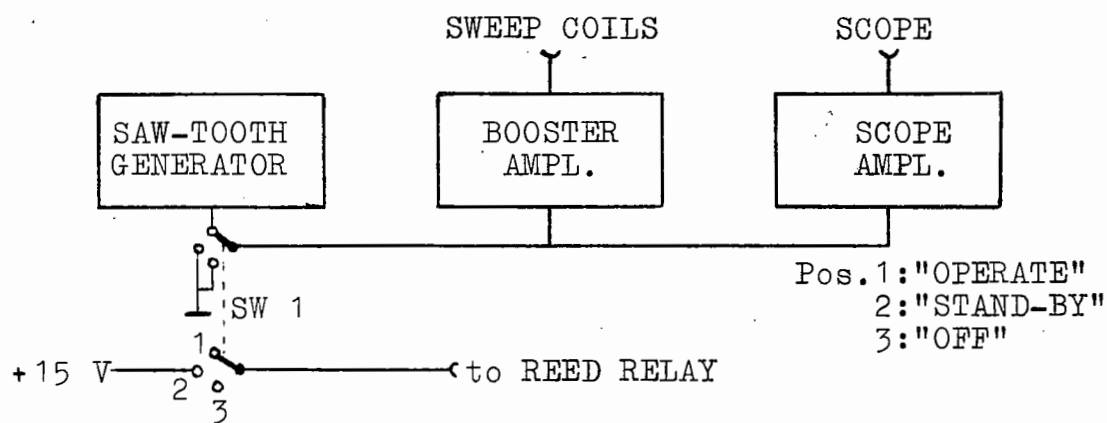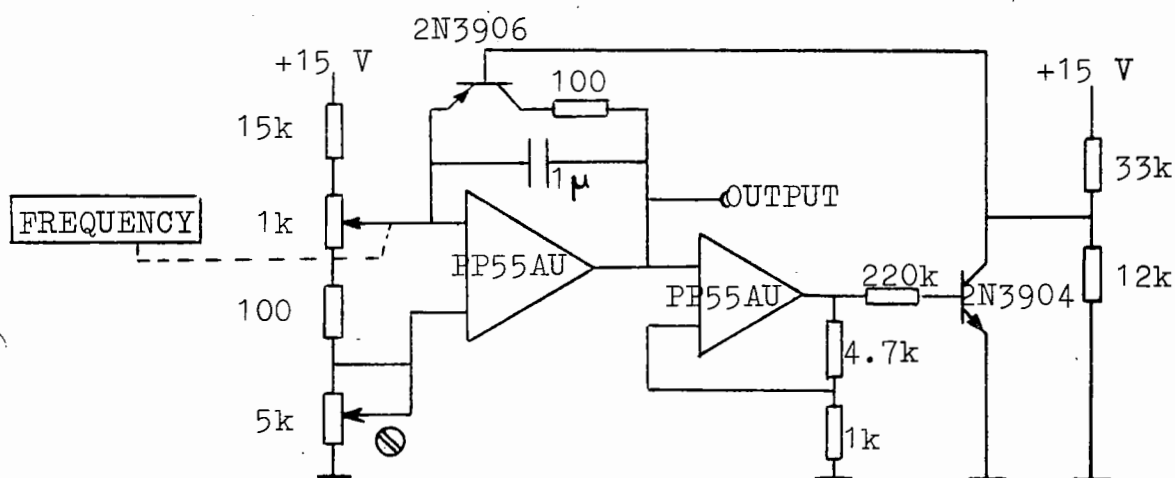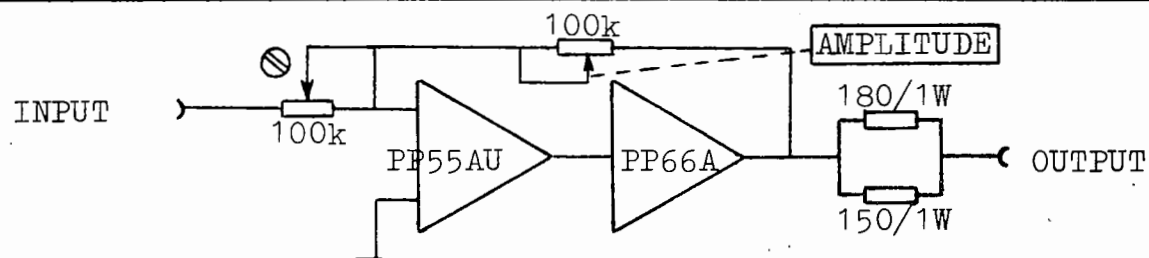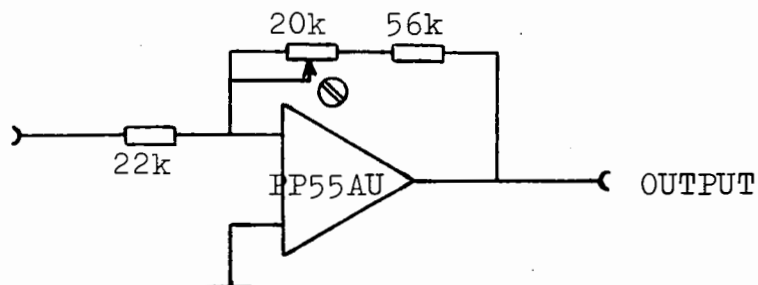
LABORATORIUM VOOR ORGANISCHE SCHEIKUNDE DER UNIVERSITEIT VAN AMSTERDAM

-SOLID STATE LINEAR SWEEP-

SWEEP COILS   SCOPE

| SAW-TOOTH GENERATOR | BOOSTER AMPL. | SCOPE AMPL. |

Pos.1:"OPERATE"
    2:"STAND-BY"
    3:"OFF"

SW 1

+15 V   1
    2
    3   to REED RELAY

fig.1 BLOCK DIAGRAM

2N3906

+15 V

15k

100   1μ

FREQUENCY   1k

OUTPUT

PP55AU

100

PP55AU   220k   2N3904

4.7k

5k

1k

+15 V

33k

12k

fig.2.1 SAW-TOOTH GENERATOR

AMPLITUDE

100k

INPUT

100k   PP55AU   PP66A

180/1W

150/1W

OUTPUT

fig.2.2 BOOSTER AMPLIFIER

20k   56k

22k

PP55AU

OUTPUT

fig.2.3 SCOPE AMPLIFIER

LABORATORIUM VOOR FYSISCHE CHEMIE

Driehuizerweg 200, Nijmegen
Telefoon (08800) 5 83 33

FACULTEIT DER WISKUNDE
EN NATUURWETENSCHAPPEN
KATHOLIEKE UNIVERSITEIT
NIJMEGEN, NEDERLAND

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

U.S.A.

Uw kenmerk	Uw brief van	Ons kenmerk

Datum 12-8-1969

Onderwerp   Nuclear Magnetic Resonance on alkali metal-amine solutions.

Dear Professor Shapiro,

We have investigated with NMR the properties of alkali metal-amine
solutions. Our first experiment has been performed on lithium-ethyl-
amine solutions. We have studied the resonance of the protons, the ^{7}Li
and the ^{14}N nuclei.

a) Proton-NMR

In figure 1 a typical result is shown. All signals are shifted to high
field with respect to pure ethylamine.
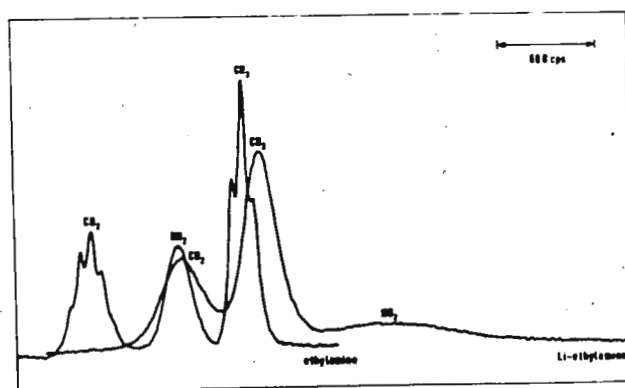
Figure 1:
^{1}H-NMR spectrum of a
0,46 solution of Li in
ethylamine at 60 Mc/s
and -73°C.

The shifts becomes less going in the molecule further away from the
nitrogen. The shift increases and the line broadening decreases with
increasing temperature.

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132-25

FACULTEIT DER WISKUNDE
EN NATUURWETENSCHAPPEN
KATHOLIEKE UNIVERSITEIT
NIJMEGEN

Geadresseerde Prof. Shapiro   Ons kenmerk   Datum 12-6-1969   Blad No 2

All proton shifts (neglecting bulk susceptibility corrections) depend
linearly on each other while varying concentration or temperature. **Figure** 2
shows the dependence for different concentrations
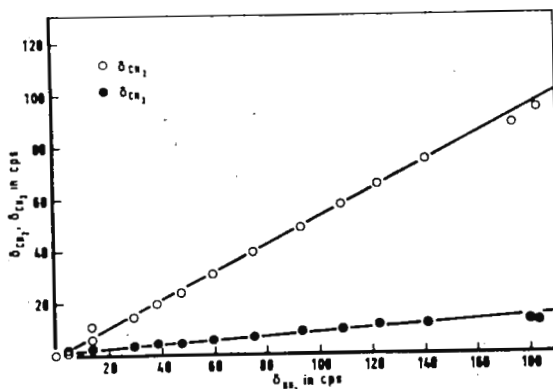
Figure 2:
Shifts of the CH_2 and CH_3
protons versus the shift of
the NH_2-protons for different
concentrations of Li in
ethylamine.

Assuming that no spin pairing occurs one can estimate a lower limit for
the NH_2-proton density on the electron from the contact shift.
At -65°C the nuclear density in a 0,5 M solution of Li in ethylamine is
equal to:

$$\rho(r_H) \approx -2 \times 10^{21} \text{ cm}^{-3}$$

b) ^{7}Lithium and ^{14}Nitrogen-NMR

The resonance signals are broadened and shifted to low field. As **references**
are used respectively lithium perchlorate in water and pure **ethylamine.**
From the shifts one can estimate the following lower limits for the
nuclear densities on the electron in a 0,5 molar solution again **assuming**
that no spin pairing occurs:

$$\rho(r_{7_{Li}}) = 0,55 \times 10^{21} \text{ cm}^{-3} \qquad \text{(at } -65^\circ\text{C)}$$

$$\rho(r_{14_N}) = 3,4 \times 10^{22} \text{ cm}^{-3} \qquad \text{(at } -65^\circ\text{C)}$$

Conclusions.

(i) Comparing $\rho(r_{14_N})$ with the ESR results of Tuttle[1] assuming that we are looking at the same species suggests that we have at most 10% unpaired electron spins in a 0,5 molare solution which results in a bulk susceptibility correction of $\pm$ 3 cps. Using this information about spin pairing all nuclear densities are a factor ten greater than the estimated lower limits based on no spin pairing.

(ii) The absolute value of the ratio $\rho(r_{14_N})/\rho(r_H)$ is 17. Almost the same ratio has been estimated with ESR[2] for this system. The knight shift data of nitrogen are too inaccurate to check the constancy of this ratio as function of temperature and concentration[3].

(iii) The behaviour of the proton shifts with temperature means that we get more paramagnetic species in the solution by increasing temperature. This might be caused by a decoupling of paired spins via a reaction like

$$Li_2 \leftrightarrows 2Li$$

(iv) In the lithium-ethylamine system the only paramagnetic species are the solvated electron and the solvated lithium atom (the monomer). If the solvent molecules in the solvation shell are in rapid equilibrium with solvent molecules in the bulk of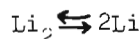 the solution then the measured contactshifts refer to averaged shifts. In the solution the following equilibrium may exist between the paramagnetic species:

$$(Li^+)_{solv} + e^-_{solv} \leftrightarrows Li_{solv} \cdot$$
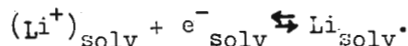
The observed linear relationship between the proton shifts can now be explained in two ways.

a) The equilibrium is shifted extremely to the right for the concentrations (0,05-0,5 M) and temperature region (-73°C up to + 30°C) studied. In this case we are looking at only one paramagnetic species which explains the linearity between the proton shifts.

b) The equilibrium is not shifted to one of the extremes sited but it is impossible to discriminate between the two paramagnetic species because the ratio of the nuclear densities are equal in both species and again a linear dependence between the proton shifts is expected.

1) Selma Bar-Eli and T.R. Tuttle Jr. J. Chem. Phys. 40, 2508(1964)

2) R. Catterall, Proceedings of Colloque Weyl II, in press

3) K.S. Pitzer, Proceedings of Colloque Weyl I, Solutions métal-ammoniac,
   Benjamin Inc., New York, 1964.

B.J.J. Hendriks   T.R. Tuttle Jr.   E. de Boer.

UNILEVER RESEARCH LABORATORY

THE FRYTHE, WELWYN, HERTS.

TELEPHONE : WELWYN 5121

Your Ref.

Our Ref. EF/BLM

13th August, 1969.

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

<u>Use of NMR in the study of ionophorous antibiotics</u>

Dear Professor Shapiro,

Although the number of practising NMR spectroscopists is now large and seems to be increasing exponentially, the proportion of these who work in the area of biophysics is remarkably small. This may be because the spectra of big "biological" molecules are aesthetically rather displeasing (i.e. broad and horrible), or it may be because samples tend to be difficult to handle. Perhaps if we outline here some ways in which we have been using NMR in this field we may persuade other members of the fraternity to keep us company.

As we see it, high resolution NMR can play two rôles in biophysics: it can serve as an aid to the determination of structures and conformations of molecules in solution, and it can be used as a tool to follow molecular interactions. The former rôle is of course a familiar one to NMR spectroscopists, although it is surprising how many biologists seem to be unaware of any methods of obtaining molecular structural information other than by X-ray diffraction (which is, of course, almost useless in solution studies). The latter rôle is less familiar to spectroscopists, but is of great importance in biophysics: one just follows changes in chemical shifts or relaxation times (line widths) as a function of temperature, pH, concentration, molar ratios of different substances, etc. Used thus, NMR is simply another physico-chemical tool in the armoury of the biophysicist, except that it has one great advantage over other techniques such as calorimetry, conductivity measurements, electrochemical measurements etc. : NMR is a molecular technique, and so it can distinguish between events occurring at different parts of a molecule.

We have been studying some cyclic polypeptide and depsipeptide antibiotics which have the property of transporting alkali metal cations across natural and artificial membranes. It has been shown that these molecules form lipid-soluble complexes with the cations, in some cases in an ion-specific fashion; for example, valinomycin, which is a naturally-occurring cyclic depsipeptide with the formula

- 2 -

$(D\text{-}val \rightarrow L\text{-}lac \rightarrow L\text{-}val \rightarrow D\text{-}hyisoval)_3$, binds K^+ much more readily than Na^+. The spectrum of the complex dissolved in $CDCl_3$ is quite different from that of free valinomycin, and we were able to analyse the spectrum and deduce from the values of the coupling constants and from some infra-red data the conformation of the valinomycin -K^+ complex. The ring forms a "crown" with the ion in the centre, and three carbonyls from the ester linkages project inwards above the ion, with another three below, thus forming a six-coordinated complex by ion-dipole interaction. The hydrophobic groups on the outside of the complex render it lipid-soluble, thus allowing the ion to be transported across the membrane. Similar results have now been published by other workers (V.T. Ivanov et al., Biochem. Biophys. Res. Comm. 34, 803 (1969)).

The above is an example of the use of NMR in structure determination. We have also used it to follow molecular interactions in the study of these ion-transporting antibiotics. Valinomycin and alamethicin, a cyclic polypeptide containing nineteen amino acid residues, both interact strongly with phospholipids. Phospholipids form a large proportion of the content of biological membranes, and can be made into bimolecular films which show many of the properties of natural membranes; their interaction with the ion-transporting antibiotics is therefore of fundamental importance to an understanding of ion transport across membranes. Phospholipids form large aggregates in water, but when dispersed by ultrasonic irradiation they give a high resolution NMR spectrum (in which the most intense signal arises from the CH_2's of the long alkyl chains). We found that the addition of a small quantity of alamethicin or valinomycin to a dispersion of phospholipid (lecithin or phosphatidyl serine) in D_2O caused a dramatic reduction in the high resolution signal from the lipid (i.e. a broadening of the signal such that much of it is lost in the baseline). This is caused by the formation of lipid-antibiotic aggregates in which there is little internal motion of the lipid molecules and which have a slow overall tumbling rate, so that correlation times are long and relaxation times short. By following the reduction in signal (with respect to an external reference) as a function of molar ratio of antibiotic/lipid, we have found equilibrium constants for the interaction and the number of lipid molecules aggregated by each antibiotic molecule. In the case of phosphatidyl serine and alamethicin, this number is 600, and so clearly there is some sort of cooperative effect taking place. This is of great importance in the understanding of the mode of action of antibiotics and for lipid-peptide interactions in general. This work is to be published shortly.

We hope that the above may have aroused some interest in spectroscopists looking for a field in which to apply their skills.

Yours sincerely,

Elliot Finer

E.G. FINER (subscription credit)

Alan Flook

A.G. FLOOK

UNIVERSITY OF CALIFORNIA, RIVERSIDE

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DEPARTMENT OF CHEMISTRY   RIVERSIDE, CALIFORNIA 92502

August 13, 1969

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

Title: Hydrogen Bonding Effects on Amide Rotational
Barriers

Dear Barry:

We have determined the concentration dependence of
the rotational barrier of N,N-dimethylacetamide in the
solvent formamide. Rate constants were obtained using
total lineshape analysis.[1] The rotational barrier for
DMA is higher for DMA-formamide solutions as can be
seen from the portion of our data given below.

Amide	Solvent	Conc. Mole %	E_a kcal/mole	log A	$\Delta F^*_{298.2}$ kcal/mole
DMA-d_3	neat	100	19.6 ± 0.3	13.8 ± 0.2	18.2
DMA-d_3	formamide	9.8	21.3 ± 0.6	14.2 ± 0.3	19.4

Intermediate concentrations of DMA in formamide give
intermediate values of ΔF^* which define a smooth curve
in a plot of ΔF^* versus mole-% DMA in formamide. The
increased rotational barrier is attributed to ground
state stabilization through hydrogen bonding as shown
in Figure 1.

B. L. Shapiro
August 13, 1969
Page 2

$$HCONH-H\cdots O\overset{\delta-}{\diagdown}\underset{CD_3}{\overset{}{\diagup}}\overset{\delta+}{C}=N(CH_3)_2$$
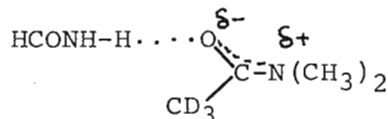
Figure 1

The rotational barrier for neat DMA probably represents that for DMA self-association dimers $(DMA)_2$.[2] However, a comparison of our data (<u>vide supra</u>) with those[3] for DMF in carbon tetrachloride suggests that the true rotational barrier (ΔF^*) for monomeric DMA should be even lower than that shown for the neat solution.

Complete details, data, and arguments are presented in the manuscript which is now in press for <u>J. Phys. Chem</u>.

Sincerely yours,

Bob

Robert C. Neuman, Jr.
Associate Professor of Chemistry

RCN:mm

References

1. See R. C. Neuman, Jr., and V. Jonas, <u>J. Am. Chem. Soc</u>., <u>90</u>, 1970 (1968).

2. R. C. Neuman, Jr., W. Snider, and V. Jonas, <u>J. Phys. Chem</u>., <u>72</u>, 2469 (1968).

3. M. Rabinovitz and A. Pines, <u>J. Am. Chem. Soc</u>., <u>91</u>, 1585 (1969).

NORTHERN ILLINOIS UNIVERSITY

DEKALB, ILLINOIS 60115

THE MICHAEL FARADAY LABORATORIES

DEPARTMENT OF CHEMISTRY

August 15, 1969

Area Code 815

Telephone 753-1181

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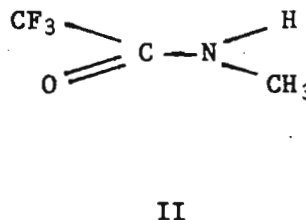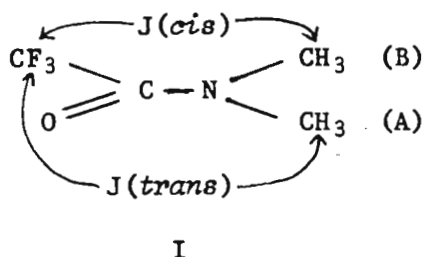Texas A & M University
College Station, Texas 77843

Trifluoroacetamides: $^5J_{HF}$ (*cis*) > $^5J_{HF}$ (*trans*) and Observation of $^6J_{HF}$ (*cis*)

Dear Barry:

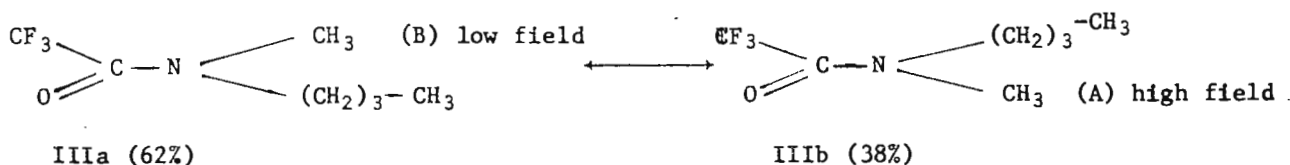Although proton-fluorine coupling over five bonds in trifluoroacetamides (I) has been

observed before[1-3], the relative magnitude of J_{HF} (*cis*) and J_{HF} (*trans*) has not previously been established. It has been suggested, however, that the *cis* coupling constant may be larger than the *trans*[1].

The proton NMR spectrum of I reveals a quartet for both N-methyl groups, with J_{HF} = 1.60 cps for the lower field quartet, and J_{HF} = 0.65 cps for the quartet to higher magnetic field. We have made the peak assignments (and therefore determined that J (*cis*) is indeed larger than J (*trans*) in I) by a combination of indirect methods. These methods have been used to make assignments in other amides[4]. The assignment for dimethylformamide (high field N-methyl peak from protons *cis* to the carbonyl oxygen atom) was later confirmed by NOE[5].

As the methods of assignment have already been presented in detail[4], we will mention here only that (a) benzene solution studies of I indicate that the protons at position B resonate to lower field than those at A, and therefore that J_{HF} (*cis*) is larger than J_{HF} (*trans*). (b) Our IR studies of N-methyltrifluoroacetamide in CCl₄ solutions indicate that the *trans* configuration predominates (II). From the assignment in (a), J_{HF} in II would be expected to be closer to J_{HF} (*trans*) in I. Its value is 0.67 cps.

(c) Peak assignments for N-methyl-N-n-butyltrifluoroacetamide (III) are:

$$CF_3-\underset{O}{\underset{\|}{C}}-N\begin{cases}CH_3 \quad \text{(B) low field}\\ (CH_2)_3-CH_3\end{cases}$$

IIIa (62%)

$$\longleftrightarrow$$

$$CF_3-\underset{O}{\underset{\|}{C}}-N\begin{cases}(CH_2)_3-CH_3\\ CH_3 \quad \text{(A) high field}\end{cases}$$

IIIb (38%)

The most intense N-methyl peak is the one to lower field with J_{HF} = 1.65 cps, whereas the higher field protons are coupled by only 0.70 cps. All studies concur in the assignment of $^5J_{HF}$ (*cis*) > $^5J_{HF}$ (*trans*) for N-methyl trifluoroacetamides. It may be possible to extend the assignment to all N-methyl fluoroacetamides, as your work[6] has shown that the lower field N-methyl protons of $CFCl_2-CON(CH_3)_2$ and $CF_2Cl-CON(CH_3)_2$ are also more highly coupled to fluorine.

We have been able to detect $^6J_{HF}$ in N,N-diethyltrifluoroacetamide in CH_2Cl_2. At 60 Mcps, the center peak of the lower field methyl triplet has a line width at one-half maximum intensity of 1.8 cps, while the corresponding value for the high field triplet is 1.2 cps. With fluorine decoupled, both peaks have a line width of 1.2 cps. Peak assignment leads to the conclusion that it is the methyl protons of the N-ethyl group *cis* to the CF_3 group which are coupled to fluorine with $^6J_{HF}$ (*cis*) ~ 0.2 cps.

References:

(1) M. T. Rogers and J. C. Woodbrey, J. Phys. Chem., **66**, 540 (1962).

(2) Yu. A. Cheburkov, Yu. A. Aronov, E. I. Fedin, P. V. Petrovskii, and I. L. Knunyants, Doklady Akad. Nauk. SSSR, **169**, 128 (1966).

(3) M. J. Sewell, TAMU NMR Newsletter, No. 128, 34 (1969).

(4) Laurine A. LaPlanche (Graham) and M. T. Rogers, J. Am. Chem. Soc. **85**, 3728 (1963).

(5) F. A. L. Anet and A. J. R. Bourn, J. Am. Chem. Soc., **87**, 5250 (1965).

(6) P. C. Adlaf and B. L. Shapiro, unpublished results.

Sincerely,

Lori

Laurine L. Graham

University of East Anglia

From Professor N. Sheppard F.R.S.

School of Chemical Sciences
University Plain
Norwich NOR 88C
Telephone Norwich ~~52651~~ 56161

15th August 1969

Dear Barry,

Restricted Rotation in Chlorinated Propanes

Attempts to obtain NMR spectra of molecules dissolved in stretched rubbers

I apologise that my scientific subscription to the TAMU Newsletter is
a little behind hand.   We are incidentally happy to honour the academic
charge for the Newsletter and I have returned the order form under
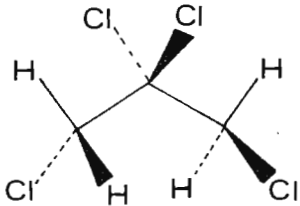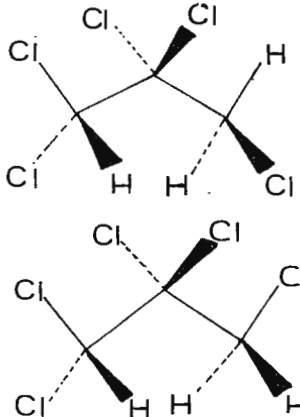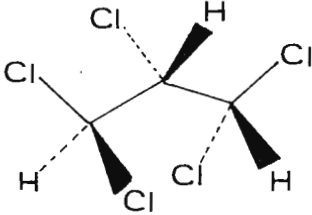separate cover.   We have two topics to bring to the attention of your
readers.

Restricted Rotation in Chlorinated Propanes

By the combined application of NMR and infrared spectroscopy we have
been able to identify the conformations of the more abundant rotamers
in a large number of chloropropanes.   Amongst these are 1,2,2,3-tetra-
chloropropane and 1,1,2,3,3- and 1,1,2,2,3-pentachloropropane which
exist mainly as the single conformers shown in Table 1.   Each of the
conformers shown has a spectroscopically indistinguishable mirror imaged
form with which it can interconvert and recently we have used variable
temperature NMR techniques to determine the thermodynamic parameters
for the internal rotation processes.

At room temperature the NMR spectrum of 1,2,2,3-tetrachloropropane
consists of a single line corresponding to the rotationally averaged
signals of each proton in the equivalent terminal methylene groups.
Below -80°C the signal broadens rapidly passing through coalescence
at about -100°C to give a single sharp AB quartet at -120°C and below.
The terminal methylene group of 1,1,2,2,3-pentachloropropane also gives
rise to the same type of NMR spectral changes with temperature, only
now the coalescence temperature is -54°C.   Both these systems were
analysed using an AB line-shape program to give the rate of inter-
conversion at each of several temperatures from which ΔH* and ΔS*
for the internal rotation processes were determined (Table 1).

The spectral changes associated with 1,1,2,3,3-pentachloropropane
are more complex, the spectrum corresponding to an exchange modified
AMX spin-system at 100 Mc/s.   At room temperature the separate
signals of the two different terminal methylene groups are averaged
to one doublet of coupling 5.7 cps to the central methine proton.
Below -90°C this doublet broadens rapidly, passing through coalescence
at about -120°C, to give a pair of doublets at -140°C.   Although these
have not been completely resolved the high field doublet shows a trans
coupling and the lower field doublet a gauche coupling to the central
methine proton.   Line-shape analysis has again been applied and the
thermodynamic parameters determined.

Table 1

Molecule	Most Stable Conformer	ΔH^* Kcal mole^{-1}	ΔS^* e.u.
1,2,2,3-Tetra-Chloropropane		6.55 ± 0.8	-11.2 ± 3.5
1,1,2,2,3-Penta Chloropropane		10.15 ± 0.5	- 5.2 ± 2.5
1,1,2,3,3-Penta Chloropropane		6.72 ± 1.0	- 4.6 ± 4.0

Attempts to obtain NMR spectra of molecules dissolved in stretched rubbers

We have recently been attempting to obtain NMR spectra from molecules
oriented in stretched rubbers. Although we have so far had no success
nevertheless even this information might be of interest to some of your
readers. Also in the attempt we obtained some fairly interesting data
on the line widths of the resonances of the rubber molecules themselves.
We were kindly supplied with some cylindrical samples of natural rubber
by the Dunlop Research Centre in Britain. Some of these were prepared
by extrusion, and some by moulding, and these turned out to have very
considerably different line widths for the resonances from the rubber
molecules although the samples superficially had rather similar physical
properties. The line widths were about 400 Hz (operating at 100 MHz
for protons) for the extruded samples, whereas moulded samples had much
greater half widths of about 3600 Hz. We imagine that this must reflect
reduced general mobility of the chains in the moulded samples. When

we dissolved orthodichlorobenzene in these rubbers so as to cause the
cylindrical samples to swell, in the extruded sample the solvent proton
resonance was narrow (of width about 20 c/s) whereas in the moulded
samples the solvent merely contributed to the very broad resonance
from the rubber itself.

We had hopes that on stretching the rubbers we would obtain NMR spectra
from oriented molecules in some measure similar to those nowadays often
studied in liquid crystals, but we have so far had no success although
we have varied both the degree of cross-linking in the rubber, and also
the proportion of 'solute' dissolved in it.   It may be that the solute
molecules turn over too slowly to give averaged 'high resolution'
spectra;   alternatively perhaps they occur in sufficiently different
environments in the interstices between rubber chains that they have
different degrees of orientation, and translational motions are too
hindered to average out either the orientations or the effects of
intermolecular broadening mechanisms.

As far as we know the only earlier reference in the literature to work
of this type is made in Buckingham and McLauchlan's review article
in Volume II of "Progress in NMR Spectroscopy".   Here they comment
that W.G. Schneider was able to resolve a 1,2,1 triplet from toluene
dissolved in a lightly cross-linked butadiene-styrene rubber that
had been swollen in a NMR specimen tube.   However recent correspondence
with Bill Schneider reveals that their sample did in fact contain
considerable cross-linking and we are continuing to pursue our
exploratory studies in this field.

<div align="center">Yours sincerely,</div>

I. Gazzard   K. Price   N. Sheppard

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

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

August 14, 1969

313.06

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

<u>Proton Relaxation Studies of K_2ReH_9</u>

Dear Barry:

Rolf Johannesen and Tom Tsang and I have just completed some
proton wide-line and relaxation time (T_1) studies of K_2ReH_9.
From crystallographic studies it has been shown that there are
two distinct types of $ReH_9^=$ anions designated by type "a" and
type "d". The activation energies for internal reorientation
of the $ReH_9^=$ anions, and their rms errors, are 9.9 ± 0.4 and
25.0 ± 0.8 kilojoules per mole (2.4 ± 0.1 and 6.0 ± 0.2 kcal/
mole) respectively for type "a" and "d" sites. Our results
suggest that the barriers are determined by nearest neighbor
$ReH_9^=$ - $ReH_9^=$ interactions. There are five nearest neighbor
Re located 5.5Å from the d-site, but only two nearest neighbor
Re at that distance from a-site (the next nearest neighbor Re
distance is about 9.6Å).
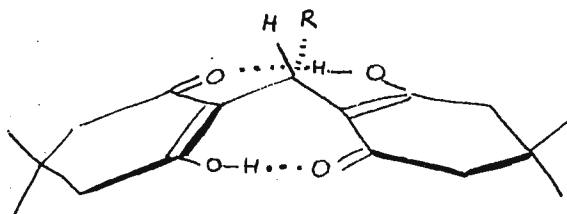
Regards,

T. C. Farrar
Crystallography Section

Princeton University DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

August 18,1969.

Dear Barry,

"A little pyridine goes a long way"
We have been investigating molecules of the type I, prepared by a simple condensation
of dimedone with the appropriate aldehyde :

I

These exist solely in the dienolic form shown; no evidence for the existence of
ketonic forms has been found[1]. Internal rotation around each of the C-C bonds to the
CHR bridge exchanges the methyl groups syn and anti with respect to the bridge.
The barriers to these rotations have been studied by nmr using the approximation of
two uncoupled sites. This assumption is found to be adequate from the excellent
linearity of the Arrhenius plots.
We have studied the effect on the activation parameters of adding a small amount
of proton acceptor. When R = $CH_2C_6H_5$, the coalescence temperature goes from + 65°C
in $CHCl_2$-$CHCl_2$ (an inert solvent) to - 57.5°C in a deuteriochloroform-pyridine
mixture (1:2 ratio). The apparent activation energies are respectively 16.9 kcal./
mole and 10.3 kcal./mole[2], which is a very large variation. We have therefore
carefully measured the rates in two solvent mixtures - $CDCl_3$ with 5 % pyridine,
and $CDCl_3$ with 10 % pyridine - while maintaining the solute concentration constant.
Each spectrum was recorded at least 4 times at the same temperature and digitalized
on punched paper tape. The temperature was measured with a $MeOH/Me_2O$ capillary
inserted into the sample tube, and precalibrated with a thermocouple. We have also
accounted for the temperature dependence of the limiting shifts by verifying
their linearity below coalescence, and extrapolating to estimate their values at
temperatures above coalescence. The temperature intervals were of the order of 5°
and about 10 different temperatures were used for each sample.

/ ...

The activation parameters are listed below :

	5 % pyridine	10 % pyridine	
ΔH^*	12.2 ± 0.4	9.4 ± 0.4	kcal./mole
ΔS^*	-11.3 ± 1.2	-17.3 ± 1.2	e.u.
ΔG^*	15.5	14.6	kcal./mole

The results clearly confirm that pyridine is solvating the enolic protons in the transition state and thus lowering the barrier :

transition state   (inert solvent)

                                    (+ proton acceptor)

initial state
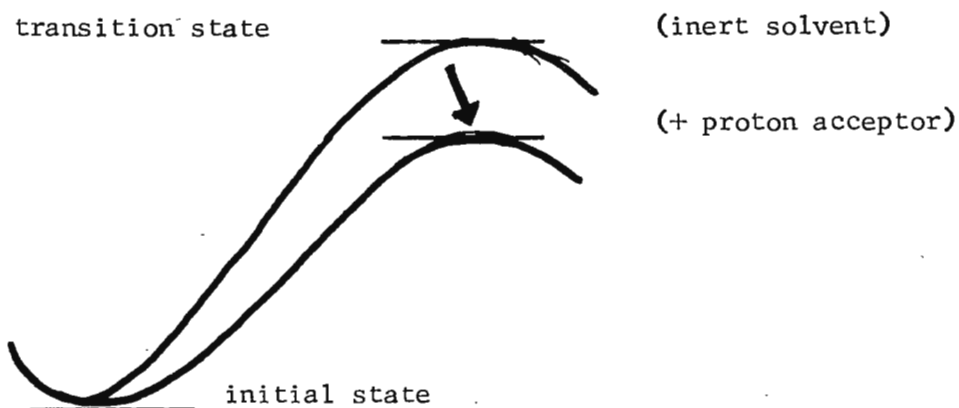
Apparently the molecule does not have to revert to the keto form in order to rotate.

This work was conducted at the Lund Institute of Technology in Lund, Sweden, and WEF wishes to gratefully acknowledge the hospitality and assistance of Professor Sture Forsén and Mr. Törbjörn Drakenberg.

(1)   S.Forsén,W.E.Frankle,P.Laszlo,and J.Lubochinsky,J.Magnetic Resonance, 1, 327 (1969).

(2)   cf. Table 3 in ref.(1); see also H.Zimmermann and F.Strohbusch,IITNMR 112-25.

William Ernest Frankle   Pierre Laszlo

RELIABILITY OF SPECTRAL ANALYSIS

It must be the umpteenth time that someone is complaining about the ambiguities of spectral analysis.We would like to add our voice to that of some of our fellow-sufferers and request that spectral analyses be not relied upon unless there is mutual compatibility of the parameters derived from the spectra of the same sample obtained at two different frequencies such as 60 and 100 MHz.

The rms is not a sufficient criterion.

In many cases a number of sets of parameters would equally well fit the experimental data.Here is one example :

ITERATION   9   R M S ERROR =   0.050

PAR SET	NO. SPINS	SPIN	ISO		INPUT PARAMETERS	BEST VALUES	STANDARD DEVIATION
1	1	0.5	1	W(1) =	313.230	313.381	0.031
1	1	0.5	1	W(2) =	313.230	313.381	0.031
2	1	0.5	1	W(3) =	304.570	304.494	0.037
2	1	0.5	1	W(4) =	304.570	304.494	0.037
3				A(1,2)=	0.531	2.044	0.089
4				A(1,3)=	6.634	7.336	0.071
5				A(1,4)=	1.283	0.727	0.051
5				A(2,3)=	1.283	0.727	0.051
4				A(2,4)=	6.634	7.336	0.071
6				A(3,4)=	8.133	9.392	0.123

ITERATION   3   R M S ERROR =   0.051

PAR SET	NO. SPINS	SPIN	ISO		INPUT PARAMETERS	BEST VALUES	STANDARD DEVIATION
1	1	0.5	1	W(1)=	313.390	313.295	0.050
1	1	0.5	1	W(2)=	313.390	313.295	0.050
2	1	0.5	1	W(3)=	304.568	304.506	0.028
2	1	0.5	1	W(4)=	304.568	304.506	0.028
3				A(1,2)=	1.102	0.271	0.224
4				A(1,3)=	6.986	7.017	0.066
5				A(1,4)=	0.858	1.122	0.043
5				A(2,3)=	0.858	1.122	0.043
4				A(2,4)=	6.986	7.017	0.066
6				A(3,4)=	8.713	7.726	0.203

Fata _viam_ _invenient_,as one would say before the advent of Parkinson,Peter,_et_ _al_. !

<div align="center">

With all best regards,

Sincerely,

</div>

Arnold Speert

Pierre Laszlo

ARGONNE NATIONAL LABORATORY

August 20, 1969

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

ISOTOPE HYBRID PROTEINS FOR NMR

Dear Barry:

The technique of simplification of a complex spectrum by
the judicious introduction of deuterium can now be applied in
a simple and direct way to protein molecules. The main re-
quirement is to be able to grow organisms in 99.8 percent D_2O,
a capability that is not excessively difficult or expensive
to acquire. We at this Laboratory have been culturing algae
in D_2O for a number of years.[1] Since these algae are grown
autotrophically (CO_2 is their only source of carbon) all of
their cellular components are fully deuterated. More recently
we have begun adding some ordinary ($^1H-$) amino acids to these
cultures to see if the fully deuterated algae would take them
up and incorporate them into cellular proteins to give $^1H-^2H$
hybrid proteins. The PMR spectrum of such an isotope hybrid
protein will show only the ^1H-amino acids and thus present a
highly simplified protein spectrum. As Figure 1 shows, our
efforts have met with some success. The spectrum is that of
the total hydrolyzate of purified algal protein, yet the only
proton resonances are those of leucine, methionine and phenyl-
alanine.

Other amino acids such as alanine, tyrosine, valine and
glutamic acid can also be incorporated singly or in combination
into algae growing in D_2O. We have been pleasantly surprised by
the minimal amount of redistribution of protons into other amino
acid side chains. In addition to hybrid proteins, one can, of
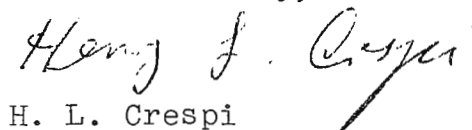
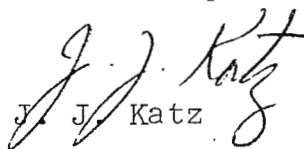Professor Bernard L. Shapiro   -2-   August 20, 1969

course, also extract other biological molecules, such as the chlorophylls, of unusual isotopic composition. Thus, chlorophyll fully deuterated except for CH_3 in the carbomethoxy group at position 10 can be isolated from algae grown in D_2O with exogenous ^1H-methionine. The method seems a particularly useful one for the hydrogen isotopes because it requires ^1H rather than ^2H-amino acids as substrate[2] and no doubt will also be applied to the formation of isotope hybrid molecules of ^{15}N, ^{13}C and eventually ^{17}O.

Yours sincerely,

H. L. Crespi

J. J. Katz

HLC:JJK/skj

References:

(1) J. J. Katz and H. L. Crespi, Science, 151, 1187 (1966).

(2) For a procedure utilizing ^2H-amino acids and heterotrophic organisms, see J. L. Markley, I. Putter, and O. Jardetzky, Science, 161, 1249 (1968).
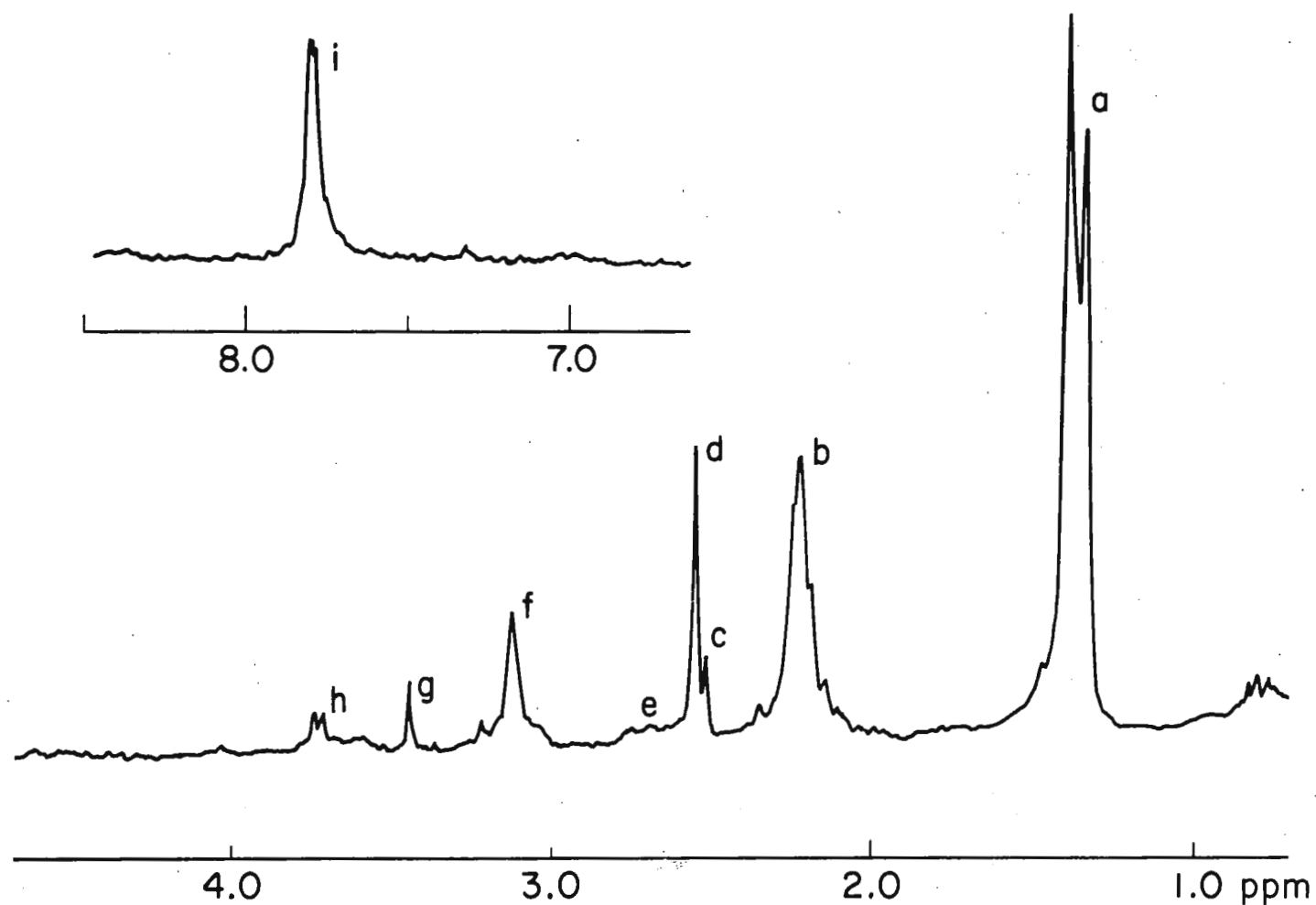
Fig. 1. The pmr spectrum of an acid hydrolyzate of ^{2}H-phycocyanin (^{1}H-leucine, ^{1}H-methionine, 1H-phenylalanine). The proton resonances are as follows: a, methyl groups of leucine; b, -CH-CH$_2$-grouping of leucine; c, acetate methyl (added as internal standard); d, methionine methyl; e, -CH$_2$-of methionine (C-3), broad; f, -CH$_2$- of methionine (C-4); g, unidentified; h, -CH$_2$- of phenylalanine; i, phenyl group of phenylalanine.

**PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL**
4056 BASEL, SCHWEIZ - KLINGELBERGSTR. 82
TEL. 43 04 22
VORSTEHER: PROF. DR. P. HUBER

Basle, August 22nd 1969.ri

Prof. Dr. P. Diehl.

Prof. B.L. Shapiro
Department of Chemistry
Texas University
College Station, Texas 77843

Postdoctoral Position Available.

Dear Barry,

I will have funds available for a postdoctoral
position for one year, beginning November 1st 1969 (or later).
The work will involve NMR exclusively (spectra of oriented
molecules). Any person interested should write to me as soon
as possible.

Sincerely yours

Peter

Prof. Dr. P. Diehl.

22 August 1969

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

GORILLA GORILLA

Dear Barry,

Since you were shown to be so surprisingly misinformed on the Felidae, could we tell you about the gorilla (derived from the Greek Gorillai, an African tribe of hairy women[1]). You may think this is simply a close relative of the chimpanzee (but less arboreal, less erect and much larger) whereas in fact it stands for Gismo[2] for Observing the Relaxation of Individual Lines using a Lock-in Amplifier.

Gorilla is descended from an earlier device described by Vold et al.[3] Two strong (non-selective) pulses are applied to a proton spin system; the first turns the magnetization through 180°, then t seconds later a 90° pulse generates a free induction decay. Since the Fourier transform of this signal is the slow-passage high resolution spectrum, the evolution of the intensity of each line can be followed as a function of t from its initial inverted state back to the erect thermal equilibrium posture. Under certain circumstances this gives the spin-lattice relaxation time of the individual lines.

The origin of this new species can be traced back to earlier Fourier transform experiments with an internal proton lock during pulsed operation.[4] Rather than monkey with a computer, we have dispensed with the Fourier transformation step by exploiting the natural selectivity of a lock-in detector, tuning this very narrow "window" to one line at a time. A similar filtration of a Carr-Purcell spin-echo train gives the individual spin-spin relaxation times. Field/frequency stabilization can be critical, particularly for the spin-echo measurements where it appears that the phase of the free precession of a typical spin must not drift significantly during the time that echoes are observed (10 to 100 secs). Internal proton and internal fluorine locks have been tried. The figure shows the different spin-lattice relaxation rates for the four groups of protons in p-dimethylaminobenz-aldehyde (proton A is ortho to the aldehyde group).

Yours sincerely,

Ray

Ray Freeman

Howard Hill

Howard Hill

1. Webster's Third New International Dictionary; no Barry, nothing to do with that topless establishment.
2. Gismo (or gizmo), n. A gadget, hickey Lauterburiensis.
3. R. J. Vold, J. S. Waugh, M. P. Klein and D. E. Phelps, J. Chem. Phys. 48, 3831 (1968).
4. FT 100 accessory; cf. S. Gross, R. Graves and P. Rose, TAMUNN 131, 4 (1969).

ALDEHYDE PROTON

RING PROTON A

RING PROTON B

N-METHYL PROTONS

$t = \infty$
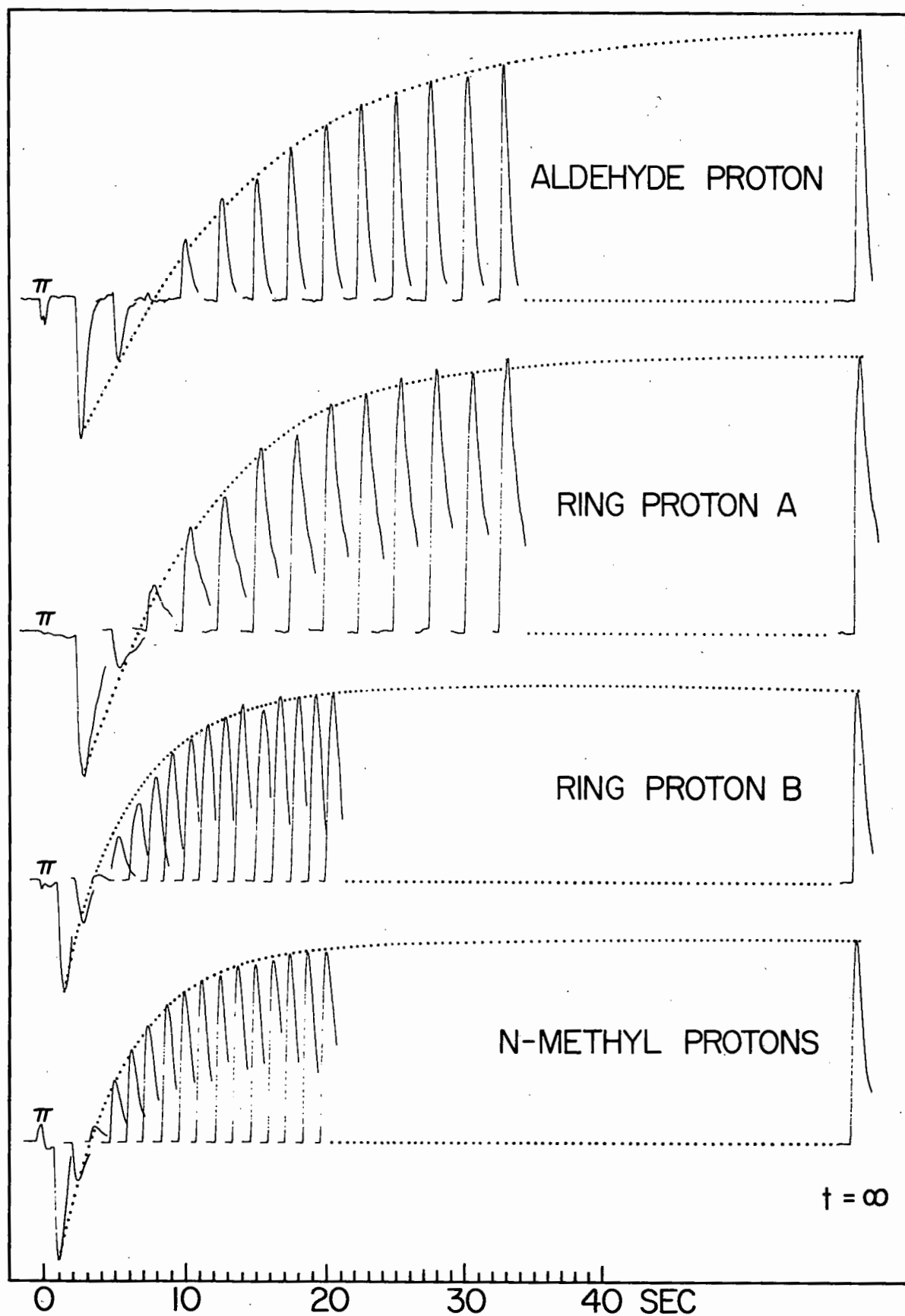
MERCK INSTITUTE
FOR
THERAPEUTIC RESEARCH
RAHWAY. NEW JERSEY 07065

August 27, 1969

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

PMR vs. Assignments of Tyrosines in Nase

Dear Barry:

Please consider this letter an initial contribution for my personal copy
of the T.A.M.N.M.R. Newsletter. My address from October will be Division
of Computer Research and Technology, National Institutes of Health, Bethesda,
Maryland. I will be using the new 220 MHz spectrometer there for protein
studies in collaboration with Chris Anfinsen's group.

A number of recent publications[1-3] may be of interest. However, what I
wish to mention are recent experiments designed to obtain independent
assignments of the 7 tyrosine (Tyr) resonances in staphylococcal nuclease
(Nase). A number of largely deuterated analogs of this enzyme have been
under intensive study in this laboratory. Some of the Tyr residues are known
to be involved in the activity of this enzyme, and John Markley[4] has studied
the effects of inhibitor (pTp) on these resonances. It is not possible to
apply the technique which was utilized for the assignment of the histidine
residues of ribonuclease[5], since the conditions required for ring proton
exchange in Tyr would cleave peptide bonds. I have therefore attempted to
prepare the selectively nitrated derivatives of Nase as described by Anfinsen
and coworkers[7], utilizing the technique of affinity chromatography[8] for their
purification. A Nase analog containing 3,5-deutero-Tyr
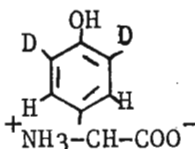
has been prepared, and is being used to aid these assignments since its
aromatic spectrum in PMR is a singlet.

Best regards

Jack S. Cohen

Jack S. Cohen, Ph.D.

/drw

References:

1. J.S. Cohen, Nature, 223, 43 (1969)
2. G. Roberts, D. Meadows, E. Dennis, J. Cohen and O. Jardetzky, Proc. Natl. Acad. Sci., 62, 1151, (1969)
3. W. Horsley, H. Sternlicht and J.S. Cohen, Biochem. Biophys. Res. Comm., in press.
4. J.L. Markley, Ph.D. Thesis, Harvard, 1969.
5. D. Meadows, O. Jardetzky, R. Epand, H. Ruterjans and H. Scheraga, Proc. Natl. Acad. Sci., 60, 766, (1968)
6. P. Cuatrecasas, S. Fuchs, and C. Anfinsen, J. Biol. Chem., 243, 4787,(1968).
7. P. Cuatrecasas, M. Wilchek and C. Anfinsen, 61, 636, (1968).

UNIVERSITY OF KENTUCKY

LEXINGTON. KENTUCKY 40506

COLLEGE OF ARTS AND SCIENCES
DEPARTMENT OF CHEMISTRY

August 25, 1969

Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas   77943

Dear Barry,

Lately we have been investigating dilute biopolymer solutions. To obtain a spectrum of satisfactory signal-to-noise ratio signal averaging of many hours is required. In spite of this, the resulting base line is quite noisy, with existing peaks ill-defined and varying greatly in width, similar to results obtained in other macromolecular systems where concentration and conformation determine peak area and line shape. Analysis of these spectra includes determinations of chemical shift by interpolation, peak area by planimetry and FWHM by direct measurement. Aside from being extremely time consuming, these techniques can be quite subjective, particularly when establishing a base line for area and FWHM determinations.

To combat these problems a program, MULPLOT, has been written which accomplishes the following: 1) takes raw digital data and performs a "variable-smooth" to reduce noise, 2) determines chemical shifts, relative peak area and FWHM, and 3) plots the results.

The variable-smoothing function routine is an important part of this program. Since a macromolecular system may yield spectra having widely varying FWHMs, a fixed point smoothing function is usually inadequate. For example, a broad smoothing function will treat a narrow peak as noise, tending to flatten and distort it. Thus the ability to have at the disposal of every data point a varying-width smoothing function is essential.

Chemical shifts are determined by observing the first derivative of the digitized spectrum. Areas are determined by a slightly modified trapisoidal method. The plotting is accomplished using a Calcomp 750 plotter. (Output is also printed so the plotter is not essential.)

Professor Bernard L. Shapiro
August 25, 1969
Page 2

Since computer memory was not a problem, no attempt was made
to shrink the program to minimum size. On an IBM 360/50 it requires
ca. 100K. With some modification in output the memory requirement
could be reduced significantly. The present program will handle
1024 data points (from a C-1024 CAT) and up to five smoothing
iterations. Reduction of either the number of data points or the
number of iterations will drastically reduce storage requirements.

An example of the plotter output is shown in the accompanying
figure. These spectra consist of 1024 channels yielding an in-
herent resolution limitation of 0.25 Hz/channel for a 250 Hz scan.
The smoothed spectrum was obtained after one iteration using a
maximum smoothing function containing fifteen points. Detection
of the highfield peak after smoothing shows how a peak in the raw
spectrum may go undetected until some noise is removed. While we
have not performed exhaustive tests, present indications are that
the maximum error in areas of distortion of lines is less than a
few percent.

More specific information concerning MULPLOT is available
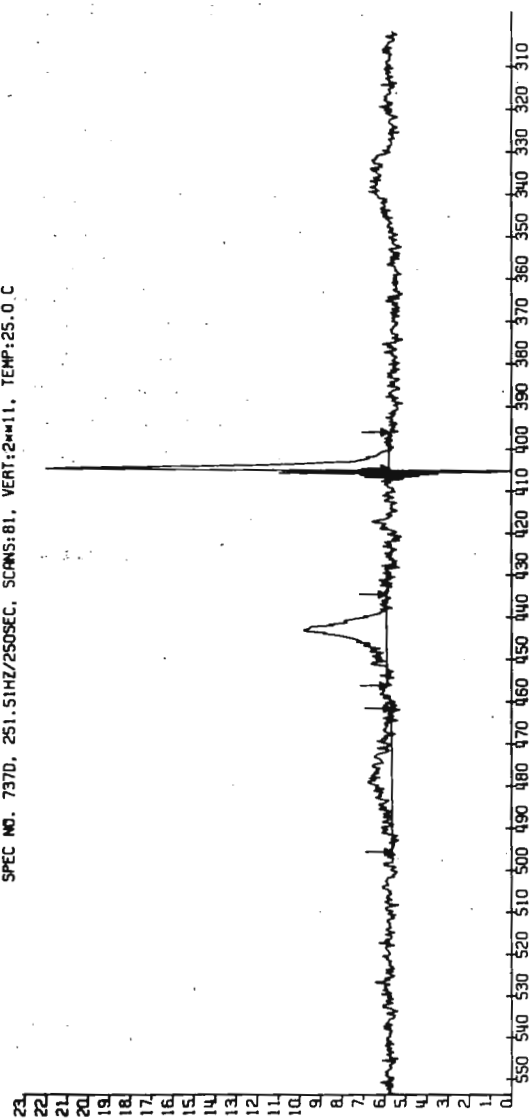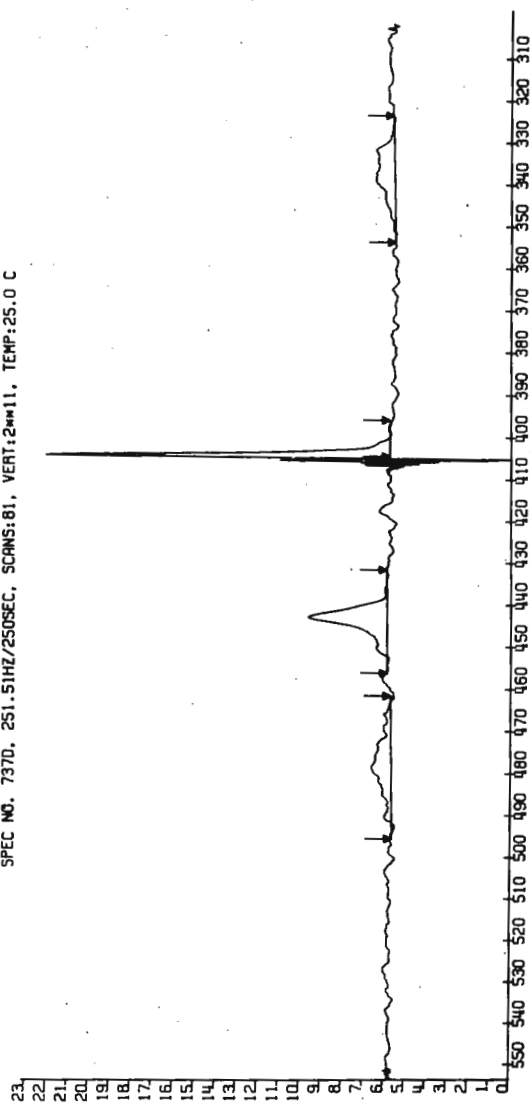on request.

Yours truly,

Stanford L. Smith

James L. Alderfer

Title: Doing It More But Enjoying It Less? - - Go "MULPLOT"

SPEC NO. 737D, 251.51HZ/250SEC, SCANS:81, VERT:2mm11, TEMP:25.0 C

SPEC NO. 737D, 251.51HZ/250SEC, SCANS:81, VERT:2mm11, TEMP:25.0 C

CARBON-13 NMR DATA GENERATION AND COMPILATION*

Monday, October 6, 1969

Tower Room No. 10, Disneyland Hotel - 9:30 A.M.

An informal session to facilitate communication among those both actively engaged and potentially interested in any aspect of ^{13}C NMR spectroscopy. Topics to be discussed include: needs for standard practices in reporting ^{13}C NMR data; referencing substances and conventions; types of ^{13}C NMR data compilation needed now and in the future; the availability, present and future, of enriched ^{13}C materials. In connection with such enriched ^{13}C substances, one or more presentations from representatives of the U.S. Atomic Energy Commission are expected, and ample opportunities for discussion of this important issue will be provided.

This session is being held under the auspices of the NMR Data Generation and Compilation Program sponsored by the Office of Standard Reference Data of the National Bureau of Standards. Attendance by all interested persons is cordially invited. Anyone interested in attending and contributing to this session is asked to make his desires known to B. L. Shapiro, Department of Chemistry, Texas A&M University, College Station, Texas 77843.

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* Special session at the Pacific Conference on Chemistry and Spectroscopy (combined 15th Western Regional Meeting, American Chemical Society and 8th National Meeting, Society for Applied Spectroscopy), Disneyland Hotel, Anaheim, California, October 6-10, 1969. Program and registration information may be obtained by writing Dr. W. F. Ulrich, Beckman Instruments, Inc., Scientific Instruments Division, 2500 Harbor Blvd., Fullerton, California 92634; (714) 871-4848.

On Tuesday, October 7, there will be an all-day Symposium On Carbon-13 NMR Spectroscopy. (Chairman, John L. Jungnickel, Shell Development Company, Emeryville, California.) The symposium will consist of invited papers by J. D. Roberts, L. F. Johnson, D. M. Grant, J. B. Stothers, G. E. Maciel, R. J. Kurland, F. A. Bovey, P. C. Lauterbur, H. Sternlicht, and R. A. Friedel.

On Wednesday morning, October 8, there will be a session of submitted NMR papers.

B.L.S. - 8/6/69

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