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Newsletter

No. 157
OCTOBER, 1971

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Deadline dates: No. 158: 1 November 1971
No. 159: 6 December 1971

All Newsletter correspondence, etc., should be addressed to:

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

Dartmouth College HANOVER · NEW HAMPSHIRE · 03755

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

September 3, 1971

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

Longitudinal Relaxation Times of Spin-Decoupled Protons

Dear Professor Shapiro:

We have decoupled via double irradiation two non-equivalent sets
of spin coupled protons, and employed the saturation recovery
method to demonstrate the feasibility of measuring relaxation times
for such a system. A dilute solution polytrimethylene oxide in carbon
tetrachloride was examined at two temperatures, and the proton T_1's
for the collapsed pentuplet and triplet are given below.

	Triplet	Pentuplet
$27^{O}C$	$.69 \pm .05$	$.68 \pm .05$
$48^{O}C$	$.75 \pm .04$	$.94 \pm .05$

The experimental method for the determination of proton relaxation
times by the saturation recovery technique is reported by Van Geet
(Anal.Chem.,37,983(1965)). We have made the following modifications
to his method. We employ a standard Varian HR-60 nmr spectrometer
locked on external sulfuric acid. The manual and sweep oscillators
are replaced by Monsanto Model #3100A digital frequency synthesizers
in order to minimize signal drift. The H_2 field is applied to the
center of the chosen multiplet, while the sweep frequency is adjusted
to correspond with the resonance position of the single peak.
Saturation is induced by switching the H_1 power to its maximum value
with a relay. When saturation is complete, the H_1 field is decreased,
and the recovery is monitored on a Varian C-1024 time averaging computer.

Sincerely,

Michael J. Gerace   Karl F. Kuhlmann
Research Associate   Assistant Professor

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

CHEMICAL CENTER

PHYSICAL CHEMISTRY 2

Lund, September 3, 1971

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

Dear Barry,

Title: PMR studies of mesomorphous phases.

In our study of mesomorphous phases consisting of n-oktyl-amine (OA), OAHCl and water, we have observed fine structure in the water pmr signal[1]. It was found possible to derive this line shape assuming anisotropic magnetic susceptibility effects - either microscopic or macroscopic - in the lamellar-like mesomorphous phases (fig. 2). An example of both theoretical and experimental lines is shown in figure 1 for spinning and non-spinning samples.

Signals from molecules dissolved in the mesomorphous phases might be expected to show similar effects, but it is only when the nucleus under observation experiences dipole coupling to an even number of equivalent nuclei that this can be observed. If it is coupled to an odd number of nuclei, the signal will be completely smeared out due to the variation in this dipole coupling with the orientation of the molecule. When it is coupled to an even number of equivalent nuclei the central signal will always be observable. For the compounds given in the table this type of spectral behaviour has been observed for a lamellar mesophase consisting of H_2O, OA and HCl (3:5.5:1.5)

$\Delta\nu_{susc}$ (for a definition see fig. 2) is positive when the intensity maximum is to high field for a non-spinning sample.

THE LUND INSTITUTE OF TECHNOLOGY
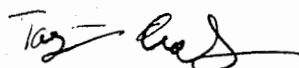
H$_2$O	1.17	CH$_3$OH	0.1	CHCl$_3$	-2.00
HCOO$^-$	0.83	CH$_3$CN	0.17	CH$_3$CCl$_3$	-0.67
CH$_3$COO$^-$	0.67	(CH$_3$)$_4$	0.20		

(CH$_3$)$_4$N$^+$ is a symmetrical ion and should hence not be oriented in the meso-phase. The shift, $\Delta\nu_{susc}$, of (CH$_3$)$_4$N$^+$ must thus be due to some macroscopic effect. This might be the difference in magnetic susceptibility between the water and the hydrocarbon parts of the liquid crystal. $\Delta\nu_{susc}$ increases with decreasing amount of water. An extrapolation to zero per cent water gives a shift of 0.45 ppm (see figure 3), which corresponds to a difference in the susceptibility of ca 2 $\cdot$ 10^{-6} between water and OA in the direction of the long axis of the OA molecules, which is not an unrealistic value.
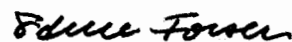
All of the compounds that dissolve in the water part give non-spinning spectra like that in the figure 1, whereas CHCl$_3$ and CH$_3$CCl$_3$ give spectra with the intensity maximum to low field. Thus it seems possible to decide from this whether added molecules are in the water or the hydrocarbon part of the meso-phase, since CHCl$_3$ and CH$_3$CCl$_3$ are assumed to be in the hydrocarbon part. The low shifts for methanol and acetonitrile may be due to a distribution of the molecules between the two parts of the liquid crystal, but with fast ex-change.

The fact that the shift is different for different compounds indicates that other effects than the difference in the macroscopic susceptibilities must be involved. Most likely the orientation of the molecules in the mesophase relative to the lamellar layers is of importance.

Yours sincerely

Torbjörn Drakenberg   Sture Forsén

Reference

Drakenberg, T., Johansson, Å. and Forsén, S., J. Phys. Chem. 74 4528 (1970)

Figure 1.

$\Delta\nu_{susc}$

Non-spinning sample

S   S

Spinning sample

Figure 2.

Figure 3.

$\Delta\nu_{susc}$ (ppm)

0.5

0.4

0.3

20   40

% H_2O

OSWEGO

September 8, 1971

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

Dear Barry:

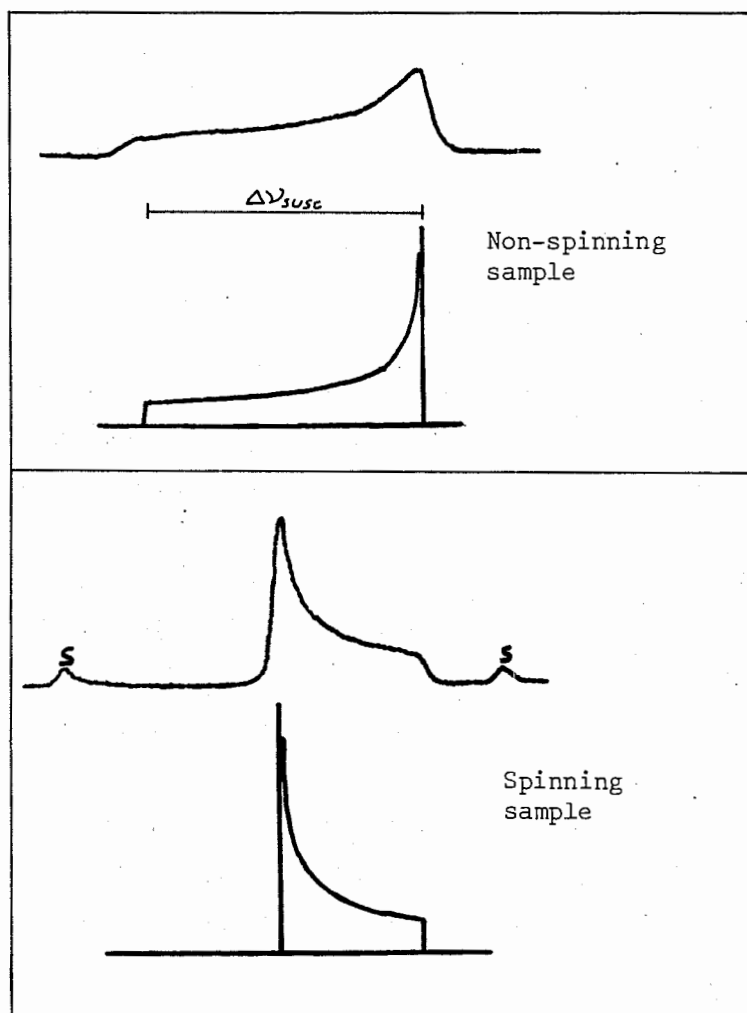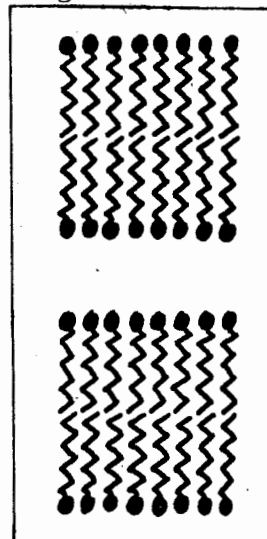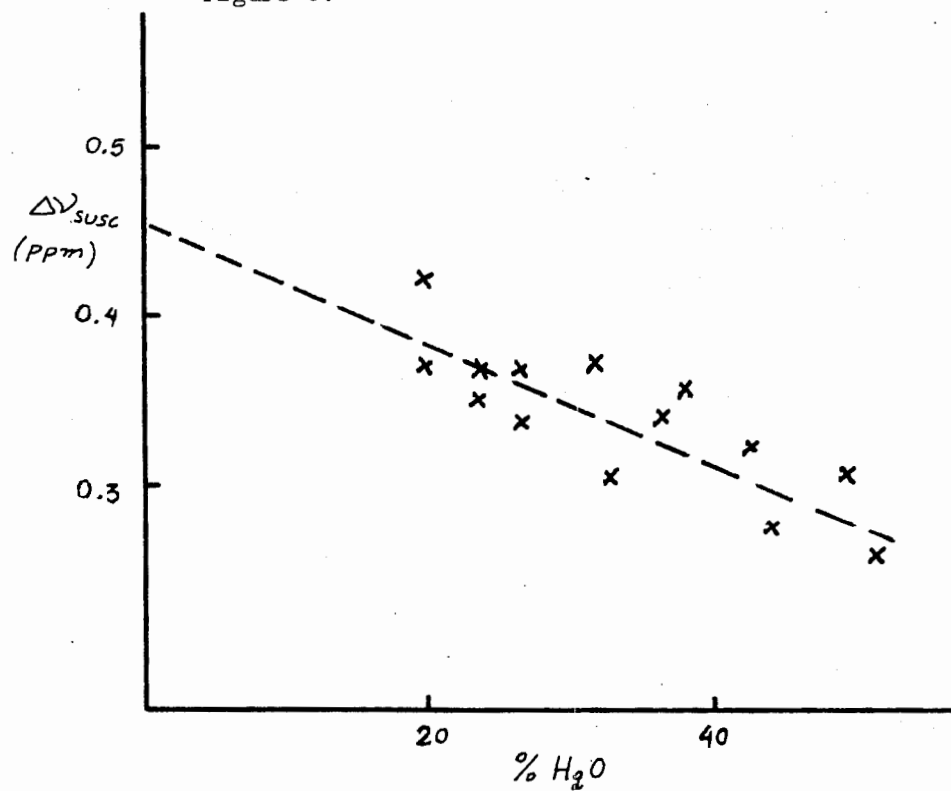### Sodium NMR of Aqueous Salt Solutions

We have measured the chemical shift of the magnetic resonance of sodium-23 in aqueous solutions of $NaClO_4$ and NaOH. The shift is proportional to the mole fraction $\underline{N}$ of the salt up to saturation, and is respectively 24.0 $\underline{N}$ (25°C) and -21.7 $\underline{N}$ (27°C) in ppm. relative to the aqueous sodium ion at infinite dilution. The result is interpreted by the formation of short-lived contact ion pairs with a formation constant close to 1. The shift of $NaBPh_4$ is zero, suggesting that no contact ion pairs are formed with this large anion. Higher temperature displaces the resonance downfield, $-3.65 + 900/\underline{T}$ for 5.59 $\underline{m}$ NaCl and $-5.79 + 950/\underline{T}$ for 8.3 $\underline{m}$ NaOH relative to infinite dilution. The relaxation rate $1/\underline{T}_1 = 1/\underline{T}_2$ increases steadily for $NaClO_4$ solutions, but shows an indefinite break for NaOH solutions around $Na/H_2O = 0.10$. When corrected for the viscosity, the break disappears, and $1/\eta\,\underline{T}_2$ for NaOH increases steadily. The viscosities at 26° of the solutions are given as a polynomial in $\underline{M}$.

The work was done jointly with Dr. G. J. Templeman, and has been submitted to J. Am. Chem. Soc. A few extra preprints are available.

Sincerely yours,

Anthony L. Van Geet

ALVG:mlk

Anthony L. Van Geet
Associate Professor of Chemistry

BOSTON COLLEGE

A University of 10 Colleges and Schools

CHESTNUT HILL, MASSACHUSETTS 02167

Department of Chemistry

September 9, 1971

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

Dear Barry:

Since the Pople and Bothner-By model for substituent effects on $^2J_{HH}$ [J. Chem. Phys., 42, 1339(1965)] is basically a symmetry argument, we felt it should be applicable to other types of two-bond couplings, and in particular, $^2J_{CH}$:
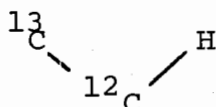
In this case, substituents may be attached to either ^{13}C or ^{12}C. Consideration of the symmetry properties of the orbitals in the CCH chain leads to the prediction that removal of o-electrons from ^{12}C will increase $^2J_{CH}$, whereas electron-withdrawal from ^{13}C should decrease it. Data in the litera-ture [Mol. Phys., 18, 491(1970)] show this to be the case.

We've looked at solvent effects on $^2J_{CH}$ in the following molecules:
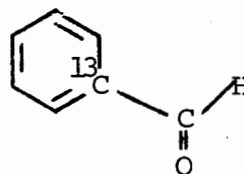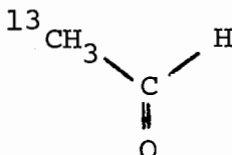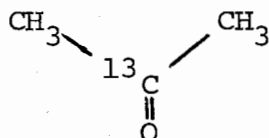
Solvent	CH_3CHO	C_6H_5CHO	$(CH_3)_2CO$
RCOOH	+26.4	+24.2	−5.76
$CDCl_3$	+27.2	+24.6	−5.89
$(CH_3)_2CO$	+27.4	--	−5.94

The variations, which appear to be outside of experimental error, indicate the effect of solvents to depend on the point of attachment of the oxygen to the coupling chain.

As is the case for $^2J_{HH}$ in formaldehyde, the positive sign of $^2J_{CH}$ in the aldehydes may be ascribed to back-donation of lone pair electrons into an orbital of the type

$$H - +C - +C.$$

Hydrogen bonding leads to a reduction in back-donation and $^2J_{CH}$ becomes more negative. In the case of acetone, the figure below suggests

that back-donation of lone pair electrons will be into an orbital of the type

$$H - +C+ -C$$
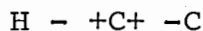
leading to a negative shift in $^2J_{CH}$. Hydrogen bonding should then cause it to become more positive, as observed.

We will be taking delivery of a Perkin-Elmer R-24 spectrometer in the next few weeks and I had hoped to be able to provide a report on its operation, but that will have to wait until my next letter.

Regards to all.

Sincerely,

Dennis J. Sardella
Associate Professor

Short title:- Solvent effects on $^2J_{CH}$.

Laboratorio dei composti del carbonio contenenti etero-atomi e loro applicazioni
Consiglio Nazionale delle Ricerche

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li. 11/9/1971

Dr.B.L.Shapiro
Dept. of Chemistry

Texas A and M University   <u>Title</u>: Partially oriented
College Station   thieno thiophen.
Texas 77843 - USA

Dear Dr.Shapiro,

please consider this letter as the first contri-
bution of C.A.Boicelli, who wants to be placed in your mailing
list. The financial contribution will arrive (hopefully) in short
time.

We have obtained the 100 MHz spectrum (JEOL PS 100)
of thieno (2, 3-b) thiophen (I) partially oriented in nematic
phase at both 78° degrees (p,p' di-n-hexyloxyazoxybenzene) and at
probe (30°) temperature (Merck Phase IV), **reported in the figure.**

(I)
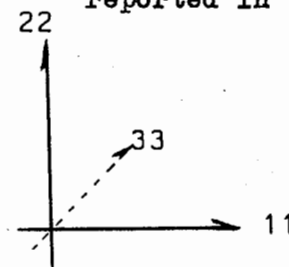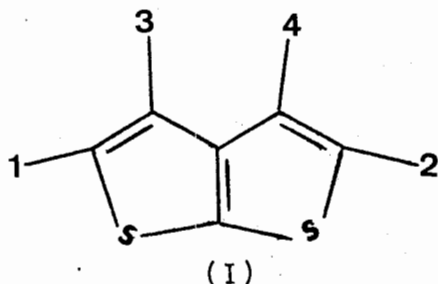
The spectral parameters are as follows:

	T = 78°	T = Probe
$\Delta\nu$	0.0	11.92 ± 0.38
D12	- 55.45 ± 0.57	- 40.65 ± 0.71
D13	-686.15 ± 0.38	-480.93 ± 0.35
D14	-103.63 ± 0.44	- 77.87 ± 0.40
D34	-513.38 ± 0.82	-392.26 ± 0.71
J13	+ 3.60 ± 0.57	+ 4.06 ± 0.52
J34	- 0.176	- 0.176
J14	- 0.034	- 0.034
J12	+ 1.166	+ 1.166
R.M.S.	1.29	1.08

It has been possible to determine the absolute sign of J13 as positive since even if introduced as negative in the calculation the iterative process revert its sign.

The value of the other J's were taken from the isotropic spectrum recorded in CCl_4 (where J13=+5.254, R.M.S.=0.029) and their signs can thus be regarded as absolute.

The ratios of interprotonic distances were determined and compared with those (A) calculated for the same molecule (1) assuming the C-H bond (1.08 $\overset{o}{A}$) as bisecting the corresponding angles (taken equals to those of the trans isomer (2)) and with those obtained from a molecular model built up with the parameters (3) of two thiofen rings (B).

	Experimental		Calculated	
	T=78°	T= Probe	A	B
R_{12}/R_{34}	2.100	2.129	2.153	2.157
R_{13}/R_{34}	0.837	0.798	0.822	0.850
R_{14}/R_{34}	1.673	1.663	1.697	1.697

The elements of the orientation matrix were also determined
$S_{11} = 0.128\pm.008$ $S_{22} = 0.079 \pm 0.005$ at 78° degrees and
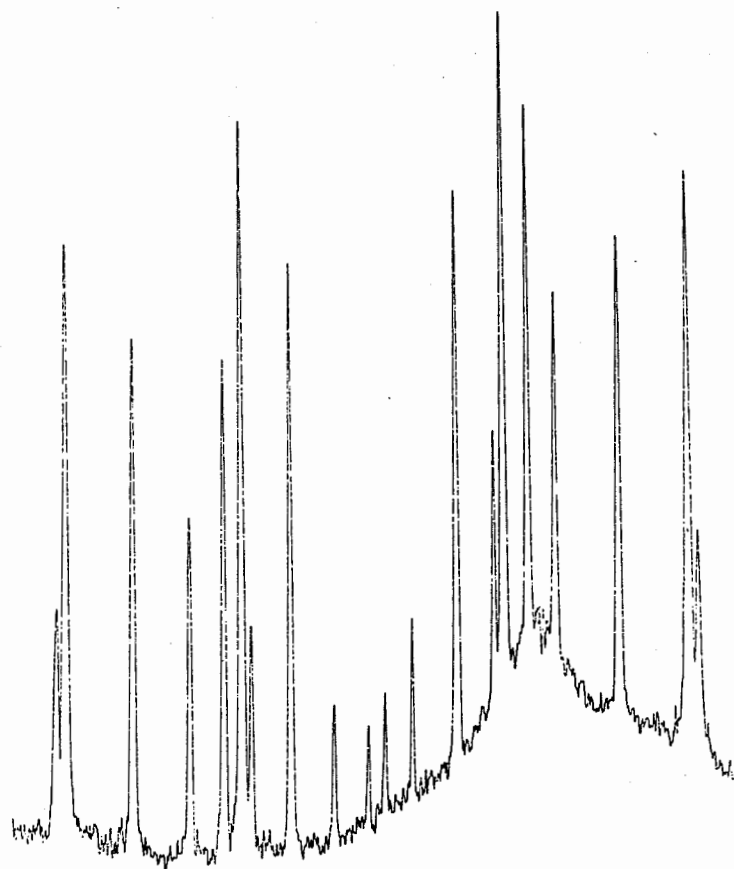$S_{11} = 0.108\pm.002$ $S_{22} = 0.028 \pm.002$ at 30° degrees.-

References
1) N. Trinajstic-A.Hincliffe - Croactica Chimica Acta, $\underline{39}$, 119, (1967)
2) E.G. Cox-R.J.J. Gillat-G.A. Jeffrey-Acta Cryst.,$\underline{8}$,356, (1959)
3) B. Bak -D. Christensen-J.Rastrup-Andersen- E. Tannenbaum-J. Chem. Phys. $\underline{25}$,892 (1955).

C. Andrea Boicelli and Ludovico Lunazzi

606. cps

THE UNIVERSITY OF NORTH CAROLINA
AT
CHAPEL HILL
27514

DEPARTMENT OF CHEMISTRY

September 13, 1971

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

H_1 Inhomogeneity and T_1 Measurements

Dear Barry:

In attempting to measure T_1 using the standard π-τ-$\pi/2$ pulse sequence the inhomogeneity in H_1 can lead to significant errors. Suppose that the r.f. field strength can be approximated by $H_1 + \Delta H_1$. When H_1 is applied for the time $t_{\pi/2}$ to produce a $\pi/2$ pulse the error in rotation angle resulting from ΔH_1 will be $\delta = \gamma(\Delta H_1)t_{\pi/2}$. Van Putte has shown that the magnetization after the $\pi/2$ pulse is $M_x = M_o^{\pi}(1 - <\delta^2>/2)$ using simple geometrical arguments, and that after a $3\pi/2$ pulse the magnetization becomes $M_x = -M_o(1 - 9<\delta^2>/2)$.[1] The correction $<\delta^2>$ can thus be measured quite easily.

We have extended Van Putte's analysis using a density matrix formulation in order to treat the situation in which $\tau \sim T_1$, T_2 and $T_1 \sim T_2$. A straight forward analysis leads to the recovery curve

$$\frac{M_o - M_x(\tau)}{M_o} = 2\{1 - <\delta^2>[1 + f(\tau)]\}e^{-\tau/T_1} \qquad (1)$$

where M_o is the magnitude of the equilibrium magnetization and $M_x(\tau)$ is the signal amplitude measured after the $\pi/2$ pulse in the π-τ-$\pi/2$ sequence. In this notation the free-induction decay after a single $\pi/2$ pulse is given by $g(t) = f(t)e^{-t/T_1}$ where $f(0) = 1$, and the form of $g(t)$ can easily be measured.

Returning to the π-τ-$\pi/2$ experiment we can solve Eq. (1) for the time of the null ($\tau = \tau_o$) and thereby obtain the equation:

$$T_1 = \frac{\tau_o}{\ell n2 - <\delta^2>[1 + 2g(\tau_o)]} \qquad (2)$$

This equation differs from Van Putte's result only by the term containing $g(\tau_o)$ in the denominator. We have found that Eq. (2) gives accurate values of T_1 for $<\delta^2> \gtrsim 0.1$. With our Magnion room temperature probe the minimum attainable value of $<\delta^2>$ is about 0.06.

Sincerely yours,

Anil Kumar   Charles S. Johnson, Jr.

AK:CSJ:bs

1) K. van Putte, J. Magn. Resonance, 2, 174 (1970).

**UNIVERSITE DES SCIENCES ET TECHNIQUES
DU LANGUEDOC**

R. JACQUIER
Professeur
Place Eugène Bataillon
34 - MONTPELLIER

Tél. : (67) 72.42.01 et 72.29.44 (Poste 803)

Le 13 Septembre 1971

Professeur B.L. Shapiro
Department of Chemistry
Texas A and M University
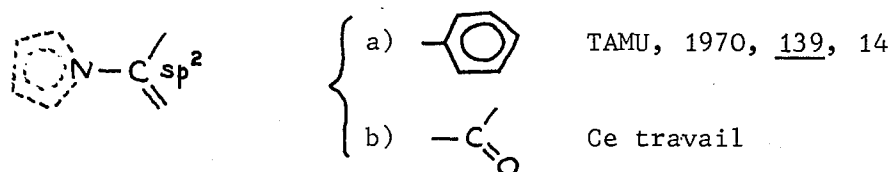College Station

TEXAS, 77843

U.S.A.

Titre :

CONFORMATION D'AZOLIDES.

Cher Professeur Shapiro,

En continuant nos recherches sur l'utilisation de la RMN pour
la détermination de la conformation préférentielle des dérivés N-substitués
des azoles, nous avons examiné le cas des dérivés N-acétylés.

a) ⬡   TAMU, 1970, <u>139</u>, 14

b) —C⟨O   Ce travail

Il s'agit de déterminer la constante d'équilibre K correspondant
aux deux conformations d'un azolide :
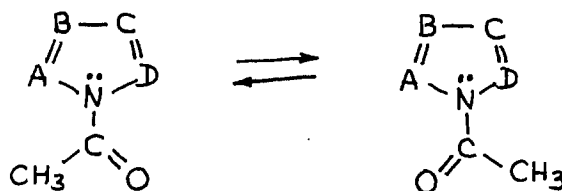
avec A, B, C et D égal soit à =CH soit à =N .

Les études à basse température n'ont pas donné de résultat (vrai-
semblablement parce que l'équilibre est fortement déplacé dans un sens) sauf
dans le cas du pyrrole (*). Pour ce produit nous avons attribué le signal
aux champs faibles au proton qui est en vis-à-vis de l'oxygène du carbonyle,
en accord avec DAHLQUIST et FORSEN (J. Phys. Chem., 1969, <u>73</u>, 4124) et
contrairement à MATSUO et SHOSENJI (Chem. Comm., 1969, p. 501).

(*) Nous avons réussi à bloquer la rotation dans le cas du carbométhoxy-1
pyrazole et du carboxamido-1 pyrazole, mais dans ce dernier cas c'est la
liaison C-NH_2 et non la C-N(pyrazolique) qui est affectée.
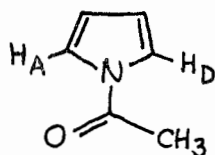
à - 40° $\delta_A = 7,53$ $\delta_D = 7,15$

$\delta_A - \delta_D = 0,38$

$\Delta_{CO} - \Delta_{Me} = 0,38$

CH₃   COCH₃
$\delta = 6,60$ $\delta = 7,27$

à 27° $\delta_A = \delta_D$

$1/2\,\Delta_{CO} + 1/2\,\Delta_{Me} = 0,67$

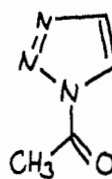donc $\Delta_{CO} = 0,86$ et $\Delta_{Me} = 0,48$.

       Si l'on admet que ces incréments sont les mêmes pour tous les azoles (dans le cas de l'imidazole le % obtenu est le même en considérant H_A que H_D), on arrive aux pourcentages de conformères suivants (à $\pm$ 5 %), en comparant les déplacements chimiques dans le $CDCl_3$ à 27° des produits N-CH₃ (le produit NH ne convient pas à cause de la tautomérie) et N-COCH₃ :
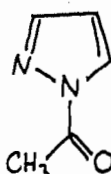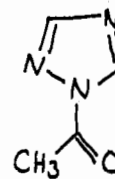
20%   100%   95%   100%

       Dans le cas de l'acétyl-1 tétrazole-1,2,3,5 l'effet sur le proton en β est trop faible pour permettre de déterminer la conformation (vérifié par l'étude de l'acétyl-1 triazole-1,2,5). L'acétyl-1 tétrazole-1,2,3,4 n'est pas stable.

       Une étude par rayons x (ESCANDE et LAPASSET, Acta Cryst., 1971, sous presse) confirme la structure E de l'acétyl-1 pyrazole.

       Des calculs EHT et CNDO/2 sont en cours pour expliquer quantitativement la prédominance de la conformation E quand il y a un atome d'azote en position 2.

       Veuillez croire, cher Professeur Shapiro, à l'assurance de nos sentiments les meilleurs.

J. ELGUERO   R. JACQUIER

UNIVERSITE DE PROVENCE – CENTRE DE SAINT-JEROME
FACULTÉ DES SCIENCES DE MARSEILLE · SAINT-JÉROME
13 · MARSEILLE (13ᴱ)
TÉL.: 50-31-61

September 14, 1971

DÉPARTEMENT DE CHIMIE ORGANIQUE
LABORATOIRE DES ORGANOMÉTALLIQUES
PROFESSEUR J. C. MAIRE

^{13}C Nmr STUDY OF TRIMETHYLSILYLBENZENES

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

Dear Dr. SHAPIRO,

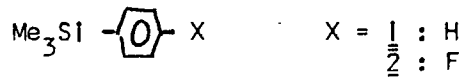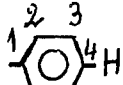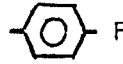Once again I come under the blue-paper law. Thank you for the TAMUNMR reminder. In connection with our current studies on pπ-dπ interactions in the aromatic derivatives of IVth group elements, we had occasion to examine the ^{13}C NMR spectra of some trimethylsilylbenzenes. Particulary puzzling are the results obtained for 1 and 2

$$Me_3Si - \langle O \rangle - X \qquad X = 1 : H$$
$$2 : F$$

^{13}C chemical shifts obtained at 25,14 MHz, referred to benzene are given in the table below

	C_1	C_2	C_3	C_4
Me₃Si —⟨O⟩—H	– 12,3	– 5,7	– 0,3	– 1,4
⟨O⟩– F	4,4	– 0,9	14,3	–35,1
Me₃Si —⟨O⟩– F	– 2,7	– 2,2	18	–30,3
^{13}C shift predicted according to additivity	– 7,9			–36,4
deviations (cal.–mes.)	– 5,2			– 6,1
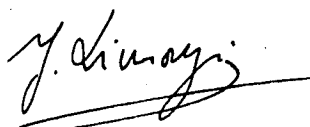
It can be seen that the additivity rule (G.E.MACIEL, J.J.NATTERSTAD, J.Chem.Phys. 1965, 42, 2427 and references therein) does not hold. Now, it has been pointed out by the same authors that deviations from additivity of appreciable magnitude, at the fluorine substituted carbon, occur only with (-R) para substituents, therefore we may assume that the silicon atom can make use of its empty 3d orbital to form a partial double bond with the phenylring. The study of a series of substituted trimethylsilylbenzenes is in progress.

Sincerely yours.

Y. LIMOUZIN   J. C. MAIRE

Me₃Si—⟨ ⟩ with ring positions labeled 1, 2, 3, 4

C_1

C_2

C_3

C_4

δ

-10

0
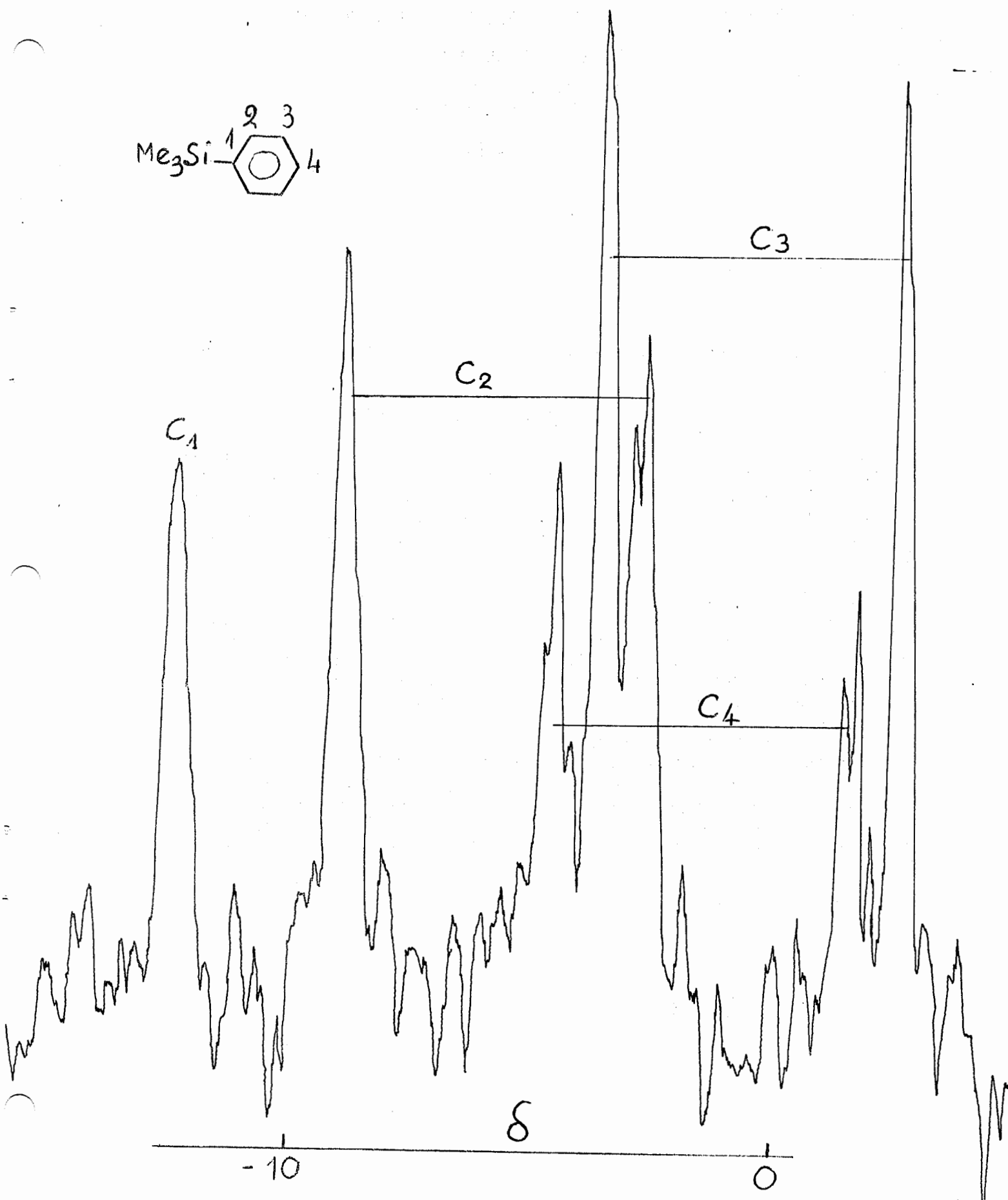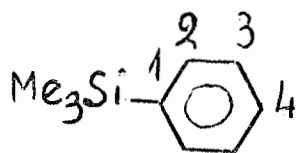
United States Department of the Interior

BUREAU OF MINES

4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

September 14, 1971

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

Dear Barry:

Our primary interest during the past several months has been in the field of

SULFUR-33 MAGNETIC RESONANCE SPECTROMETRY.

Four representative, but slightly overmodulated, ^{33}S NMR spectra are shown in figure 1. Chemically shifted peaks are evident from the figure in spite of the very broad lines observed. In contrast to these results, we have obtained spectra of two compounds, powdered sphalerite (ZnS) and dilute sulfuric acid, that give much narrower lines (linewidths much less than 0.5 gauss)

In order to obtain ^{33}S spectra without using unreasonable periods of signal averaging, H_1 levels in excess of that available from the Varian V-4311 were required. Amplification of the output of the V-4311 was accomplished with the aid of an ENI model 310L rf power amplifier. In the case of neat carbon disulfide, a 2.4 increase in signal-to-noise resulted. A saturation curve for carbon disulfide is shown in figure 2.

In reply to a question asked of me during my presentation at the 1971 ENC meeting at Gainesville, we were unsuccessful in our attempts to observe the ^{33}S resonance in elemental sulfur even after several days of time-averaging. We were also not able to reproduce the results of Karr and Schultz (Spectroscopy Letters, 1, 205-210, 1968) who reported observing the sulfur resonance in elemental sulfur dissolved in carbon disulfide.

Further work in ^{33}S NMR is in progress.
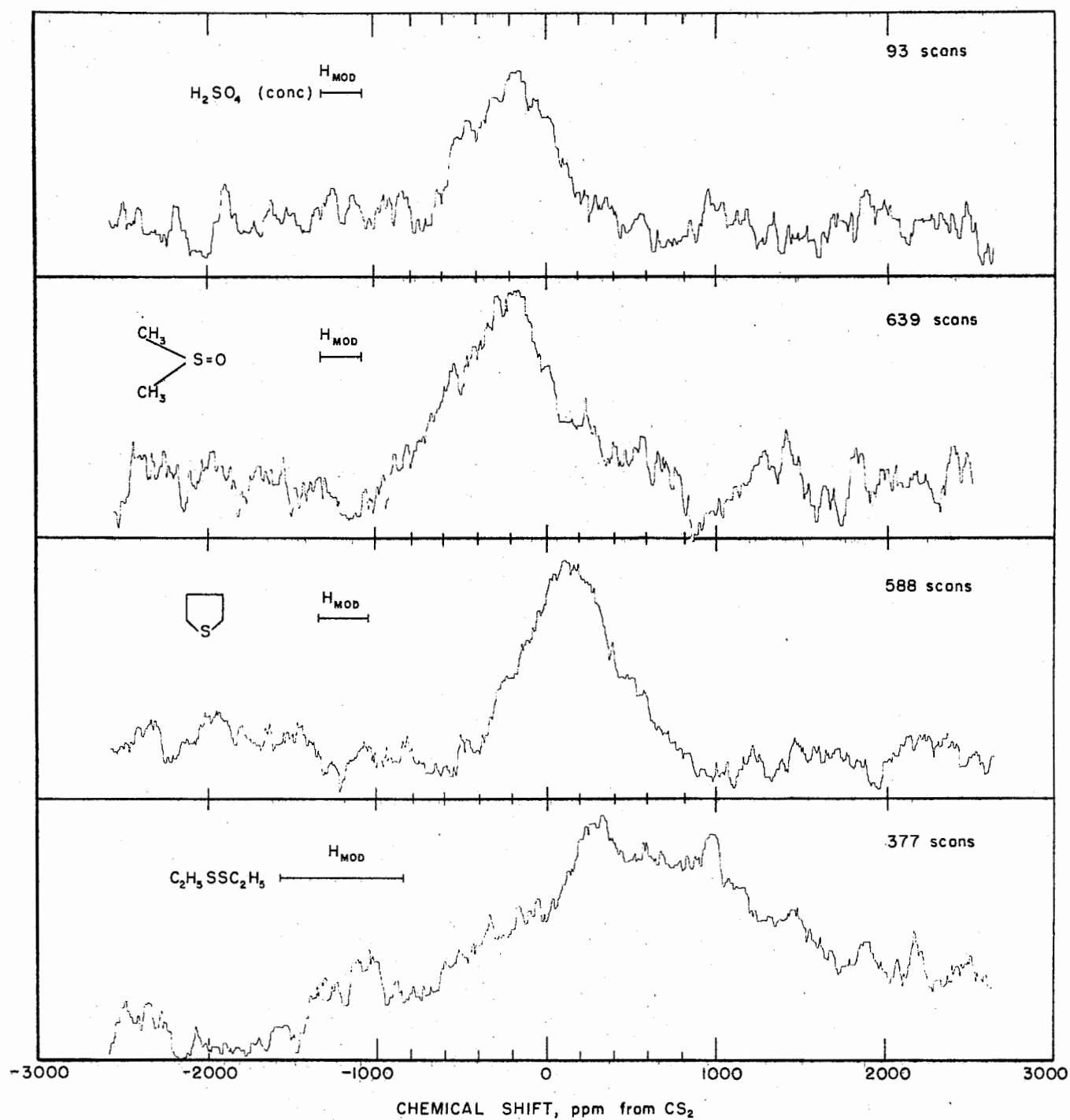
Sincerely yours,

H. L. Retcofsky

R. A. Friedel

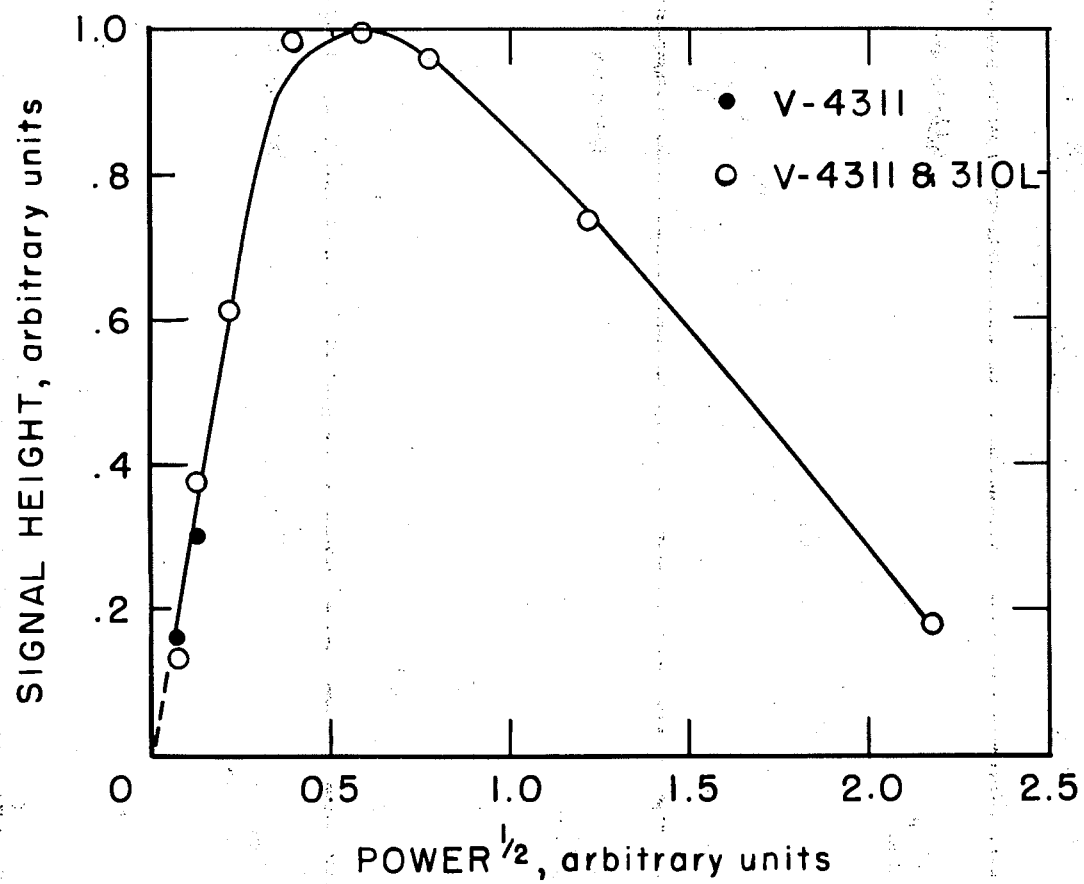Fig. 1 ^{33}S NMR spectra of selected compounds.

Figure 2 – Saturation curve for the ^{33}S resonance of CS_2.

L-11904

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SOUTHAMPTON
SO9 5NH

TEL. 0703-56331
TELEX 47661

16th September, 1971.

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

Dear Barry,

Simplification of spectra of oriented molecules by H-D decoupling.

The use of liquid crystal solvents to give spectra of partially oriented solutes is limited to small molecules because of the multitude of lines obtained when the number of interacting nuclei exceeds about eight. Similar difficulties, of course, occur for isotropic samples, and the technique of spin decoupling may be often used to give simpler spectra. For proton spectra homonuclear decoupling does not work for oriented samples because the spectra are invariably strongly coupled. However, if some of the protons are replaced by deuterium the H-D spin-spin coupling (scalar plus dipolar) is now always a first-order interaction and can be virtually removed by double resonance. There is one added difficulty in decoupling deuterium spins in that the deuterium spectrum is dominated by the interaction between the electric field gradient and the deuterium quadrupole moment, hence the spectra are in two regions separated typically by a few KHz. To decouple the deuterium one must irradiate at two points and moreover a large amount of Rf power is needed to remove the large dipolar couplings. We have achieved such decoupling using a phase modulated Rf centred at the deuterium frequency, so that the frequency spectrum of this signal has strong components at $\pm W_m$, the modulation frequency. The signal source was a Schlumberger frequency synthesizer, and as power amplifier we used the amplification stages of a Heathkitt transmitter type SB-401. The power was supplied to the sample via extra coils wound parallel to the 100 MHz transmitter coils and having a Q of about 20. As an example of the removal of H-D interactions the figure shows the spectrum of CH_3CD_2OH dissolved in a nematic phase. The spectrum is almost first order and consists of a large triplet from CH_3 protons split almost equally by the two

2.

D nuclei and the OH proton, to give sextets. The OH resonance is similarly split by both OH and CD_2. Spectrum B shows the effect of irradiating at 15,350,080 Hz coherently phase modulated at 760 Hz, and also noise modulated at 430 Hz. The coupling to the CD_2 group is removed giving much sharper resonances. To achieve the decoupling about 20 W of Rf power was provided by the amplifier.

We plan to use this technique on molecules which without decoupling do not give a resolvable spectrum, and hence be able to study systems with many protons. Decoupling does seem practicable as a technique, particularly bearing in mind the crudity of our irradiating coils; thus with a properly designed probe it should be possible to decouple with much less power from the amplifier.
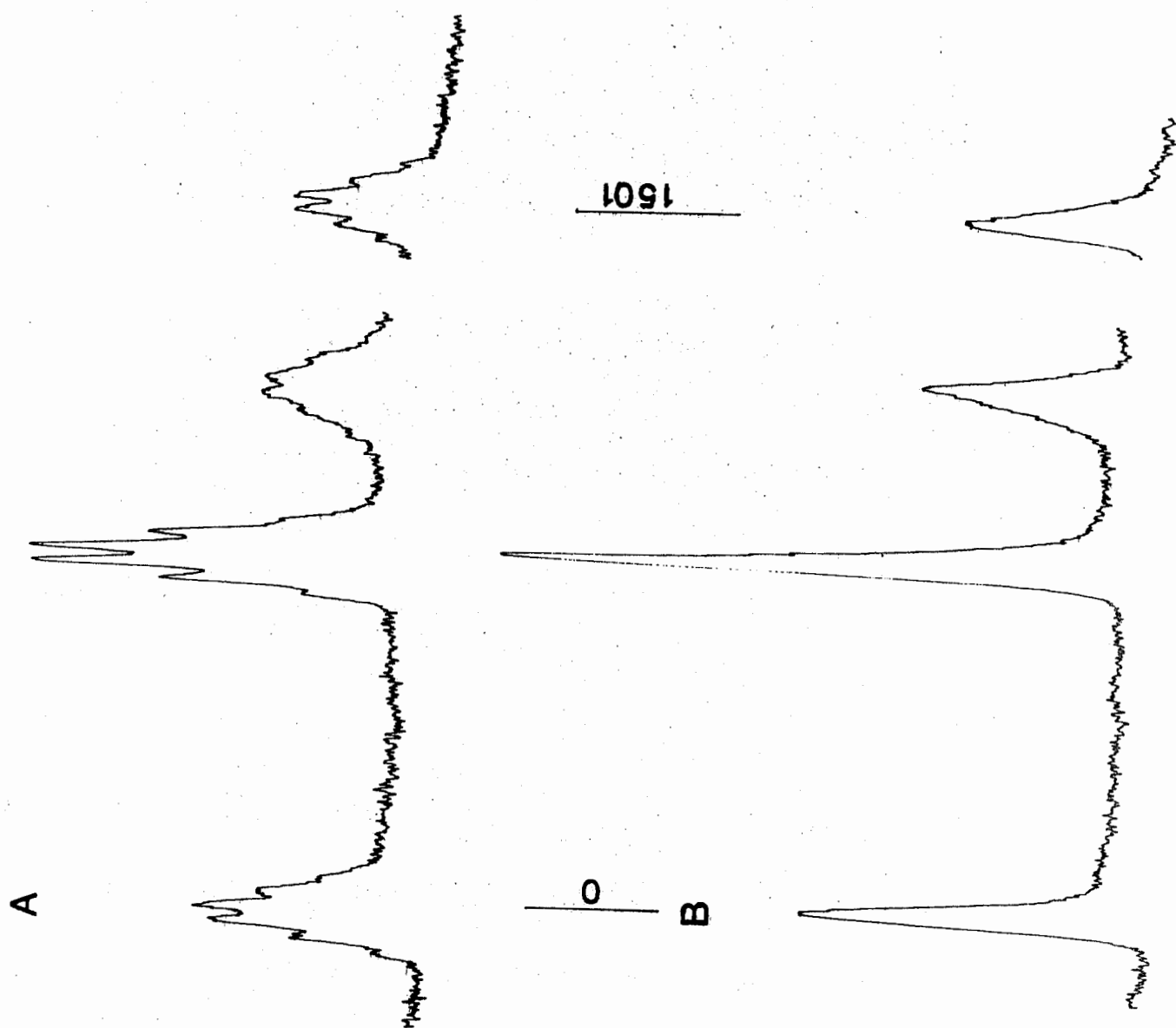
The phase and noise modulator was designed and built by Trevor Wilmshurst of the Department of Electronics, and we also are indebted to Virgil Barboiu, who spent some time here on leave from Iassy, Rumania, for designing the transmitter coils.

Best wishes,

Jim Emsley

J.W. Emsley,   J.C. Lindon,   J. Tabony.

A

B

1091

0

RUTGERS UNIVERSITY *The State University of New Jersey*

September 17, 1971
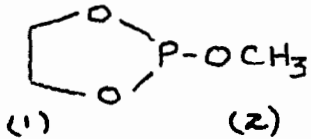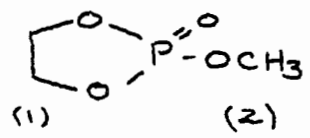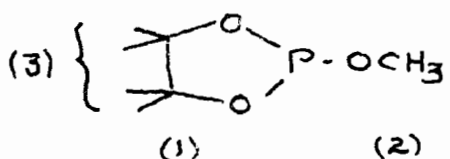
Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Dear Professor Shapiro:

Carbon-13 NMR Spectra of Cyclic Phosphorus Compounds.

We have updated our Varian HA-100 spectrometer with the wide sweep accessory and noise decoupler so we can now do ^{13}C nmr. The modification has been completely satisfactory however obtaining the data is time consuming since we must use the C-1024 to accumulate. Having a vast stock of phosphorus compounds, we decided to investigate some of these first.

We employ an external $^{13}CH_3I$ lock and an eight mm sample tube, all samples are neat except for the adamantyl phosphite (VII) which was run in chloroform. The shifts reported are in ppm relative to tetramethylsilane and the coupling constants are J_{C-O-P} or $J_{C-C-O P}$ in Hz.

I

(1)   64.5 (J = 8.9)
(2)   48.7 (J = 7.1)

II

(1)   67.1 ($w_{1/2}$ = 5)
(2)   54.8 (J = 6.5)

III

(1)   83.7 (J = 7.1)
(2)   49.1 (J = 22.5)
(3)   24.6 & 25.2
        or 24.9 (*J* = 7)

IV
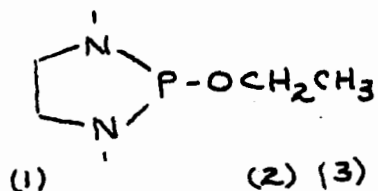
(1)   53.4 (J = 10.5)
(2)   57.9 (J = 6.0)
(3)   17.3 ($w_{1/2}$ = 6.5)

V
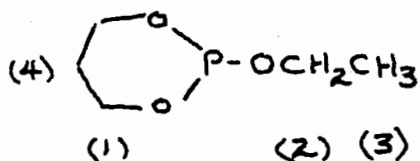
(1)   58.9 ($w_{1/2}$ = 5.5)
(2)   58.2 (J = 19.2)
(3)   16.6 (J = 4.5)
(4)   28.6 (J ~ 5)

VI
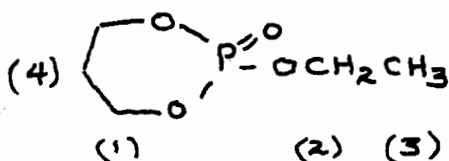
(1)   69.1 (J = 7.3)
(2)   62.8 (J = 5.1)
(3)   15.8 (J ~ 6)
(4)   26.2 (J = 6.5)

VII
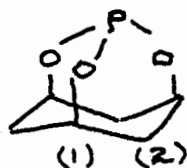
(1)   67.4 ($w_{1/2}$ = 4.0)
(2)   36.0 (J = 4.7)

VIII
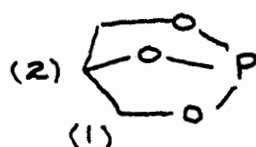
(1) 67.9 ($w_{1/2}$ = 4.0)
(2) 75.0 (J = 5.5)

IX
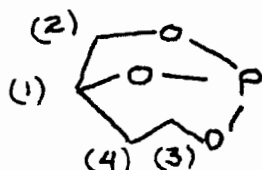
(1) 71.8 (J = 3.0)
(2) 68.3 (J = 6.0)
(3) 59.1 ($w_{1/2}$ = 4.0)
(4) 32.1 (J = 5.0)

    It is of interest to note that a carbon in a six membered ring cyclic phosphite shows no coupling, or very small coupling, to phosphorus (atom (1) of compounds V, VII and VIII). This is not the case for the corresponding phosphate (VI) nor the five membered ring compounds.

The assignments of the ^{13}C absorptions for the 3,2,1 phos-phite (IX) are based partly on CW decoupling experiments (in benzene). The 71.8 ppm absorption must be associated with a tertiary carbon, the other carbons are all secondary. Atom (4) is the most shielded, thus we assign it the 32.1 ppm absorption. The fact that carbon (3) is part of a six membered ring makes us feel that it absorbs at 59.1 ppm with little if any coupling to phos-phorus.

We are continuing to investigate these types of compounds including some phosphoranes.

Sincerely yours,

Dorothy Z Denney

DZD:mhs   Dorothy Z. Denney   Dennis W. White[*]

[*]current address

c/o Peace Corps Ghana

P.O. Box 5796

Accra North

Ghana

THE UNIVERSITY OF ROCHESTER

COLLEGE OF ARTS AND SCIENCE

RIVER CAMPUS STATION

ROCHESTER, NEW YORK 14627

DEPARTMENT OF CHEMISTRY   September 21, 1971

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

^{13}C NMR of Organic Radicals

Dear Dr. Shapiro:

We have recently been attempting to obtain natural abundance ^{13}C spectra of some organic free radicals. This type of investigation presents some special experimental difficulties because of the extremely short ^{13}C relaxation times (ca 100-200 µ sec.). Our experiments have been conducted with a pulsed spectrometer which is interfaced with a Digital Equipment PDP-12 computer. Initial attempts to obtain spectra from the Fourier transform of signal averaged free induction decays were somewhat unsuccessful because of problems in synchronizing the computer with the spectrometer (2-4 µ sec. of jitter between the sync. pulse and the start of data acquisition), the relatively long time to digitize a given point (20 µ sec/point), and field independent instrumental signals which are associated with the high powered pulse.

We have found that we can observe the ^{13}C spectra of some radicals through use of a PAR boxcar integrator in a field swept pulsed experiment. In this mode of operation, the gate of the boxcar is opened for a time longer than the free induction decay after each pulse and the field is swept. The boxcar integrates the free induction decay over the time which the gate is opened. Since only the DC components give a non zero integral, the normal absorption spectrum is obtained when the field is swept. The output of the boxcar can be recorded directly or fed into the computer for normal signal averaging. A typical spectrum obtained by this technique is shown in the figure. This technique is analogous to a C.W. experiment but takes advantage of the higher power available from the pulsed spectrometer.

This technique is intrinsically less efficient than taking the Fourier transform of a computer averaged free induction decay. We are presently building a new clock for the PDP-12 which should give us better synchronization and hope to add a faster analog to digital converter in the near future. In addition we are trying to develop a data processing technique which will remove instrumental artifacts associated with the high powered R.F. pulse.

As an additional point we might note that we have been using a radio frequency magic tee to isolate the receiver from the transmitter. This device allows the use of a single coil probe without using $\lambda/4$ length cables
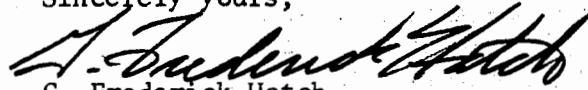
Dr. Bernard L. Shapiro   -2-   September 21, 1971
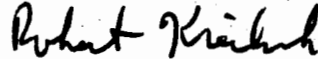
and eliminates some of the diode switches. High powered magic tees are available from Electron Navigation Industries, Rochester, New York.

Sincerely yours,

G. Frederick Hatch

Robert Kreilick

RK:lcb
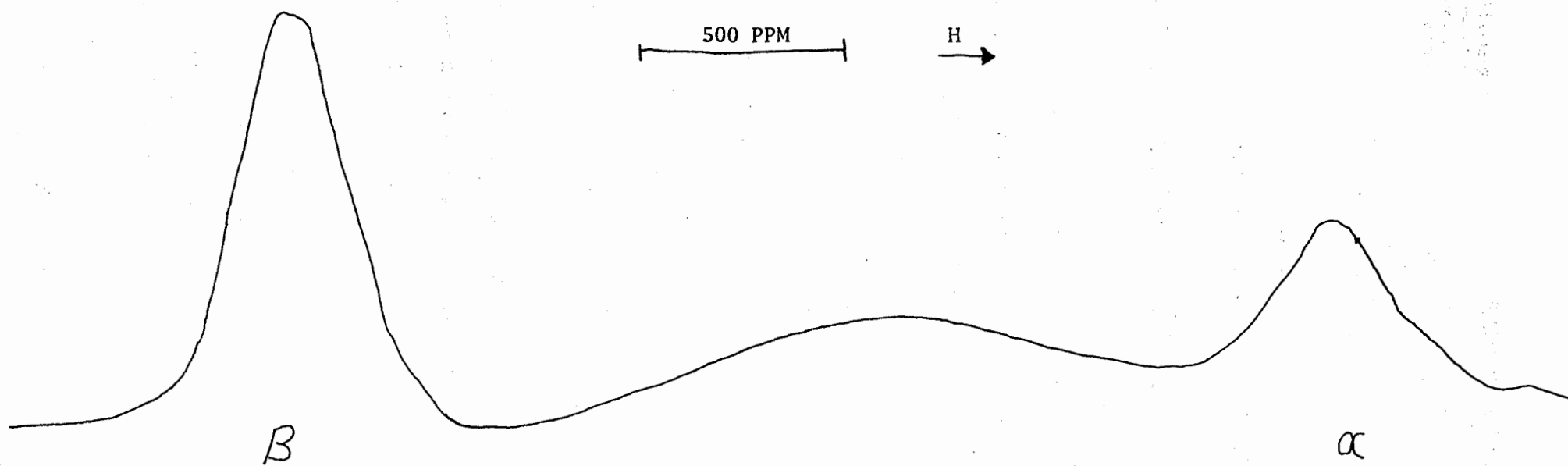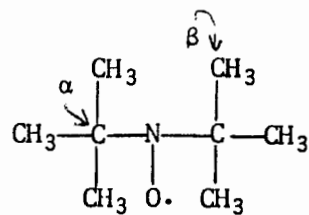
NMR SPECTRUM OF:

500 PPM

H →

β

α

ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT

Albrecht Mannschreck, Bernd Kolb

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

Cyclohexadienones. — Postdoc

Dear Professor Shapiro,

our interest in enamines and hydrazones[1] led us to investigate compounds like $\underline{1}$ (representing one resonance structure of an enamine) and $\underline{2}$ (representing a hydrazone). The τ-values for t-Bu^2/ t-Bu^6 and for H^3/H^5 may be reversed as we have no compelling evidence for these correlations.

(Figures represent τ-values in d_6-acetone.)
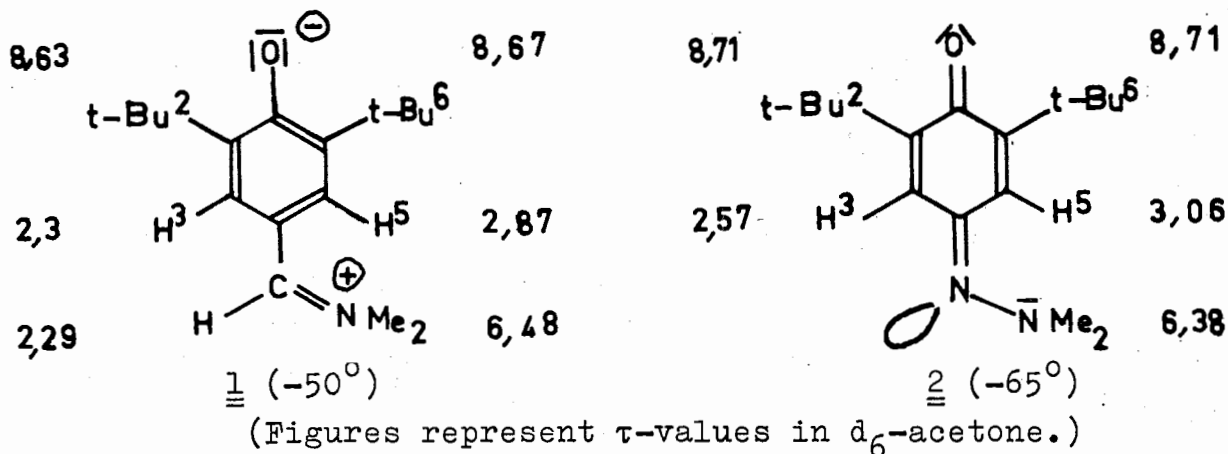
At low temperature compound $\underline{1}$ in d_5-pyridine/CD$_2$Cl$_2$, 6:1, shows two N-methyl signals which coalesce at -46°; $\Delta G_c^{\neq} = 12.4 \pm 0.2$ kcal/mole represents the barrier to rotation about the C–N bond. The C–C barrier[2] amounts to 14.5 ± 0.4 kcal/mole, obtained by coalescence of the H^3 and H^5 doublets ($J_{35} = 3$ Hz) at $+18^{\circ}$ in d_5-nitrobenzene. Therefore, this compound must be described by both, the dipolar benzenoid imonium resonance structure $\underline{1}$ and a quinoid resonance structure with the C=C–$\overline{\text{N}}$ fragment. On the other hand, $\underline{2}$ is depicted correctly by the quinoid formula, while no benzenoid resonance structure contributes significantly to the

ground state. This is true because the N-methyl signal is not split in the solvents we tried ($\Delta G_C^{\neq} < 10$ kcal/mole) and because the H^3 and H^5 doublets ($J_{35} = 3$ Hz) do not broaden at $+135°$ and below ($\Delta G_C^{\neq} > 21$ kcal/mole). We suggest the following reason for this striking difference[3]: The barriers for $\underline{1}$ show that the cyclohexadiene system attracts electrons. In $\underline{2}$ this attraction is roughly compensated by the polarization $\text{C=}\overline{\text{N}}\text{-} \longleftrightarrow \overset{\oplus}{\text{C}}\text{-}\overset{\ominus}{\overline{\text{N}}}\text{-}$ of the hydrazone bond.

Compounds $\underline{1}$ and $\underline{2}$ are protonated at the carbonyl oxygen in a CF_3COOH/C_3F_7COOH mixture. An imonium ion $RCH=\overset{\oplus}{N}Me_2$ is formed from $\underline{1}$, a diazenium ion $RN=\overset{\oplus}{N}Me_2$ from $\underline{2}$. We are now looking at the cis-trans isomers of similar diazenium ions[4] by n.m.r.

This fall, we shall move to another university: Regensburg, Bavaria. The address will be:

Fachbereich Chemie
Universität Regensburg
D-84 Regensburg, Germany.

A T-60 and an XL-100 spectrometer are in operation; ^{13}C and FT facilities are promised by Varian for december 1971. A postdoctoral position is vacant.

Sincerely yours,

Albrecht Mannschreck   Bernd Kolb

1) A.Mannschreck and U.Koelle, Tetrahedron Letters 1967, 863;Chem. Ber. 102, 243 (1969); Angew.Chem.Internat.Edit. 8, 528 (1969).
2) The height of this barrier is unusually solvent dependent:14.8 kcal/mole ($25°$) in d_6-acetone; 15 ($22°$) in d_5-pyridine/CD_2Cl_2, 6:1; >16 ($>46°$) in CS_2; 20.3 ($89°$) in d_8-toluene. Comments are welcome.
3) A.Mannschreck and B.Kolb, Chem.Ber., submitted for publication. Preprints available.
4) A.Mannschreck and T.Burgemeister, unpublished results.

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

September 28, 1971

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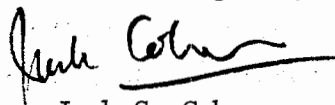College Station, Texas, 77843

Dear Barry:

In response to your timely reminder I will briefly summarize our current work,

1) We have obtained chemical shift data at 60 MHz for the imidazole ring protons of histidine and its carboxyl and amino blocked derivatives. The titration data over a wide pH range for these resonances show inflections in the titration curves due to interaction (competition for protons) between the amino and carboxyl groups and the imidazole side chains. (Sachs, Schechter and Cohen, J. Biol. Chem., in press).

2) A general equation has been derived for such titration curves resulting from interaction between two titrating groups. Computer curve-fitting enables the characteristic pK values for these model systems to be obtained (Shrager, Cohen, Heller, Sachs and Schechter, submitted to Biochem.).

3) These curve-fitting methods have been applied to extensive titration data obtained at 220 MHz for the His C2 proton resonances of ribonuclease. Our analysis indicates that the two active site histidine residues (12 and 119) are not interacting with each other as has been suggested, but His 119 is interacting with a group of pK 4.5, which is probably the carboxyl of Asp-121 (manuscript in preparation). This work has been summarized recently (Fed. Proc., 30 1293 (1971), Abst. 162nd ACS Natl. meeting, Biol. Chem. No. 160, Washington, D.C., 1971).

Your readers may also be interested in two other recent publications. The folding of S. Nuclease, Magnetic Resonance and Fluorescence Studies of Individual Residues, H. Epstein, A. N. Schechter and J. S. Cohen, Proc. Natl. Acad. Sci. (US) 68 2042 (1971). PMR Studies of Cyclic Derivatives of Phosphorus Oxy-acids, G. M. Blackburn, J. S. Cohen and I. Weatherall, Tetrahedron 27 2903 (1971).

Kindest regards,

Jack S. Cohen
Physical Sciences Laboratory

Title: Son of His

NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

OTTAWA, CANADA
K1A OR6

29th September 1971

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

SOME COMMENTS ON THE XL-100 FT SYSTEM
- $^3J_{^{31}P-^{13}C}$ COUPLINGS IN NUCLEOTIDES - DMSO BEWARE AGAIN.

Dear Barry:

We have had an XL-100-15 for 18 months; for the last 8 months
we have also been operating in FT mode on ^{13}C and ^1H. The
instrument has had a lot of down time, but most of this can
be attributed to its being the prototype. When it operates,
it does so extremely well. Since the FT installation was
completed the instrument has been running 24 hrs/day,
7 days/week with very little difficulty. Figure 1 is a Fourier-
transformed ^1H spectrum (1000 Hz wide, disregard absolute ppm)
of an 0.01M solution of β-pseudouridine in D_2O containing 0.1M
DSS and approximately 0.2M HDO. The strong DSS and HDO peaks
give an opportunity to test the dynamic range of the FT system.
Figure 2 gives a 125 Hz blowup of the ribose region of the
spectrum. On comparison with the c.w. spectrum run under
optimal conditions[1], it is clear that the FT spectrum contains
no aberrations due to dynamic range or poor resolution. The
intrinsic resolution of this spectrum is 1 Hz. If one had
narrower lines in the spectrum he would be in more trouble
however, due to the intrinsic limitation that number of data
points taken = 2 × acquisition time × sweep width. To get a
reasonable number of data points for higher resolution one
would have to go to a longer acquisition time, which would mean
a lot of time spent looking at the very weak part of the free
induction decay. Thus, he would have lost the principal
advantage of FTNMR - building up S/N rapidly. Neveretheless,
for studies of medium to large biological molecules, with line-
widths generally > 1 Hz, the instrument performs quite well.

.....2

Professor B. Shapiro   2   29 September 1971

Turning to ^{13}C, we show in Fig. 3 a proton noise-decoupled
Fourier-transformed spectrum (54K accumulations) of polyuri-
dylic acid (molecular weight 130,000) and comparison with the
spectra of uridine (12K) and uridine-5'-phosphate (12K).
These are spectra of 0.2M solutions in D_2O at 37°C with 5000 Hz
sweep widths in 4096 points (resolution 2.4 Hz). Data acquisi-
tion time and pulse delay time are 0.4 and 0.8 sec. respectively.
Couplings between ^{13}C and ^{31}P are manifest in the spectra of all
nucleotides. Two bonds $^{31}PO^{13}C$ couplings are centered around
5 Hz while three bond $^{31}POC^{13}C$ couplings vary between 2-9 Hz
and apparently depend on dihedral angle in a manner similar to
the Karplus relationship for $^1HCC^1H$ and $^{31}POC^1H$ three bond
couplings. These couplings can be resolved in the spectra of
polyU when we do a 2500 Hz transform. They should prove very
useful in determining the backbone conformations of poly-
nucleotides.

The gyrocode decoupler works fine on high power – we use it
regularly to decouple ^1H from ^{13}C or ^{31}P. It is low on power
for ^1H-^1H decoupling, but remarkably free of beats. We have
decoupled groups of lines separated by only 20 Hz. We have
not as yet received any of the other decoupling bands.

Thus, on the whole the spectrometer satisfies most of the cri-
teria we established when be bought it. The biggest problem
for us has been finding optimal conditions for running spectra –
pulse widths, acquisition times, pulse delays, etc. This would
be the same for any spectrometer.

In last year's TAMU NMR[2] I mentioned that we had noticed some
weird effects of DMSO on aromatic amino acids. Since then
Roxanne Deslauriers has found that this solvent causes rapid
denaturation of the octapeptide hormone lysine vasopressin.
Many studies have already been reported on biological compounds
in this solvent, so I feel obliged to repeat the warning.

Yours sincerely,
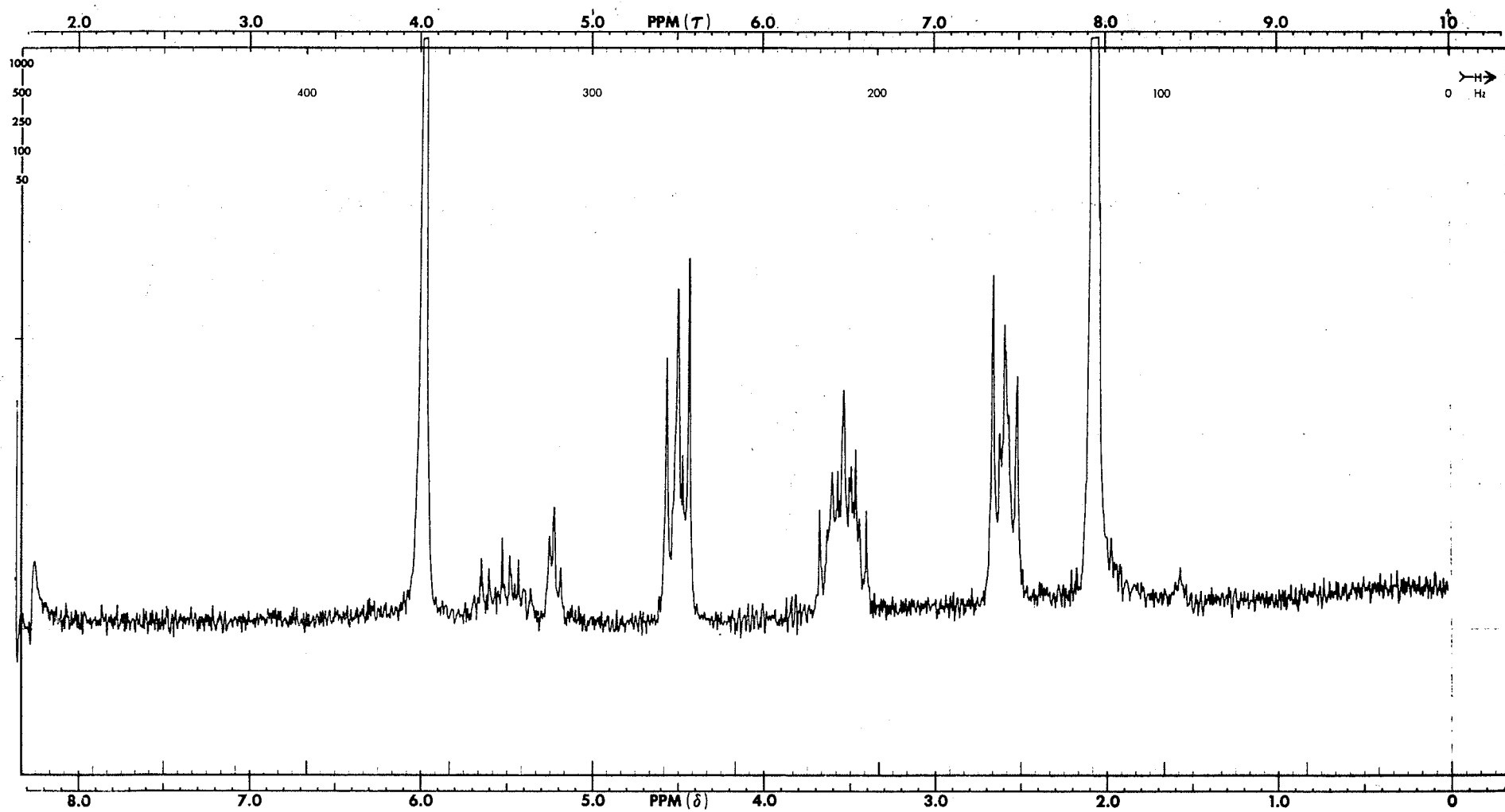
Ian C.P. Smith   H.H. Mantsch
ICPS:hsc

[1] F.E. Hruska, A.A. Grey, and I.C.P. Smith, J.A.C.S. 92, 214
    4088 (1970).

[2] I.C.P. Smith, TAMUNMR 146, 21 (1970).

Fig.1

Fig.2

Fig.3

4000   3000   Hz   2000   1000   0

PPM

193.5   128.5   78.4   41.9
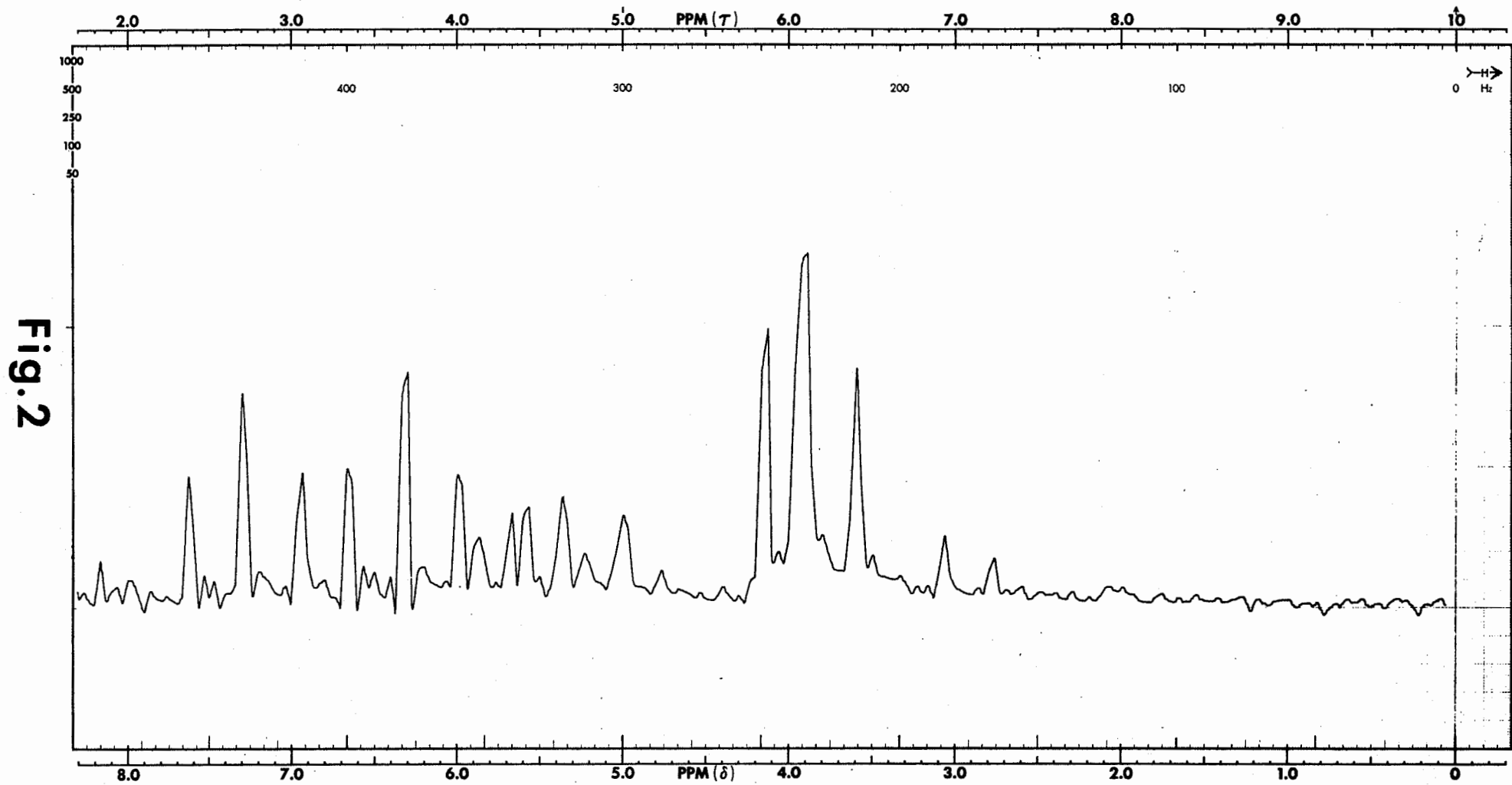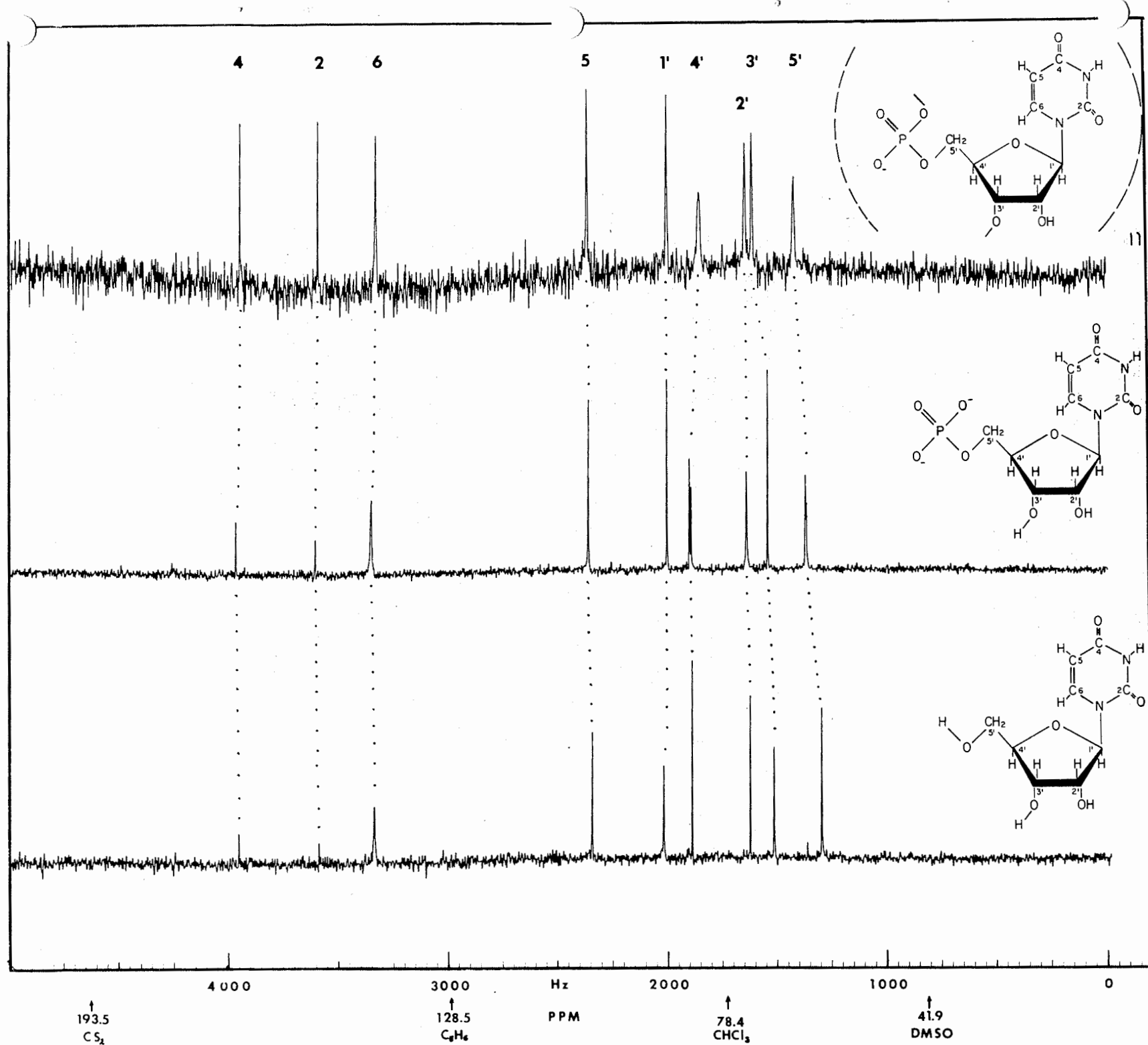CS₂   C₆H₆   CHCl₃   DMSO

157-35

BP RESEARCH CENTRE

SUNBURY-ON-THAMES

MIDDLESEX

ENGLAND

FAST SUB-ROUTINE FOR MATRIX DIAGONALISATION IN NMR COMPUTER PROGRAMS

The method for diagonalisation of symmetric matrices which has been used most extensively in computer programs for NMR spectral analysis is that due to Jacobi. The Jacobi method of matrix diagonalisation is an infinite iterative process, employing successive 2 by 2 rotations, the procedure being terminated in practice when the off-diagonal elements are smaller than some preset value. By comparison with more modern procedures, the Jacobi method is slow and subject to larger round-off errors because of the many operations involved. Therefore a reduction in computer run time may be effected by using a more efficient diagonalisation procedure. This is important if diagonalisation time is the limiting factor.

The more modern methods for diagonalising a symmetric matrix involve two steps: first the reduction of the matrix to tridiagonal form and then diagonalisation of the tridiagonal matrix to yield the eigenvalues and eigenvectors. The most efficient method for finding the eigensystem is based on Householder's tridiagonalisation of a symmetric matrix (1), followed by the QL algorithm for tridiagonal matrices (2). The first part of this method, the tridiagonalisation step, is fast and involves a finite iterative process. The algorithm then used to diagonalise the tridiagonal matrix is also fast, incorporating techniques by which each eigenvalue and eigenvector is found independently, so reducing round-off errors. The combination of these two algorithms can effect a significant reduction in computing time compared with the Jacobi method of diagonalisation; the larger the matrices to be diagonalised, the greater is the time saving.

R.A. Davidson

for S.A. Knight

(1) R.S. Martin, C. Reinsch and J.H. Wilkinson, Numerische Mathematik, 11, 181 (1968).

(2) H. Bowdler, R.S. Martin, C. Reinsch and J.H. Wilkinson, Numerische Mathematik, 11, 293 (1968).

Texas
A
M **&**

University
N – M – R
Newsletter

POLICIES AND PRACTICAL CONSIDERATIONS

1. Policy: The TAMU NMR Newsletter (née MELLONMR, then IIT NMR Newsletter) is envisaged as a means for the rapid exchange of information between active workers in the field of nuclear magnetic resonance. As such, it will serve its purpose best if the participants impart whatever they feel will be of interest to their colleagues, and inquire concerning whatever matters interest them. Since the participant is clearly the best judge of what he considers interesting, our first statement of policy is "We print anything". (This is usually followed by the mental reservation "that won't land us in jail".) Virtually no editorial functions are performed, although I feel the time has come when contributions dealing with the likes of how to clean spectrometer cooling coils, still another discovery of non-equivalent methylene protons, etc., should not be considered adequate. The TAMU NMR Newsletter is not, and will not become, a journal. We merely reproduce and disseminate exactly what is sent in. Foreign participants should not feel obliged to render their contributions in English.

2. Subscriptions: A single subscription is $50.00 per year. A 50% academic or personal discount is available. Organizations and individuals are also invited to consider becoming a Contributor or Sponsor of the Newsletter and to have their organization's name appear in the appropriate list on the back of each month's Newsletter, as well as the satisfaction of knowing they are helping keep the Newsletter in a solvent configuration. We will be happy to provide further details to anyone interested.

We are willing to send your issue by air-mail if you are willing to pay the rather formidable air-mail postage; rates and ground rules on request.

Participation is the prime requisite for receiving the TAMU NMR Newsletter; in order to receive the Newsletter, you must make at least occasional contributions to its contents. We feel that we have to be ruthless in this connection and the following schedule is in effect: Eight months after your last contribution you will receive a "Reminder letter". If no contribution is then forthcoming ten months after your last contribution, you will receive the "Ultimatum letter", and then the next issue will be your last. If you are dropped from the mailing list, you can be reinstated by sending a contribution, and you will receive back issues (as available) and forthcoming issues at the rate of nine per contribution. Frequent contrubutions are encouraged, but no "advance credit" can be obtained for these. In cases of joint authorship, either contributor, but not both, may be credited - please indicate to whose account credit should be given.

PLEASE NOTE: A subject of considerable interest and concern to several present and potential TAMU NMR Newsletter participants - as well as to ourselves - is whether the Newsletter ought to contain material which either appears essentially simultaneously in the formal literature (or is presented at a meeting) or is definitely scheduled to appear very shortly (i.e., within a few weeks) after it would appear in the Newsletter. Our attitude is that a TAMU NMR Newsletter contribution should not duplicate, summarize or abstract material which has been published or which will appear in the formal literature within a small number of weeks of the Newsletter account. On the other hand, let it be firmly emphasized that if the appearance in a journal is several months away - as is frequently the case - a brief account (as an abstract with or without a "Preprint Available" notice, a separate informal account, a selection of material from the manuscript, or what have you) sent in to the TAMU NMR Newsletter fulfills one of the very functions which we feel this Newsletter can provide. We trust that a participant will in each case himself apply the criterion of whether or not his contribution will communicate some subject matter to the Newsletter audience before they could read it elsewhere.

3. Public Quotation: Public quotation of Newsletter contents in print or in a talk is expressly forbidden (except as follows), and reference to the TAMN NMR Newsletter by name in the scientific literature is never permissible. We remind you that in order to quote results or use material from the Newsletter, it is necessary, in each individual case, to obtain the prior permission of the author in question and then to refer to the material quoted as a "Private Communication".

If your copy of the Newsletter is shared with other readers, it is your obligation as the actual recipient of the Newsletter to see that these other readers of your copy are acquainted with and abide by the statements of policy and practical considerations.

4. Practical Considerations: (a) All contributions to the TAMU NMR Newsletter should be sent to the undersigned and will always be included in the next issue if received before the deadline dates, which appear on the cover of each issue.

(b) Contributions should be on the minimum (NOTE!!) number of 8-1/2 x 11" (21 x 27.5 cm) pages printed on one side only, with at least 3/4" (2 cm) margins on all sides. Black ink, typing, drawings, etc., on white paper are good; grey or blue ink, typing, etc., on anything is ghastly - i.e., high contrast is essential. We are not equipped to deal with large size pieces of paper - e.g. A-60 charts.

Please conserve space by avoiding double spacing (except where necessary), ultra-wide margins, half-filled pages, etc. In general, please plan and construct your contribution so as to fill the minimum number of pages needed. On the other hand, drawings and spectra lose both eye-appeal and utility when they are too small. However, it should rarely, if ever, be necessary for a contribution to exceed four pages in length, including figures.

Since reproductions of various kinds do not themselves reproduce too well, contributors are urged to submit their photographic originals to us (if the size does not exceed 8-1/2 x 11"), and we will be happy to return these if requested. Some law of physics says that photographic reproductions of fuzzy or blurred originals never come out less fuzzy or blurred.

(c) Please provide short titles of all topics of your contributions, as this will ensure accuracy in preparing the title-page index.

(d) Please do not send in manuscripts, theses, books, etc., and ask us to be your consciences in selecting what should and shouldn't go into the Newsletter.

5. Suggestions: They are always welcome.

B.L.Shapiro
10-4-7

Address for all contributions and inquiries:

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

FROM THE DEPARTMENT OF INORGANIC, PHYSICAL AND INDUSTRIAL CHEMISTRY

DONNAN LABORATORIES GROVE STREET P.O. BOX 147 LIVERPOOL L69 3BX   TEL: 051 – 709 · 6022 EXT.

SECOND   INTERNATIONAL   SYMPOSIUM

ON NMR   SPECTROSCOPY

3rd to 7th July 1972.

The above symposium, organised by the Chemical Society NMR Discussion Group, will take place at the University of Surrey at Guildford.

The programme will consist of lectures by invited speakers and contributed papers dealing with all aspects of high resolution nuclear magnetic resonance spectroscopy. Anyone wishing to present a paper should submit a title and short synopsis (not more than 250 words) to the undersigned, NOT LATER THAN 1st FEBRUARY 1972. Authors of accepted papers will be required to produce a more detailed abstract according to a prescribed format. These abstracts will be circulated beforehand to those proposing to attend the symposium. All enquiries concerning the meeting should be sent to Dr. John F. Gibson, The Chemical Society, Burlington House, London, W1V OBN.

Les Sutcliffe

Dr. L. H. Sutcliffe,
Chairman, NMR Discussion Group.

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