Texas A & M University N-M-R Newsletter

RECEIVED MAY 2 8 1974

No. **188**

May, 1974

Deadline Dates: No. 189:   3 June 1974
                  No. 190:   1 July 1974

All Newsletter Correspondence, Etc. Should Be Addressed To:

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

SPONSORS:

Abbott Laboratories
Bruker Scientific, Inc.
JEOL, Inc.
Dr. R. Kosfeld, Abt. Kernresonanz, Inst. f. Phys. Chemie, TH Aachen (Germany)
The Lilly Research Laboratories, Eli Lilly and Company
The Monsanto Company
Unilever Research (U.K.)
Union Carbide Corporation
Varian, Analytical Instrument Division

CONTRIBUTORS:

The British Petroleum Co., Ltd. (England)
Eastman Kodak Company
E. I. DuPont DeNemours & Co.
International Business Machines Corp.
Nicolet Instrument Corporation
The Perkin-Elmer Company
The Procter & Gamble Company, Miami Valley Laboratories
Shell Development Company

ADVERTISERS:

Bruker Scientific, Inc.   - see p. 2
Electronic Navigation Industries - see p. 14
JEOL, U.S.A., Inc.   - see inside back cover
Nicolet Instrument Corporation   - see p. 24
Nuclear Magnetic Resonance, Ltd. - see p. 30
Varian Instrument Division   - see outside back cover
Wilmad Glass Co., Inc.   - see inside front cover

UNIVERSITY OF CALIFORNIA, BERKELEY

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO   SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY   BERKELEY, CALIFORNIA   94720

March 28, 1974

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

Dear Barry:

We have constructed a device which is quite useful for nmr in all types of systems. This has several novel features, e.g.:

1. Produces a 11166 pulse 387τ sequence with independently adjustable widths and delays. This eliminates all shifts and couplings in any spectrum, including chemical shifts, Kondo shifts, scalar coupling, dipolar coupling, quadrupolar coupling, Knight Shifts, Day Shifts, and Suhl-Nakamura coupling, leaving a simple, clear, easily interpretable spectrum consisting of one sharp line. Analysis of this spectrum is performed automatically.
2. Eliminates automatically large extraneous peaks due to solvents. The solvent to be eliminated is selected by pushbutton out of a collection of 1704 entries. Solvent peaks may also be added.
3. Sensitivity is enhanced by transferring polarization from a large sample maintained in Saclay at 2°K. Polarization is running out so competition is keen and proposals must be submitted for permission to transfer.
4. Operates with 130 frequency synthesizers and a magnetic field calibrated according to the theorem $\omega_o = \gamma H_o$. The lock is external and operates on $^5Li - ^{11}Li$; it is powerful and can be put on another campus.
5. The machine smiles during a spin tickling experiment.
6. Equipped with a 45 KW power transmitter. This is supplied with an answering service to reply to complaints from radio amateurs in Siberia.
7. Optical detection is optional. Sensitivity is so enormous that half a photon has been detected. The other half is being kept spin-locked under close guard of a hyperfine component.
8. The device operates in any frame including the rotating, pulsating, and randomly fluctuating frames.
9. Can do DEFT, TDFT, PRFT, WEFT, LEFT, GLBM, etc., by selecting a combination of four letters. If no experiment exist for a selected combination, the device will invent one and publish a preliminary communication.

This work was hardly supported.

Best regards,

Alex Pines

AP:crh

POLITECNICO DI MILANO
ISTITUTO DI CHIMICA
20133 MILANO - Piazza Leonardo da Vinci, 32
Tel. 292.109 - 292.110

Milano, March 15th, 1974

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

Dear Professor Shapiro,

I have received today your pink letter, so I must apologize again for my delay and I send you immediately our contribution, whose title is:

" ^{1}H and ^{13}C spectra of thietane-1-oxide "

We have continued our n.m.r. investigations on four-membered rings, in particular thietanes. In thietane derivatives only a few complete analysies have been published, whereas many stereochemical assignments are based on approximate n.m.r. results. Moreover the absence of complete experimental data of unsubstituted molecules and the lack of knowledge on their conformation did not allow an adequate test of the theoretical studies. We have analyzed the ^{1}H and ^{13}C spectra of thietane-1-oxide in order to determine the ring conformation and evaluate whether a correlation is possible between structure and n.m.r. parameters, particularly J's, normally used for stereochemical assignments.
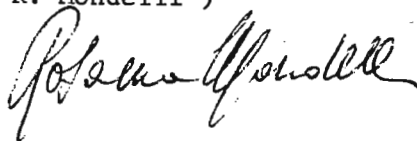
The analysis was carried out first on the spectrum at 300MHz which, although strongly coupled, gave the four chemical shifts and the approximate values of the three-bond couplings and $^2J_{CD}$. The refinement of these parameters and the determination of the remaining ones were obtained by iterative procedure, performed on the spectrum at 100 MHz (fig. 1). From the n.m. r. data in the range of temperature + 190° and - 140°C, evidence was obtained that a strongly puckered structure with the sulphinyl oxygen equatorial is rather more populated than the other one, although the ring inversion rate is fast enough to average the coupling constant values even at low temperature. Increasing the temperature, a slight increase in the population of the less stable conformer (sulphinyl oxygen axial) has been deduced from variations of $^3J_{AC}$ $^3J_{BD}$ $^4J_{BB'}$ and $^4J_{AA'}$.

A complete discussion on the coupling constant values in thietane-1--dioxide and related four-membered heterocycles will appear shortly in a full paper.

The ^{13}C spectrum without ^{1}H decoupling is reported in Figure 2 together with all the coupling constant values, that could be obtained complete of their signs from the 2nd order analysis.

Sincerely yours

(R. Mondelli)
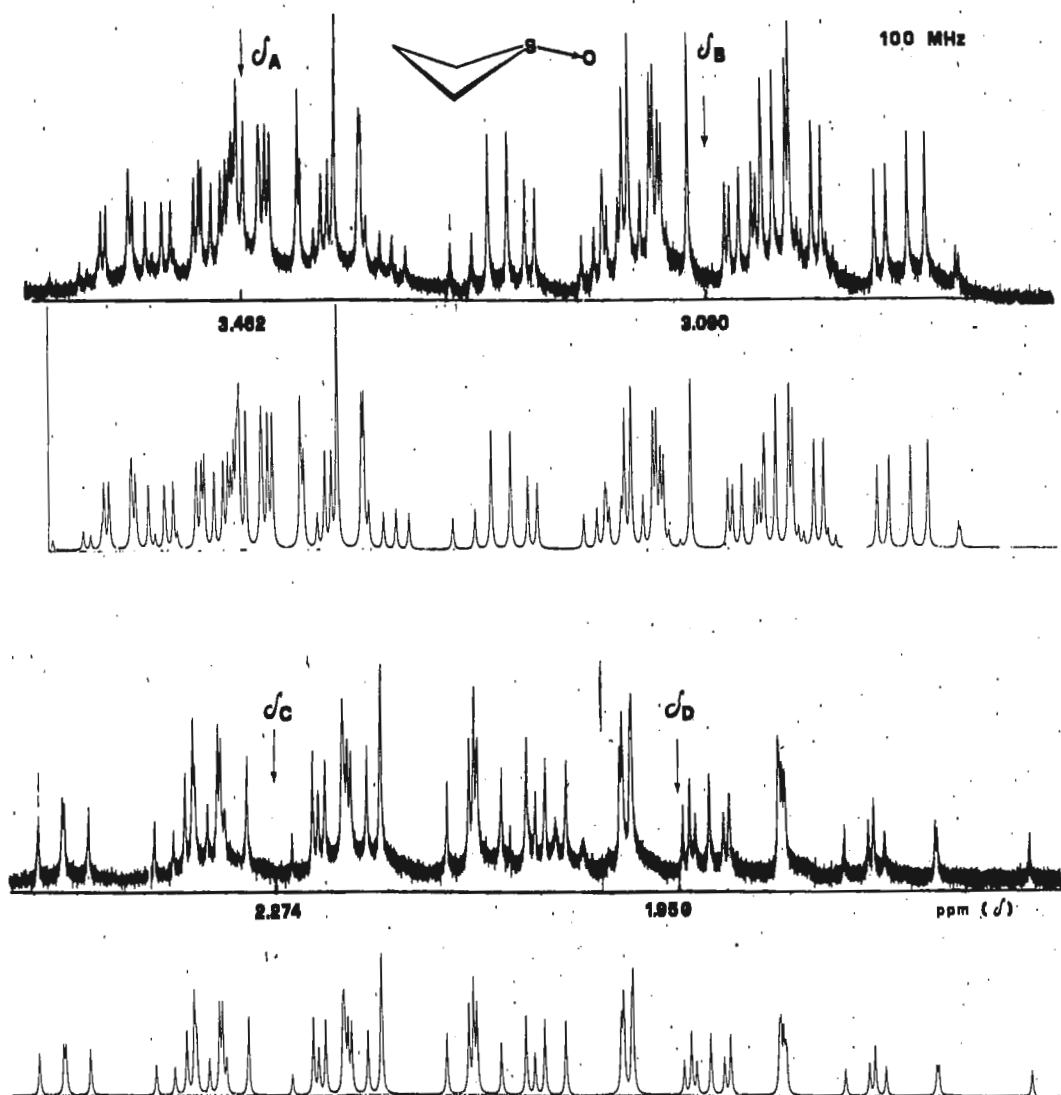
Figure 1

$^2J_{AB}$	$-$ 10.29 $\pm$ 0.005* Hz	acetone-d_6 30°C
$^2J_{CD}$	$-$ 12.69 $\pm$ 0.006	RMS 0.031
$^3J_{BD}$	$+$ 12.53 $\pm$ 0.005	
$^3J_{AC}$	$+$ 1.83 $\pm$ 0.005	*The probable error for
$^3J_{BC}$	$+$ 10.63 $\pm$ 0.006	each parameter should be
$^3J_{AD}$	$+$ 7.49 $\pm$ 0.005	increased at least by a
$^4J_{AA'}$	$+$ 6.10 $\pm$ 0.008	factor of two.
$^4J_{BB'}$	$-$ 0.57 $\pm$ 0.007	
$^4J_{AB'}$	$-$ 0.95 $\pm$ 0.006	

$^{1}J_{C_\alpha H_{ax}}$	+ 141.0
$^{1}J_{C_\alpha H_{eq}}$	+ 147.0
$^{1}J_{C_\beta H_{ax}}$	+ 135.5
$^{1}J_{C_\beta H_{eq}}$	+ 144.5
$^{2}J_{C_\alpha H_{ax}}$	− 3.5
$^{2}J_{C_\alpha H_{eq}}$	− 3.0
$^{2}J_{C_\beta H_{ax}}$	− 4.0
$^{2}J_{C_\beta H_{eq}}$	− 2.2
$^{3}J_{C_\alpha H_{ax}}$	+ 13.0
$^{3}J_{C_\alpha H_{eq}}$	+ 3.5

C_α — 53.3 C_β — 10.4   25 MHz   ppm (δ)
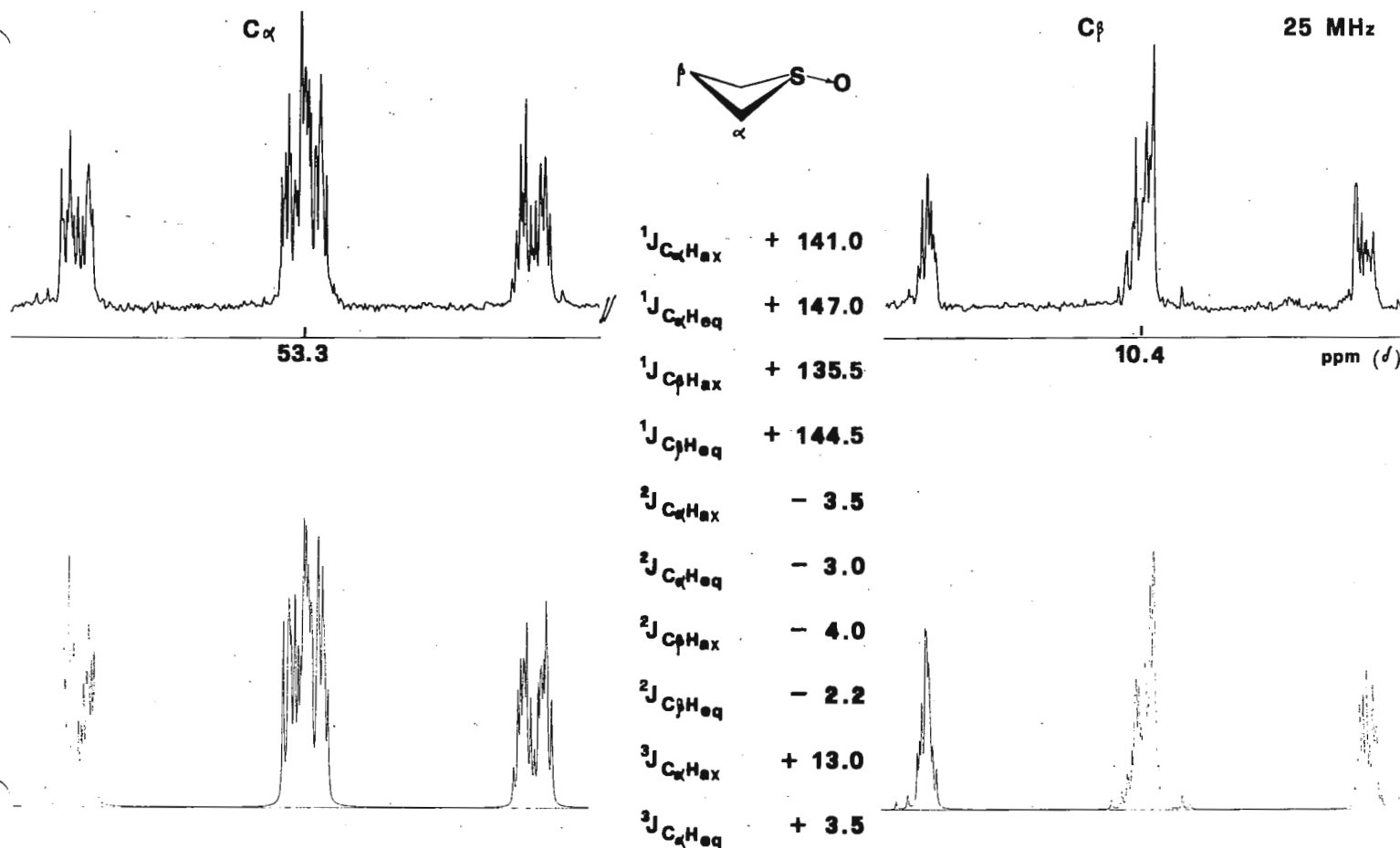
YESHIVA UNIVERSITY

BELFER GRADUATE SCHOOL OF SCIENCE

2495 Amsterdam Avenue / New York, N.Y. 10033 / (212) 568-8400

29 March 1974

Dr. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77043

Dear Barry,

I am also interested in an organic chemist interested in
working on novel compounds of Se (non-toxic), Te and I.
Salary is $8000-$8500. The position begins after Sept. 1.

Yours sincerely,

Jeremy I. Musher

April 1, 1974

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

TITLE: A simple instrumentation amplifier between an NMR and signal
        averaging computer.

Dear Barry:

Please credit this contribution to the Standard Oil (Indiana) subscription.

We would like to describe a simple and effective amplifier to provide
signal conditioning between an existing NMR spectrometer and the Analog to
Digital converter (ADC) of a signal averaging system. The circuit is
suitable for both CW and FFT operation. It provides a high degree of
common mode rejection in order to avoid ground loops and noise pick-up.
It will also generate a $\pm 10V$ offset voltage to properly DC null the NMR
signal before it reaches the ADC. As a result the experimenter may obtain
optimal digital resolution and long signal averaging times without over-
ranging the storage word in the computer system.

Referring to the attached schematic, A_1 and A_2 are respectively, a variable
voltage reference and a summing amplifier. A_3, A_4 and A_5 form a classical
differential instrumentation amplifier. Each input may be floated relative
to ground. In normal operation, inputs 2 and 3 are connected to the analog
output of the NMR receiver. A shield may be connected to the common of the
circuit. It is essential that this shield is not connected to the spec-
trometer or the noise rejection properties of the amplifier will be lost.
The resistors around A_5 must be closely matched to achieve the highest
possible common mode rejection ratio. The signal from the instrumentation
amplifier is summed with the variable reference voltage in A_2. The meter
circuit on the output of A_2 provides a convienent means to null any DC
component from the NMR signal before the signal is passed on to the
computer for averaging.

Additional details of the circuit include two zener diodes across the
input to protect against pulse break-through damage. A spring loaded
switch increases the sensitivity of the meter circuit momentarily for
precise balance near DC null. The decoupling scheme is shown. This scheme

B. L. Shapiro
April 1, 1974

and proper layout practices must be employed to avoid oscillation. The basic bandwidth of the circuit is about 100 KHz with a gain of unity. The bandwidth may be restricted by the addition of C_x to the feedback path of A_2. A more effective approach is to use a tunable active filter on the output circuit, before the ADC. The operational amplifier types illustrated were carefully chosen for their almost ideal phase shift vs frequency characteristics and should not be substituted.

This circuit has been used successfully between a Bruker HFX-90 and a Nicolet 1070, an XL-100 and Nicolet 1080 and in installations involving IBM computer systems.

We hope that this circuit will prove helpful to anyone who is attempting to optimize the transfer of analog data between an NMR and signal averaging computer, regardless of the types involved.

Sincerely yours,

Joe Ray
Standard Oil, Inc. (Indiana)

Bob Santini
Department of Chemistry
Purdue University
W. Lafayette, IN. 47907

GJR:slk

3300 pf

C_x

100K

33K

50K

150K

330K

A_1

33K

33K

A_2

C_x 33K

200K

2K

P.B.—M.C.—N.O.

OUTPUT

+15V

−15V

10-TURN

25-0-25 μA

IN-914A

INPUT

3

1

2

IN4753

A_3

A_4

5K*

5K*

5K*

5K*

5K*

A_5

* = 0.1% RESISTOR
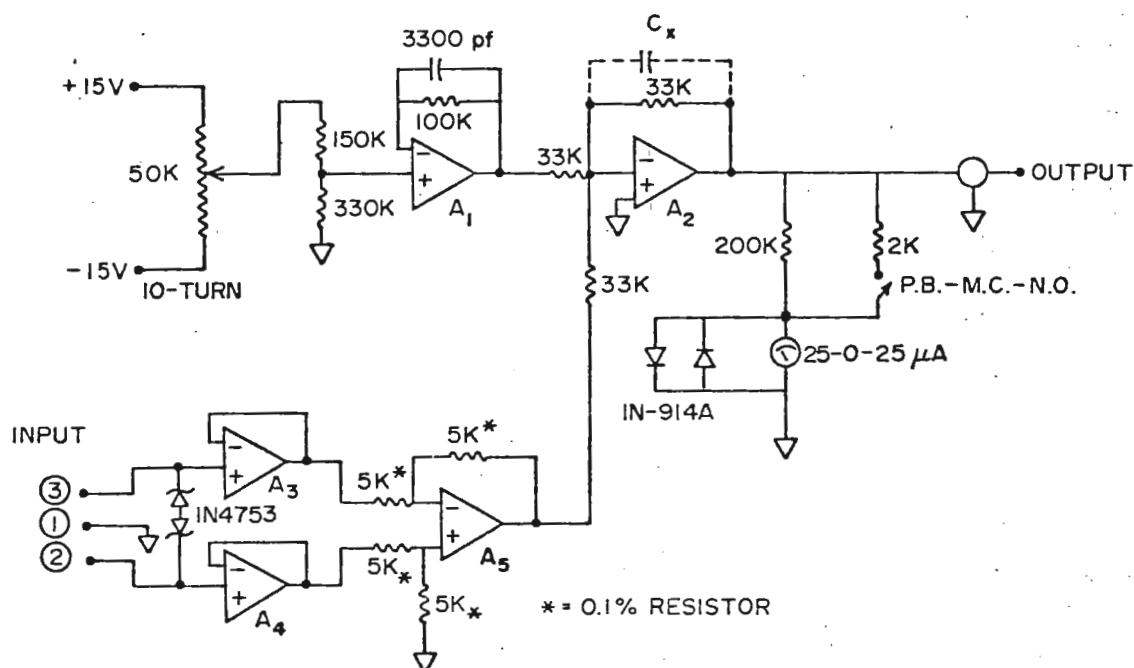
A_1 to A_5 = MOTOROLA
MC-1456CG
or
SIGNETICS
5556C

LARGE BYPASS CAPACITORS
ARE TANTALUM TYPE

C_x = RISETIME ADJUSTMENT—
IS OPTIONAL

250ma

100K

+15V

COMMON

−15V

ANALOG DEVICES
#902

POWER SUPPLY

DECOUPLING SCHEME

+15V

−15V

A_1

A_2

1μf

1μf

.01

.01

A_3

A_4

A_5

4.7

4.7

.01

.01
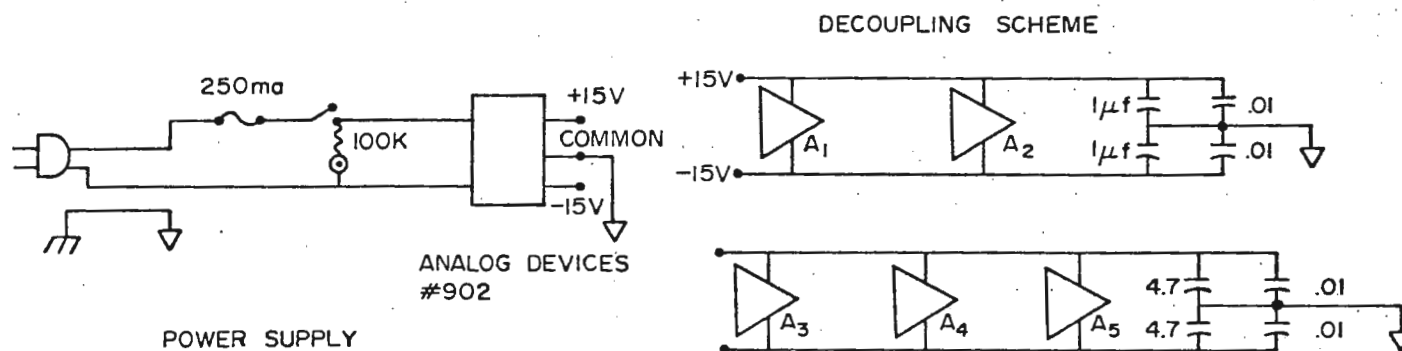
Hunter College

OF THE CITY UNIVERSITY OF NEW YORK | 695 PARK AVENUE, NEW YORK, N.Y. 10021 | DEPARTMENT OF CHEMISTRY

Telephone
360-2351

April 11, 1974

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

Dear Barry:

Title: Postdoctoral Position Available

I am seeking a postdoctoral research associate for a one- or two-year
period beginning 1 September 1974 to collaborate in doing nitrogen-15 nmr.
The research areas include structure-chemical shift correlations, medium effects
on chemical shifts, and applications to biochemically and pharmacologically
important compounds. We also are determining coupling constants between
^{15}N and other nuclei. All the chemical shift work is carried out at the natural-
abundance level of ^{15}N on a JEOL PS/PFT-100 spectrometer with deuterium lock.
In addition, we have become involved in some aspects of instrument modification.

Interested individuals, who should have some nmr experience and preferably
some acquaintance with FT nmr, should contact me at the above address.

Hunter College is located in the upper east side of Manhattan and is easily
accessible to all parts of New York City. Needless to say, we are an equal
opportunity employer.

See you in Raleigh.

Sincerely,

Bob

Robert L. Lichter
Assistant Professor

RLL:bd

UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

Department of Chemistry
(803) 777-5263

April 1, 1974

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

TITLE: Hydrocarbon ^{13}C Chemical Shifts and Postdoctoral Position Available

Dear Barry:

We have been involved recently with the development of a semi-empirical theory of nmr chemical shifts, which could be applied to any atom in the first long row of the periodic table. To properly check the calculations for hydrocarbons, we obtained the ^{13}C chemical shifts of seven hydrocarbons, i.e., CH_4, C_2H_6, C_3H_8, C_4H_2, C_2H_2, C_3H_4, and C_2H_4. These shifts were determined on a Varian CFT-20 in CS_2 solvent with 10% acetone-d_6 added for a lock material. The temperature was -80°C. The data are summarized in the accompanying table. It is important to note that the value of the chemical shift between CH_4 and C_2H_6 is -11.23 ppm. Our value is excellent agreement with the one reported by Strong, et al., J. Magn. Resonance, 9, 145 (1973).

Also I would like to let your readers know of the availability of a nonteaching postdoctoral position in my laboratories. The research involves the study of the nmr parameters (shifts and T_1's) for the pyridine dinucleotides interacting with several enzymatic systems. The nuclei of interest are ^{1}H, ^{2}H, ^{13}C, ^{15}N and ^{31}P. Furthermore, the postdoctoral (hopefully) will be involved in some fundamental modification to the XL-100, e.g. quandrature phase detection, etc. The salary for this position is $8500. The University of South Carolina is an equal opportunity/ affirmative action employer.

I would ask any interested individuals to write or phone me (803-777-6039) for further information.

Sincerely,

Paul D. Ellis
Assistant Professor

PDE/scc

Carbon-13 Chemical Shifts of Some Representative
Hydrocarbons

Chemical Shift

Compound	$\delta (CS_2)^a$	$\delta (TMS)^b$	$\delta (CH_4)$
CH_4	195.61	2.8	0.0
C_2H_6	184.38	−8.4	−11.23
$\underline{CH}_3CH_2\underline{CH}_3$	175.67	−17.1	−19.94
$CH_3\underline{CH}_2CH_3$	175.50	−17.3	−20.11
$H\underline{C}\equiv C-C\equiv \underline{C}H$	126.34	−66.5	−69.27
$HC\equiv \underline{C}-\underline{C}\equiv CH$	124.63	−68.2	−70.98
C_2H_2	119.67	−73.1	−75.94
$H_2\underline{C}=C=\underline{C}H_2$	118.18	−74.6	−77.43
C_2H_4	69.34	−123.5	−126.27
$H_2C=\underline{C}=CH_2$	−19.78	−212.6	−215.39

a) Internal CS_2 as determined on a Varian CFT-20 operating at −80°C locked to a 10% acetone-d$_6$. Positive chemical shifts denote shifts to higher shielding.

b) External TMS using the relationship $\delta (TMS) = \delta (CS_2) - 192.8$

CHIMIE ORGANIQUE PHYSIQUE

NANTES, le 4.4.74

UNIVERSITÉ DE NANTES
U E R DE CHIMIE

38, Bd Michelet - 44 - NANTES
B. P. 1044
Tél. (40) 74-50-70

Professor Bernard L. SHAPIRO
Department of Chemistry
TEXAS A-M University
College Station

TEXAS 77843

Dear BARRY,

Dependence of the coalescence temperature in two-site chemical exchange studies. A complement to Professor GUTOWSKY'S letter.

An alternative to Professor's GUTOWSKY (1) way of obtaining enthalpies and entropies of activation from the rate constant at the coalescence point, is conveniently offered by the simultaneous use of ^{1}H and ^{13}C resonance.

Some results concerning the hindered rotation around C-N bonds in amidines are represented in the table. The presence of many diastereotopic nuclei improves the quality of the method as shown for compound 2. Consideration of different sites is certainly a source of discrepancies although the intrinsic variation of the chemical shift with the temperature must not be excluded in the one-site multi-frequencies experiments.

The method making use of both ^{1}H and ^{13}C resonance is somewhat cheaper than the elegant procedure of Professor GUTOWSKY since :

Σ US $ (A 60 + HA 100 + HR 220 + further developments of superconducting solenoïds) $\gg$

Σ US $ (CFT 20 + XL 100)

It may also be noted that a twenty fold range in frequency and rates may easily be covered by this technique.

	^{1}H (a)				^{13}C (b)			
	CFT 20*		XL 100		CFT 20*		XL 100	
	$\Delta\nu_\infty$	Tc	$\Delta\nu_\infty$	Tc	$\Delta\nu_\infty$	Tc	$\Delta\nu_\infty$	Tc
$C_6H_5-N=CH-N(CH_3)_2$ 1 (a)	6.2	-	7.8	278	116	-	145	318
$C_6H_5-N=CH-N(CH_2CH_3)_2$ 2 ba b	13.4 -	-	16.8 -	275 -	128 56	-	160 70	304 294

* At the present time, the values relative to the CFT 20 spectrometer are virtual since we do not dispose of such apparatus, but this negligeable fact does not detract from the validity of the method. Other data will be abailable in ref. (2).

        The accuracy of the results is good for the ΔG^*, acceptable for the ΔH^* and poor for the ΔS^* values ; it is limited, as Professor GUTOWSKY points out, by the accuracy of the temperature measurements. With the vast shortage of funds which characterizes our day and age, greater accuracy perhaps should be looked for in a drastic improvement of the "magic box", rather improperly called "temperature controller V6040 " (4), or in self-made devices, than in superconducting solenoids.

        Sincerely yours.

G.J. MARTIN   M.L. MARTIN

	$\Delta G^*/T$ kcal.m^{-1}	ΔH^* kcal.m^{-1}	ΔS^* cal.Kelv^{-1}
1	$14.9/318 \pm 0.1$	11.9 ± 2	-8 ± 4
2	$14.3/304 \pm 0.1$	12.2 ± 1.8	-7 ± 4

(1) H.S. GUTOWSKY - TAMU Newsletter 186, 25, (1974) -

(2) M.L. FILLEUX, N. NAULET, J.P. DORIE, G.J. MARTIN - Tetrahedron Letters 1974 - in press -

(3) G.J. MARTIN, D. LE BOTLAN, M.L. FILLEUX - TAMU Newsletter, 182, 30,(1973) -

(4) I suppose that the problem of controlling the temperature in NMR inserts is not limited to this apparatus but we have not direct experience of other commercial systems.

DEPARTMENT OF CHEMISTRY

THE UNIVERSITY OF GEORGIA   ATHENS, GEORGIA 30602

404 542-2626

April 4, 1974

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

POSTDOCTORAL POSITION

Dear Prof. Shapiro:

I solicit candidates for a postdoctoral position in my laboratory to begin July 1, 1974, or as soon thereafter as possible.

The research will involve CIDNP from reactions of stable free radicals (radical anions) in low magnetic fields. CIDNP will be detected after these very fast reactions are complete using Fourier nmr spectroscopy. The radical pair theory and its parameterization will be tested through efforts to simulate the observed CIDNP spectra through calculations based on those models.
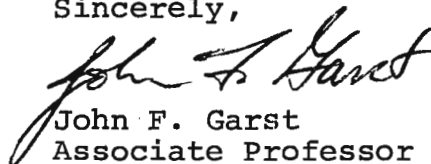
A candidate must be well versed in magnetic resonance theory as well as practice. In particular, he should be familiar with treatments of time-dependent phenomena involving fairly complex spin systems and with the associated computer programming. It would seem that the best candidates would probably be physical chemists with experience in DNP, other double resonance areas, or similar fields. Prior experience in CIDNP is not required.

A candidate must be able to work independently. His expertise will not be coincident with mine (physical organic chemistry, kinetics and mechanisms), but complementary.

The salary will be $8500/yr.

Candidates should contact me directly.

Sincerely,

John F. Garst
Associate Professor

Eidgenössische Technische Hochschule Zürich

Laboratorium für Organische Chemie

CH-8006 Zürich,
Universitätstrasse 16
Tel. (01) 32 62 11

April, 4 1974.

Prof. B. L. Shapiro

Department of Chemistry

Texas A & M University

College Station, Texas 77843

· U. S. A.

T_1 Error Analysis for the Inversion Recovery Technique

Dear Prof. Shapiro,

We have recently studied some parameters affecting the accuracy and precision of T_1 values measured by the inversion recovery technique. The most important factors are errors in signal intensity measurements, pulse inhomogeneity, and incorrect pulse width.

Errors in signal intensity measurements do not affect the accuracy of the T_1 values. Pulse inhomogeneity and incorrect 180° pulse setting, however, give raise to a systematic error. If a linear regression of $\ln(A_o - A) / 2 A_o$ on τ (or similar) is used for the evaluation, this bias is removed, as it affects only the intercept.

The precision of T_1 values is most seriously affected by the variance of the signal intensity and to a lesser degree by the pulse inhomogeneity. The accuracy of the 90° pulse does not influence accuracy and precision of the result. In practice, the contribution of the variance of τ as well as of inproper 180° pulse setting can be neglected. Pulse inhomogeneity is difficult to measure. However, as errors in pulse width are generally small, a measure for pulse inhomogeneity is

given by $I = - A_{(180^\circ - 0 - 90^\circ)} / A_{(90^\circ)}$. If one further assumes that A and

A_o are measured with equal precision, the variance of a T_1 value calculated from

a single point with given A/A_o can be estimated. In Fig. 1 the ratio between the

relative standard deviation of T_1 and the relative standard deviation of A_o is

plotted against A/A_o for two different values of the pulse inhomogeneity measure I.

$SD(T_1)/SD(A_o)$
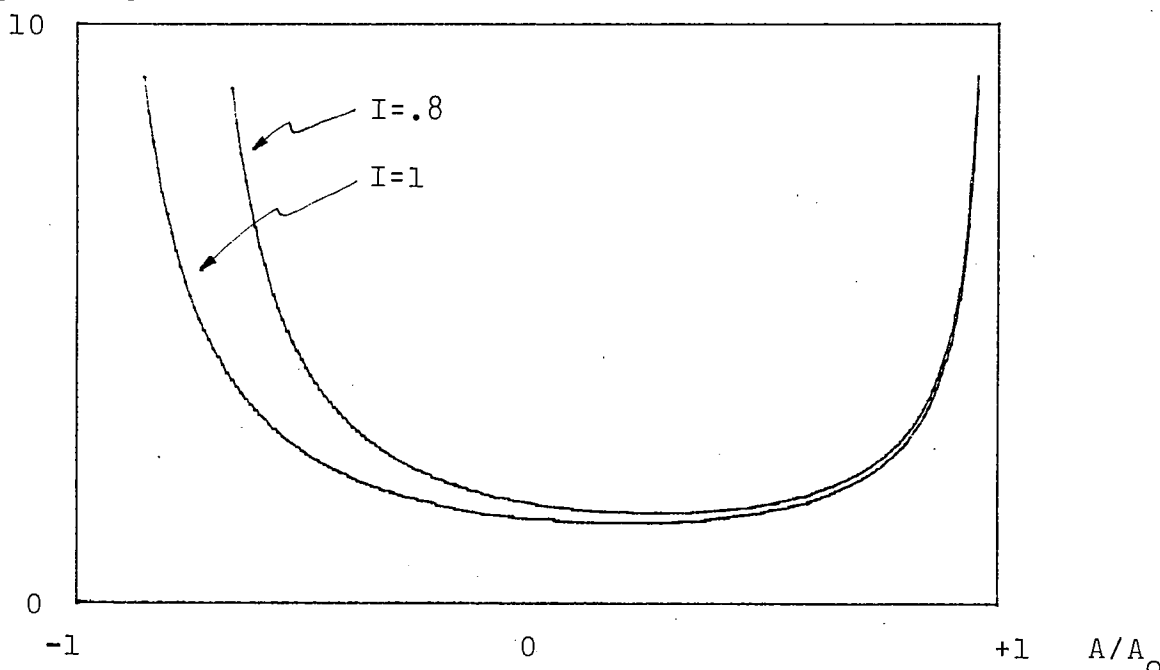
Fig. 1. Plot of the estimated ratio between the relative standard deviation of T_1 and the relative standard deviation of A_o against A/A_o.

As the precision in T_1 detoriorates rapidly for extreme values of A/A_o, it is

suggested to exclude data points with $|A/A_o|$ near 1.

A more detailed discussion will be submitted for publication in Org.Magn.Res.

Yours sincerely

J.T.Clerc   H.P.Meier   E.Pretsch

April 5, 1974

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

Dear Barry:

Allylic Couplings and Bond Fixation in α-Pyrones

Since the relationship between π-bond order and the magnitude of allylic couplings involving methyl groups is well-established, it was not surprising that the nonequivalent methyls of 4-methylaminopent-3-en-2-one had widely differing allylic couplings:
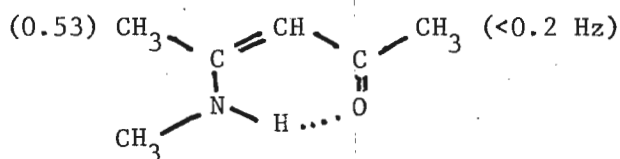
One might thus anticipate that for a system in mobile equilibrium, such as acetylacetone
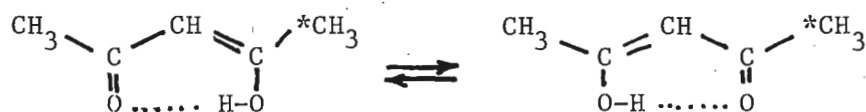
the allylic coupling should be approximately the average of those in the above model. In fact, $^4J < 0.2$ Hz, suggesting either 1) the model is a poor one, 2) there is no enol-enol equilibrium or 3) the allylic couplings in the model have opposite signs.

Professor Bernard L. Shapiro   April 5, 1974

    In an attempt to explore the possibility that systems involving considerable
bond fixation may exhibit positive allylic couplings, I looked at the spectra of
some methyl-substituted α-pyrones (supplied by Dr. George Vogel of Boston College).
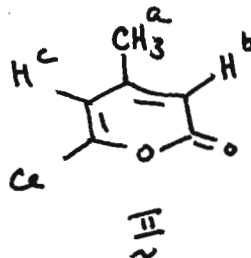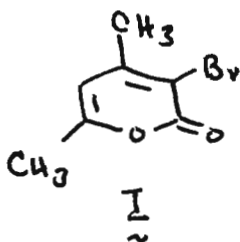
    In $CDCL_3$ solutions I exhibits methyl absorption at δ2.26 (singlet) and
δ2.21 (doublet; J = 1.0 Hz). Coupling between the methyls is δ0.2 Hz. No
sign information was obtained.

    Compound II gives a spectrum ideally suited for sign determinations. The
methyl absorption (δ2.16; doublet of doublets, J = 1.2 and 0.25 Hz) clearly
shows coupling to both ring protons (meta coupling = 1.4 Hz). Double resonance
experiments indicate

$$J_{ac} (-) \qquad J_{ab} (-) \qquad J_{bc} (+)$$
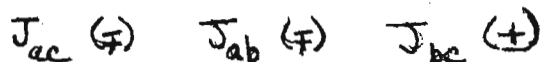
which, of course, is not supportive of the original hypothesis. The question, thus,
remains open, but the indication of considerable bond fixation in α-pyrones is
interesting and entirely consistent with their chemistry.

    Best wishes to all.

Sincerely,

Dennis J. Sardella
Visiting Lecturer

DS:bn

varian AG / Steinhauserstrasse / 6300 Zug / Switzerland / Tel. (042) 23 25 75 / Telex 78841

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

Texas 77843 U.S.A.

April, 11, 1974

Dear Barry,

Suggested Title :   Solvent suppression in proton
FT NMR on the XL-100 :
Some practical hints

With the rapid growth of biochemical applications of proton FT NMR,
instrument users are confronted with the problem of detecting weak
solute resonances (10^{-3}-10^{-5} molar) in the presence of the large residual
HDO line. The problem has in some instances erroneously been inter-
preted as one of dynamic range due to the limited computer word length.
This can easily be overcome by block averaging and double precision
storage techniques. The limitation, however, rather lies in the ADC's
dynamic range. Though the XL-100's ADC has a word length of 13 bit
(12 bit plus sign), the strong solvent response forces one to reduce the
spectrum amplitude in order to avoid overloading of the ADC. This on
the other hand means that weak signals may be below the ADC's detection
threshold. Apart from this, a solvent line, which is two orders of
magnitude more intense than the resonances of interest, render the
observation of signals near the solvent line impossible (spinning side-
bands etc.). It is for these two reasons often mandatory to suppress the
perturbing solvent line.

It should be pointed out that none of the subsequently discussed
methods is essentially new. The purpose of their presentation is rather
to compare the presently available methods with respect to their efficiency
and to encourage instrument users to apply them.

The techniques to be discussed are :

(i)   Inversion-recovery method as described by Patt and Sykes[1]
and Benz, Feeney and Roberts[2]
(ii)   Irradiation of the HDO peak
(iii)   Partial saturation using a (90°-t) sequence in the steady state
regime.

ad (i) : All this method requires is (a) a standard XL-100 program,
(b) a minor hardware modification allowing a short field gradient pulse
to be applied to the Y shim coils, (c) a precise determination of T_1 (HDO)
and (d) that T_1 (solute)$\neq T_1$ (HDO).

The idea behind the method is to apply the 90° observing pulse at the moment the HDO magnetization passes through zero. A standard (180°-t-90°-T) sequence would require $T \gg 5 \cdot T_1$ (HDO) thus excessively lengthening the experiment. Instead Benz et al.[2] have determined the steady state conditions allowing shorter values of T to be taken. After T_1 (HDO) has been determined (which is a matter of seconds), a suitable pair of t, T values can be taken from the curve on page 117 in Ref. 2. In order to allow for the steady state to build up, it is important, however, that SS = 1 is used. This means that the first four pulses will be neglected. Fig1a) shows a proton FT spectrum obtained after accumulation of 500 4-sec transients under standard conditions from a 5×10^{-3} molar solution of tryptophan in 99,75 % D_2O in a 5 mm-tube. The spectrum in Fig1b) was obtained by using a $(180^o-HSP-t-90^o-T)$ sequence under otherwise unaltered conditions. Apart from the 160-fold reduction of the HDO peak's intensity, the spectrum shows a considerably improved signal-to-noise, because of a better ADC resolution for these signals.

ad (ii) : Irradiation of the HDO peak at its exact frequency is an alternative way of suppressing the solvent resonance. This requires the FT homodecoupling accessory, in principle a simple T cable which permits the hetero decoupler output to be fed onto the observe transmitter coils. Important in this experiment is a precise setting of the decoupler frequency. This is best achieved by varying the decoupler frequency until a minimum response is observed on the oscilloscope. Fig 1 c) shows a spectrum obtained under the same conditions as the one in Fig 1 a) except that the HDO line was irradiated. The solvent suppression factor is about 30 and the signal-to-noise of the solute line comperable to that observed in Fig (b).

ad (iii) : The simplest but also the least efficient among the methods discussed, consists of applying 90° pulses. If steady state conditions are selected and T_1 (solute) $< T_1$ (HDO) this should result in a solvent line intensity reduction. The spectrum shown in Fig 1 (c) has been obtained under the same conditions as the one in Fig 1 (a) except that the first four pulses were neglected and that 90° pulses were applied.

VARIAN AG
Research Laboratory

F. W. Wehrli

F.W. Wehrli

[1] S.L. Patt and B.D. Sykes, J. Chem. Phys. 56, 3182 (1972)

[2] F.W. Benz, J. Feeney and G.C.K. Roberts, J. Mag. Res. 8, 114 (197?)

Transients : 500

$\alpha = 60°$

HDO

a)

x40

$(180° - HSP - t - 90° - T)_{500}$

$t = 5\,sec$, $T = 8\,sec$, $T_1(HDO) = 15.1\,sec$

b)

c) Transients : 500

$\alpha = 60°$

HDO irrad.

x 1.5

d) $(90°-t)_{500}$

steady state

x25
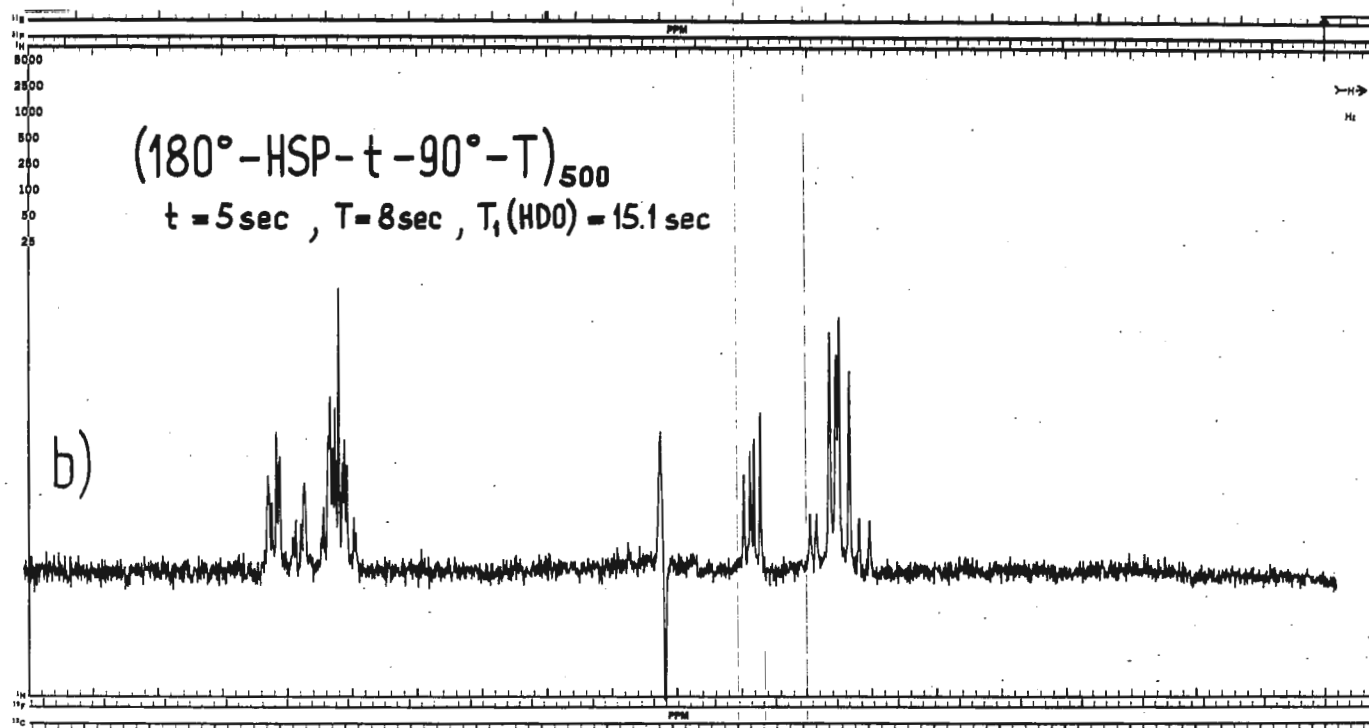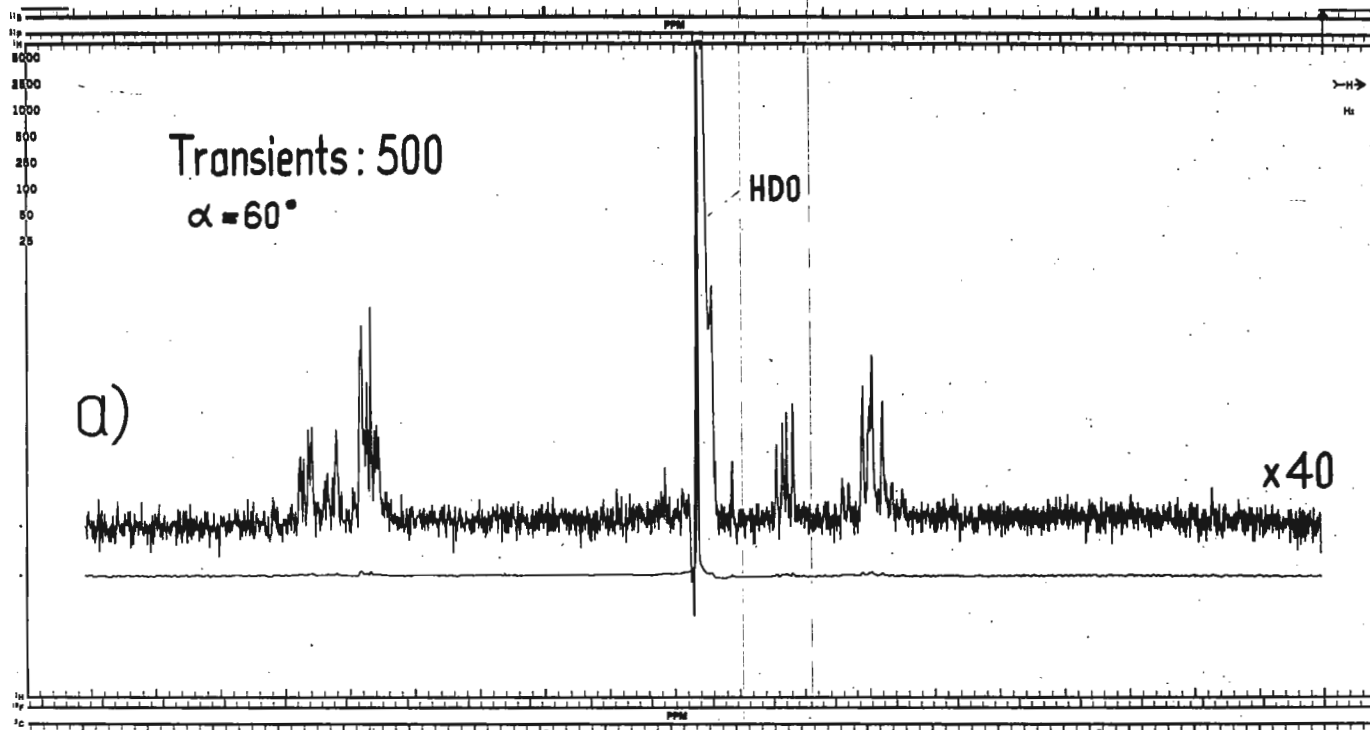
<u>Fig. 1 a)-d)</u> : 100 MHz FT spectra of 5 x 10^{-3} molar tryptophan in
99,75% D_2O (5 mm tube) under experimental conditions
as described in the text.

NICOLET
nmr data systems...
for routine research problems
and advanced applications

The Nicolet 1080 and NMR-80 data acquisition and analysis systems are in use world-wide in solving not only routine research problems but also in advancing the frontiers of nmr knowledge. These data systems are highly regarded for their timing accuracy, sensitivity, continuous display capabilities and general versatility in the conception and execution for new experiments. Some of these are:

STOCHASTIC RESONANCE — This technique involves random noise modulation of the rf excitation frequency, leading to a broadband excitation whose response is measured and Fourier transformed much as in conventional pulsed-FT nmr. Its principal advantage lies in the fact that much less rf power is needed to excite the chemical shift range of interest and that it has the same Fellgett's advantage of FT nmr.

R. R. Ernst, *J. Mag. Res. 3* 10-27 (1970); R. Kaiser, *J. Mag. Res. 3* 28-40, (1970); J. Cooper and R. Addleman, 13th Experimental Nmr Conference (1972); E. Lippmaa, private communication.

RAPID SCAN NMR — In this technique, a spectral region is swept at a rate much greater than allowed for by slow passage conditions and the resulting ringing spectrum correlated with a spectrum of a single ringing line or of a theoretical line. Its principal advantage lies in the ability to acquire data rapidly even in the presence of strong solvent lines, without requiring that these lines be part of the signal averaged data.

J. Dadok and R. F. Sprecher, 13th and 14th Experimental Nmr Conferences (1972, 1973); E. Becker, paper in press.

HOMOSPOIL T_1 SEQUENCE — This sequence allows the rapid measurement of long T_1's without the long $5xT_1$ waiting period needed by the inversion-recovery sequence. It is accomplished by a -(90-spoil-tau-90-sample-spoil)- sequence.
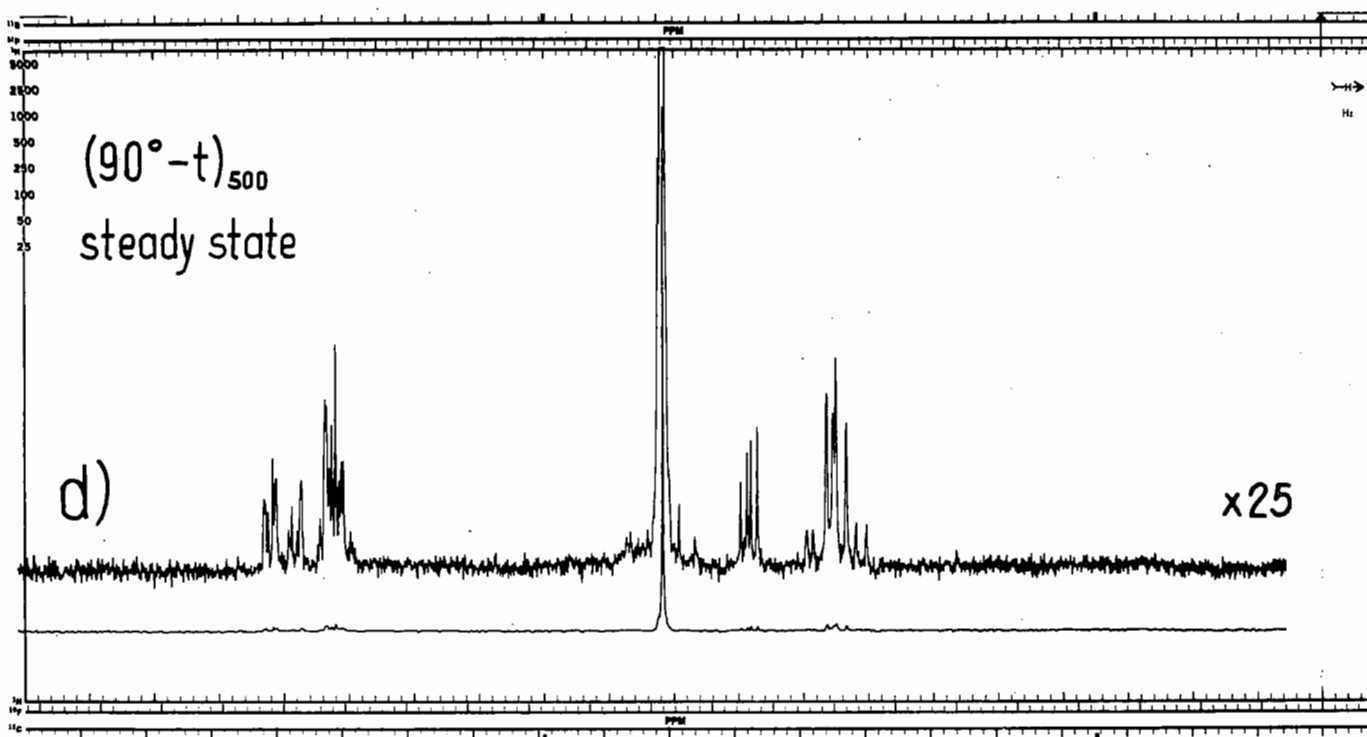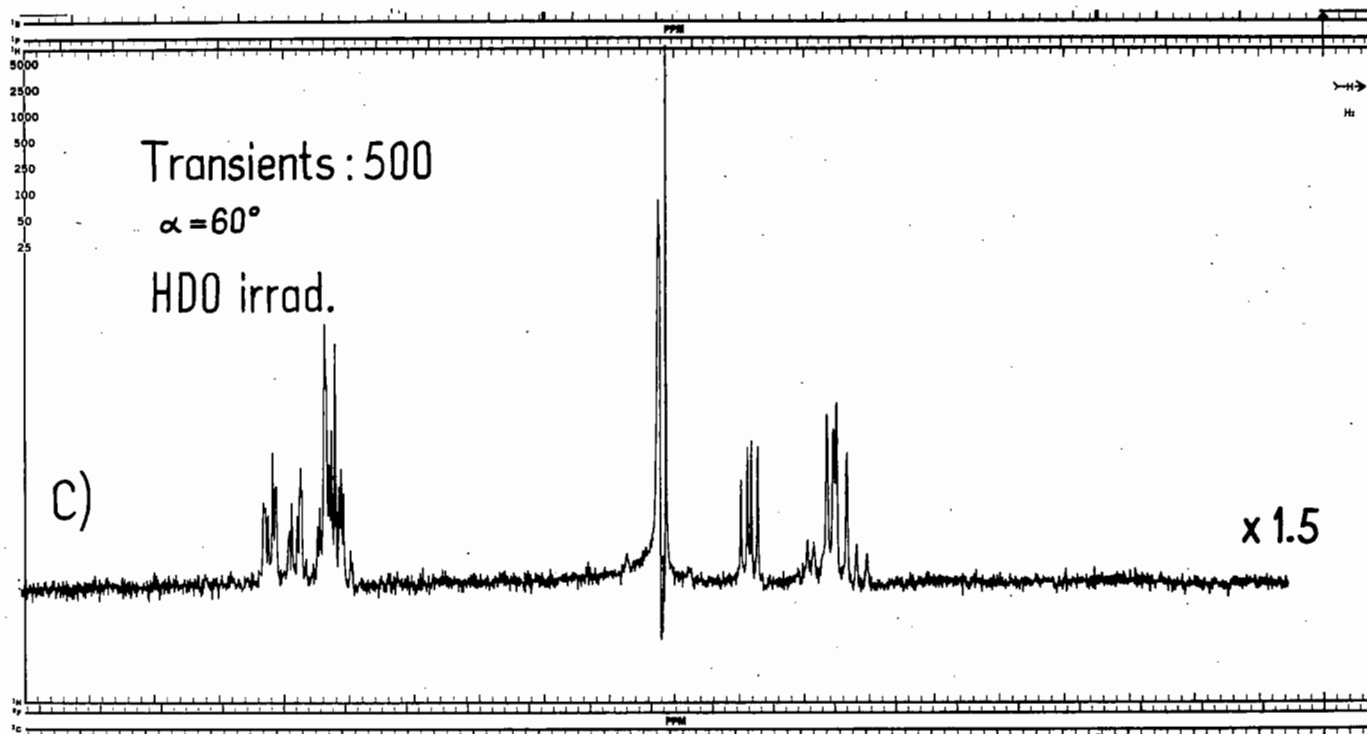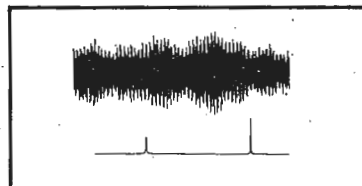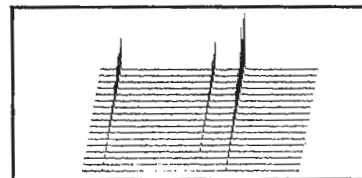

J. L. Markley, W. J. Horsley and M. P. Klein *J. Phys. Chem. 55* 3604 (1971); R. Freeman and H. D. W. Hill, *Ibid. 54* April (1971); G. G. McDonald and J. S. Leigh, Jr., *J. Mag. Res. 9* 358 (1973).

QUADRATURE DETECTION NMR — This technique allows $\sqrt{2}$ enhancement over conventional pulsed nmr since the rf carrier can be placed in the center of the spectral region and dual phase detectors used to receive the response. The two resulting free induction decays are Fourier transformed using a complex transform which results in   .e frequency domain spectrum.
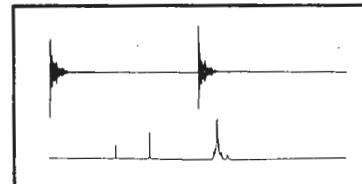
J. Schaeffer and E. O. Stejskal, 15th Experimental Nmr Conference (1974), and *J. Mag. Res.* March (1974) (in press). J. D. Ellett, etal. *Adv. Mag. Res. 5* 117 (1971)

Please p   for details on these applications or to discuss how the vers   ..R-80 data system may be used for your experiments. Complete systems start at $20,000. If you are already a Nicolet data system user, you may order free software for the above techniques from our Nicolet Users Society (NUS) library.

NICOLET INSTRUMENT CORPORATION
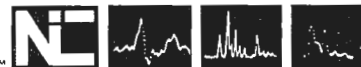
5225 Verona Road, Madison, Wisconsin 53711
Phone 608/271-3333 TWX: 910-286-2713

![University of Western Ontario crest] The University of Western Ontario, London, Canada

Faculty of Science
Department of Chemistry

April 24, 1974

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

Dear Dr. Shapiro:

POSITION AVAILABLE

I would like to draw to the attention of the readers of TAMU newsletter that the Chemistry Department, University of Western Ontario is beginning a search for a Senior Scientific Officer. I would be pleased to receive inquiries from anyone interested. A brief description follows.

Applications are invited for the post of Senior Scientific officer from persons familiar with the operation and scientific capabilities of spectroscopic instrumentation. The position involves responsibility for the maintenance and operation of major instruments in the Department with emphasis on n.m.r. and mass-spectroscopic facilities, together with an involvement in the professional or research activities of the Photochemistry Unit within the Department. The appointee will be a senior member of the support staff of the Department and should hold a Ph.D. or M.Sc. degree in Chemistry. The appointment is for 2 years in the first instance. Salary is negotiable, but not less than $12,000. Applications should be sent to Dr. H.C. Clark, Head, Department of Chemistry, University of Western Ontario, London, Ontario N6A 3K7, as soon as possible.

Yours sincerely,

H.C. Clark, Head.

Southern Research Institute

KETTERING-MEYER LABORATORY

2000 NINTH AVENUE SOUTH
BIRMINGHAM, ALABAMA 35205
TELEPHONE 205-323-6592

April 15, 1974

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

Dear Barry:

^{13}C NMR of Isomeric Dithianes.

Most of our recent ^{13}C work has been on substituted purines, but this is scheduled to appear in the Journal of Magnetic Resonance very soon (July), and, in any case, is too lengthy for the newsletter. Meanwhile, here are some ^{13}C data on a pair of cis-, trans- isomers of a 2,5-disubstituted-1,3-dithiane to keep the subscription going.
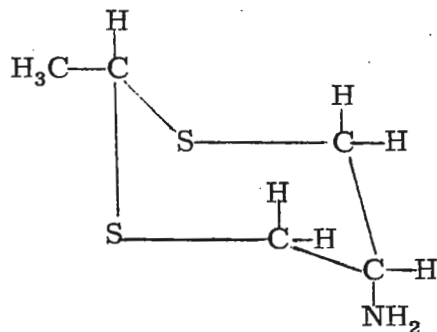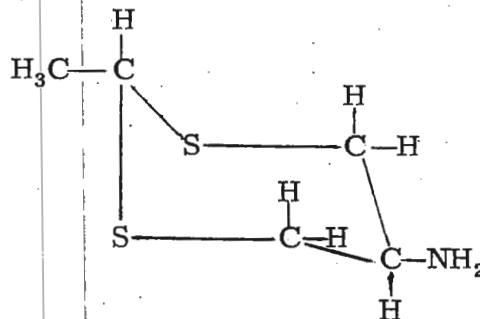
cis-   trans-

Originally, we identified these isomers by means of their ^{1}H nmr spectra, two helpful references [1,2], and Eu(fod)$_3$ addition. The ^{1}H chemical shifts of the methyl groups for both isomers are in agreement with that expected for an equatorial methyl group at C$_2$, so that the predominant conformations should be as drawn.

Both completely decoupled and proton-coupled ^{13}C spectra were obtained for each isomer. The proton-coupled spectra made it possible to assign all peaks in the spectra of both isomers, and to obtain some of the coupling constants.

Prof. B. L. Shapiro
April 15, 1974

Southern Research Institute

Chemical Shifts[3]
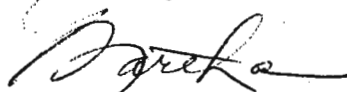
Isomer	C_2	$C_4(C_6)$	C_5	CH_3
cis-	41.82	38.62	38.72	21.06
trans-	41.00	37.89	47.69	20.00

Coupling Constants (Hz)

Isomer	$^1J_{C_2H_2}$	$^1J_{C_4H_4}$	$^3J_{C_4H_2}$	$^1J_{C_5H_5}$	$^1J_{C_{Me}H_{Me}}$	$^2J_{C_{Me}H_2}$
cis-	~153	~139	~7	138.6 ± 0.3	129.4 ± 0.3	4.3 ± 0.3
trans-	~150	~140	-	144.6 ± 0.3	129.4 ± 0.3	4.3 ± 0.3

As you will note, the only carbon with a significantly different chemical shift in the two isomers is C_5. In addition, in the proton-coupled spectra C_5 showed different splitting patterns in the different isomers. In the cis- isomer, C_5 appeared as doublet of triplets (being split by only one of the protons at $C_4(C_6)$, $^2J_{C_5H_4} = 4.7\pm0.3$). In the trans- isomer, C_5 was split nearly equally by both protons at $C_4(C_6)$, and appeared as doublet of "quintets" with $^2J_{C_5H_4} \simeq 4.5$Hz.

Sincerely,

Martha C. Thorpe
Senior Chemist
Molecular Spectroscopy

MCT:mw

1. E. L. Eliel and R. O. Hutchins, J. Amer. Chem. Soc., 91, 2703-15 (1969).

2. R. J. Abraham and W. A. Thomas, J. Chem. Soc., 335-41 (1965).

3. Chemical shifts are in ppm downfield from internal TMS, and should be accurate within $\pm$ 0.02 ppm. Solvent: $CDCl_3$.

WESTERN RESEARCH CENTER | Stauffer CHEMICALS | **Stauffer Chemical Company**
1200 South 47th Street / Richmond, California 94804 / Tel. (415) 233-9361

April 23, 1974

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

Trifluoroacetic Acid as a Solvent

We wish to caution NMR researchers on the use of trifluoroacetic acid as a solvent.

In our attempt to obtain a carbon-13 NMR spectrum of 2-hydroxy-4-(ethylamino)-6-(isopropylamino)-triazine (I) we had to use trifluoroacetic acid as a solvent. For spectral comparison, we also used the same solvent for 2-chloro-4-(ethylamino)-6-(isopropylamino)-triazine (II). To our surprise, the two carbon-13 NMR spectra were identical.
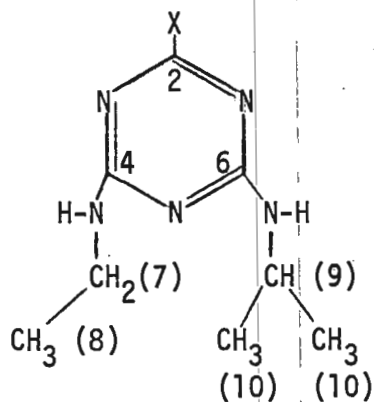
I:X = OH

II:X = Cl

The chemical shifts with respect to TMS are listed as follows:

C(2), C(4), C(6): 145.2, 149.3, 150.2
C(7)   : 33.0
C(8)   : 7.7
C(9)   : 41.6
C(10)   : 15.7

Stauffer Chemical Company

Prof. B. L. Shapiro

Upon evaporating the solvent, both compounds gave identical IR and proton NMR spectra. Apparently trifluoroacetic acid contained water which reacted with II in the presence of acid to form I.

Sincerely yours,

C. K. Tseng

A. Mihailovski

CKT/AM/1h

Deuterated Solvents
Reference Compounds
Chart Papers Etc:
Shift Reagents

NUCLEAR MAGNETIC RESONANCE LTD.

MAGNETIC HOUSE / SCRUBBS LANE / BLEDLOW RIDGE /
HIGH WYCOMBE / BUCKS / HP14 4AF

Université Claude BERNARD LYON I
Laboratoire de SPECTROSCOPIE ET DE LUMINESCENCE
43, Bld du 11 Novembre 1918
69621 VILLEURBANNE FRANCE

Dear Professor Shapiro,

T_1 measurements showing convection streams.

        In order to measure spin-lattice relaxation times of protons
at low resolution we apply the usual fast adiabatic passage technique
/1//2/, on a Varian HA-100 spectrometer operating in the H.R. mode.
For example, phenyl selenol relaxation times bave been studied in the
30°C - 150°C temperature range. When oxygen is removed /2//4/ the T_1
values of selenic proton /3/ are about 20 seconds so we can use a saw
thooth generator with a period of 1.6 s to obtain the field sweep
through the resonance.

The observed phenomenon : Magnetization recovery appears to be "normal"
-purely exponential- with a spinning sample at all temperature Fig. 1a.
But the recovery shows an important modulation when the sample is not
spinning. Fig 1b, ▬▬▬▬. This phenomenon arises from the heating of
the insert. A thermocouple threaded into the insert, shows that the
heating device generates along the axis of the sample a gradient of
temperature of about 2°C per cm when the mean temperature is 130°C. This
gradient is sufficiently stable (20-30 minutes) to allow the recording
os several experiments ; it decreases when the heating is maintained
for a long time and the modulations disappear in that case. We see that
convection motions amid the cylindrical sample are produced by the gra-
dient for temperature /5/ and that these motions influence the apparent
evolution of magnetization. Inertia caused by the spinning of the sam-
ple prevents such motions and hinders the modulation of recovery curves.
        Similar observations have been obtained with dimethyl sulfoxide
and substances dissolved in this liquid.

Quantitative analysis. Let V be the total volume of the sample and v'
be the fraction of this volume in which nuclei are adiabatically reversed.
Furthermore we suppose that only a fraction of v' induce the bulk of the
signal into the receiver coil. Let v. be this volume which is centered
at the receiver coil level and corresponds to 1 cm of the sample vertical
size. The signal in the receiver arises from two different species of
nuclei : A part of it arises from the reversed spins which were initially
in the volume v', let be $p_1(t)$ the corresponding fraction ; an other part
results from the non reversed spins which were initially outside the volu-
me v' but came into the receiver volume v because they have pulled in by
convection streams, let be $1 - p_1(t)$ the corresponding fraction. Then,

/1/ L.E. DRAIN, Proc. Phys. Soc. (London) 62 A, 301, (1949)
/2/ J.C. DUPLAN, A. BRIGUET and J. DELMAU, J. Chem. Phys. 54, 3648, (197¹⁾
/3/ L. LALEZARI and N. SHARGHI, Spectroch. Acta 23A, 1948, (1967)
/4/ R.E. RONDEAU, J. Chem. Phys. Educ. 46, 504, (1969).
/5/ J.W. EMSLEY, F. FEENEY, L.H. SUTCLIFFE, High Resolution N.M.R.
    Spectroscopy, First Edition, chapter 7, page 271, Pergamon Press (1965)

the total magnetization which influences the receiver coil may be written :

$$M_z(t) = p_1(t) M_z(t) + (1 - p_1(t))M_o \qquad (1)$$

The evolution of $M_z(t)$ is driven by the Bloch decay :

$$\frac{d}{dt} M_z(t) = \frac{M_o - M_z(t)}{T_1} \qquad (2)$$

Eq (1) and Eq (2) give :

$$M_z(t) - M_o = (M_z(t) - M_o)p_1(t) \qquad (3)$$

and finally :

$$M_o - M_z(t) = 2 M_o e^{-t/T_1} p_1(t) \qquad (4)$$

with the initial conditions :

$$M_z(0) = - M_o$$
$$p_1(0) = 1 \qquad (5)$$

The behaviour of $p_1(t)$ is reflected by the product $(M_o - M_z(t))e^{t/T_1}$ since T_1 and M_o are known and the variations of $M_z(t)$ are recorded.

Motion of "labeled" nuclei :   The experimental curves shown in Fig.2 have been obtained at 130°C with phenyl protons signals of C_6H_5SeH. The full lines represents the decay of $(M_o - M_z(t))/M_o$ and they correspond to the evolution of the magnetization of the volume v° after the spins have been reversed in the volume v'. From the preceeding curves we can the decay of $p_1(t)$ by multiplying by e^{t/T_1} * - dashed lines. We have obtained theses results using decreasing liquid heights in 5 mm o-d N.M.R. tubes successively 45,25 and 15 mm. The tubes are identically fixed in the spinner so the surface of the liquid has not the same position and v' is not constant.

Of course the quantity $(M_o - M_z(t))/M_o$ tends toward zero, but this limiting value is reached only after several oscillations. One can reasonably assume that the spins "labeled" in the volume v' at time zero will spread over the whole sample volume V after a long enough time. Then the value of $p_1(t)$ tends to the ratio v'/V which is a non zero value. This prediction is well tested by the experiment.

A close relationship exists between the period of the observed oscillations and the convection motions. These streams appear well regulated. But in course of time the streams tubes get out of shape because the mixing of the liquid and the amplitude of the oscillations of $p_1(t)$ decrases.

Cautions in high temperature N.M.R. studies.   Since this parasite effect must be carefully avoided during relaxation times measurements we though it would be useful to summarize some remarks about how to avoid it. Care must be taken even for spinning samples because the inertia introduced by rotations prevents the convection streams, it also hinders the homogeneization of the temperatures amid the samples.

We also looked at the effects of the convection currents on

_____

* The T_1's value is independently measured by the adiabatic method after the gradient has disappeared.

saturation recovery experiments /6/. The recovery of the apparent ma-
gnetization is in that case nearly exponential but with a time constant
shorther than the usual T_1's value. Indeed, the convection motions
alter the initial conditions of the different spins ; those which are
not in the volume v' at zero time, have soon recovered some magnetiza-
tion.

Finally we would like to point out that our observations pro-
vide further support to the idea that magnetic labeling of the nuclei
is a powerful method to reveal internal motions in small liquid samples
/7/.

Sincerely yours.

A. BRIGUET   J.C. DUPLAN   J. DELMAU

Fig. 1. Magnetization recovery of the phenyl protons in purum C_6H_5SeH

spinning sample

10 s

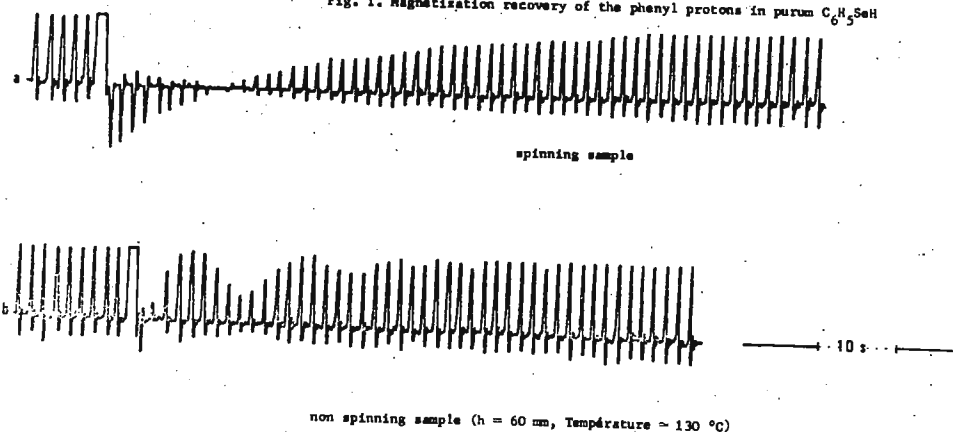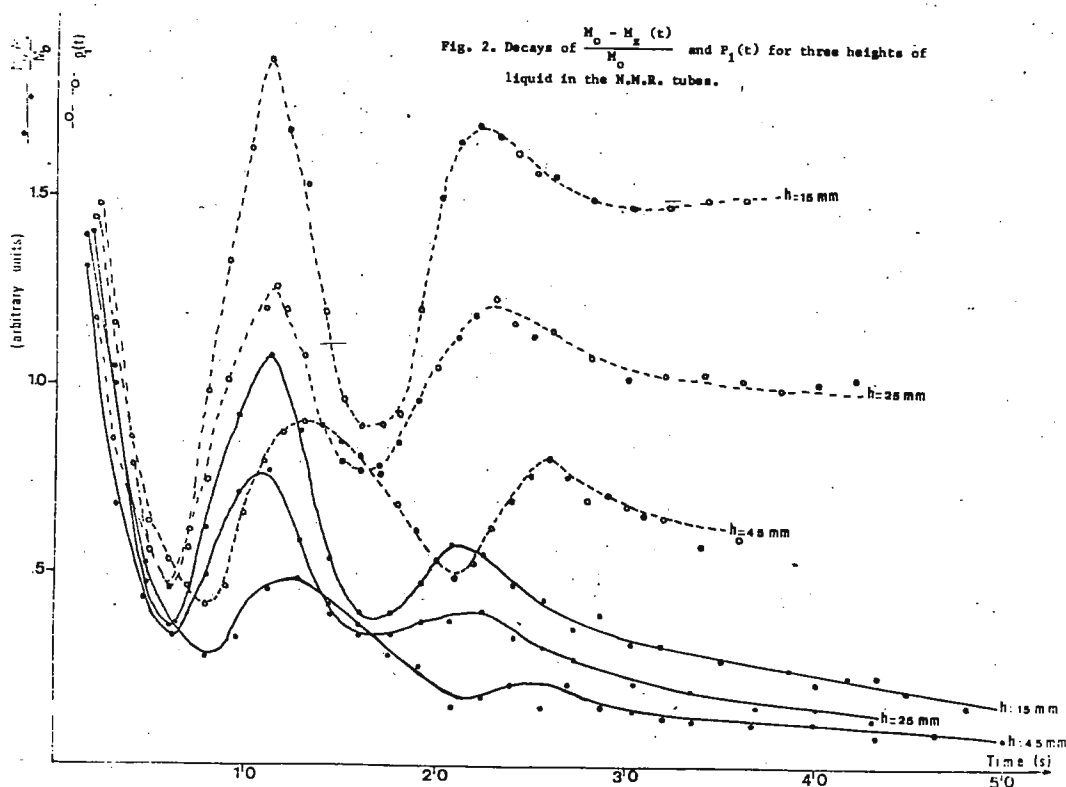non spinning sample (h = 60 mm, Temperature ~ 130 °C)

Fig. 2. Decays of $\dfrac{M_o - M_z(t)}{M_o}$ and $P_1(t)$ for three heights of
liquid in the N.M.R. tubes.

/6/ A.L. VAN GEET and D.N. HUME, Anal. Chem. 37, 979, (1965)
                                    ibid   37, 983, (1965)
/7/ J. PACKER, Mol. Phys. 17, 355, (1969)

MONTEDISON

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

27 march 1974

BLS/lmk

DIPE/CER

Dear Prof. Shapiro:

just now i have received your letter of the 25th february and I
have learnt that I will go on receiving TAMU NMR Newsletter.
I have already received the february issue and I hope you will
be able to send me the back numbers from october 73'. In the
mean time I send you the present contribution.

Subject : ^{19}F NMR analysis of fluoride of perfluorocyclo-
hexanesulphonic acid and of 3-trifluoromethyl-perfluorocyclopentane-
1-sulphonic acid.
From the electrochemical fluorination of the chloride and fluoride
of the benzensulphonic acid, beside the main product perfluoro-
cyclohexanesulphonic acid $C_6F_{11}SO_2F$ (I), also the side products
3-trifluoromethylperfluorocyclopentane-1-sulphonic acid $CF_3C_5F_8SO_2F$
(II) and $C_6F_{10}ClSO_2F$ were obtained.
We have examined with accuracy the values of the different chemical
shifts and coupling constants of I and II.
(II) is constituted of two geometric isomers cis (IIa) and trans
(IIb). Near the cis-trans isomerisation phenomenum, for each of
the two geometric isomers, two conformers in mutual equilibrium
are found: (1),(2) (see table 1). For the cis isomer the two
conformers in equilibrium are: (1) the pseudo-axial-axial conformer
and (2) the pseudo equatorial-equatorial conformer (^{1}) and form
(1) is the overwhelming ($n_1 \gg n_2$). For the trans isomer the two
conformers are: (1) the pseudo-axial-equatorial and (2) the pseudo-
equatorial-axial conformer and in this case the distribution of
the populations is $n_1 \simeq n_2$.

The attributions of ^{19}F NMR spectra of (1) were conducted in strict analogy with the Sutcliffe analysis of perfluoromethylcyclohexane $(CF_3C_6F_{11})$ [2].

In table 1 the structure formulae of (I), (IIa) and (IIb) with the labelling of the fluorine atoms are reported.

The chemical shifts were measured relatively to $CFCl_3$ and expressed in ppm according to the δ scale. The coupling constant are given in Hz but the sign was not determined.

In the next tables the small letters e, a are used for the equatorial and respectively axial fluorine atoms.

In table 2 the chemical shifts (50% v/v $CFCl_3$ solutions) and some coupling constants of (I) are reported.

In table 3 the chemical shifts and the geminal coupling constants of (IIa) and (IIb) are reported (same concentration).

We hope to be able to send within few months the present work to Organic Magnetic Resonance Journal with further explanations and details.

We are indebted to Prof. L. Cavalli of "Società Italiana Resine, Laboratori Analisi", for the helpful discussions, we had during his former activity at the "Centro Ricerche of Bollate" (Montedison SpA), and to Prof. G. Troilo of the "Istituto di Chimica Industriale-Facoltà di Ingegneria-Università di Padova" for the preparation and purification of the products.-

Yours sincerely
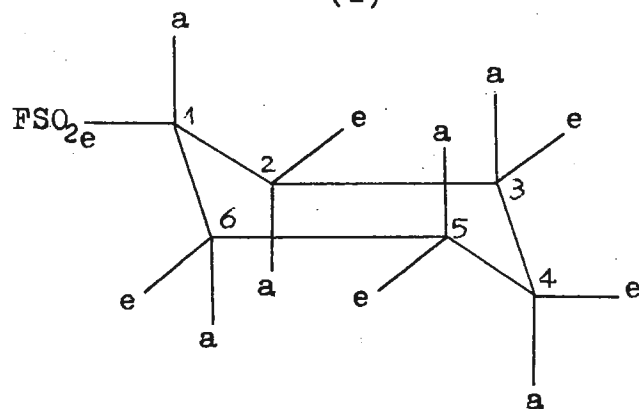
Giorgio Gurato
(Giorgio Gurato)

Giorgio Zenoni
(Giorgio Zenoni)

References
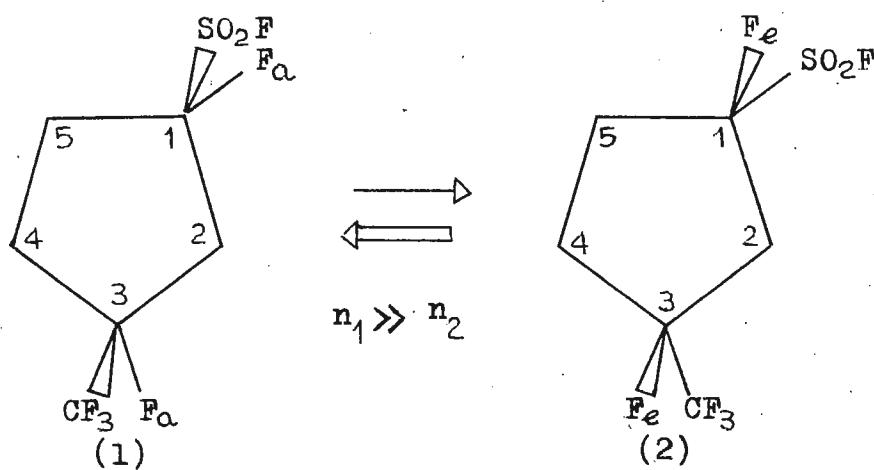1) E.L.Eliel,N.L.Allingher,S.J.Angyal and G.A.Morrison –Conformational Analysis.Interscience Publishers.New York, pag. 202
2) W. Jolley, L.H. Sutcliffe and S.M. Walker–Trans. Faraday Soc. I(64), 269(1968)

Table 1

(I)

(IIa) cis

$n_1 \gg n_2$

(1)   (2)

(IIb) trans

$n_1 \simeq n_2$

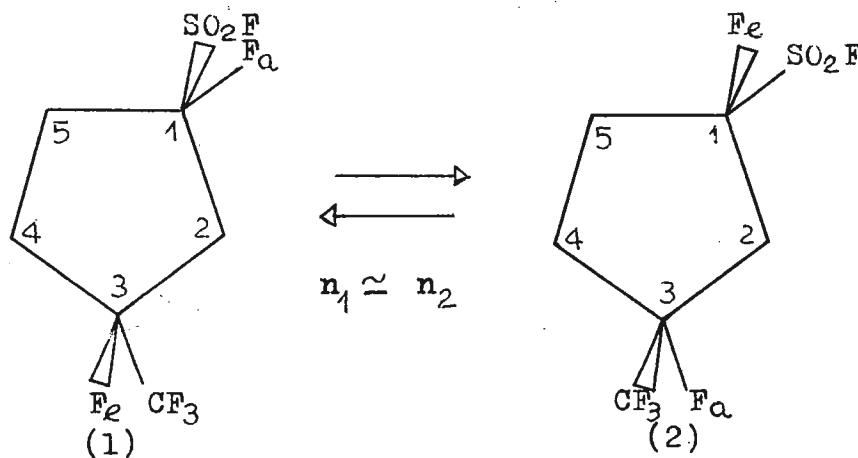(1)   (2)

Table 2

NMR data of (I)

Chemical shifts (ppm)   Coupling constants (Hz)

δ(1e)   = +63.5   J(2a-2e)=J(6a-6e) = 295 ± 0.5

δ(2a,6a) = - 117.1   J(3a-3e)=J(5a-5e) = 287 ± 3

δ(3a,5a) = - 122.4   J(4a-4e)   = 288 ± 3

δ(4a)   = - 123.7

δ(2e,6e) = - 129.9

δ(3e,5e) = - 139.0

δ(4e)   = - 141.7

δ(1a)   = - 165.8

Coupling constants related to 1a band (-CF)

J(1a-3a,5a) = 23.5
J(1a-2e,6e) = 15.9
J(1a-2a,6a) = 4.2
J(1a-3e,5e) = 2.1
J(1a-SO$_2$F)   = 2.1
J(1a-4a,4e) = 0.0

Coupling constants related to -SO$_2$F band
J(SO$_2$F-2a,6a) = 16.7
J(SO$_2$F-2e,6e) = 7.8
J(SO$_2$F-1a)   = 2.1
J(SO$_2$F-3e,5e) = 2.2
J(SO$_2$F-3a,5a;4a,4e) = 0.0

Coupling constants related to 4e band
J(4e-3e)=J(4e-5e)= 14.1 or 12.7
J(4e-3a)=J(4e-5a)= 12.7 or 14.1
J(4e-2e)=J(4e-6e)= 6.4
J(4e-2a)=J(4e-6a)= 1.6

Table 3

NMR data of (IIa) and (IIb)

Chemical shifts (ppm)

(IIa) cis   (IIb) trans

$\delta(SO_2F) = +\ 59.18$ $\delta(SO_2F) = +\ 59.50$

$$\delta AV(CF_3) = -\ 72.66\ \text{(cis+trans)}$$

$\delta(2a)$	$= -\ 116.52$		$\delta(2a)$	$= -\ 113.99$
$\delta(4a)$	$= -\ 119.14$		$\delta(2e)$	$= -\ 116.83$
$\delta(5a)$	$= -\ 123.90$		$\delta(5a)$	$= -\ 120.35$
$\delta(2e)$	$= -\ 123.23$		$\delta(4a)$	$= -\ 123.21$
$\delta(4e)$	$= -\ 131.76$		$\delta(5e)$	$= -\ 123.41$
$\delta(5e)$	$= -\ 132.32$		$\delta(4e)$	$= -\ 125.61$
$\delta(1a)$	$= -\ 163.41$		$\delta(1a,e)$	$= -\ 163.99$
$\delta(3a)$	$= -\ 183.87$		$\delta(3e,a)$	$= -\ 185.50$

Geminal coupling constants J(e,a) (Hz)

J cis   J trans

$J(2c) = 283.80 \pm 0.1$		$J(2t) = 276.50 \pm 0.3$
$J(4c) = 268.95 \pm 0.25$		$J(4t) = 268.48 \pm 0.55$
$J(5c) = 274.35 \pm 0.15$		$J(5t) = 270.60 \pm 0.10$

UNIVERSITÉ D'OTTAWA　　UNIVERSITY OF OTTAWA

OTTAWA ONTARIO
CANADA K1N 6N5

DÉPARTEMENT DE CHIMIE　　　　　　　　　　　　DEPARTMENT OF CHEMISTRY

April 18, 1974.

Title:　The Conformation of N-nitroso-r-2-cis-6-dimethyl-4-phenylpiperidine, I.

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

Dear Barry:

　　　　We wish to describe the results of a computer analysis of the 13-spin
system giving rise to the 220 MHz spectrum of the N-nitrosopiperidine derivative,
I.　Comparison of the vicinal coupling constants with similar parameters in the
literature provides evidence that the compound possesses a distorted chair con-
formation in which the two methyl groups are axial, e.g.
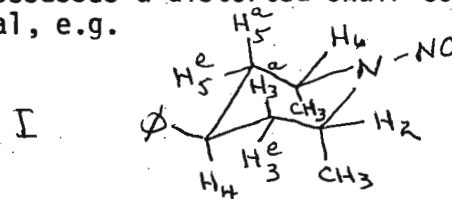
　　　　Compound I was prepared by two successive methylations of N-nitroso-4-
phenylpiperidine.　Since the 100 MHz spectrum of I was exceedingly complex the 220
MHz spectrum was run for us by Dr. A. Gray, Ontario Research Foundation, Toronto.
A portion of the spectrum showing all but the aromatic and methine proton absorptions
appears in Fig. 1A.　In order to obtain the spectral parameters for the seven protons
attached to the piperidine ring the LAOCN3 program was used.　Iterative fit by com-
puter was not used as the matching of assignments was complicated by broadening due
to unresolved long-range couplings.　Each calculated spectrum was compared to the
experimental and another calculation made with adjusted parameters until acceptable
agreement was obtained.　The calculated spectra included a first order perturbation
by the two methyl groups on both the vicinal and the next nearest protons.　Agreement
was deemed acceptable for correspondence in line positions of <0.1 Hz.　The parameters
which give the calculated spectrum shown in Fig. 1B appear in the Table.

　　　　It can be seen that coupling between protons at carbons 3,4 and 5 are typical
for protons on a cyclohexane ring.　However couplings between protons on carbons 2 and
3 (and 5 and 6) are not normal for a piperidine ring i.e. J_{ae} should be 3-3.5 Hz[1] and
one can estimate, by considering effects of electronegativity and their orientation
dependence[2], a value for J_{ee} of 2.2 Hz.　The observed J_{ae}'s (6.3, 6.5) and J_{ee}'s (1.5)
indicate the presence of a distortion due to the severe repulsive 1,3-diaxial methyl-
methyl interaction.　Should this distortion produce a 10° increase in the dihedral angle
between the two equatorial protons (ϕ_{ee}) and a concomitant increase in ϕ_{ea}, the predicted
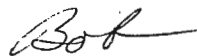
values for J_{ea} and J_{ee} would change to 5.2 and 1.0 Hz. Thus a distortion of this type can account, at least qualitatively, for the observed vicinal coupling constants.

Proton	Shift	Coupling Constants to Other Protons[a]							
	(Hz from TMS at 220 MHz)	2	3e	3a	4	5e	5a	6	CH$_3$
2	1143.5		1.5	6.5				1.0	7.0
3e	402.5			-13.7	3.2	2.3			0.2
3a	390.9				13.0				0.3
4	733.0					3.2	12.6		
5e	442.2						-13.3	1.5	0.2
5a	467.4							6.3	0.5
6	1150.5								7.0

a) effects of unresolved long range couplings were simulated by using a line-width of 1 Hz for the print out in Fig. 1B.

The conclusion that the title nitrosamine exists in a distorted chair conformation having two methyl groups axial substantiates the earlier proposals of Harris and Spragg[3] and Chow and Colon[4] that the nitrosamine of cis 2,6-dimethylpiperidine exists "predominantly" in a chair conformation having both methyl groups axial. Furthermore the parameters obtained for 1 rule out the presence of boat conformations to greater than a few percent.
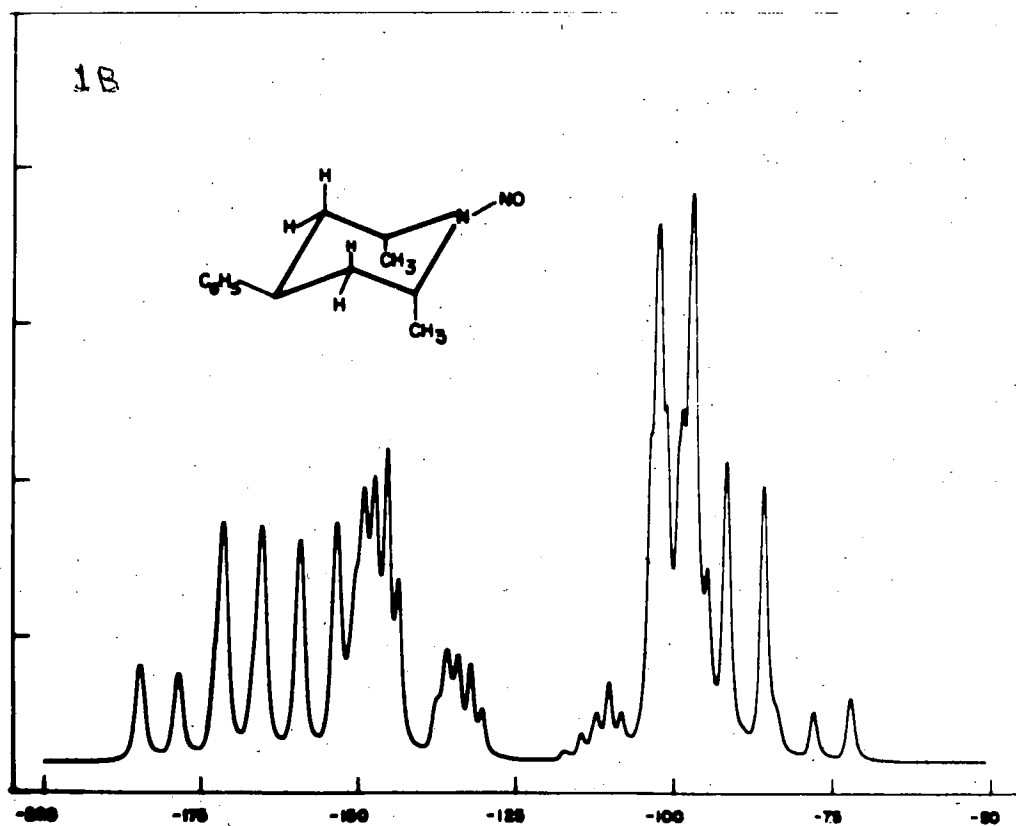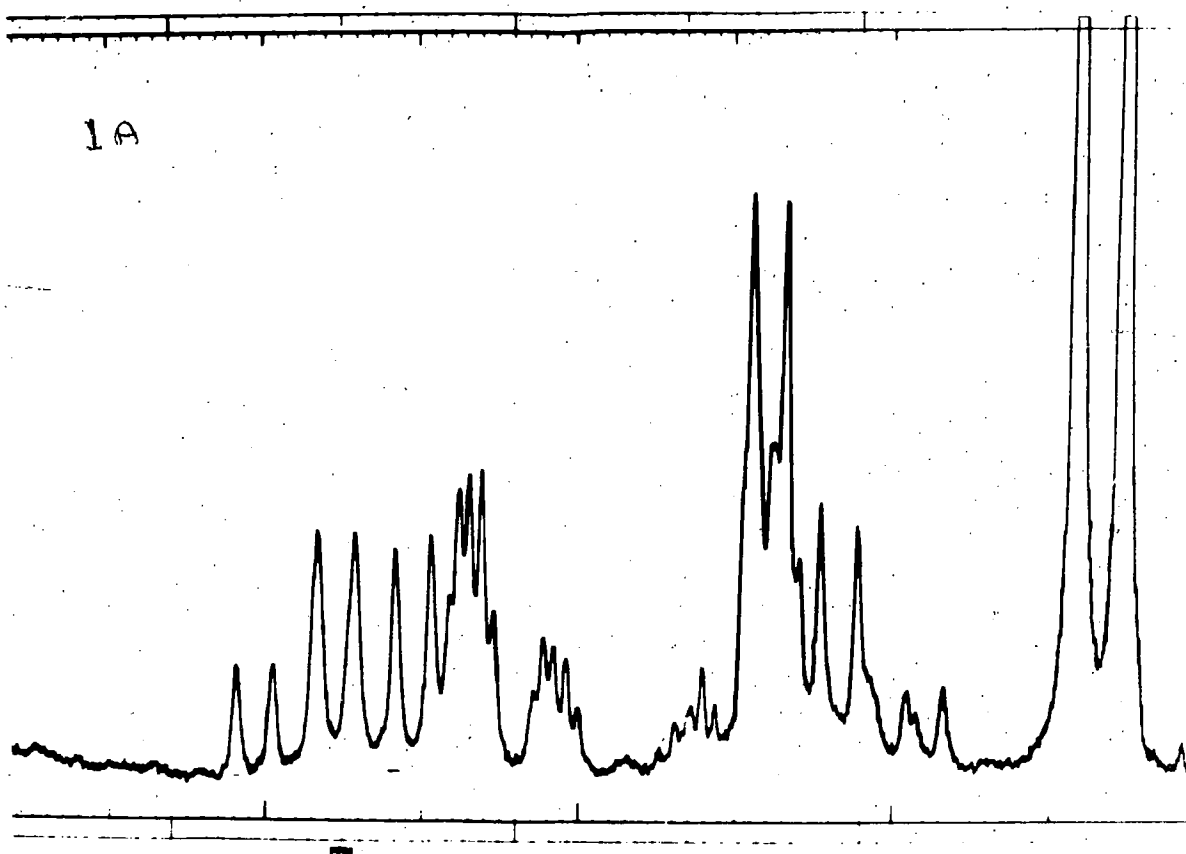
Best regards,

R.R. Fraser,
Prof. of Chemistry.

RRF/ma

1. A.F. Casey and K.M.J. McErlane, J. Chem. Soc. Perkin. I, 1972, p. 334.
2. R.J. Abraham and G. Gatti, J. Chem. Soc., B 1969, p. 961.
3. R.K. Harris and R.A. Spragg., J. Mol. Specty. 23, 158 (1967).
4. Y.L. Chow and C.J. Colon, Can. J. Chem., 46, 2827 (1968).

1A

1B

SIR GEORGE WILLIAMS UNIVERSITY

sgwu

DEPARTMENT OF CHEMISTRY

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

April 26, 1974

Dear Barry:

Spectra of Internal Rotational Isomers in a
Chiral Solvent

We have determined the proton spectra of some aryl substituted hydantoins, which are known to have slow rates of internal rotation at normal probe temperatures, in the chiral solvent (+)-phenyltrifluoromethylcarbinol.[1] Under achiral conditions, the rotational isomers of these compounds are enantiomeric.

Since, in the chiral solvent, the solvated rotamers should bear a diastereomeric relationship to each other, it is expected that they should show distinguishable nmr spectra.[1] We were interested in the extent to which the signals from corresponding nuclei in the two rotamers would be split.
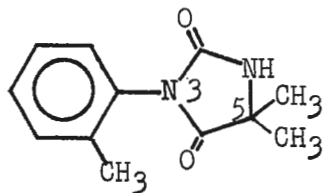
I
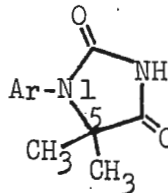
IIa   Ar = 2-methyl
IIb   Ar = 2,3-dimethyl
IIc   Ar = 2,4-dimethyl
IId   Ar = 2,5-dimethyl

Dr. Bernard L. Shapiro

We find that the extent of splitting of signals is strongly dependent on the location of the nuclei in these molecules. Thus, in the 3-aryl hydantoin, I, only the ortho methyl signals are resolvable (0.05 ppm), the 5,5-dimethyl signals being unaffected. Other 3-aryl hydantoins which were examined also failed to show additional splitting in the chiral solvent.

In the 1-aryl series (II) the 5,5-dimethyl proton signals are slightly broadened in the chiral solvent, while the ortho aryl methyl signal is split (0.12-0.13 ppm) in all cases examined. In the 2,3-dimethylphenyl compound (IIb) the meta methyl signal is split by 0.12 ppm, whereas in the 2,5-dimethylphenyl compound (IId) the meta methyl signal is split by 0.06 ppm. In contrast, the para methyl signal of the 2,4-dimethyl compound (IIc) is unsplit.

The known solvating behaviour[2] of the solvent suggests that solvation should occur by hydrogen bonding to the carbonyl groups of the hetero ring. A feasible explanation for the observed chemical shift differences between the diastereomeric solvates may be based on a model involving a secondary interaction between the π electron systems of the solute and solvent molecules such that the maximum anisotropy of the solvent phenyl group is experienced by the nuclei in the region of the solute aryl group. Thus the 5,5-dimethyl groups are affected in the 1-aryl but not the 3-aryl series. The lack of splitting of a para methyl group (IIc) may result from a similar relationship with the solvated solvent phenyl groups in the two rotamers.

Best regards,

Yours sincerely,

L.D. Colebrook
F.H. Hund
S. Icli

[1] W.H. Pirkle, J. Amer. Chem. Soc., 88, 1837 (1966).

[2] W.H. Pirkle and S.D. Beare, ibid., 91, 5150 (1969).

KEMISK INSTITUT

AARHUS UNIVERSITET

LABORATORIET FOR ORGANISK KEMI
·HANS JØRGEN JAKOBSEN

8000 Århus C, den   April 30, 1974
Telefon (06) 12 46 33   HJJ/ATL

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

Dear Professor Shapiro:

Selective Population Transfer (SPT) in FT NMR.

A Useful Technique Equivalent to TSI in CW NMR

In connection with our interest in analysis of unde-coupled ^{13}C FT NMR spectra, we would like to inform your read-ers of a technique that we have applied in numerous cases for assignment and relative sign determination of ^{13}C-X coupling constants in ^{13}C spectra [1]. Furthermore, in molecules with degenerate proton transitions (e.g. AX_n spin systems; $A = {}^{13}C$, $X = {}^{1}H$), the method may be especially useful for sensitivity enhancement [2].

The SPT technique is equivalent to the transitory selec-tive irradiation (TSI) experiment in CW NMR [3], i.e. a spe-cific transition in the ^{1}H satellite spectrum is perturbed in a manner so as to approach inversion of the corresponding ener-gy level populations. Thus in a ^{13}C FT experiment a weak irra-diating field $\underline{H}_2$ field ($\gamma \underline{H}_2/2\pi = 0.1$-$0.5$ Hz) is applied to one of the ^{1}H transitions during a time τ, given by $\gamma \underline{H}_2 \tau = \pi$ (i.e. $\tau = 1$-5 sec), immediately before probing the ^{13}C intensity change by excitation with a strong $\underline{H}_1$ rf pulse. Almost complete popula-tion inversion may be obtained for molecules where $T_1 \gg \tau$ (T_1 is the shortest spin-lattice relaxation time for all connected transitions). In a repetitive $\underline{H}_1$ pulse experiment the $\underline{H}_2$ field is simply gated as described by Freeman and Hill [4]. This pulse sequence has also recently been applied by Pachler and Wessels to the ^{13}C spectrum of chloroform [5]. The SPT ^{13}C spectra in figures 1 and 2 serve to illustrate the application of the tech-nique for assignment and relative sign determination of ^{13}C-X couplings, and for sensitivity enhancement in ^{13}C FT NMR, re-spectively.

For comparison with first order spectral intensity dis-tributions arising from ordinary equilibrium populations (i.e. the binomial coefficients), we have calculated (fig. 3) the rel-ative intensities for the A transitions in AX_n ($A = {}^{13}C$, $X = {}^{1}H$) spin systems immediately after the SPT technique has been ap-plied to one of the lines (degenerate transitions) in the X dou-blet. This has been performed assuming complete population in-

version between the levels for the degenerate transitions and using $\gamma_H/\gamma_C = 4$. As seen in figure 2 the relative intensities in the enhanced spectra are in good agreement with those predicted (fig. 3).

A few preprints (refs. [1] and [2]) are available.

Sincerely yours,

H. J. Jakobsen   R. S. Hansen   S. Aa. Linde   S. Sørensen

[1] S.Sørensen, R.S.Hansen and H.J.Jakobsen, J.Magn.Resonance, 1974.

[2] H.J.Jakobsen, S.Aa.Linde and S.Sørensen, J.Magn.Resonance, 1974.

[3] R.A.Hoffman and S.Forsén, "Progress in Nuclear Magnetic Resonance Spectroscopy" (J.W.Emsley, J.Feeney and L.H.Sutcliffe, Eds.), Vol.1, p.p.34, 87 Pergamon Press, Oxford, 1966.

[4] R.Freeman and H.Hill, J.Magn.Resonance, 5, 278 (1971).

[5] K.G.R.Pachler and P.L.Wessels, J.Magn.Resonance, 12, 337 (1973).
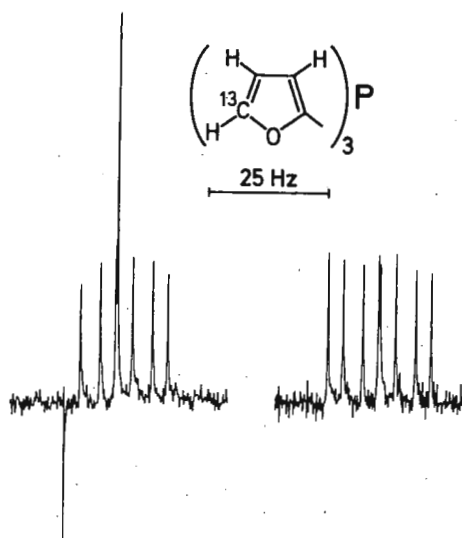
Figure 1. 25.16 MHz ^{13}C SPT NMR spectrum (Varian XL-100-15 spectrometer, S124-XL Fourier transform accessory, Varian 620L 16K computer) of the C5 carbon in tris-2-furylphosphine; high frequency (low field) part is at the left and low frequency (high field) part at the right. The spectrum was obtained by application of the SPT technique to the highest frequency line in the H4 satellite spectrum, $\gamma H_2/2\pi = 0.25$ Hz and $\tau = 2.0$ sec. The experiment shows that

$$^2J_{C5-H4} > {}^3J_{C5-H3},$$

$$^1J_{C5-H5} \times {}^3J_{H4-H5} > 0,$$

$$^3J_{C5-H3} \times {}^3J_{H3-H4} > 0$$

(i.e. $^3J_{C5-H3} > 0$), and

$$J_{C5-P} \times {}^4J_{H4-P} > 0$$

(i.e. $J_{C5-P} > 0$).

Figure 2. ^{13}C NMR spectra of the carbonyl carbon atom in acetone ($^2J_{CCH}$ = 5.92 Hz). (a) Normal undecoupled spectrum. (b) and (c) SPT spectra obtained by gated irradiation of the low (b) and high (c) frequency line in the ^{1}H inner satellite doublet spectrum, $\gamma H_2/2\pi$ = 0.45 Hz and τ = 1.1 sec. All spectra were obtained from 25 transients and recorded on an absolute intensity scale. For relative intensities see fig. 3.

Figure 3. Relative intensities for the A spectrum of AX_n (A = ^{13}C and X = ^{1}H) spin systems. (a) Relative intensities corresponding to the populations at thermal equilibrium (Pascal triangle). (b) Relative intensities corresponding to complete inversion of the equilibrium populations for the degenerate transitions due to one of the lines in the X doublet (γ_H/γ_C = 4).

AUTHOR   INDEX

Varian has an NMR system for every application...

for instance, the new CFT-20 for Carbon-13

Varian, world leader in magnetic resonance spectroscopy, offers a complete selection of NMR spectrometers, from low-cost instruments designed to solve the typical problems of industrial and academic laboratories to the ultimate in research systems.

EM-300X

World's lowest priced, high resolution NMR system. A really economical thermostatted 30-MHz permanent magnet system that produces highly informative spectra on a wide variety of compounds. Like higher performance proton spectrometers, it uses 5-mm samples, contains a built-in integrator, has a homogeneity adjust circuit for fast tune-up, and includes a flatbed recorder with precalibrated chart paper. Its ruggedness, small size, low weight and easy operation make it ideal for routine analyses and teaching applications.

EM-360

A legend in its own time. Reaction from hundreds of scientists who have seen it in operation has been unanimous: with its resolution (0.6 Hz), its sensitivity (18:1), and most of all, its extremely low price, the 60-MHz EM-360 is being hailed as one of the most outstanding contributions to the field of NMR to come along in years. And it's available with a lock/decoupler accessory.

T-60A

A brand new, old reliable spectrometer. The old, reliable part of the T-60A is a heritage of fine workmanship and dependability inherited from the renowned System T-60.

The brand new aspect includes a wide range of improved features—sensitivity in excess of 30:1; resolution better than 0.3 Hz; resolution stability of 0.5 Hz per day; more sweep widths; and more sweep times. Yet even with all this improved capability, the T-60A costs no more than the System T-60 before it.

CFT 20

CFT-20

Varian's newest instrument, the first low-priced NMR spectrometer specifically designed for ^{13}C spectroscopy. Its low impedance electromagnet is double-thermally insulated for excellent long-term stability. And the magnetic field is so homogeneous, the CFT-20 can accommodate 10-mm sample tubes for room temperature experiments and 8-mm sample tubes over the temperature range of $-80°C$ to $+200°C$. The operating console houses a keyboard for entering operating parameters and experimental commands; an oscilloscope that can display alphanumeric characters or spectral data; an X-Y plotter; and a built-in 620L-100 minicomputer with 8,192 words of memory. If that's not enough, the CFT-20 also features: internal pulsed deuterium lock; continuous wave, noise modulated and gated decoupling; Autoshim™; and a built-in read only magnetic tape cassette for loading programs. Best of all is the price. Ask about it. You'll be surprised.

XL-100

The industry standard. A pulsed-Fourier transform or frequency swept high resolution 23.5-kG spectrometer. It features observing capability from 7 to 100 MHz and decoupling range from 2.9 to 58 and 94 to 100 MHz for continuous wave, noise decoupling or INDOR experiments. The availability of homo- or heteronuclear internal lock on ^{1}H, ^{19}F, and ^{2}H, and external lock on ^{1}H and ^{19}F provides locking flexibility. Fourier transform operation, T_1 measurements, homonuclear decoupling and solvent elimination techniques are also routine XL-100 operations. The XL-100 can be tailored to meet single purpose or multi-departmental NMR needs.

SC-300 and SC-360

For the highest performance in commercially available high resolution NMR spectrometers. The SC-300 (300 MHz) and SC-360 (360 MHz) spectrometers are engineered for use in applications requiring the highest magnetic field strengths—liquid crystal, biological, biopolymer, and biochemical studies. Accessories are available for observation of other nuclei in both continuous wave and Fourier transform modes.

If you'd like more information on any of these systems, see your local Varian representative or write Varian Instrument Division, 611 Hansen Way, Palo Alto, California 94303.

varian instruments (W)