CT

Texas A & M University N-M-R Newsletter

No. 198

March, 1975

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No. 200: 5 May 1975

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.

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 198

198-1
CHIMIE ORGANIQUE PHYSIQUE

UNIVERSITÉ DE NANTES
U E R DE CHIMIE

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

NANTES, le 30.1.75

TITLE : A method for peak elimination in ^{13}C spectroscopy

Dear BARRY,

Inversion recovery pulse sequence (1) and selective saturation (2) have been proposed to achieve a good solvent peak elimination and to overcome efficiently the striking problem of the dynamic range of NMR computers. Recently, a more sophisticated machine has been claimed to suppress all peaks but one in the NMR spectra (3). However, this spectrometer is not yet commercially available, so we have tried to find a method which could be carried out on routine machines.

A signal can be suppressed quite efficiently by heating or cooling the sample and it is not even necessary to regulate and measure accurately the temperature. A typical run is shown on the figure ; the doublet located at ~35 ppm from TMS is easily eliminated by a slight increase of 55 degrees.

Incidentally, this experiment points out how difficult it is to obtain a good signal to noise ratio near the coalescence point. If we do wish to obtain it we must then accumulate a great number of transients but this procedure may create another problem of dynamic range !

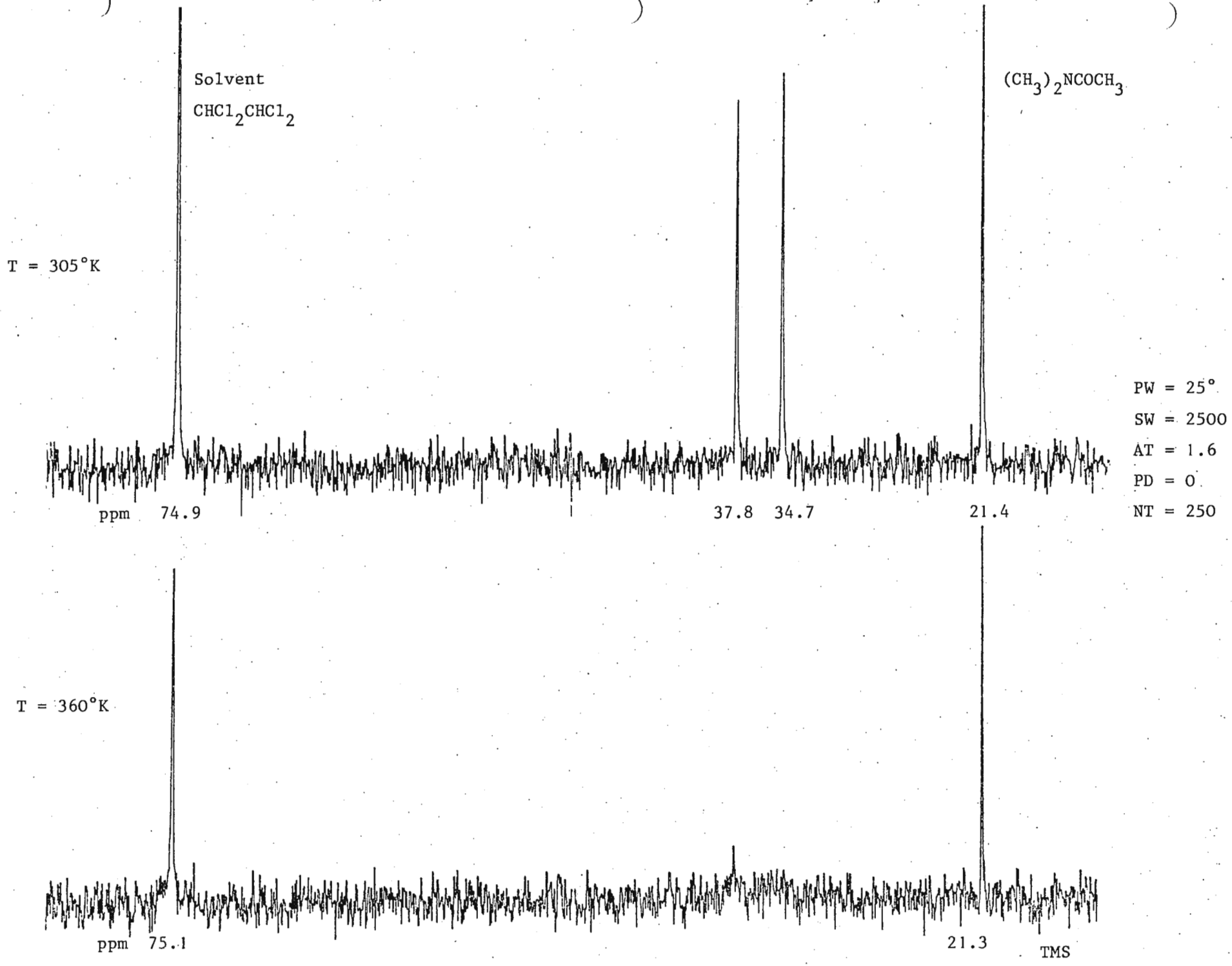
Yours sincerely.

G.J. MARTIN

(1) F.W. BENY, J. FEENEY, and G.C.K. ROBERTS - J. Magn. Res. 8, 114 (1972).

(2) J.P. JESSON, P. MEAKON, G. KNEISSEL - J. Amer. Chem. Soc. 95, 618 (1973).

(3) A. PINES - Tamu NMR Newsletter 188, 1 (1974).


Solvent
$CHCl_2CHCl_2$
$(CH_3)_2NCOCH_3$
T = 305°K
PW = 25°
SW = 2500
AT = 1.6
PD = 0
NT = 250
ppm 74.9
37.8 34.7
21.4
T = 360°K
ppm 75.1
21.3
TMS

198-2

UNIVERSITÉ DE LYON
FACULTÉ DES SCIENCES

LABORATOIRE DE SPECTROSCOPIE ET LUMINESCENCE

43, Bd DU 11 NOVEMBRE 1918
69 - VILLEURBANNE
TÉL. (78) 52.07.04 et 52.12.29

Villeurbanne, January 31, 1975

Titre : Du bon emploi des formules de "coalescence"

Cher Professeur Shapiro,

La formule de Gutowsky et Holm(1) qui donne la durée de vie des sites à la coalescence des raies RMN $\tau = \sqrt{2} / 2\pi(\nu_A - \nu_B)$ est largement utilisée dans l'étude des échanges. Dans le cas où la différence $(\nu_A - \nu_B)$ est importante devant la largeur de raie $1/\pi T_2$ son emploi est parfaitement légitime car c'est sous cette condition qu'elle a été établie. Par contre si cette condition n'est plus réalisée on ne peut se contenter de cette approximation, la valeur du temps de vie pour laquelle la coalescence est obtenue dépend de la largeur de raie imposée en général par l'inhomogénéité du champ magnétique H_o.

Nous vérifions ceci en observant les résonances des méthyles en 5 du diméthyl - 5.5 dioxanne - 1,3 qui s'échangent entre deux conformations également probables l'écart de fréquence $\nu_A - \nu_B = 23$ Hz.

Alors que la coalescence a lieu à - 61°C pour des raies fines ($L_{TMS} \simeq 1/\pi T_2 = 1,75$ Hz) (fig I), elle a lieu à - 64°C dans un champ moins homogène $L_{TMS} = 9$ Hz (fig II,III,IV).

On peut reprendre le calcul qui donne à partir de la forme de raie (2) $g(\nu)$ la condition de coalescence en ne négligeant plus les termes en $1/\pi T_2$ devant $(\nu_A - \nu_B)$. On obtient alors la coalescence lorsque

$$\tau = \frac{\sqrt{2}}{2\pi(\nu_A - \nu_B)}\left(1 + \frac{3\sqrt{2}}{8}K + \frac{3}{8}K^2\right) \quad \text{en posant } K = \frac{1}{\pi T_2(\nu_A - \nu_B)}$$

avec $\frac{1}{T_2} = \frac{1}{T_{2vrai}} + \frac{1}{T_{2inhomogène}}$ et en se limitant aux termes du second ordre en K.

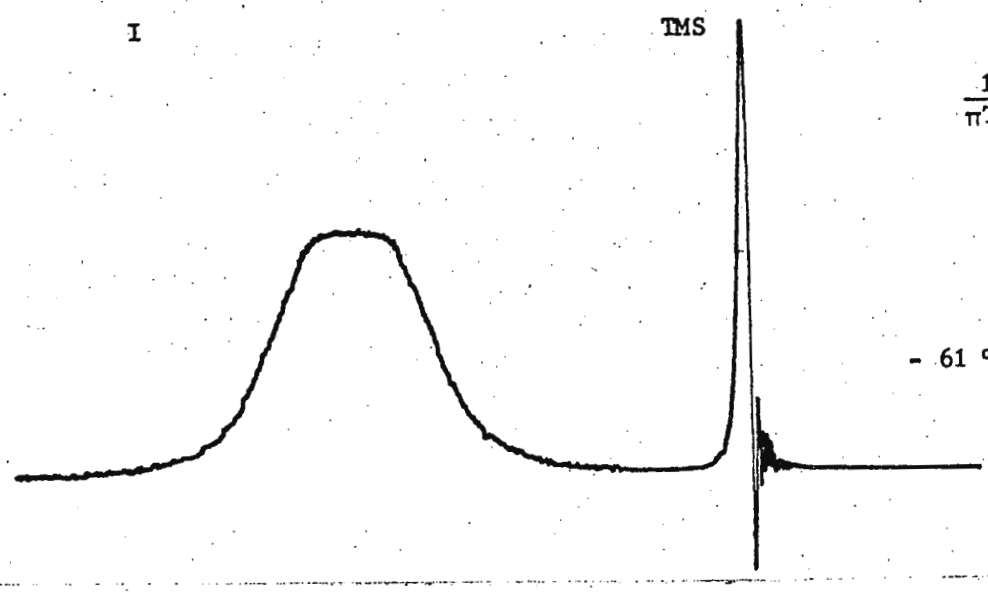
L'augmentation du rapport K déplace bien la coalescence vers les basses températures. Certes pour illustrer ce déplacement de la température de coalescence nous avons utilisé des champs très inhomogènes, il va sans dire que pour des valeurs de $(\nu_A - \nu_B)$ plus faibles cet effet devient important même en champ homogène.

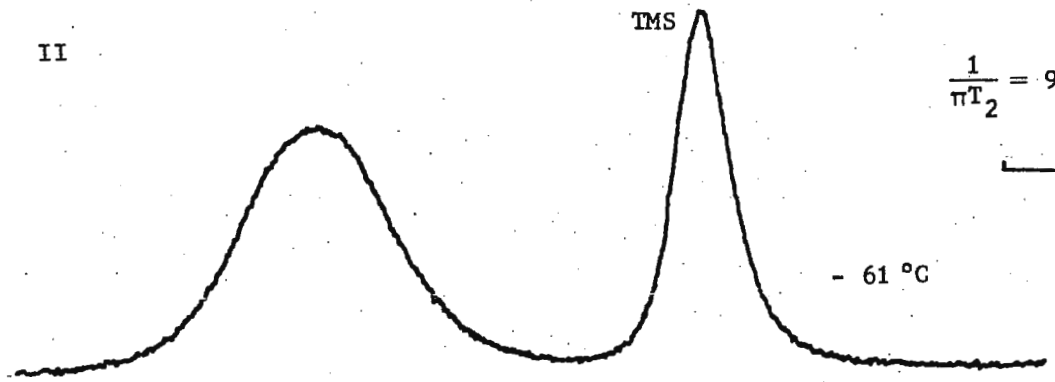
Recevez cher Docteur Shapiro nos sentiments les meilleurs.

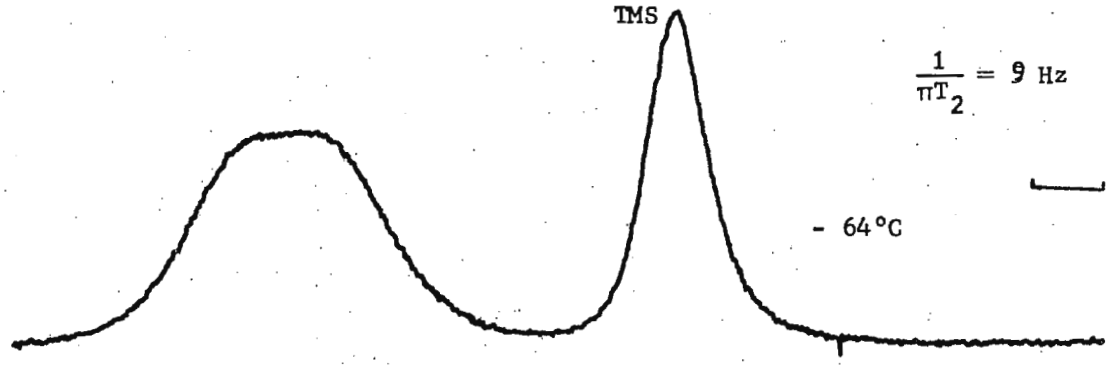
J. DELMAU J.C. DUPLAN A. BRIGUET G. TETU

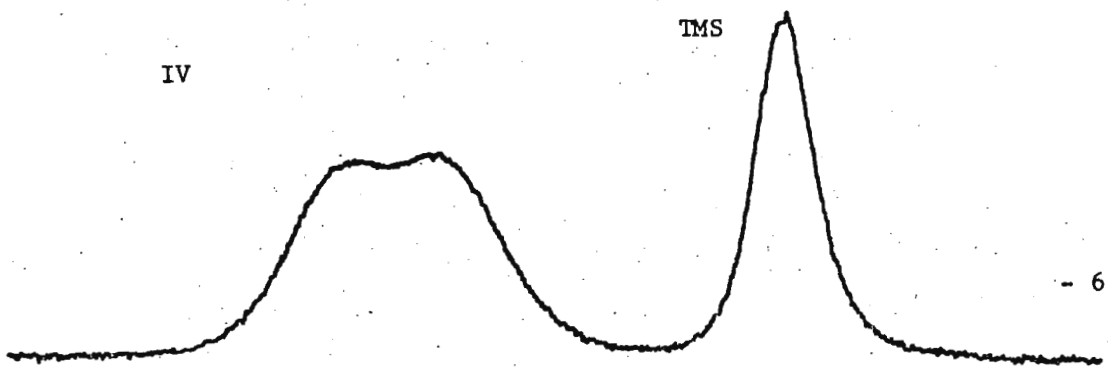
(1) H.S. GUTOWSKY, C.H. HOLM J. Chem. Phys. 25, 1228, (1956).

(2) High Resolution Nuclear Magnetic Resonance
J.A. POPLE, W.G. SCHNEIDER, H.J. BERNSTEIN Mc Graw Hill(1959)


I
TMS
$\frac{1}{\pi T_2}$ = 1,75 Hz
10 Hz
- 61 °C

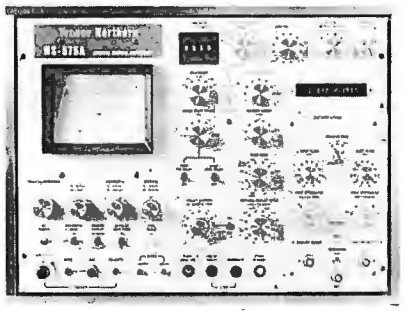

II
TMS
$\frac{1}{\pi T_2}$ = 9 Hz
10 Hz
- 61 °C


III
TMS
$\frac{1}{\pi T_2}$ = 9 Hz
10 Hz
- 64 °C


IV
TMS
$\frac{1}{\pi T_2}$ = 9 Hz
10 Hz
- 65 °C

Multi-budget systems for multi-discipline applications...Tracor Northern signal averagers.

Data once thought to be unobtainable due to its fringe position is now easily captured by Tracor Northern's signal averagers. The adaptability and versatility of our powerful systems is proven by their daily use in fields like spectroscopy, electronics, physics, medicine, mechanical vibration studies and analytical chemistry to name a few.



NS-575A Digital Signal Analyzer. The most advanced fixed program signal averaging system.

Over 400 signal averaging installations provide the background and expertise in designing the 575A. Implementation of the most sophisticated production techniques enables us to offer these features as standard:

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* 4 digit thumbwheel time base control. 10 uSec. to 10 Sec. per address.
* Pre and post analysis delay.
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* Digital display of address, data, and number of sweeps performed.
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* 7 data processing modes.

To provide users with extensive flexibility and versatility, over 20 plug-in modules are available for:

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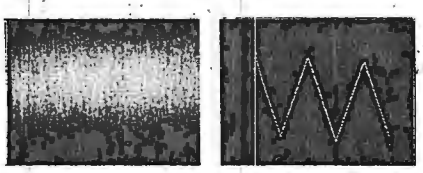

Left: NS-575A with Biomation plug-in module examines severe noise situation. Right: 100KHz triangular waveform is detected after 1024 sweeps (real time = 8 sec.).

* 10 nSec. per address averaging with Biomation Transient Recorder.
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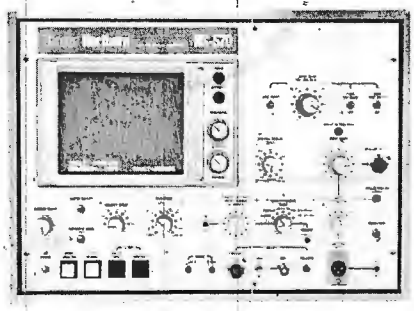
* High resolution waveform digitizing.

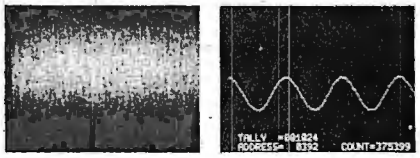


NS-570. A unique low cost signal averaging system.

Years of design experience have gone into Tracor Northern's NS-570 to produce a system ideal for dedicated averaging and MCS applications. No other system available today can match the 570's low cost and state of the art features. And no other system comes close to the 570's ease of operation.

Built into this unique system are 6.5″ Tektronix oscilloscope, data processor and continuous display. The solid state memory is available in 1024 or 2048 with 2^{20}-1 counts per address.

To make sure our system operates within yours, we offer options like character generator display and NMR synchronizer with easy



Left: NS-570 in a direct averaging application examines a severe noise environment. Right: Sine wave is detected after 1024 sweeps (real time = 20 sec.).

to operate NMR controls. Like the main system, options are low cost.

Both the 575A and 570 are compatible with Tracor Northern accessories which aid data manipulation . . . readout/readin via teletype, high speed paper tape punch and reader, reel to reel and cassette magnetic tape and EIA compatible devices. And interfaces are available for DEC-11, H-P 9800 and Nova series computers.

If you're not sure about your application for signal averaging, give us a call. Our applications assistance department will be able to advise you based on years of experience and over 400 installations. We undoubtedly have worked in a situation similar to yours so we can talk results before you decide. Would you take anything less from the leader?

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Naperville, Illinois 60540
312-420-5111

January 30, 1975

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

Subject: ^{13}C Studies of Ethylene-Propylene Copolymers

Dear Barry:

We received our Varian CFT-20 in June and it has been churning out data ever since then. One of the problems we have been working on is the structure of ethylene-propylene copolymers. The samples we studied were prepared with a standard stereoregular catalyst system which produced polymers containing, within our limits of detection, no propylene head-to-head or tail-to-tail inversions. Also, due to the relatively low concentration of propylene in the copolymers we examined, peaks due to stereo-inversions are expected to be too small to be detected under the conditions we employed. The relative structural simplicity of these samples led to a sharpening of several spectral regions which allowed assignment of certain tetrad and pentad sequences. Following the nomenclature of Carman[1] a methylene carbon is designated by two Greek letters which indicate its position relative to flanking methine carbons. Thus the underlined carbon in the structure $\overset{C}{\overset{|}{C}}$-$\underline{C}$-C-C-$\overset{C}{\overset{|}{C}}$ is an $\alpha\gamma$ CH_2. The methine and methyl carbons are denoted by ^tC and CH_3 respectively. A "typical" spectrum is shown in Figure 1 and the chemical shifts are listed in Table I.

As reported in the literature[2] we also find a discrepancy in the total methine area compared to the total methyl area. In all cases we have studied, the ^tC-PPE resonance is larger than the CH_3 PPE resonance. In order to avoid uncertainty in calculating percent composition we derived the following equations which avoid using either the ^tC areas or the CH_3 areas.

$$P = I_{\alpha\alpha} + \tfrac{1}{2}(I_{\alpha\gamma} + I_{\alpha\delta})$$

$$E = I_{\beta\beta} + I_{\beta\delta} + \tfrac{1}{2}I_{\delta\delta}$$

$$P + E = 1$$

Our results show that the measured CH_3 area is incorrect. We are presently examining this problem.

P. E. Johnson J. R. Knox G. J. Ray

GJR:sls

1. C. J. Carman and C. E. Wilkes, Rubber Chem. Tech., 44, 781 (1971).
2. C. E. Wilkes, C. J. Carman and R. A. Harrington, J. Polym. Sci., Symposium No. 43, 237 (1973).

TABLE I

Peak Assignments and Chemical Shifts for an Ethylene-Propylene Copolymer

Peak	Assignment	δ^a	Peak	Assignment	δ^a
			11a	$\beta\delta$ PE(E)$_n$EP	27.1
1	$\alpha\alpha$ PPPP	46.3	11b	$\beta\delta$ PEEP	27.2
2	$\alpha\alpha$ PPPE	45.8	12	$\beta\beta$ EPEPE	24.7
3	$\alpha\alpha$ EPPE	45.6	13	$\beta\beta$ PPEPE	24.6
4	$\alpha\gamma$	37.8	14	$\beta\beta$ PPEPP	24.4
5	$\alpha\delta$	37.4	15	CH_3 PPPPP	21.6
6	^{t}C EPE	33.1	16	CH_3 PPPPE	21.4
7	^{t}C PPE	30.7	17	CH_3 EPPPE	21.2
8	$\gamma\gamma$	30.3	18	CH_3 PPPEE + PPPEP	20.7
9	$\delta\delta$	29.8	19	CH_3 EPPEE + EPPEP	20.5
10	^{t}C PPP	28.7	20	CH_3 EPE	19.8

[a]Chemical shift in ppm from TMS.

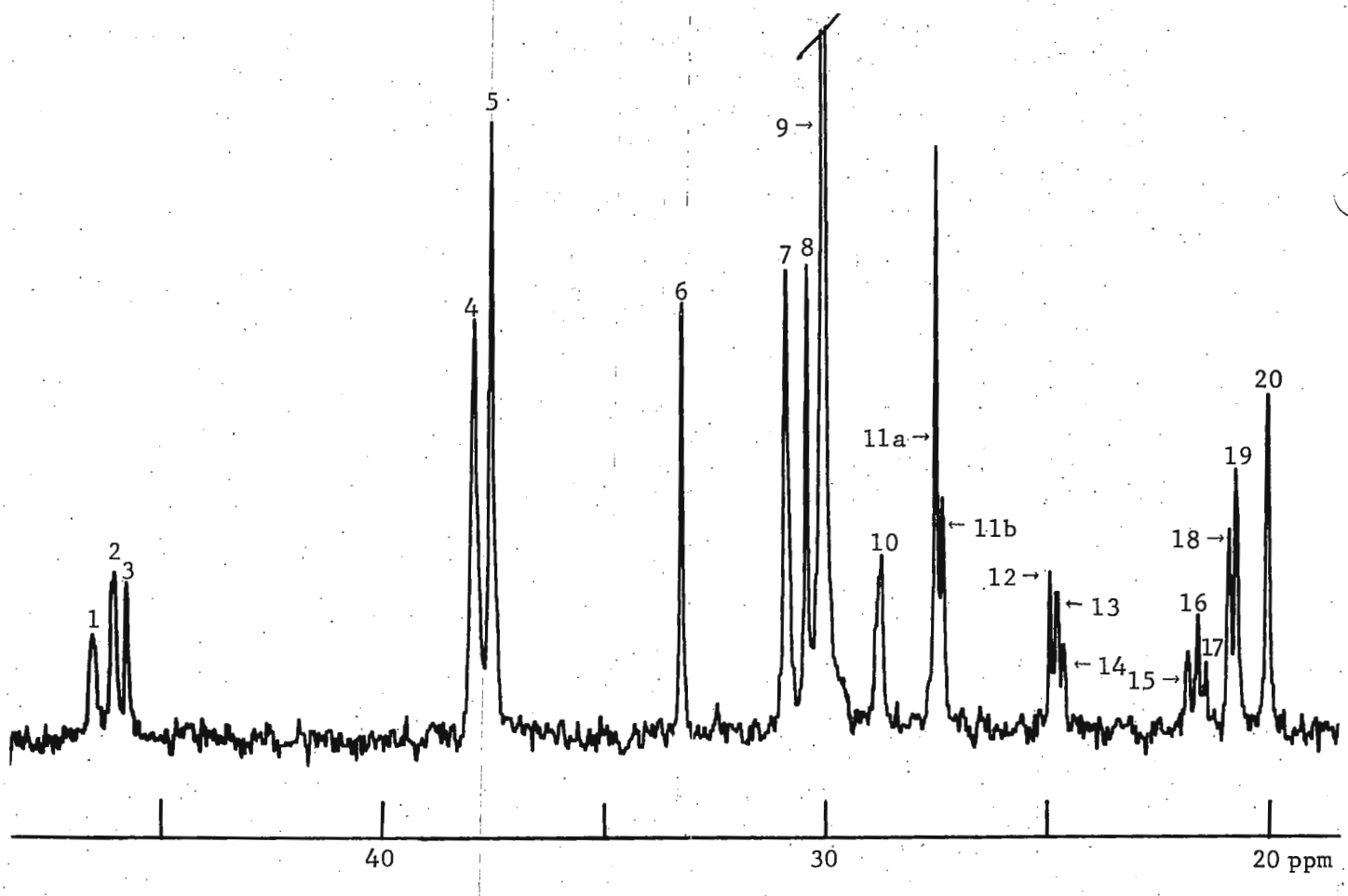

Figure 1

^{13}C-NMR Spectrum of an Ethylene-Propylene Copolymer

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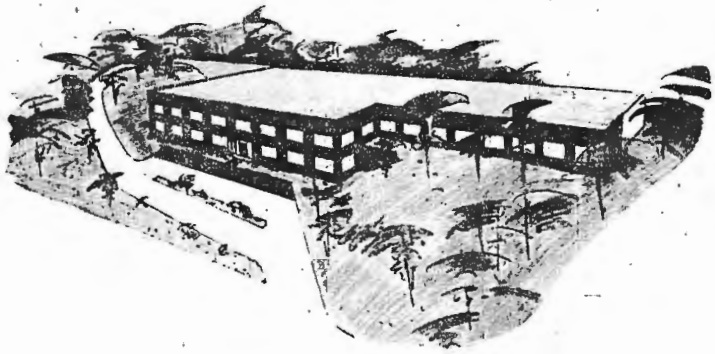

February 3, 1975

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

RE: Post-Doctoral Openings

Dear Barry:

We would like to inform our readers that Bruker Scientific, Inc., of Elmsford, New York, and Bruker Magnetics, Inc., of Burlington, Massachusetts, have now formally reorganized at our new North American Headquarters in Manning Park, Billerica, Massachusetts.

Our new facility encompasses very comprehensive application facilities, including our complete line of high resolution and pulsed spectrometers, as well as super conducting spectrometers.

We have immediate openings for post-doctoral fellows in high resolution NMR, ESR, and infrared spectroscopy. Individuals with extensive experience in these areas are urged to contact me at our new address in Billerica immediately.

In addition, similar openings are available in our R&D and application laboratories in Karlsruhe, West Germany and Zurich, Switzerland. Applicants for these positions are urged to contact Mr. Tony Keller, Bruker Physik A.G., 7501 Karlsruhe-Forchheim, Am Silberstreifen, Deutschland.

Yours sincerely,

Christian I. Tanzer

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Bruker Spectrospin Ltd.
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Mississauga, Ontario, Canada L4W1E4
Phone — 416-625-2375

198-9

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

NATIONAL HEART AND LUNG INSTITUTE

Computer File Searching of CMR Spectra

February 2, 1975

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

Dear Dr. Shapiro:

Our group at NIH has been studying the possibility of assembling a file of CMR spectra for research purposes and I am writing to solicit opinions from workers in the field.

We have done a great deal of work with large files of mass spectral data and a little with files of PMR spectra. As a result, we have most of the software necessary for the efficient handling of large data bases and we felt that CMR spectra are well-suited to this approach and furthermore, that the time is ripe for such a program.

At present, we envisage a file in which each CMR spectrum is represented by the observed chemical shifts, the name, molecular weight, molecular formula and structural formula of the compound and a source (or literature) reference. Also to be included in the data base, as available, would be intensities, T1 values and observed or predicted results of off-resonance observations.

As with the remainder of our chemical data base, the file will be resident on the NIH time-shared PDP-10 and would be searched in real time with chemical shifts, partial or complete molecular formulas or molecular weight or combinations of any two of these. Once a single spectrum has been retrieved from the file, any of the optional parameters that are available could be used by the investigator as secondary checks.

The question of assignments is more difficult. We certainly want to retain established assignments in the data base but have not decided how we are to identify individual carbon atoms in each specific molecule. Standard numbering systems probably are inadequate and so we plan to store with each spectrum a graphical representation of the numbered

Professor B. L. Shapiro February 2, 1975

molecule. This will only be accessible via a graphics display terminal but such an approach will allow us to retain the data pending a general solution to the problem which we hope may lie in the use of connection tables, probably in conjunction with CAS registry numbers.

We shall provide printed and computer readable copies of the files to all collaborators at appropriate intervals and for those interested, we also hope to be able to provide access to our PDP-10 on which the file and all the related software will reside. Such access was provided to many mass spectroscopists during the development of the NIH mass spectral search system and was deemed by many to be a useful arrangement.

We would very much appreciate readers' views on all these matters and would also like to ask if any groups would be prepared to supply CMR data to help us in building a large file. We can handle such data in any form (written, cards, tape, etc.) and would be ready to discuss the matter in order to create as little work as possible on the part of the contributor.

Sincerely,

G. W. A. Milne
Laboratory of Chemistry

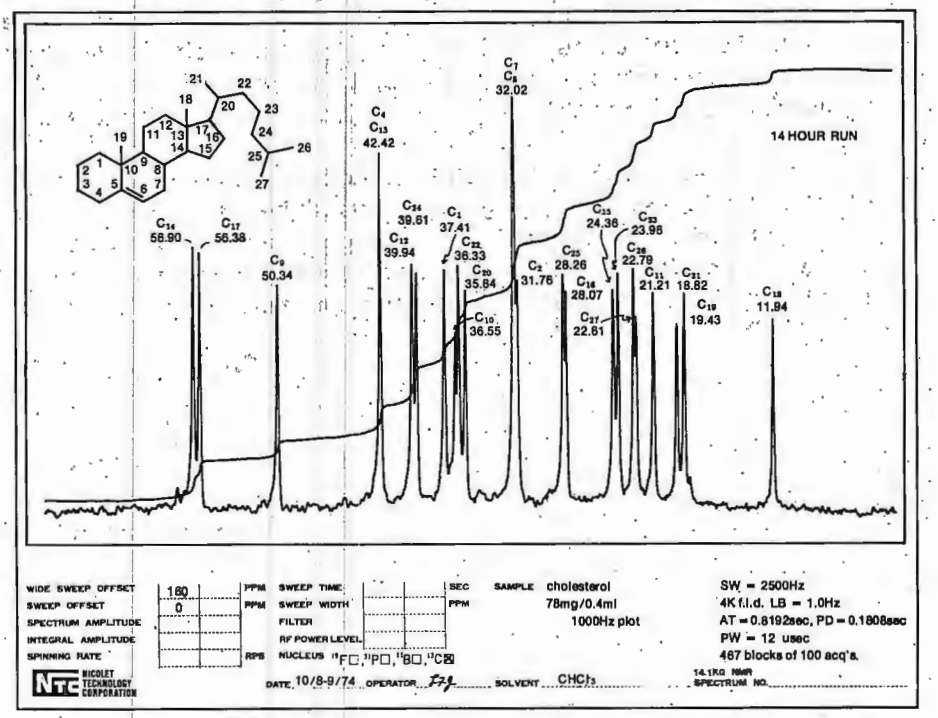
Transform your T-60 for ^{13}C spectra with a Nicolet TT-7 pulsed FT system.

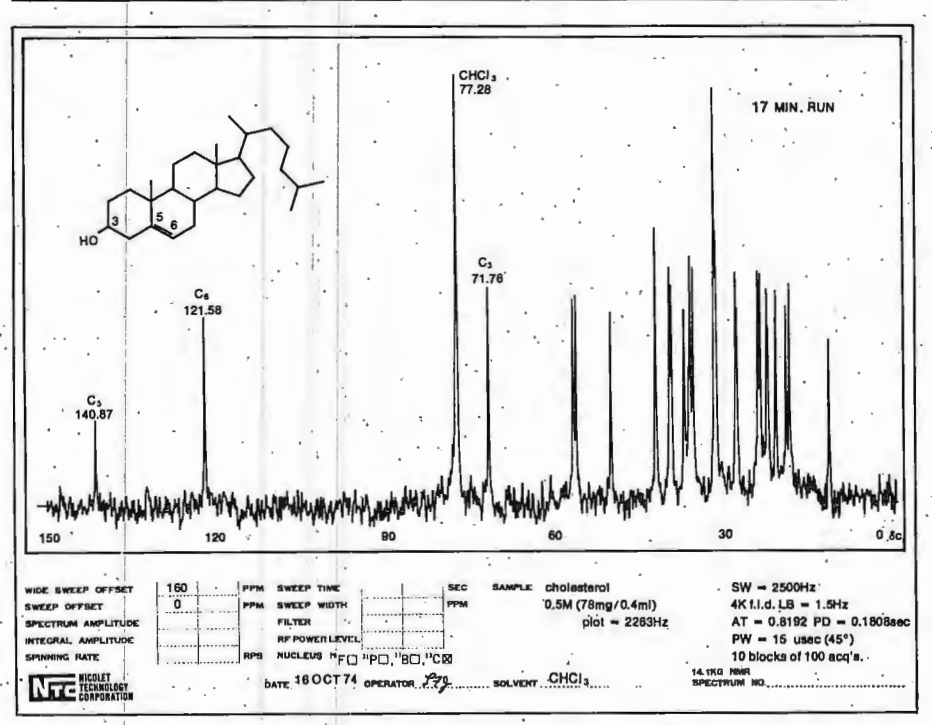
You can update a T-60 for ^{13}C measurements at a fraction of the cost of a new, dedicated system with the Nicolet TT-7 pulsed FT nmr accessory. The sensitivity provided by this combined system is comparable to that of instruments specifically designed for ^{13}C spectroscopy. Features offered with the TT-7/T-60 combination include: ■ ^{13}C spectra on 50 mg samples in 15 minutes; ■ 6.5 mm sample size; ■ no lock material required (expensive deuterated solvents are not required); ■ long-term runs of 12 hours or more are made possible through computer peak registration techniques which compensate for field drifts; ■ decoupling accessory for selective proton decoupling, noise decoupling, and gated decoupling; ■ expandable to 16K transform size; ■ optional T_1 (relaxation time) measurements unattended using multi-pulse inversion recovery techniques.

Signal input, accumulated free induction decays, or transformed spectra can be displayed on the TT-7's cathode ray tube for visual monitoring. The spectra can be plotted using the T-60 recorder and digital integration of spectra can be viewed or plotted as well.

The TT-7's ease of use is incomparable. Not only will it provide increased sensitivity and/or sample throughput of your T-60, but it will also provide an excellent Fourier transform training facility. The basic TT-7 system will provide computer calculations of theoretical nmr spectra of up to six spins.

Phone or write today for more detailed information.





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Faculty of Science
Department of Chemistry
519/885-1211

February 12, 1975.

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

Dear Barry;

Both in São Paulo and Waterloo, we are engaged in studies of lyotropic liquid crystals by NMR methods. For those who use the nematic phases for ordering ions or molecules, it is of considerable interest to obtain phases which have the maximum composition range for the components and also the maximum tolerance of the impurity concentration which is to be ordered by the phase. In wide surveys of such nematic systems which have proved very interesting in themselves, we have discovered that the Cesium decyl sulphate/decanol/water/electrolyte system is the best so far.

The accompanying diagram illustrates the large range of nematic behaviour. It is also of interest to note that this system will allow spinning in both cryogenic solenoids and conventional magnets to improve resolution. The figure represents nematic compositions in the following manner;-

1. Weight of Cesium decyl sulphate 50 parts.
2. Weight of D_2O defined by numbers which represent parts by weight at the ends of the horizontal bars in the figure.
3. Decanol contents are (a) 2 parts by weight (b) 3 parts (c) 4 parts (d) 5 parts (e) 6 parts and (f) 7 parts. The increase in decanol content in general increases the nematic range.

Outside the horizontal bars the phases become isotropic, lamellar, solid or 2 phase regions as indicated.

Addition of complex ion or simple electrolytes up to about 5 weight % is generally possible if solubility problems are not encountered. Flautt and Lawson [J. Am. Chem. Soc. 89 5489 (1967)] actually report two types of nematic phases one of which cannot be rotated with any velocity in a conventional magnet with retention of single liquid crystal behaviour and another with more electrolyte added (Na_2SO_4) which can be rotated to improve resolution. All nematic phases with Cesium decyl sulphate, whether they contain balanced electrolyte or not, belong to the second class which we have called type II phases. The nematic axis is actually perpendicular to the field requiring a small orientation time for selection of the unique spinning axis in conventional magnets but practically no orientation time in cryogenic solenoids.

We are trying to put some science into lyotropic nematic phases and call it "Synthetic Physical Chemistry". Keith Radley has just finished his Ph.D. on this topic and has now gone to the Liquid Crystal Institute at Kent State.

With kind regards,

Len.

LWR/es

L.W. Reeves.

(P.P.)/(I.) TWO PHASES

f. 120 — 88

POWDER PATTERN

e. 104 — 72

d. 80 — 56

c. 60 — 44

b. 44 — 36

ISOTROPIC

a. 34 — 28

SOLID

198-14

BROWN UNIVERSITY *Providence, Rhode Island • 02912*

DEPARTMENT OF CHEMISTRY

February 6, 1975

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

Dear Barry,

As I sit on my hands awaiting anxiously the delivery of our WP-60 so that we may get on with the serious business of doing pulsed CIDNP, I have been amusing myself by serving as a consultant on an interesting chemical exchange problem encountered by my colleague, Tom Morton. Lest you interpret my silence of the past few months as an indication of a death-wish with regard to my TAMU NMR Newsletter subscription, I will relate to your readers the nature of this project.

Deceptively Simple Chemical Exchange

Tom and David Bomse, a senior at Brown, have recently prepared tetraisopropylethylene (I) which is hindered enough to require cooperative motion of the alkyl groups of the sort shown below.

I

The nmr spectrum is nearly first-order at 60 MHz. and exhibits coalescence effects involving both the methyl and methyne proton signals at around room temperature. We are presently working with Tom to refine his data with a total lineshape analysis using linearized least squares fitting[1]. The slow exchange spectrum of I consists of a total of 9 pairs of lines (two septets and two doublets). Intensity borrowing is negligible, however, and the exchange process can be described quite accurately as nine simultaneous two-site exchanges, i.e. the much more time- and hardware-consuming density matrix approaches should be unnecessary. Since the spectrum is described *in toto* by one lifetime, two chemical shift differences, one coupling constant, probably a single T_2, a couple of scaling parameters and a predetermined set of intensities, it should be possible to determine the exchange

Professor B. L. Shapiro February 6, 1975

rate with unusually good precision. We have, in principle, nine times as much data to work with as is usual in such simple problems. We plan to put this precision to good use by comparing the rate of the conformation change in I with that in the compound with deuterium substituted at the methyne positions.

We have been aided in our TLS analysis by the development of a set of utility I/O subroutines written for our PDP-8/E which make it possible to program A/D and D/A functions in FOCAL. These routines were written by Paul Barbara who calls the package ACME (Automatic Collection of Machine Effluence)! Our goal is to combine the data acquisition and refinement functions in a single, essentially automatic, TLS operation using the PDP-8. Similar procedures are applicable to extracting data from CIDNP spectra--once the WP-60 arrives on our doorstep.

[1] S. L. Spassov, et.al., OMR, 3, 551 (1971); L. M. Jackman, et.al., ibid, 1, 109 (1969); L. Fischer, J. Mol. Spectros., 40, 414 (1971).

Sincerely yours,

Ron Lawler

Ronald G. Lawler
Professor of Chemistry

RGL:EAF

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198-18

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

Ihr Zeichen	Ihre Nachricht vom	Unser Zeichen	Tel. Durchwahl:	Datum
		LE/UH	7008 362/363	February 26th, 1975

Subject: A. XL-100-Decoupler Offset for Selective Heteronuclear Decoupling
-------- B. CFT-20 Spinner

Dear Dr. Shapiro,

A. We have recently performed a series of $^{13}C\{^{1}H\}$ -selective decoupling experiments as a method of assigning close lying carbon signals in aromatic compounds. To find the right decoupler offset is, of course, a prerequisite. The usual method, i.e. observing the residual ^{13}C, ^{1}H-coupling of the TMS ^{13}C-signal as a function of the decoupler offset and extrapolating to $J_r = 0$ is a rather tedious job, especially if one doesn't want to have too much TMS in the solution to be studied. With the Varian XL-100 there is a much easier way, obviously intended by the manufacturer, but not immediately obvious to the user. This is the recipe

a) Run the ^{1}H spectrum first FT-wise, pulsing at the high-field side of the spectrum.

b) Determine the offset of the TMS signal from the pulse position.

c) Add this number to your sweep offset.

The resulting figure gives the exact decoupler offset required to decouple the ^{1}H TMS signal during observation of the X nucleus, e.g. ^{13}C (provided one uses the same solution and the same lock signal). In other words: the sweep offset necessary to pulse on TMS is identical with the decoupler offset necessary to decouple TMS.

B. A useful hint for CFT-20 owners: the silver mirror on the spinner, required to measure the spinning rate, wears off in a matter of weeks. If it is replaced by a coating of white correction fluid, it works beautifully again (and seems to be more durable).

Please credit this contribution to Ernest Lustig's suscription.

Yours sincerely,

Ludger Ernst

Ludger Ernst

198-19

National Research Council Canada
Conseil national de recherches Canada

Division of Chemistry
Division de chimie

File Référence

February 6, 1975

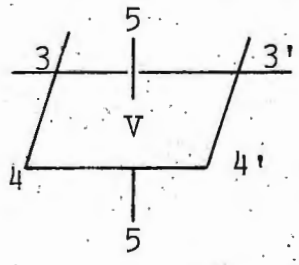
Dr. Bernard L. Shapiro,
Department of Chemistry,
Texas A&M University,
College Station, Texas 77843,
U. S. A.

Dear Barry,

Fluorine Resonance in VF_5

Thank you for your excellent handling of the mail situation. Our postal employees are not as able as they once were.

There has been a lot of study of averaging mechanisms in pentafluorides and of their state of aggregation, neat and in solution. One of the most reactive and least studied of these compounds has been vanadium pentafluoride. (Can. J. Chem. 52, 2236 (1974)). We have finally been able to resolve fine structure from spin coupling in a dilute solution of SO_2ClF and CF_2Cl_2 at -140°C. The VF_5 exists as chains of octahedra joined by cis-fluorine bridges. The spectrum may be fitted by the following parameters where the spin couplings are in Hertz and the chemical shifts are p.p.m. to low field of $CFCl_3$.



$\delta_3 = -13$ $\quad J_{3-3'} = 9$ $\quad J_{4-4'} = 9$

$\delta_4 = -627$ $\quad J_{3-4} = 122$ $\quad J_{4-5} = 122$

$\delta_5 = -536$ $\quad J_{3-4'} = 214$

$J_{3-5} = 122$

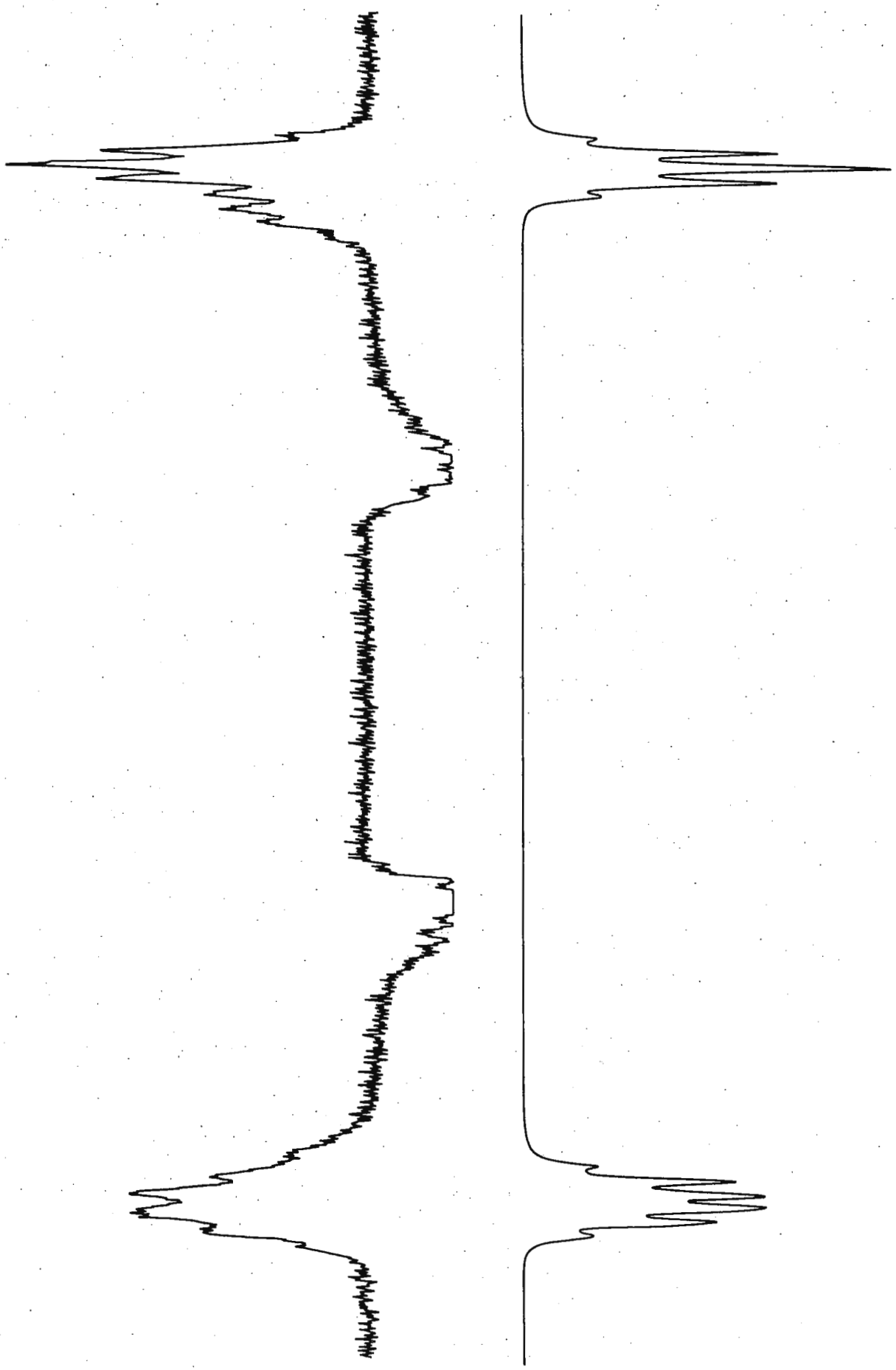
Experimental and theoretical spectra are shown on the figure for the non-bridging fluorines. Extra lines arise from the end groups.

Best wishes,

S. Brownstein.

SB/gm

Ottawa, Canada
K1A 0R9



UNIVERSITY OF BRADFORD

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Telephone 33466 Ext. 288, 498.
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DWJ/scs

School of Studies in Chemistry

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

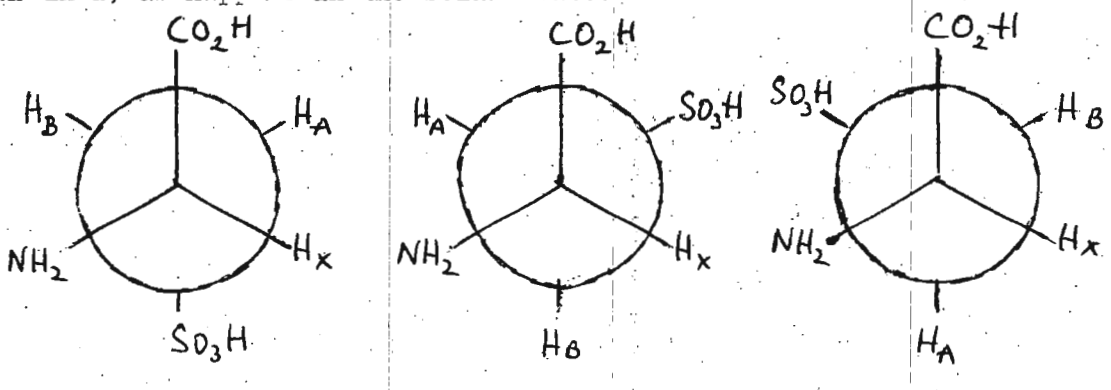
7 February 1975

Dear Dr. Shapiro,

Rotamers of sulphur-containing aminoacids in acid solutions

Following our previous 60 MHz ^{1}H measurements on sulphur-containing aminoacids in basic D_2O solution[1], and 220 MHz ^{1}H measurements of deceptively simple spectra of other aminoacids[2,3], we report some 220 MHz spectra of sulphur-containing aminoacids recorded by Dr. B.J. Dale (now at Abbott Laboratories, Queenborough, ME11 5EL, England) in acid solution. Geminal protons were assigned by analogy with the vicinal coupling constants of 8.8 and 3.2 Hz in cysteine. The fractional populations of the side-chain rotamers, derived by a Pachler procedure[4], are not very dependent on the size of the side-group, and show that for several acids the rotamer with carboxyl and sulphur-containing groups gauche is surprisingly highly populated over a wide pD range. Increase of temperature tends to equalise the populations and to decrease the chemical-shift difference between the two geminal protons. For S-carboxymethyl cysteine and S-methyl cysteine (whether at low pD or in zwitterion form at higher pD), and for S-t-butyl cysteine and S-benzyl cysteine at low pD, the geminal coupling constant of the methylene hydrogens is closely similar, near to 14.9 Hz.

In L-cysteic acid, the chemical shift of the methine proton exhibits two downfield shifts, each of 0.5 p.p.m., presumably owing to protonation, first of $-NH_2$ and then of $-COO^-$ and $-SO_3^-$ groups. Small J_{AX} indicates sparse population of one rotamer throughout the pD range studied. In basic solution, rotamer I with carboxyl and sulphonic groups trans is assumed predominant. Rotamer III, despite being unfavourable sterically, is appreciably populated in both acid and base, and may be stabilized by an intramolecular hydrogen bond (which would also occur in I) as happens in the solid state.



I II III

Analogous PMR determinations have been made of relative rotamer residence times of phenylalanyl, tyrosyl, tryptophyl, and histidyl dipeptides and tripeptides in acidic and basic solution. Three kinds of temperature dependence are observed: little change, for most compounds; tendency towards equalization, as for L-trypophyl-L-tyrosine in base; and divergence, as for L-phenylalanyl-L-leucine in acid solution.

Yours sincerely,

J.A.G. Drake D.W. Jones H. Pakdel

1. K.D. Bartle, D.W. Jones and R.L'Amie, J. Chem. Soc., Perkin II, 646 (1972).
2. B.J. Dale and D.W. Jones, Spectrochim. Acta, A, in the press.
3. TAMO NMR Newsletter 177, 48 (June, 1973).
4. K.G.R. Pachler, Spectrochim. Acta, 20, 581 (1964).

198-23

University of East Anglia

From Professor A.R. Katritzky

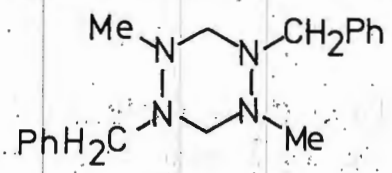
School of Chemical Sciences
University Plain, Norwich NOR 88C
Telephone Norwich (0603) 56161
Telegrams UEANOR NORWICH

7th February, 1975

Dear Barry,

Spectacular Spectral Changes with Temperature Variation: Part I

The room temperature spectrum of 1,4-dimethyl-2,5-dibenzyl hexahydrotetrazine (I) displays, in the N-CH_2 region of the p.m.r. spectrum (220 MHz), two singlets of equal intensity, one for the four ring methylene and one for the four benzyl methylene protons. A spectrum of the same region at -80°, however, reveals the most dramatic changes. A veritable forest of peaks occur, a careful analysis of which (later confirmed by the investigation of specifically deuterated samples) proved to be the superposition of six AB quartets of roughly equal area: i.e. twenty four peaks in all. As shown in the Figure, most of these peaks are well resolved though, unsurprisingly, some overlap does occur.

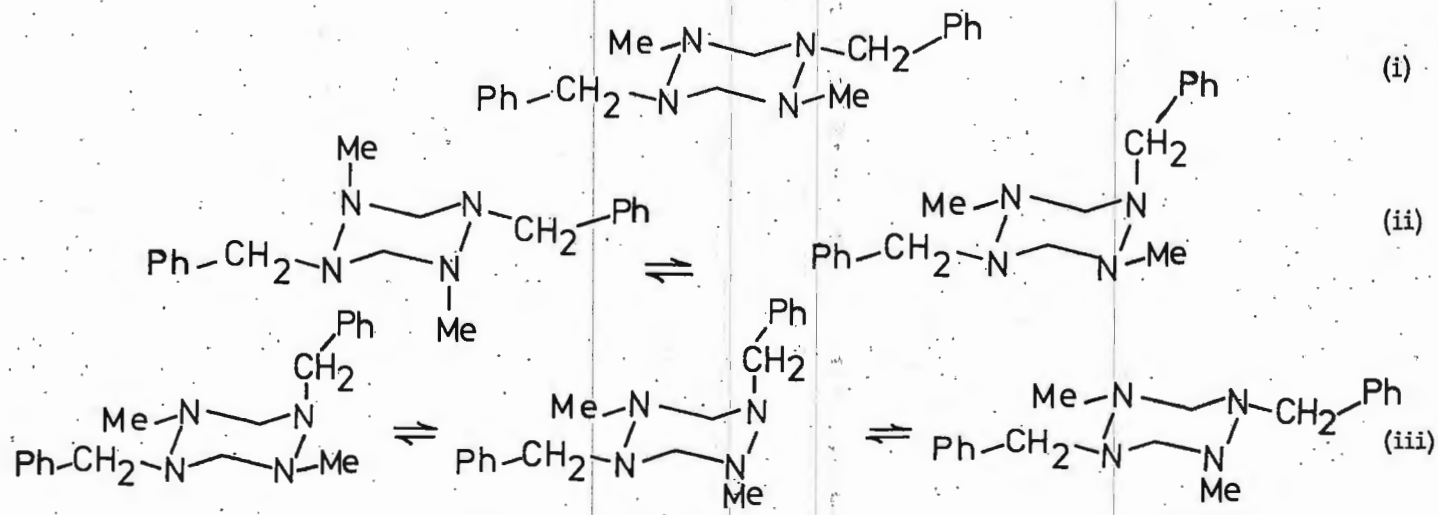


I

The explanation lies in the fact that at -80° we have slowed down all the ring inversions and also those N-inversions which are of the "passing" type (see Ref.). This results in the isolation of three sets of conformers (Scheme), of which two sets are populated. The full story will be unfolded in a forthcoming paper in J. C. S. Perkin II.

Best wishes, Yours sincerely,

V. J. Baker, A. R. Katritzky, J. P. Majoral.

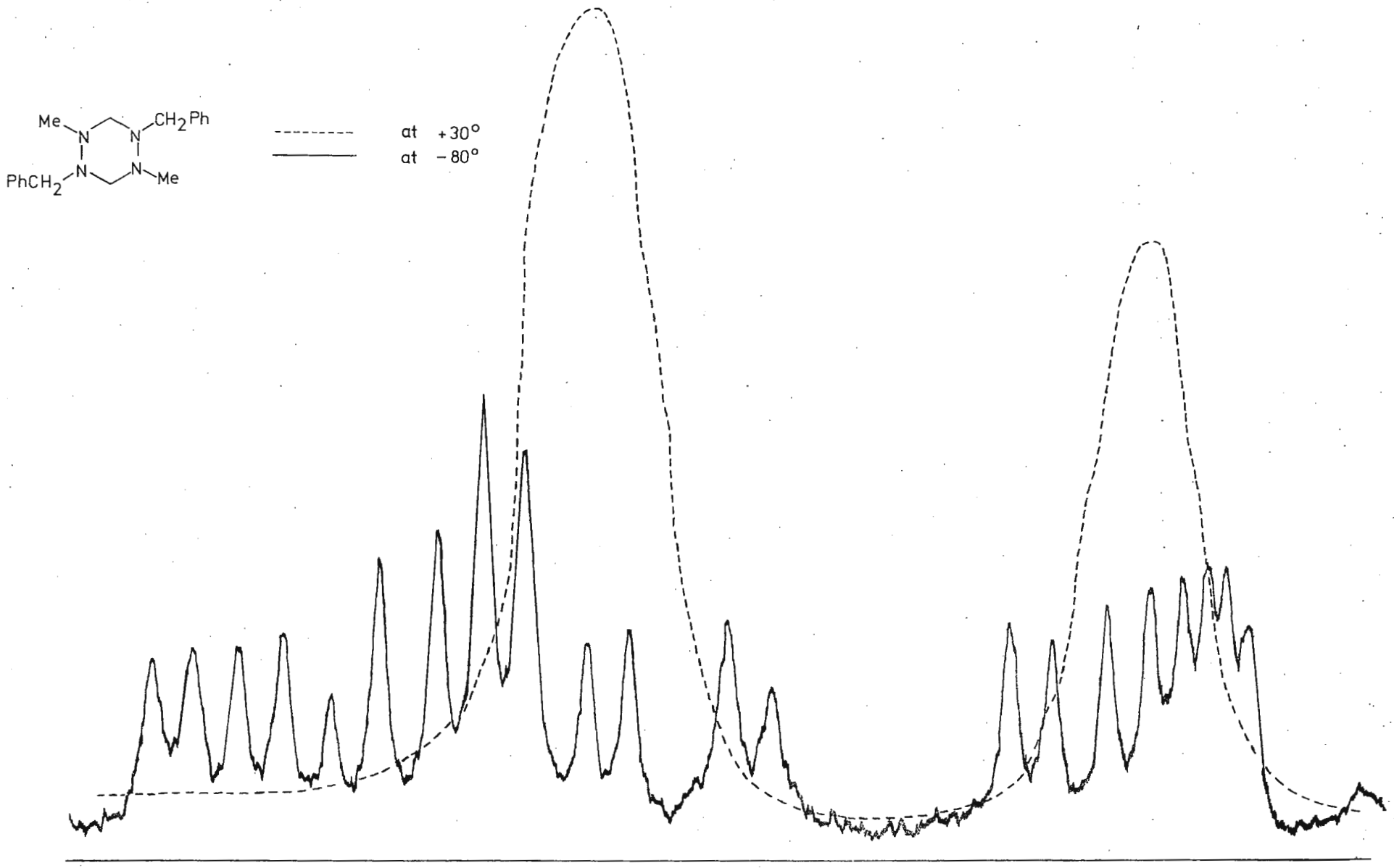


(i)

(ii)

(iii)

Ref. R.A.Y. Jones, A.R. Katritzky, K.A.F. Record, and R. Scattergood, J.C.S. Perkin II, 1974, 406.



198-24

198-25 Laboratorium
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Zürich

8006 Zürich,
Universitätstrasse 6

February 18, 1975

Professor B L. Shapiro
Department of Chemistry
TEXAS A&M UNIVERSITY
College of Science
College Station
T E X A S 77843

A Suggested Reference for Platinum-195 Chemical Shifts

Dear Prof. Shapiro,

In continuing our ^{195}Pt nmr studies we have noticed that there seems to be the usual uncertainty concerning referencing. We would like to suggest that the $PtCl_6^{2-}$ ion might prove suitable since:

1. It is commercially available
2. It appears at one end of the ^{195}Pt spectrum (complexes of nitrogen, phosphorus, arsenic, olefins and many others are all to high field of this ion).
3. In the concentration range 0.3M to 0.03M the chemical shift of Na_2PtCl_6 is essentielly invariant (unlike the $PtCl_4^{2-}$ ion which does satisfy criteria 1 and 2).

Your readers might also be interested to learn that while the line width of the Platinum signal in the $PtCl_4^{2-}$ ion is approximately 25Hz we have observed that in some complexes of nitrogen (I = 1) and arsenic (I = 3/2) widths may be of the order of 100 Hz or more.

Please credit this contribution to the "account" of Prof. L. M. Venanzi.

Sincerely,

G. Ballimann

Paul Pregosin

G. Ballimann

Dr. P. S. Pregosin

15530/26

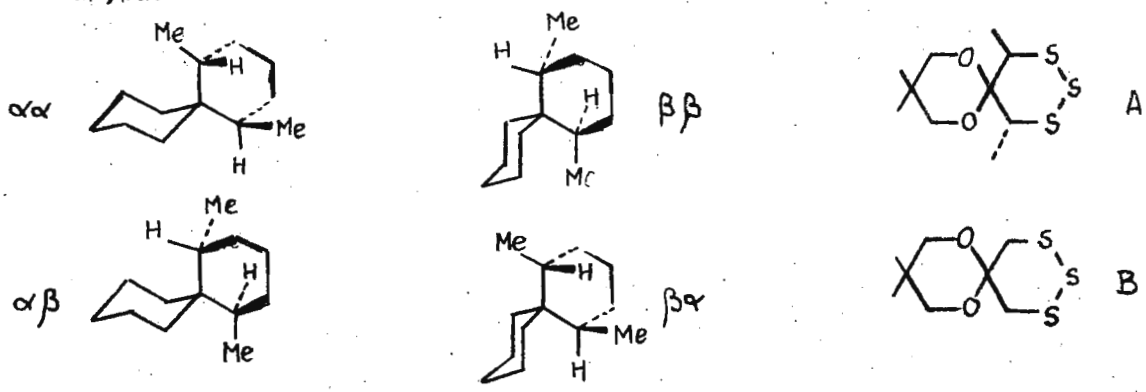
STATE UNIV. of GENT
ORGANIC CHEM. DEPT.
LAB. for NMR SPECTROSCOPY
Prof. M. ANTEUNIS
Krijgslaan 271 — GENT B — 9000
BELGIUM

LABORATORIUM
voor
ORGANISCHE CHEMIE

B-9000 GENT, 21 FEB. 1975
KRIJGSLAAN 271 - S 4 Tel. 22 57 15
(België-Europa)

Dear Barry,

We have studied the ring reversal of some trans-1,5-diMe-spiro[5.5]-undecanes. There are two pairs of equistructural chair conformations, say αα,ββ and αβ,βα.



The αα,ββ pair must be strained, because of the Me that sticks above the plane of one ring (Me inside strain, cfr energy of an axial t.Bu group). Therefore, the pair αα,ββ should not contribute significantly to the ground state properties of the compound. Interconversion between αβ and βα requires a double ring reversal: after topomerization of only one ring αα or ββ is formally obtained. Presumably the strain present herein causes the other ring to flip concertedly. We then expect that (i) both rings of the spiro compound should topomerize at the same rate (ii) the strain present in the prospective forms αα,ββ should cause a higher barrier to reversal than in the spiro compound without Me substituents.

C. Becu at this laboratory succeeded in preparing the title compound (A) and the parent compound B. Here we have in one spiro compound two heterocycles whose rates of topomerization are greatly different, (1) a 1,3-dioxane ring, usual barrier ≈10 kcal/mole (2) a 1,2,3-trithiane ring, usual barrier ≈14 kcal/mole. Moreover, the Me inside strain of the αα,ββ conformation in compound A must be maximized because of (i) the short C-O bond (ii) the large free energy difference ≈7 kcal/mole between the chair and the boat form of 1,3-dioxane. From a DNMR study of A (observing the Me signals) we have indeed found the same barrier to ring topomerization ≈16 kcal/mole for both rings. On the contrary, and as expected along the lines of previous reasoning, the 1,2,3-trithiane ring in B has the usual barrier of ≈14 kcal/mole.

D. Tavernier.

M. Anteunis.

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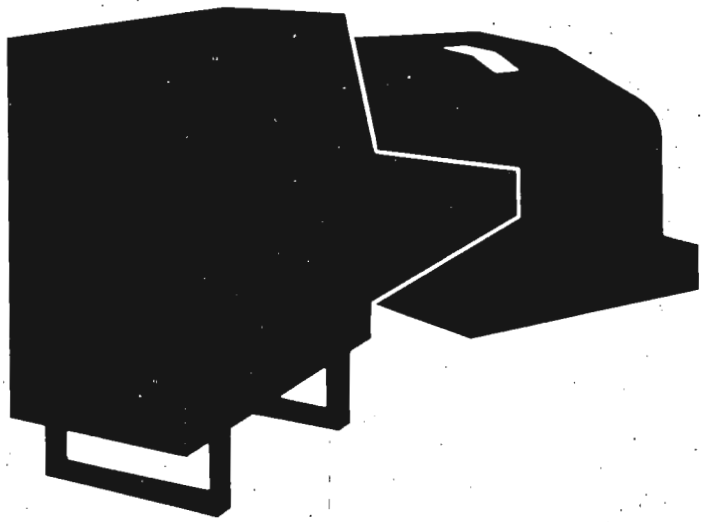

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COLORADO SEMINARY
UNIVERSITY OF DENVER
UNIVERSITY PARK • DENVER, COLORADO 80210

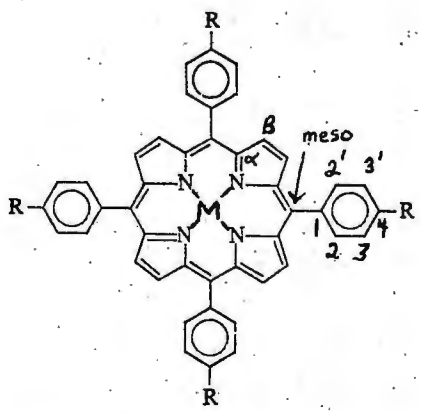
DEPARTMENT OF CHEMISTRY / 303•753-2436

February 21, 1975

Dear Barry:

Title: ^{13}C NMR of Metalloporphyrins

In conjunction with a Varian ^{13}C Workshop at the University of Denver, we recently had the opportunity to obtain the ^{13}C nmr spectra of some metalloporphyrins on a CFT-20. The results are presented in the accompanying Table. Spectra were run in $CDCl_3$ solution at ca. 35° with a ca. 20° pulse and ca. 1 sec. acquisition time. 10,000 to 60,000 transients were accumulated for each sample. Carbons are numbered as in the diagram. All shifts are in ppm downfield of TMS. Carbon fluorine coupling constants in Hz are in parentheses.



Assignments of the resonances in tetrakis-(para-isopropylphenyl)porphyrin (H_2(p-iPr-TPP)) and its complexes were based on comparison with the reported spectrum of zinc tetraphenylporphyrin (Zn(TPP))[1] and the expected effect of alkyl substitution on the phenyl-ring carbon shifts.[2] The reported spectrum of α,α,α-trifluoromethyltoluene[3] was used to assign resonances in tetrakis(para-trifluoromethylphenyl)porphyrin (H_2(p-CF_3-TPP)) and its complexes. The spectra of the octaethylporphyrin (OEP) complexes were assigned by analogy with spectra of H_2(OEP) and Zn(OEP).[4] In all cases the assignments are consistent with the integration of the spectra provided allowance is made for the longer relaxation times of the quaternary carbons.

The assignment of the resonances in the spectra of tetrakis(ortho-tolyl)-porphyrin (H_2(o-Me-TPP)) and its complexes is less obvious. The o-CH_3 is on carbon 2'. The α-C signal in the free porphyrin exhibited characteristic broadening[4] and was readily assigned. The β-C was assigned on the basis of intensity. C_1 is the only quaternary carbon expected at the high field end of the spectrum. The two quaternary carbons in the region 139-142 ppm must be $C_{2'}$ and meso-C. The signal at 141.6 ppm in the free porphyrin remains unsplit in the complexes, while the signal at 139.7 in the free porphyrin is split into two on complex formation. It seems likely that the former is meso-C and the latter $C_{2'}$ since the phenyl carbons are more likely to detect the sidedness of the porphyrin complex than are the porphyrin ring carbons. Whichever way the assignments are made, the meso-C resonance in H_2(o-Me-TPP) and its complexes is 2-6 ppm upfield of its position in the less sterically hindered porphyrins, suggesting a strain contribution to the shift. A similar contribution to the shift of $C_{2'}$ could explain the fact that it is ca. 6 ppm

TABLE I

^{13}C NMR OF METALLOPORPHYRINS

Compound	α	β	meso	C_1	C_2	C_2'	C_3	C_3'	C_4	R	L
H_2(p-iPr-TPP)	146.8	131.1	148.2	120.2	134.7		124.7		139.6	CH 34.1 CH_3 24.3	
In(p-iPr-TPP)Cl	149.6	132.7	148.6	121.9	134.8 (broad)		124.8		139.1	CH 34.1 CH_3 24.3	
TiO(p-iPr-TPP)	148.7	132.6	148.7	123.8	134.7		125.0		139.1	CH 34.1 CH_3 24.3	
Ru(CO)(p-iPr-TPP)(py)	143.8	131.8	147.7	121.7	134.4 134.2		124.3 124.6		140.2	CH 34.2 CH_3 24.3	py 144.2, 121.3 CO 180.3
H_2(p-CF_3-TPP)	146.5	131.4	145.6	119.1	134.7		123.9 (3)		130[a]	124.7[a]	
In(p-CF_3-TPP)Cl	149.5	133.1	145.2	120.7	135.2 134.4		124.1 (3.5)		131.0 (32)	124.5 (272)	
TiO(p-CF_3-TPP)	148.4	132.9	145.2	122.6	134.9 134.5		124.1		131.0 (32)	124.7 (268)	
Ru(CO)(p-CF_3-TPP)(THF)	143.9	132.0	146.1	120.9	134.1 134.5		123.5		130.2 (32)	124.7 (272)	THF 64.2, 33.5 CO 180.1
Ru(p-CF_3-TPP)[P(OMe)$_3$]$_2$	143.8	131.8	147.0	120.8	134.0		123.3		129.5 (32)	b	47.7
Ru(p-CF_3-TPP)(t-Bu-NC)$_2$	143.3	131.6	147.1	120.2	134.2		123.4		129.5 (32)	b	CH_3 29.1
H_2(o-Me-TPP)	146.7	130.8	141.6	119.0	134.0	139.7	124.3	129.3	128.5	21.4	
In(o-Me-TPP)Cl	149.5	132.4	141.2	120.6 120.8	133.5 134.5	139.1 140.8	124.2 124.5	129.3 129.5	128.7	21.1 21.6	
TiO(o-Me-TPP)	148.5	132.3	141.2	122.4 122.6	133.8 134.2	139.3 140.4	124.3 124.6	129.4 129.6	128.8	21.0 21.9	
Zn(TPP) [c]	150.8	132.5	143.3	121.6	134.9		127.5		128.0		
H_2(OEP) [d]	e	140.9	96.0							CH_2 19.7 CH_3 18.3	
In(OEP)Cl	146.9	143.4	97.9							CH_2 20.0 CH_3 18.5	
Ru(CO)(OEP)(THF)	141.7[f]	141.5[f]	98.5							CH_2 19.9 CH_3 18.5	THF 63.0, 21.9 CO 184.
Zn(OEP) [d]	146.7	141.1	96.2							CH_2 19.8 CH_3 18.8	

[a]Estimated by comparison with complexes. β-C obscures part of each quartet in free porphyrin. [b]Not observed. [c]Spectrum in d_5-pyridine/D_2O, from ref. 1. [d]Spectru( ) $CDCl_3$ from ref. 4. [e]Not reported. [f]Assignments may be interch( )d.

downfield of C_2 rather than the 8.9 ppm expected for methyl substitution.[2] The other ambiguity concerns the assignment of $C_{3'}$ and C_4. The methyl substituent is expected to shift the carbon ortho to it ($C_{3'}$) 0.7 ppm downfield and the carbon para to it (C_3) 2.9 ppm upfield.[2] Therefore we expect about 4 ppm between resonances of C_3 and $C_{3'}$. This suggests that the signal at 124.3 ppm in the free porphyrin is the resonance of C_3 and either the signal at 128.5 or 129.3 is due to C_3, the other to C_4. The splitting of the 129.3 signal into two signals in the complexes would seem more likely for $C_{3'}$ than C_4, but it is not conclusive evidence for the assignment.

Several features of the spectra are noteworthy. The shift of the α-C appears to be very sensitive to metal ion with Ru shifting it upfield ca. 3 ppm from the free porphyrin, TiO ca. 2 ppm downfield, and InCl ca. 3 ppm downfield. Shifts for the same porphyrin with different metal ions vary by 1-2 ppm for both β-C and meso-C. Shifts for carbons in peripheral alkyl groups or phenyl rings are much less sensitive to changes in metal. The sensitivity of the ^{13}C shifts of α-C, β-C, and meso-C to changes in metal ion indicate that considerable care must be exercised in the choice of a diamagnetic reference compound in studies of paramagnetic shifts in metalloporphyrins.

Nonequivalence of carbons due to slow axial ligand exchange and restricted rotation of phenyl rings was observed in all the M(p-CF_3-TPP)X complexes and in Ru(CO)(p-iPr-TPP)(py). Chemical shift differences (in ppm) due to nonequivalence are of comparable magnitude to the shift differences in the proton spectra.[5] In H_2(o-Me-TPP) the various isomers due to methyl orientations do not give resolvably different spectra. In the M(o-Me-TPP)(X) complexes many of the peaks are split into two resolvable peaks, implying that the chemical shifts may be primarily dependent on the relative orientation with respect to the axial ligand.

A more detailed discussion of the comparison between the ^1H and ^{13}C spectra will be published shortly.

Sincerely,

Gareth R. Eaton Sandra S. Eaton

1. K. Wuthrich and R. Baumann, Helv. Chim. Acta. 56, 585 (1973).
2. G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972 p.81.
3. L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra: A Collection of Assigned, Coded, and Indexed Spectra", Wiley-Interscience, New York, 1972, #225.
4. R. J. Abraham, G. E. Hawkes, and K. M. Smith, J. C. S. Perkin II, 627 (1974).
5. S. S. Eaton and G. R. Eaton, J. C. S. Chem. Commun. 576 (1974).

198-31

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From

Tel.

DEPARTMENT OF CHEMISTRY

concordia university

February 11, 1975

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

Dear Barry:

CONVERSION OF AN HA-100 TO ^{13}C FT OPERATION

We have recently converted our HA-100 spectrometer, which was equipped with the Varian C.W. ^{13}C package, to FT operation. The design of the system was based on the need to use available equipment as much as possible. Of the C.W. ^{13}C components, the V-3512 heteronuclear decoupler and the V-4311 r.f. unit (with modifications) were retained in the new configuration.

Pulse control and timing is carried out by means of a Tektronix 2600 Series instrumentation system with two pulse generator and two ramp (delay) generator plug-in units. One pulse generator is employed to switch a Digilab 400-2 Pulser (gated power amplifier) which boosts the r.f. signal from the V-4311 r.f. unit. The other pulse generator controls the computer via the interrupt system. One ramp generator controls pulse interval timing, being triggered in synchronization with the audio reference frequencies. The other ramp generator, triggered synchronously with the r.f. pulse, provides a delay before the start of data acquisition and switches off the signal to the audio frequency phase detectors during and immediately after the pulse by controlling a blanking amplifier. Broadband phase detection in the analytical channel is provided by a modified PAR 128 phase detector. We built our own blanking amplifier and audio-frequency filter circuitry.

At present we are restricted to a homonuclear internal lock, using a decoupled solvent line or a capillary. The pulsed lock system is easier to use and is more stable than was the original C.W. homonuclear lock system.

Professor Bernard L. Shapiro February 11, 1975

A Hewlett-Packard 2114A computer (8K) is used for data acquisition and processing, with 4K of memory available for data collection and transformation. Mass storage for data is available on magnetic tape. We frequently store our FID's in case re-processing might be required at a later stage. Transformed spectra can also be stored on tape if necessary. Scope display is used during processing, while hard copies of spectra are obtained using a Complot digital plotter. The usual processing routines, such as exponential and trapezoidal digital filters, are available. Writing and de-bugging the software was by far the most time consuming aspect of the conversion.

The principal current application of the FT system is to obtain the ^{13}C spectra of nitrogen heterocycles.

Yours sincerely,

Laurie

L.D. Colebrook
Professor of Chemistry

LDC/ac

198-33

University of Durham Department of Chemistry

Science Laboratories, South Road, Durham, DH1 3LE
Telephone: Durham 64971 (STD code 0385)

11th February, 1975.

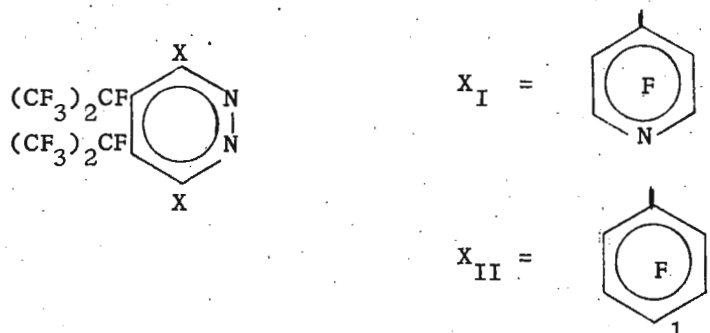
Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A and M University,
College of Science,
College Station,
Texas 77843,
U.S.A.

Dear Professor Shapiro,

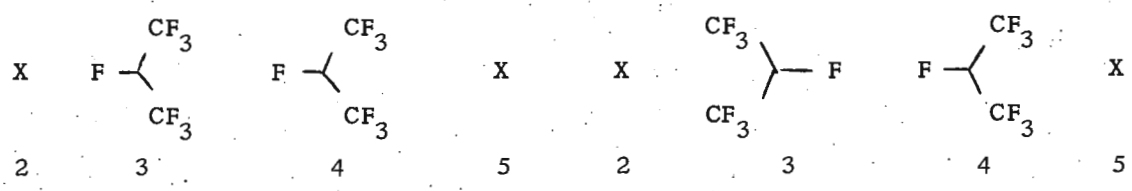
Rotational isomers in perfluorobisisopropylpyridazines - four adjacent rotors.

We hope this letter is fast enough to ward off the dreaded pink note.

Recently we observed the ^{19}F spectra of several perfluorobisisopropyl pyridazines:



which have already been reported in the literature[1] with directly measured ^{19}F parameters. Previous studies[2] have indicated that, unlike the perfluoro-t-butyl and -methyl groups, the rotation of a $(CF_3)_2CF$ group can be frozen at lower temperatures and the preferred orientations easily deduced. Normally the relative stability of the various conformations appears to be dependent on (i) adjacent or even distance bulky substituents and (ii) the position of substitution e.g. adjacent to nitrogen in aromatic azines usually leads to a sufficiently large 'hindrance gradient' to stop rotation. In particular the two CF_3 groups of $(CF_3)_2CF$ are usually forced to take up a position of minimum crowding, orthogonal to the aromatic substrate. Our results support this observation but show enhanced C<u>F</u> deshielding - greater than previously observed or expected and the result (from some approximate calculations) of the spatial proximity of both ^{19}F atoms and CF bonds. In essence the following rotational isomers were found - represented in the plane of the pyridazine ring and ignoring vibrational effects:



MAJOR ISOMER MINOR ISOMER

where the planes of X and the substrate are also approximately orthogonal. The internal rotors are almost locked together. In the initial analysis, this structural information was overlooked. We can hopefully measure the relative steric hindrance of X substituents by (i) the relative proportions of the rotamers or (ii) from tertiary fluorine shifts, and the series is being extended.

Yours sincerely,

R.S. Matthews A. Royston

Chemical Shifts (upfield of internal $CFCl_3$)

Assignment			I		II	
			Major	Minor	Major	Minor
	CF_3	4b	69·00	>71	69·23	>71·37
	CF_3	5b	71·56		72·14	
X	a-F	2'6'	88·09	88	136·47/140·62	137·57
X	a-F	3'5'	137·95/142·23	139·09	160·80	160·80
X	a-F	4'	-	-	147·51	150·25
	t-F	4a	145·94	163·90	147·98	163·54
	t-F	5a	172·42		172·46	

1. R.D. Chambers, M. Clark, J.A.H. MacBride, W.K.R. Musgrave and K.C. Srivastava, J.C.S. Perkin I, 1974, 125.

2. R.D. Chambers, R.P. Corbally, T.F. Holmes and W.K.R. Musgrave, J.C.S. Perkin I, 1974, 108, and references therein.

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- 1.7MHz to 560MHz usable coverage
- Thin film construction
- 8dB noise figure
- Failsafe

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DEPARTMENT OF CHEMISTRY TUFTS UNIVERSITY MEDFORD, MASSACHUSETTS 02155

February 24, 1975

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

"Nmr Calculations on the PDP-11"

Dear Barry:

I have recently been working on a program for the theoretical calculation of nmr spectra (sometimes incorrectly called simulation) for our departmental PDP-11/40 with a LAB-11 peripheral for display, etc. The program is now done and is being used in course work and to some extent in research. It will calculate a 2-7 spin system, superimpose a Lorentzian line width, and plot either the theoretical (stick) or Lorentzian line spectrum using a constant speed plot. It also allows variation of the chemical shifts, coupling constants and spectrometer frequency individually after the spectrum is displayed and, of course, will also vary the width of the display and the "offset." Incidentally, it also prints out the transitions and intensities in fixed point.

In the course of this project, it occurred to me that there might be other people engaged in this or similar projects who have not noticed the possibility of a couple of computer-nik tricks to speed up the calculation. The first of these is one originally implemented by Juers, Boettcher, Hull and Zimmerman[1] in a PDP-8 program. In this program the transitions are not saved in memory unless there is sufficient room, and they are stored only in a 1024 word stick figure display buffer, thus saving significant space.

The other tricks which make assembly language ideal for this program are the ability to store the basis functions as individual bits of a word. Thus the basis function $\alpha\beta\beta\alpha\beta\alpha$ is stored as 011010 where beta = 1 and alpha = 0. This becomes useful in two places. First, when the spin Hamiltonian matrix is set up[2], the off-diagonal elements are given by

$$H_{uv} = 1/2\ J_{ij}\ W$$

where W = 1 if basis function u and basis function v differ only in the interchange of spins i and j and W = 0 if the above is not true.

The function W can be calculated by performing the exclusive OR between the two basis functions and then finding only two bits on in the product. The exclusive OR is a hardware instruction in many minicomputers and allows a complex comparison very rapidly. For example, if the two basis functions are, in a 5-spin system, 01011 and 01101, the operation

(01011).XOR.(01101) = 00110

which has only bits 3 and 4 turned on. Thus, the matrix element will be 1/2 J_{34}.

Similarly, when the intensities are calculated after matrix diagonalization, the intensities I_{km} are given by

$$I_{km} = \left(\sum_{i}\sum_{j} C_{ik}C'_{jm} X_{ij}\right)^2$$

where the C and C' terms are the "old" and "new" eigenvectors and X_{ij} if the old basis function i and the new basis function j differ only in the interchange of 1 spin. X_{ij} is zero otherwise. The exclusive OR of these two basis functions followed by counting the number of differences will again find the right answer very quickly. In computers not having the exclusive OR, it may be simulated by subtracting the AND from the inclusive OR. A copy of a spectrum of ODCB is attached to prove the thing really works.

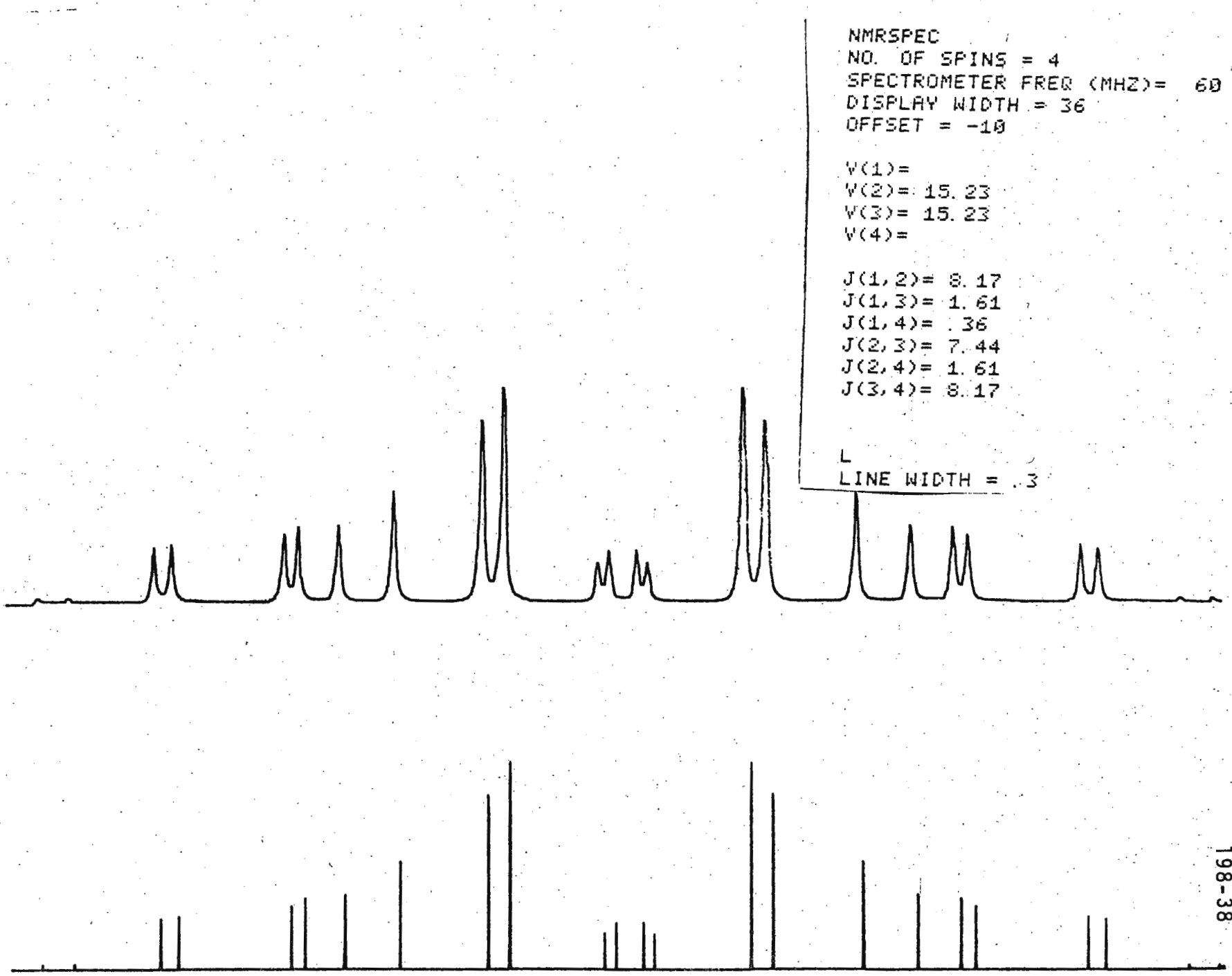
Regards,

Jim Cooper

James W. Cooper
Assistant Professor

1. DECUS program number 8-194, May, 1969.

2. See, for example, E. D. Becker, High Resolution Nmr.


NMRSPEC
NO. OF SPINS = 4
SPECTROMETER FREQ (MHZ)= 60
DISPLAY WIDTH = 36
OFFSET = -10
V(1)=
V(2)= 15.23
V(3)= 15.23
V(4)=
J(1,2)= 8.17
J(1,3)= 1.61
J(1,4)= .36
J(2,3)= 7.44
J(2,4)= 1.61
J(3,4)= 8.17
L
LINE WIDTH = .3

198-39

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DE STRASBOURG

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1, rue Blaise Pascal
67008 STRASBOURG Cedex
Téléphone ~~361.57.15.2~~ 61-48-30
Boite postale 296/R8

Professeur J.-M. LEHN

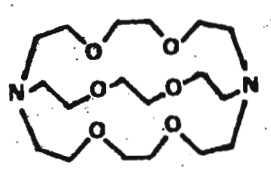
STRASBOURG, le 11 Février 1975

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

THALLIUM-CARBON COUPLING CONSTANTS

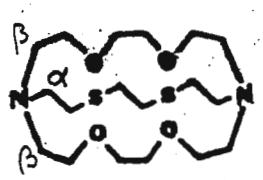
Dear Barry,

Since the trend is more and more towards NMR of nuclei other than protons, we wish to "pay" our subscription in thallium currency. Some time ago we have been measuring ^{13}C spectra of several thallium cryptates, i.e. thallium ($TlNO_3$) complexes of the macrobicyclic ligands I and II ($CDCl_3$ solution; XL-100/15 FT spectrometer). The $^{203,205}Tl$ - ^{13}C coupling constants listed below have been measured (at 30°C for I and 5°C for II).



I

Coupled Carbon	Coupling Constant
CH_2-N	12Hz ± 0.5
CH_2-O	10Hz <1Hz



II

CH_2-S	11Hz 51Hz
CH_2-N (α)	9Hz
CH_2-N (β)	12Hz
CH_2-O	12Hz <1Hz

Whereas all three types of protons show appreciable coupling to the thallium nucleus in the proton spectrum (J. Amer. Chem. Soc. 92, 2916 (1970)), one of the two sets of $\underline{C}H_2O$ carbons does not display any coupling. Similarly, a large difference in Tl-^{13}C coupling is also found for the two kinds of $\underline{C}H_2S$ carbons.

A tentative assignment would indicate that the stronger coupling in these two cases is with $NCH_2\underline{C}H_2O$ and $NCH_2\underline{C}H_2S$ and the weaker coupling with the central $O\underline{C}H_2\underline{C}H_2O$ and $S\underline{C}H_2\underline{C}H_2S$ carbons.
This might point to a special role of Tl....N coordination in the spin-spin coupling mechanism. It may be stressed that these Tl-^{13}C, as well as the former Tl-^{1}H (loc.cit.) couplings represent spin-spin interactions between nuclei separated by a non-covalent, coordination bond.

Finally, whereas the thallium splittings are well resolved at 30°C for the $TlNO_3$ cryptate of I (see also loc. cit.), the cryptate of II shows a coalescence of the ^{13}C doublets at about +15°C, indicative of Tl^+ exchange in chloroform.

Best regards,

Yours sincerely,

Jean-Marie

J.P. Kintzinger, J.M. Lehn

198-41

PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT TÜBINGEN

7400 TÜBINGEN, den 12.2. 1975
Morgenstelle
Telefon (07122) 71 2423

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

Ihr Zeichen Unser Zeichen Lu/Ru Ihre Nachricht vom

^{67}Zn - NMR at low concentration

Dear Professor Shapiro,

Continuing our investigations on less common nuclei in aqueous solutions, for instance the Fourier Transform NMR-investigations of ^{67}Zn (Ref. 1, 2, 3) we have succeeded in measuring ^{67}Zn-signals at low concentrations. This work has been done with regard to the occurence of Zinc in biological systems. In such systems the concentration of the metal nuclei is usually very small and is in the range of some millimoles/kg H_2O.
In the figure 1 a FT NMR signal of ^{67}Zn is given with some typical experimental parameters.
Further work in this low concentration field also with other metal nuclei is running.

Sincerely

B.W. Epperlein O. Lutz A. Schwenk

Ref. 1 The Magnetic Moment of ^{67}Zn and the Shielding of Zinc Ions by Water
B.W. Epperlein, H. Krüger, O. Lutz, A. Schwenk
Phys. Letters 45A, 255 (1973)

Ref. 2 ^{67}Zn NMR Anomalous Solvent Isotope Effect in Aqueous Solutions
B.W. Epperlein, H. Krüger, O. Lutz, A. Schwenk
Z. Naturforsch. 29a, 660 (1974)

Ref. 3 Fourier Transform Nuclear Magnetic Resonance Studies of ^{67}Zn
B.W. Epperlein, H. Krüger, O. Lutz, A. Schwenk
Z. Naturforsch. 29a, 1553 (1974)

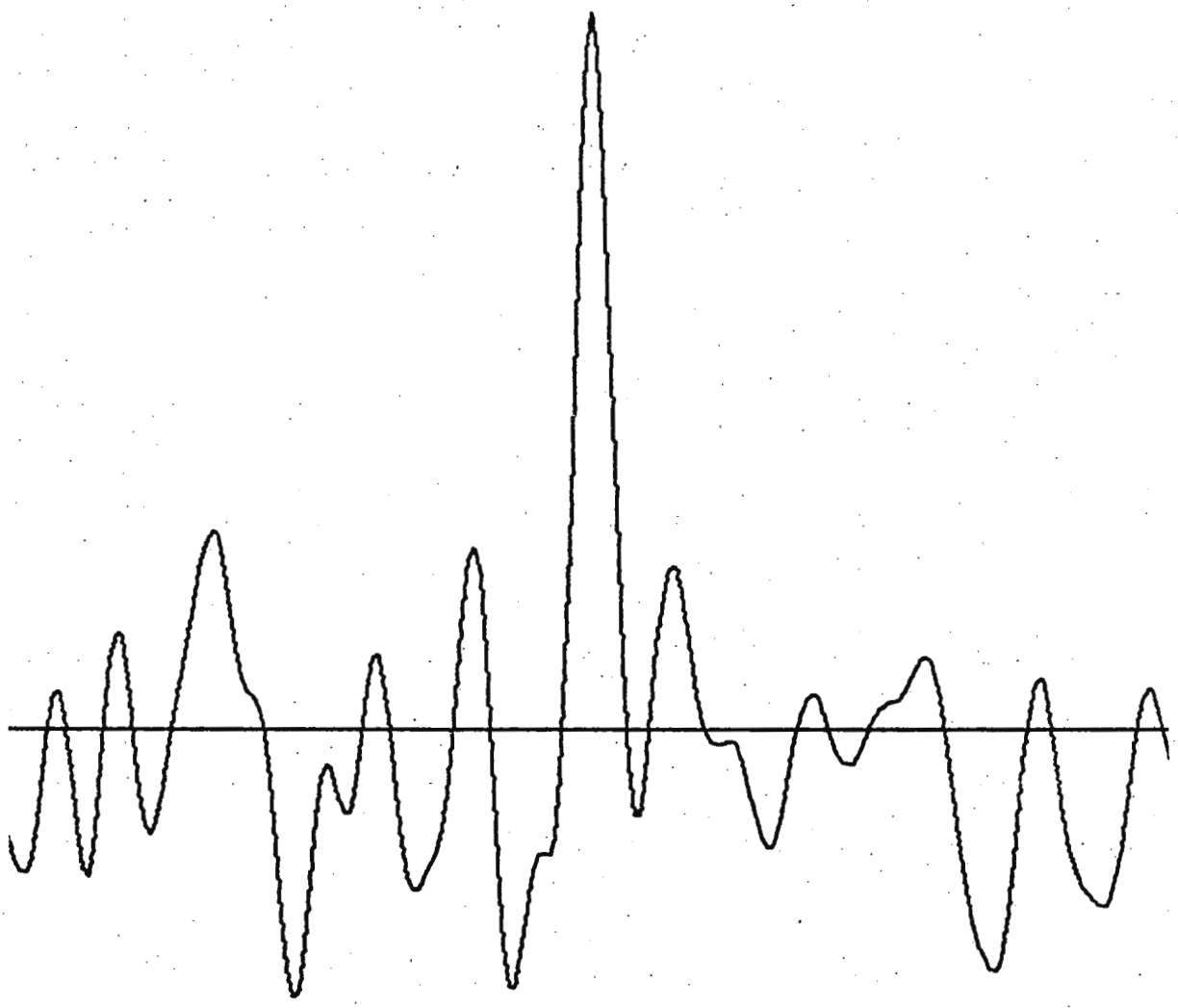


Figure 1 : ^{67}Zn-NMR-absorption-line at 4.814 MHz. Sample: 0.014 molal aqueous $Zn(ClO_4)_2$ solution, line width 40 Hz, spectrum width 1070 Hz, measuring time 3 h, pulse frequency 50 Hz, sample volume 1 ml.

198-43

RUTGERS UNIVERSITY *The State University of New Jersey*

SCHOOL OF CHEMISTRY
Ralph G. Wright Laboratory
William Rieman Laboratory
New Brunswick, New Jersey 08903

February 26, 1975

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

Title: Carbon - Phosphorus Coupling Constants

Dear Professor Shapiro:

During our continuing research on the chemistry of hypervalent molecules we routinely obtain the ^{13}C nmr spectra of all new molecules. In the case of phosphorus compounds we occasionally see some most unexpected coupling constants. For example the absolute value of the J_{COP} in compounds 1, 2 and 3. As the oxidation state of phosphorus changes the $-OCH_3$ carbon's coupling constant goes from 0 to 12 Hz while the analogous ring carbon shows the opposite trend.

We are surprised at the size of the three bond coupling to phosphorus of the trifluoromethyl carbons in 3, the observed spectrum is an unmistakable double quartet. Maybe 17 Hz isn't that large when compared to the 12.8 Hz three bond coupling seen in the biacetyl - triethyl phosphite adduct 4.

We have spent some time, but with no success, attempting to locate the ^{13}C resonance due to the olefinic carbons in 3. We are planning to obtain the nmr spectrum of the sample in the presence of chromium acetylacetonate in hopes that the carbons will be relaxed and that the compound will not be decomposed.

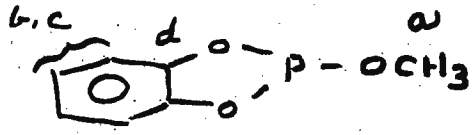
Sincerely yours,

Dorothy Z Denney

Dorothy Z. Denney

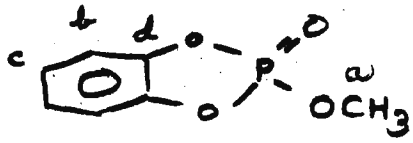
DZD:mhs

^{13}C nmr Data



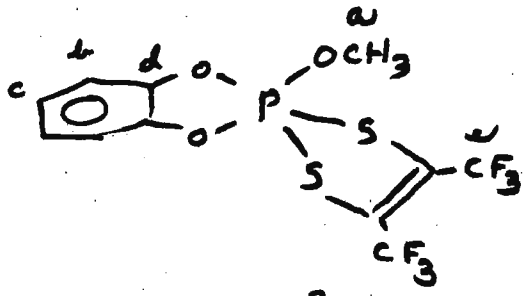
1

a	49.92 (s)
b	111.71 (s)
c	122.72 (s)
d	146.19 (20)



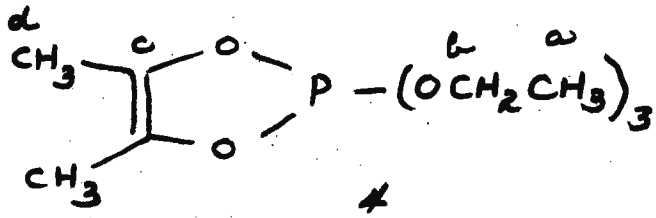
2

a	57.03 (7)
b	113.23 (13.6)
c	124.62 (s)
d	145.02 (4)



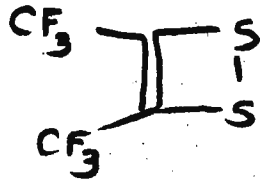
3

a	56.35 (12)
b	111.15 (15)
c	123.15 (s)
d	145.13 (s)
e	120.57 J_{CF} = 276
	J_{CCSP} = 17



4

a	15.9 (7.5)
b	62.5 (10)
c	128.2 (2)
d	9.9 (12.8)



5

a	117.8 (272)
b	124.5 (44)

Now the XL-100A NMR Spectrometer lets you think small.

Thanks to another Varian first, a 1-mm Insert Accessory for the XL-100A Pulsed-Fourier Transform NMR Spectrometer, scientists such as biochemists and pharmaceutical chemists who have to work with limited sample quantities can obtain rapid proton NMR analysis of microgram samples.

Using the insert, it's possible to run spectra of 50 μg or less of sample. Spectra run thusly are obtained in less than 17 minutes, yet are superior to 8-hour runs in a 5-mm tube. Sensitivity for a fixed amount of sample can improve from 4- to 6-fold when the 1-mm Insert Accessory is used.

The two spectra of Δ^9-tetrahydrocannabinol (THC) shown here demonstrate the dramatic results possible using the 1-mm Insert. Spectrum A, of a concentrated sample in a 5-mm tube, serves as a comparison for the other spectra. Spectrum B (20 μg of sample in a 1-mm tube) and Spectrum C (20 μg of sample in a 5-mm tube) were run under identical conditions. Note the well-defined peaks in the spectrum run using the 1-mm Insert.

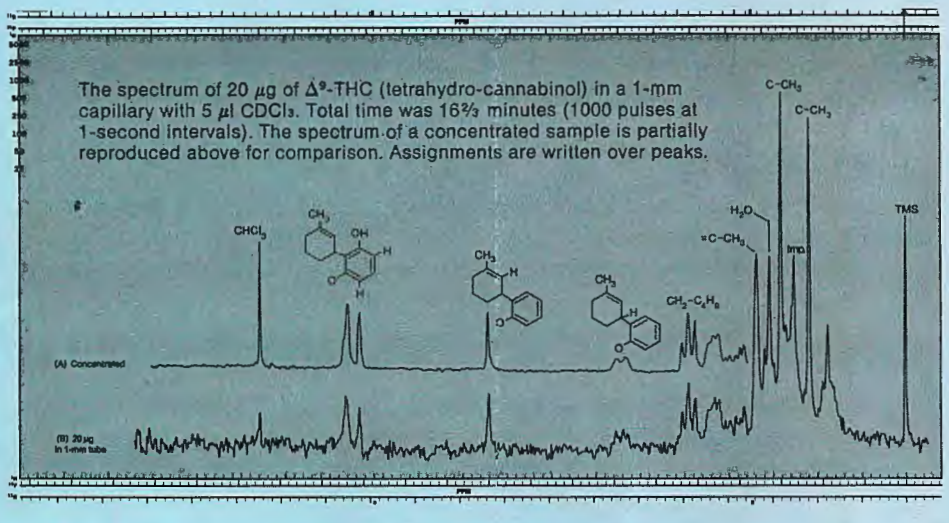
This innovative approach is successful since reducing the sizes of both the sample tube and the receiver coil ensures maximum coupling of the available nuclear magnetic moments with the coil. It permits the use of commercially available capillary tubes costing less than one cent each.

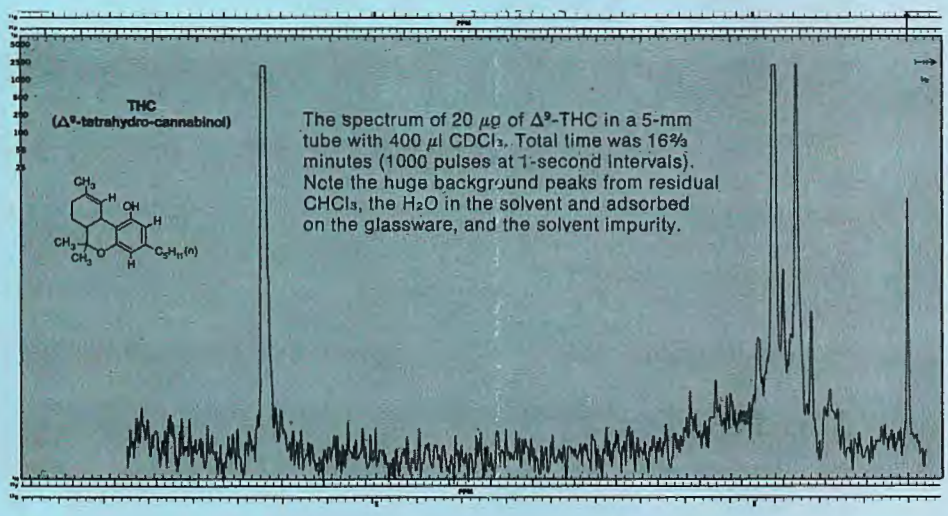
To interchange the 1-mm Insert with standard XL-100A inserts, merely take one out, put in the other, retune and balance. The sample is dissolved in 5 μl of an NMR solvent containing TMS for a reference. It is then transferred into a 1-mm sample tube by using a drawn out glass pipette or a hypodermic syringe. This eliminates the bubble problems which sometimes arise with the use of microcells in larger tubes. The resulting column length is about 10 mm, assuring freedom from line shape distortion. Since spinning produces no vortex, spinning speed is not a critical factor.

The sample volume in the 1-mm Insert is so much less than the 400 μl required for 5-mm tubes that use of deuterated species becomes more economical.

The 1-mm capillary has its own spinner turbine attached. Unlike other existing techniques designed to accommodate small quantities of samples, there are no plugs to adjust and no sample positioning is necessary. Proper positioning is automatic thereby assuring reproducible homogeneity.

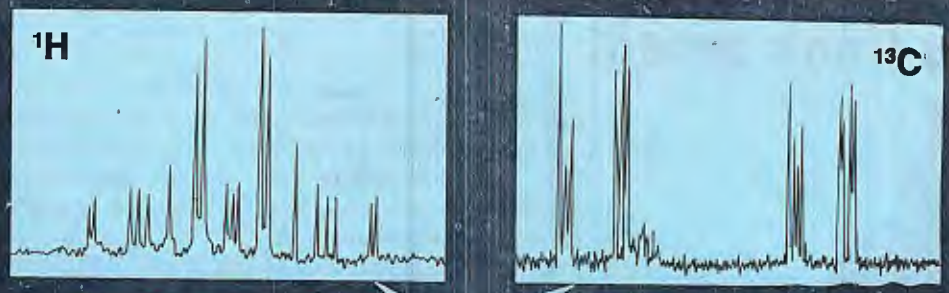
Write for a copy of Varian's Application Report NMR-2, which describes the XL-100A Insert Accessory in more detail.

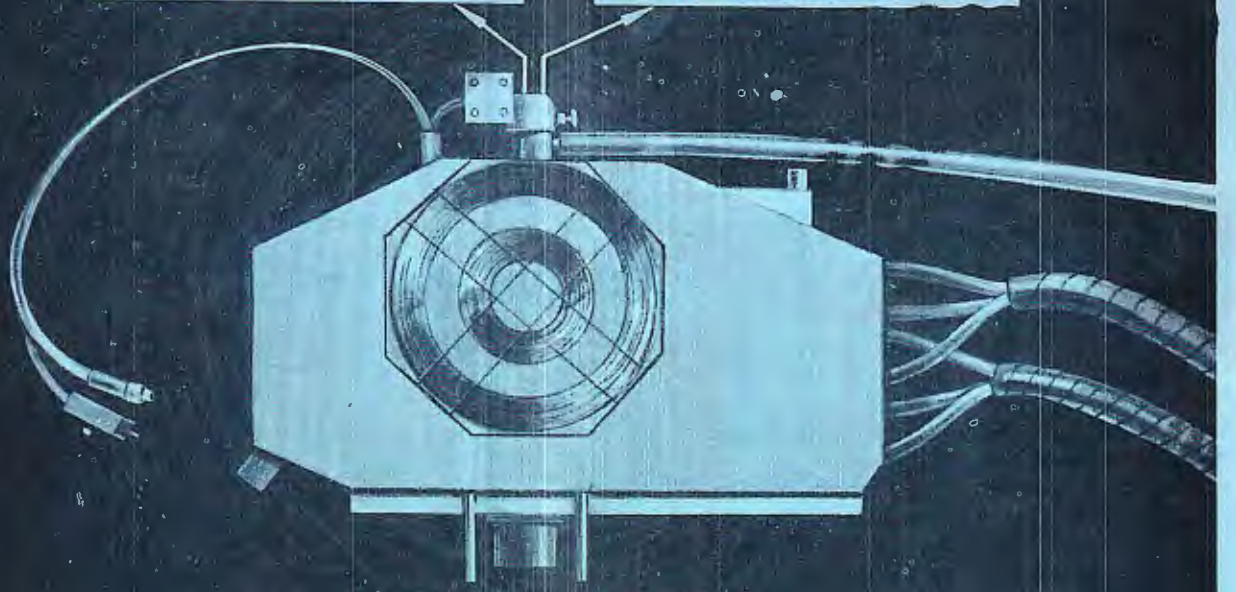




Varian Associates
611 Hansen Way, Box D-070
Palo Alto, California 94303

varian





Our FX60 ^{1}H/^{13}C Dual Probe makes even Lighter Work of FT NMR Spectroscopy

Now with the FX60 you can change frequencies from ^{13}C to ^{1}H or vice versa, **without touching the probe.** You **observe within seconds** because two simple operations, that just about anyone can perform, are all that's required.

The development of this remarkable high resolution, 10mm sample VT **dual capacity probe** means that lock resonance conditions remain identical when changing from one frequency to another.

Daily sample output can increase dramatically because it is no longer required to spend precious time relocating, establishing the lock and re-adjusting field homogeneity.

Call or write for information or demonstration.

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Analytical Instruments, Inc.

235 Birchwood Ave. Cranford, NJ 07016
201—272-8820

Spectra: ^{1}H of ODCB; ^{13}C of ODCB with proton spin-coupling.