

Texas

A
M &

University

N - M - R

Newsletter

No. 189

June, 1974

G. N. LaMar Research Associate Position Available	1
F. Ciampelli and E. Santoro NMR Determination of 1,2 Units in Polybutadienes	2
J. F. Rodrigues de Miranda and C. W. Hilbers Non-Exponential Relaxation of the Methyl Protons of Acetrisoate in Solution	5
J. S. Davies, R. J. Thomas and M. K. Williams NMR Spectra of Diastereoisomeric Di-Valyl Peptides	8
D. E. Williams HNMR Shift-Structure Correlations of Silicones	10
J. W. Cooper Homospoil T_1 Sequences	13
R. J. Highet Some INDOR Experiments on Leucodrin	16
J. M. Miller Postdoctoral Fellowships Available	18
S. S. Eaton and G. R. Eaton Phenyl Ring Rotation in Metal Complexes of Tetraphenylporphyrin Derivatives	19
P. Bladon Nematic Phase Spectra of Benzo-2,1,3-oxa-, thia-, and -selenadiazole	22
I. C. P. Smith, G. W. Stockton and C. F. Polnaszek Deuterium NMR As A Probe of Biological Membranes; Wide Sweeps on the XL-100?	24
R. D. Green Recent Ramblings From Regina	27
G. C. Levy Position Available: NMR Instrumentation, Research Associate	29
D. Tavernier Rate Process in an Acylhydrazone	30
D. N. Lincoln and V. Wray Measuring Line Positions in FT Mode; Programs LAOCOON and LASS	31

(Cont'd. on p. (i))

A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.

SPECTROSCOPIC RESEARCHERS...

HERE ARE 6 GOOD REASONS WHY IT PAYS TO STANDARDIZE ON WILMAD!

- **WORLD'S LARGEST SINGLE SOURCE.** We are the world's largest single source for glassware, accessories, and supplies for spectroscopic research.
- **MOST COMPLETE LINE.** Our line of glassware, accessories, and consumable supplies for spectroscopy now includes everything you need for your investigations . . . except the spectrometer.
- **NO SACRIFICE IN QUALITY.** Our operations are based on a policy of never sacrificing quality in order to meet a competitive price. No investigator wants to jeopardize accuracy, uniformity, stability, and repeatability just to save a few pennies.
- **MOST SAMPLE TUBES.** We have produced more sample tubes for spectroscopy than any other supplier in the world.
- **STANDARD OF EXCELLENCE.** Wilmad accuracy and precision in sample tubes have become the reigning standard of excellence in the industry. (Even the equipment manufacturers use Wilmad NMR sample tubes.)
- **A DESERVED REPUTATION.** With almost 20 years of pioneering in glassware, accessories and supplies for spectroscopic research, we have earned a reputation for reliability which supersedes monetary value.

**WRITE TODAY FOR
FREE CATALOGS**

If you don't have our two Catalogs covering the WILMAD line of Glassware, Accessories, and Supplies for spectroscopic research (NMR, EPR, IR and MS), write or call today. Wilmad Glass Company, Inc., U.S. Route 40 and Oak Road, Buena, N.J. 08310, U.S.A. Phone: (609) 697-3000.



WILMAD

PIONEERS IN ACCESSORIES AND SUPPLIES FOR SPECTROSCOPY

H. E. Simon Nuclear Transverse Cross Relaxation	32
P. C. Lauterbur In Vivo NMR Zeugmatography	34
L. W. Reeves Another Non-Tetrahedral Tetrahedral Ion in an Oriented Electrical Double Layer	36
P. S. Pregosin and L. M. Venanzi The Concentration Dependence of the ^{195}Pt Chemical Shift in the PtCl_4^{2-} Ion	38
R. J. Goodfellow Postdoctoral Research Assistant	39
B. L. Shapiro Drawings and Figures in the TAMU NMR Newsletter	39
E. A. Williams, J. D. Cargioli and W. T. Hatfield A High-Low Power Switching System for a TT 1020 High Power RF Pulse Amplifier Incorporated into an XL-100 Spectrometer	40

Deadline Dates: No. 190: 1 July 1974 No. 191: 5 August 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, Incorporated
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. 12
Electronic Navigation Industries	- see p. 4
JEOL, U.S.A., Inc.	- see inside back cover
Nicolet Instrument Corporation	- see p. 28
Varian Instrument Division	- see outside back cover
Wilmad Glass Co., Inc.	- see inside front cover

UNIVERSITY OF CALIFORNIA, DAVIS

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

May 7, 1974

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

Title: Research Associate Position Available

Dear Barry,

The Department of Chemistry is seeking qualified applicants for a Research Associate position whose responsibilities entail the routine operation of primarily FT and CW NMR spectrometers and a mass spectrometer, as well as some UV and IR spectrometers. Some minor responsibilities involve supervision of laboratory assistants in the preparation of standards for the analytical laboratory.

The Department currently has a Joel MH-100 and A-60 CW NMR spectrometer and a Joel PS-100 FT NMR spectrometer equipped with a Digilab NMR-3 data system.

A B.S. degree in chemistry and four years experience in spectroscopy, or an M.S. with three years experience are required; at least one year must involve nmr. Some experience in FT NMR operation would be desirable.

The starting salary would be in the range \$12,000 - 13,000 per year with all fringe benefits, and the position could commence July 1, 1974 or thereafter.

I would be grateful if readers could bring this notice to the attention of interested personnel. Any direct inquiries or questions should be directed to:

Mr. William Hapgood, Business Manager
Department of Chemistry
University of California
Davis, California 95616

Sincerely yours,

Gerd N. La Mar
Associate Professor
of Chemistry

GNL/ds

MONTECATINI EDISON S. p. A.

SEDE IN MILANO - C. [REDACTED] 374.500.000.000 I.V.

[REDACTED] 374.500.000.000 I.V.
Iscri. Trib. Milano - Reg. Soc. 355 Vol. 10 Fasc. 84.

CENTRO RICERCHE DI BOLLATE

Bollate, March 8, 1974

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

Si prega indirizzare la risposta a:
 MONTECATINI EDISON S. p. A.
 Centro Ricerche di Bollate
 Via S. Pietro 50
 20021 - BOLLATE (Milano)

REF. 7536

Dear Professor Shapiro:

NMR DETERMINATION OF 1,2 UNITS IN POLYBUTADIENES

The determination of the microstructure of polybutadienes is a problem that has been widely studied by infrared and nuclear magnetic resonance spectroscopies¹⁾. The main difficulty is due to the fact that, especially when 1,2 units are present, a process of cyclization may take place with a corresponding decrease in the total unsaturation²⁾. In addition to such a phenomenon, some effect due to the tacticity of 1,2 units and possibly to the distribution of the different types of microstructures increases the difficulties involved in the determination of the absorptivities required for the I.R. determination. As a result, the I.R. methods that show a satisfactory precision for 1,2 units determination, may undergo a considerable loss in accuracy (5-10% or more).

The N.M.R. methods may use, for the determination of the 1,2 units both the 4.5-5.5 δ region (5.40 δ for 1,2 plus 1,4 units and 4.95 δ for 1,2 units only) and the 1.0-2.5 δ region (2.1 δ for 1,2 plus 1,4 units and 1.2 for 1,2 units only). The region of 1.0-2.5 δ is influenced by the presence of cyclized units that by increasing the 1.2 δ peak cause an error in excess for the 1,2 units content. Unfortunately from our experience on a large number of determinations under different conditions, we also find that the 4.5-5.5 δ

MONTECATINI EDISON S. P. A.

region, and in particular the peak at 4.95δ , is sensitive to the scanning condition (Rf power). This indicates a strong disposition to saturate also by using "normal" conditions leading to errors in defect for the 1,2 units content.

Only if the same 1,2 units content is obtained from both regions, the determination must be unaffected by such types of errors. If the 1,2 units content obtained from 1.0-2.5 δ region is higher than that obtained from 4.5-5.5 δ region, cyclization and/or scanning conditions close to saturation are present; at this point we suggest to try to remove saturation effect by changing the scanning conditions (Rf power, concentration, scanning speed). In order to check the absence of saturation, we suggest to follow the behavior of the ratio between 1.0-2.5 region area and 4.5-5.5 region area versus the Rf power. After succeeding in such a job, the 1,2 units content is determined from the 4.5-5.5 δ region and on the basis of this value, we can use the other region to get an idea of the degree of cyclization. The precision that we generally obtain is of the order of $\pm 5\%$ of the determined amount of 1,2 units.

If somebody among the readers knows the values of relaxation times of polybutadiene protons, we would appreciate learning any available information.

Yours truly,

Federigo Ciampelli *Ettore Santoro*

Federigo Ciampelli Ettore Santoro

References:

- 1) Y. Tanaka, Y. Takeuchi, M. Kabayashi, H. Tadokoro, J. Polymer Sci. A2, 9 43 (1971).
- 2) J. L. Binder, J. Polymer Sci. B4, 19 (1966).

ENI

The world's leader in solid state rf power amplifiers

Once upon a time if you wanted broadband RF power, you had to settle for bulky tube-type power amplifiers. No more. Because ENI has developed a full line of all-solid-state

Class A power amplifiers, covering the frequency spectrum of 10 kHz to 560 MHz, with power outputs ranging from 300 milliwatts to over 1000 watts. And there's more to come.

Driven by any signal generator, frequency synthesizer or sweeper, ENI's compact portable amplifiers, like the ones shown below, are versatile sources of power for general laboratory work, RFI/EMI testing, signal distribution, RF transmission, laser modulation, data transmission, NMR, ENDOR, ultrasonics and more.

Completely broadband and untuned, our highly linear units will amplify inputs of AM, FM, SSB, TV and pulse modulations with minimum

distortion. Although all power amplifiers deliver their rated power output to a matched load, only ENI power amplifiers will deliver their rated power to any load regardless of match.

We also designed our amplifiers to be unconditionally stable and failsafe—you need never fear damage or oscillation due to severe load conditions (including open or short circuit loads).

ENI instrumentation amplifiers come complete with an integral AC power supply and an RF output meter. Ruggedized amplifiers capable of operating under severe environmental conditions are available.

For a **complete** catalog of power amplifiers and multicouplers, write: ENI, 3000 Winton Road South, Rochester, New York 14623. Call 716-473-6900. TELEX 97-8283 ENI ROC.



40 WATT/ MODEL 240L

- 20KHz to 10MHz coverage
- More than 40w linear power output
- Up to 150w CW & pulse output
- Works into any load impedance
- Metered output

Extraordinary performance in a wide range of transducer drive applications. Deliver up to 150w into any load regardless of its impedance. Compatible with all signal and function generators, the 240L is a high quality laboratory instrument for ultra-sonics, biological research & electro-optic modulation.

100 WATT/ MODEL 3100L

- 250 KHz to 105MHz coverage
- More than 100w linear output
- Up to 180w CW & pulse
- Works into any load
- Unconditionally stable

Designed to replace bulkier and less efficient tube type amplifiers, the Model 3100L will provide reliable and maintenance free operation. NMR, ENDOR, ultrasonics and laser modulation are just a few of the applications for this versatile source of RF energy.

20 WATT/ MODEL 420L

- 150KHz to 250MHz coverage
- 20 Watts power output
- Low noise figure
- 45dB \pm 1.5dB gain
- Class A linearity

The widest band solid state power amplifier available at its 20w power level, the ENI 420L is a truly state-of-the-art instrument. As a drive source for high resolution acousto-optic modulators and deflectors the Model 420L is invaluable. Its Class A linearity will amplify AM, FM, TV and pulse signals with minimum distortion.

.3 WATT/ MODEL 500L

- Flat 27dB gain 2MHz to 500 MHz
- 1.7MHz to 560MHz usable coverage
- Thin film construction
- 8dB noise figure
- Failsafe

This compact unit can deliver more than 300 milliwatts from 1.7MHz to 560MHz at low distortion. A thin film microelectronic circuit is the heart of this general utility laboratory amplifier. Extremely wide band response at a very modest price.



KATHOLIEKE UNIVERSITEIT
NIJMEGEN
NEDERLAND

FACULTEIT DER WISKUNDE EN NATUURWETENSCHAPPEN

Toernooiveld
Nijmegen
Telefoon (080) 55 88 33
Telex 4 82 28 winat nl
Afdeling

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

Uw kenmerk

Uw brief van

Ons kenmerk JFRdM/JB 245

Datum May 3, 1974

Onderwerp

NON-EXPONENTIAL RELAXATION OF THE METHYL PROTONS OF ACETRIZOATE
IN SOLUTION

Dear Prof. Shapiro,

Recently a number of papers have been devoted to the study of the relaxation behaviour of methyl groups. In particular the possible influence of cross-correlations has aroused some attention since it may give rise to a non-exponential relaxation pattern. This effect will only become manifest, when the overall motion of the methyl group is highly anisotropic (1) and may therefore be of potential interest to protein and membrane studies. It can, however, easily be masked by other mechanisms like intermolecular dipole-dipole and spinrotation relaxation. Non-exponential relaxation of the methyl group has been observed (2), but there is some confusion whether this effect should be attributed to cross-correlation effects.

In a recent article Werbelow and Marshall (3) reviewed the influence of rotational characteristics of the methyl group on its relaxation behaviour and extended Hubbard's theory to the situation where the limit of extreme narrowing no longer holds, i.e. $2\omega_0\tau_c > 1$

During the course of our investigation of the binding of the renal contrast medium acetrisoate to serum albumin it appeared that the methyl group of this molecule showed an outspoken non-exponential relaxation behaviour.

In figure 1 a representative example of the longitudinal relaxation of the methyl proton is plotted together with that of the ringproton. The time dependence of the methyl group magnetization is clearly non-exponential in contrast to that of the ringproton. This observation rules out the possibility of a non-linearity in the detector system. The methyl group relaxation can be interpreted along the lines of Hubbard's theory, which predicts the following longitudinal time dependence:

JFRdM/JB 245

Nijmegen, May 3, 1974

$$\frac{\langle I_z \rangle_t - \langle I_z \rangle^{\text{eq}}}{\langle I_z \rangle^{\text{eq}} (\cos \theta - 1)} = A_1 \exp(s_1 t) + A_2 \exp(s_2 t) \quad (1)$$

Curve fitting of the experimental points to eq. 1 results in the following values for the parameters:

$A_1 = 0.14$; $A_2 = 0.86$; $s_1 = 0.09$; $s_2 = 1.34$. These values agree within experimental accuracy with those predicted by Hubbard ($A_1 \approx 1/6$; $A_2 \approx 5/6$; $s_1 \ll s_2$) for a methyl group in a molecule of arbitrary symmetry. Upon binding of acetrizate to albumin the methyl group relaxation qualitatively follows the theory of Werbelow and Marshall (3).

Sincerely,

(J.F. Rodrigues de Miranda

and

C.W. Hilbers)

1. P.S. Hubbard, J. Chem. Phys. 52, 563 (1970).
2. K. van Putte, J. Magn. Resonance 5, 367 (1971).
3. L.G. Werbelow, A.G. Marshall, J. Magn. Resonance 11, 299 (1973).

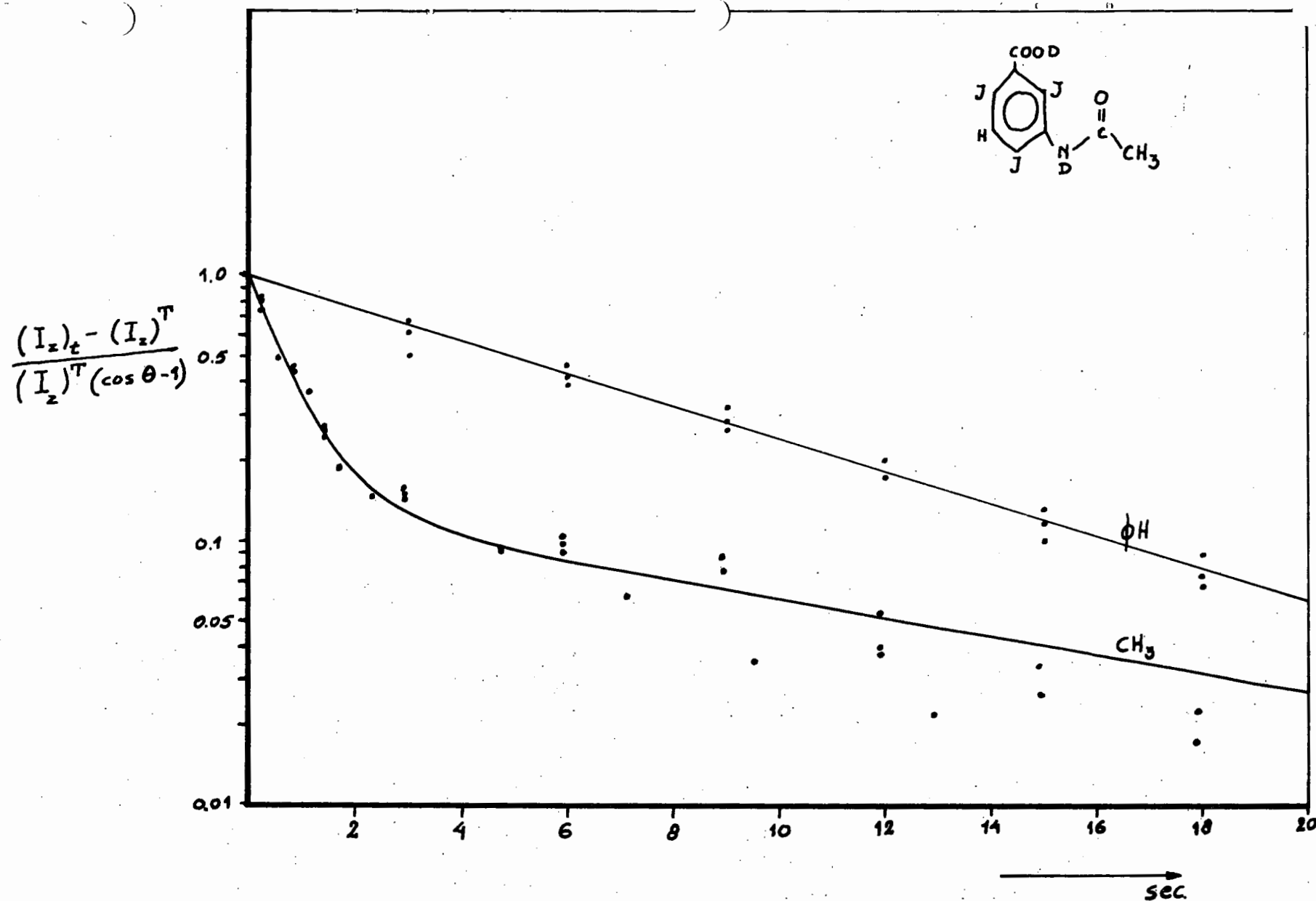


Figure 1

Longitudinal relaxation of the ringproton (ϕH) and methyl group of acetrizoate dissolved in phosphate - KCl buffer. $\mu = 0.2$; pH = 7.0 in D_2O at $32^\circ C$. The experiments were performed on a Varian XL-100 spectrometer.

Experimental points are given; the line drawn is calculated according to eq. 1 with parameter values of $A_1 = 0.14$; $A_2 = 0.86$; $s_1 = 0.09$; $s_2 = 1.34$.

UNIVERSITY OF WALES



University College of Swansea

Department of Chemistry

J. H. Pritchett M.A. Sc.D.
 Professor of Physical Chemistry and
 Head of Department
 A. Polter Ph.D.
 Professor of Organic Chemistry

SINGLETON PARK SWANSEA SA2 8PP
 UNITED KINGDOM
 TEL SWANSEA (0782) 25678

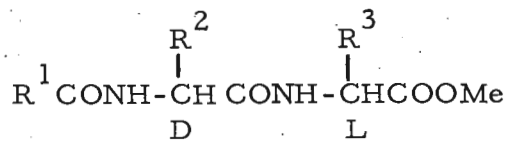
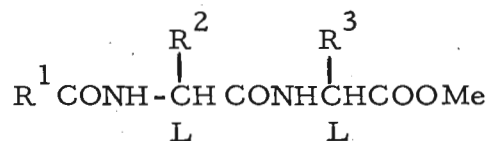
2nd May 1974

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

Dear Professor Shapiro,

N.m.r. Spectra of Diastereoisomeric Di-Valyl Peptides

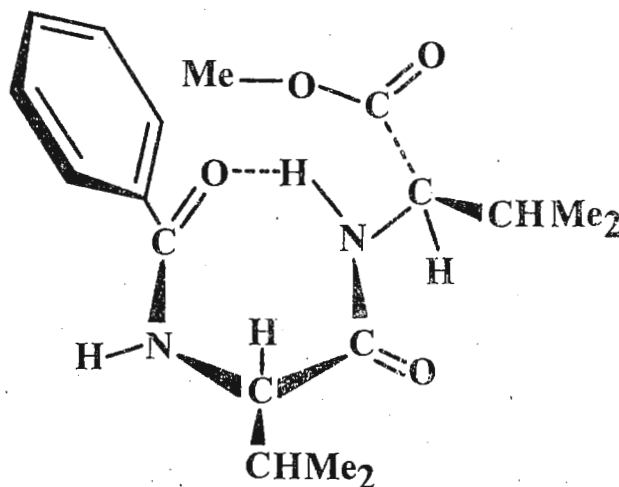
Applications¹ of p.m.r. in assessing racemisation during peptide coupling reactions have made use of differences in the magnetic shielding effects of side-chain aromatic residues in diastereoisomeric dipeptides. We can now report that a terminal benzoyl group causes a significant difference in the chemical shifts of the methyl ester protons in two diastereoisomers. Thus the peptides I and II in deuteriochloroform show methyl ester proton signals at 6.34 τ and 6.42 τ respectively. The signals

I, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{R}^3 = \text{i-Pr}$ II, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{R}^3 = \text{i-Pr}$ III, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{i-Pr}$, $\text{R}^3 = \text{Me}$ IV, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{i-Pr}$, $\text{R}^3 = \text{Me}$ V, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{i-Pr}$ VI, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{i-Pr}$.

are solvent-dependent and appear almost co-incident in d_6 DMSO. This phenomenon of separate methyl signals is also shown by diastereoisomers of methyl benzoylvalyl-alaninate (III and IV) and of methyl benzoylalanine (V and VI).

However if the benzoyl group is replaced by a benzyloxy group ($R^1 = \text{PhCH}_2\text{O}$ in the above), there is no difference in diastereoisomeric ester signals. Our thinking at the moment runs along the lines that the benzoyl group might favour the hydrogen-bonded form in the figure which might possibly induce different shielding effects on the methyl esters.

^{13}C -Spectra on I and II kindly run for us by Dr. Tony Thomas at Roche Products Ltd., Welwyn Garden City, show all the lines coincident except one secondary carbon of the valyl side-chain which appears separated by 0.25 p.p.m. in the two diastereoisomers. The significance of this result awaits interpretation.



Please credit this to Mr. Claude Haigh's account.

Yours sincerely,

John S. Davies

John S. Davies,
R. J. Thomas,
M. K. Williams.

References

1. B. Weinstein and A. E. Pritchard, J. Chem. Soc., Perkin I, 1972, 1015.

DOW CORNING

May 7, 1974

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

HNMR Shift-Structure Correlations of Silicones

Dear Barry:

The enclosed figure displays some shift-structure correlations of silicones which may be of interest to your readers. These correlations are useful for the identification of the structural groups, G, attached to silicon in compounds of the type L_3SiG , where L_3 is any combination of a variety of substituents. Most commercially interesting groups and substituents are included in these correlations.

Although the figure does not show such fine detail, the correlations are believed to be valid to within 0.05 ppm provided that nonpolar, nonaromatic solvents are used. Substantial deviations may occur if the substituent atom bonded to silicon has an atomic number greater than that of chlorine, if the substituent is a charged species, or if long range effects are induced by conformational preferences of an aromatic group in the substituent. Correlations for the SiOH and SiH groups include a more restricted range of substituents: Only hydrocarbon and siloxy substituents are included for the SiOH (DMSO) group, and polysilanes (Si-Si bonds) are not included for the SiH group.

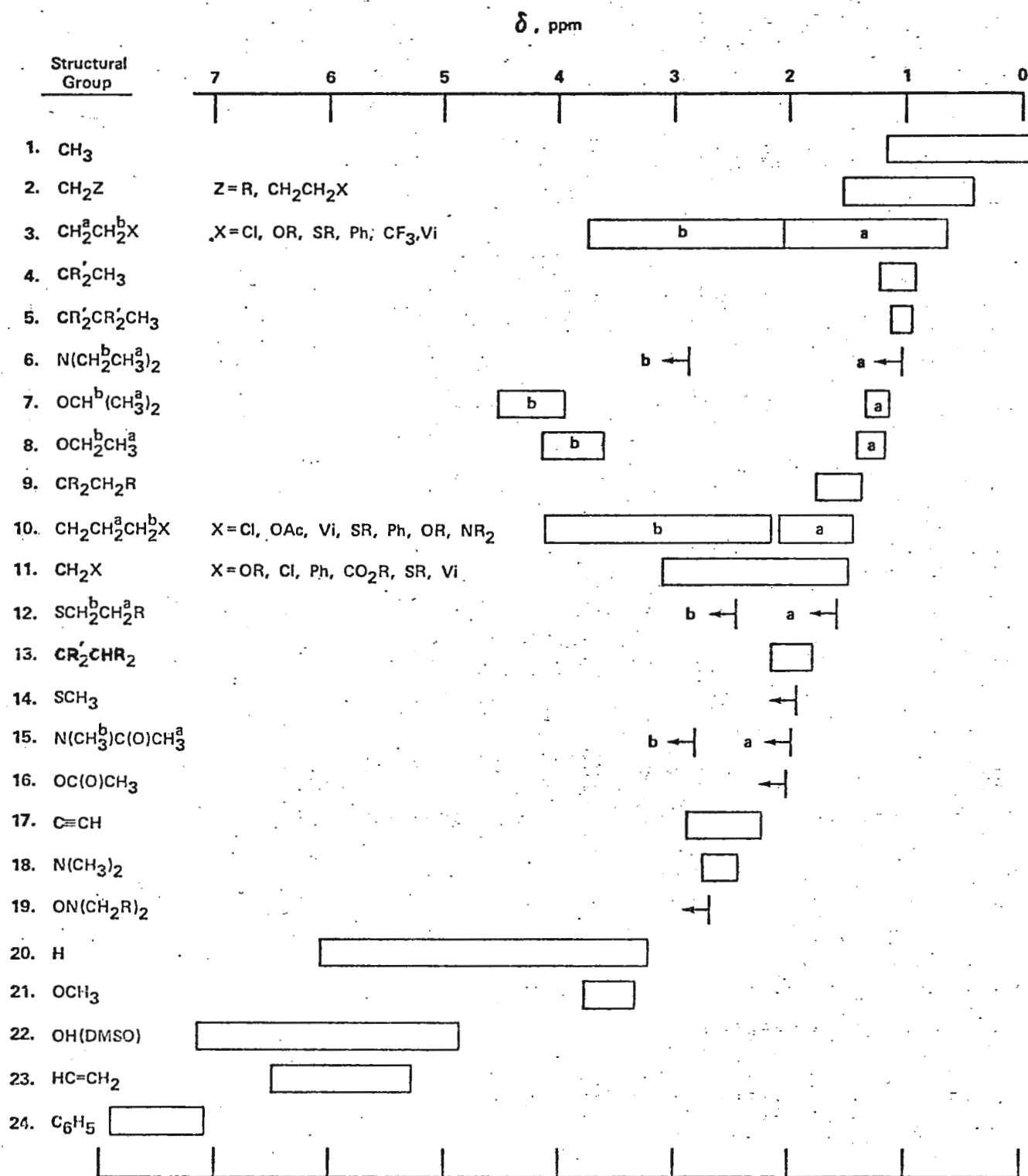
The figure is abstracted from an extensive discussion of the NMR spectra of silicones which will appear late this year (1).

Very truly yours,

Dwight E. Williams

gb
Enc.

- (1) D. E. Williams, "NMR Analysis of Silicones," Chap. 11 of ANALYSIS OF SILICONES, ed. by A. Lee Smith, to be published in December, 1974, by John Wiley & Sons, Inc.



The first High Resolution NMR Spectrometer
on the market for Fourier and PEP Spectroscopy

WH 90



Let's get acquainted!



USA BRUKER MAGNETICS INC.
One Vine Brook Park, Burlington, Mass. 01803
Tel. (617) 272-9250, Tx. 94-9493

USA BRUKER SCIENTIFIC INC.
Westch. Industrial Park, Elmsford, N.Y. 10523
Tel. (914) 592-5470, Tx. 131524

USA BRUKER SCIENTIFIC INC.
1548 Page Mill Road, Palo Alto, Calif. 94304
Tel. (415) 493-3173

CANADA BRUKER SPECTROSPIN LTD.
84 Orchard View Blvd., Toronto M4R1C2
Tel. (416) 486-7907, Tx. 21622366



189-13
NICOLET INSTRUMENT CORPORATION

5225 Verona Road, Madison, Wisconsin 53711
Phone: 608/271-3333 TWX: 910-286-2713
(formerly Fabri-Tek Instruments, Inc.)

May 14, 1974

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

Dear Barry:

TITLE: "Homospoil T_1 Sequences"

Since your dunning letter has just arrived in conjunction with my last note appearing in TAMUNMR, I gather that it didn't count.

We have been trying to repeat some T_1 sequences such as those originally suggested by Markley, Horsley and Klein¹ and by McDonald and Leigh.² Our work has been on a Bruker HX-90E converted for Fourier using the NIC-293 for controlling all pulses and ENI amplifiers for the rf portion, on the Bruker HX-270 at Florida State (courtesy of G. Levy and R. Rosanske) and on a couple of XL-100's with TTI-Nicolet Fourier accessories.

In all cases, we found that a homospoil pulse of about 10-12 milliseconds was required to cause a complete spoiling of the homogeneity unlike McDonald who mentioned a pulse in the micro-second range. The recovery of the homogeneity following these pulses was also a factor in our experiments limiting measurement of very short tau values (say, under 0.5 seconds).

I am enclosing one simple example of the T_1 's measured by both techniques which simply illustrates that we really did the work: it is of no great chemical significance. I wrote up the patch diagram of the NIC-293 along with a brief description and included it in a new T_1 program manual. I'll be glad to send a copy to anyone who's interested.

Sincerely,

James W. Cooper, Ph.D.
Applications Manager

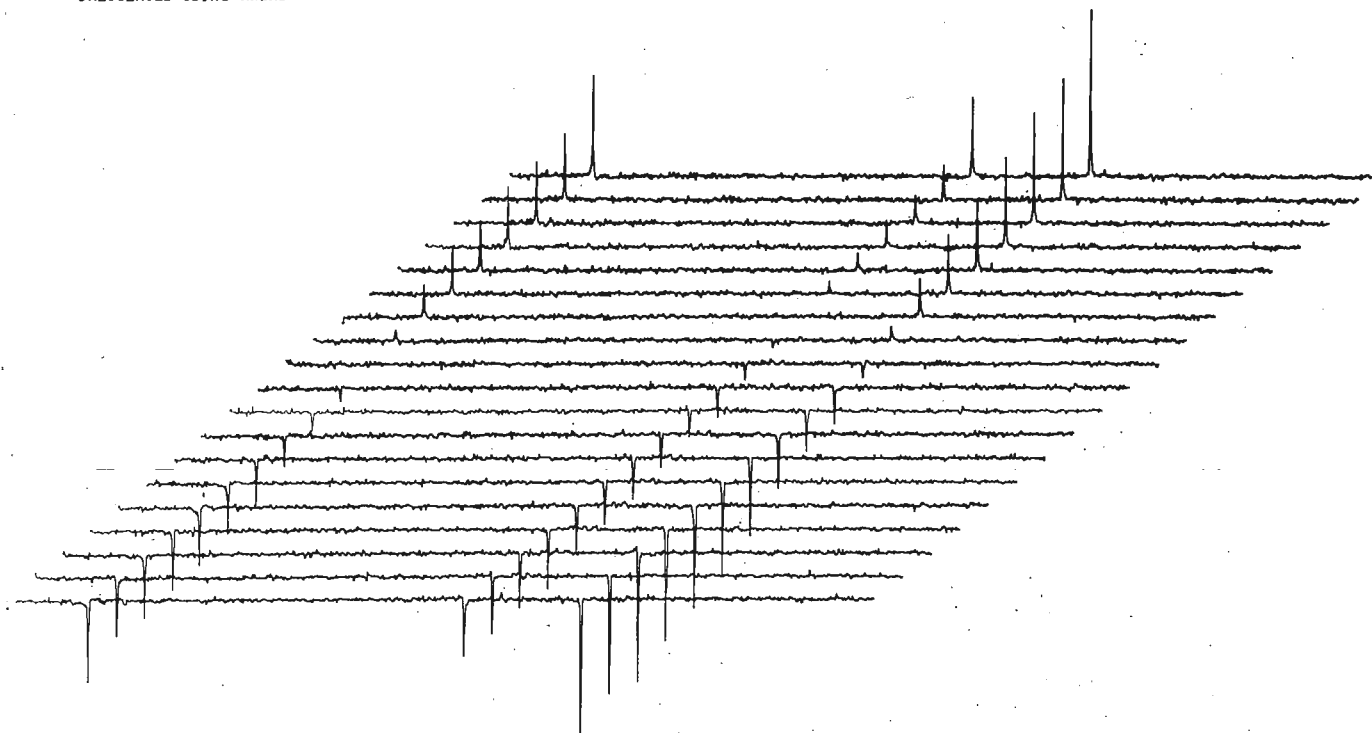
JWC/tab

1. J.L. Markley, W.J. Horsley and M.P. Klein, J. Chem. Phys. 55, 3604 (1971).
2. G.G. McDonald and John S. Leigh, Jr., J. Mag. Res. 9 358 (1973).

ISOBUTANOL PRFT

NO.	CURSOR	FREQ.	T1(SEC)	STD. DEVN.	INTERCEPT
1	192	1812.500	4.569 +-	0.013	0.726
2	1079	946.289	6.055 +-	0.016	0.812
3	1355	676.757	5.455 +-	0.013	0.651

CALCULATED USING AREAS



ISOBUTANOL PRFT
P(180)= 70.000 USEC
P(90)= 35.000 USEC

TAU VALUES
= 0.010 SEC
= 0.200 SEC
= 0.299 SEC
= 0.400 SEC
= 0.499 SEC
= 0.699 SEC
= 1.000 SEC
= 1.499 SEC
= 2.000 SEC
= 2.499 SEC
= 3.000 SEC
= 3.999 SEC
= 4.999 SEC
= 5.999 SEC
= 6.999 SEC
= 7.999 SEC
= 8.999 SEC
= 9.999 SEC
= 14.999 SEC

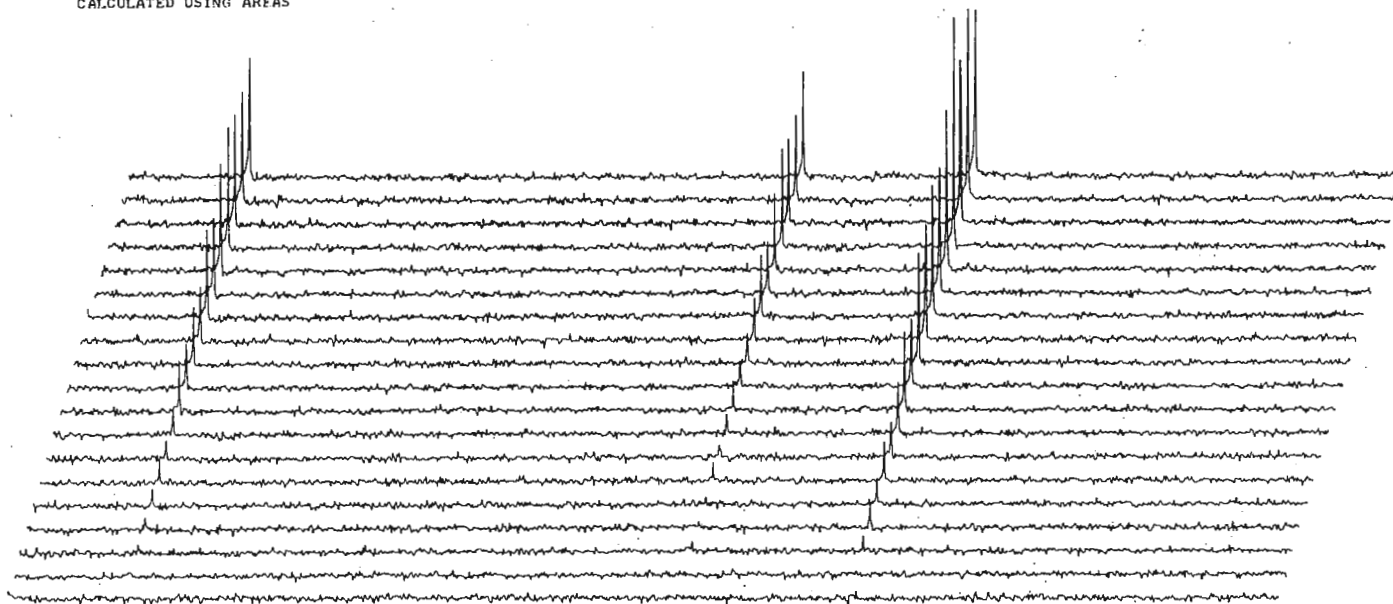
RECOVERY TIME= 14.999 SEC
P3= 100.000 USEC
D3= 0.001 SEC
P4= 0.100 USEC
D4= 0.001 SEC
TOTAL SCANS= 10

NO. OF FREQ DOMAIN POINTS = 2048
SW= 2000.000
DW= 250.000
DE= 0.000
SO= 0.000
TC= 3.000
SF= 25.144
TA= 0.000
TB= 0.000
T1= 0
T2= 0
NC= 4

ISOBUTANOL MCDONALD LEIGH

NO.	CURSOR	FREQ.	T1(SEC)	STD. DEVN.	INTERCEPT
1	192	1812.588	5.307 +-	0.032	0.021
2	1079	946.289	7.082 +-	0.024	0.033
3	1355	676.757	5.813 +-	0.024	0.015

CALCULATED USING AREAS



ISOBUTANOL MCDONALD LEIGH
P(180)= 35.000 USEC
P(90)= 8000.000 USEC

TAU VALUES
= 14.999 SEC
= 0.200 SEC
= 0.299 SEC
= 0.400 SEC
= 0.499 SEC
= 0.699 SEC
= 1.000 SEC
= 1.499 SEC
= 2.000 SEC
= 2.499 SEC
= 3.000 SEC
= 3.999 SEC
= 4.999 SEC
= 5.999 SEC
= 6.999 SEC
= 7.999 SEC
= 8.999 SEC
= 9.999 SEC
= 0.010 SEC

RECOVERY TIME= 1.099 SEC
P3= 35.000 USEC
D3= 0.008 SEC
P4= 0.100 USEC
D4= 0.001 SEC
TOTAL SCANS= 10

NO. OF FREQ DOMAIN POINTS = 2048
SW= 2000.000
BW= 250.000
DE= 0.000
SO= 0.000
TC= 0.000
SF= 25.144
TA= 0.000
TB= 0.000
T1= 0
T2= 0
NC= 0



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

NATIONAL HEART AND LUNG INSTITUTE

May 13, 1974

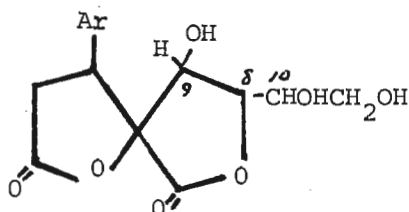
Prof. B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Barry,

Some INDOR Experiments on Leucodrin

INDOR is one nmr technique which has been little used in natural products investigations, although Burton, Hall and Steiner have shown that it is eminently suitable for studying mutarotated sugars, (Can. J. Chem., 48, 1679 (1970)), and Fujita and his colleagues have made impressive use of it in establishing the structure of the diterpene poncidin (Perkin I, 2277 (1973)).

In work with Guido Perold of the University of the Witwatersrand, we have found the technique quite valuable in investigations of the plant phenolics from Proteaceae, such as leucodrin, below:



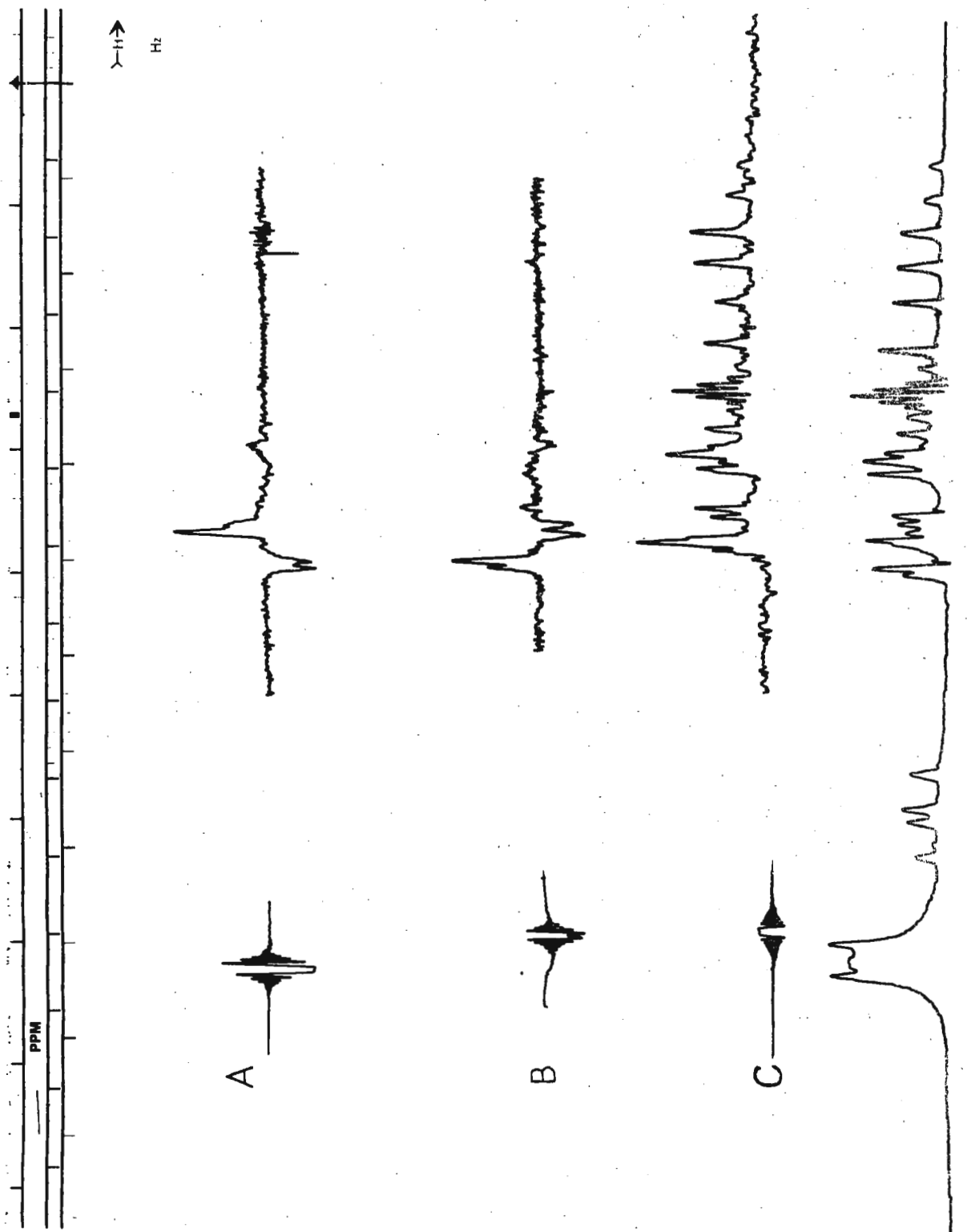
Ar = p-hydroxyphenyl

As you can see from the trace C of the accompanying spectra, a simple decoupling experiment on H-9 at $\delta 4.75$ produces a somewhat tenuous indication that H-8 occurs around $\delta 3.7$, while the INDOR runs of traces A and B provide a more precise shift value (3.71) and the coupling between H-8 and H-10 (2 Hz). The results not only confirm the assignments of Perold and Pachler (J. Chem Soc. 1918 (1966)), which were never in doubt, but promise to be useful in assigning structures to the new compounds our South African colleagues are encountering.

Yours very truly,

Bob

R. J. Highet
Laboratory of Chemistry



BROCK
University

St. Catharines, Ontario

Glenridge Campus
684-7201 Ext. 317

May 6 1974

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

Dear Prof. Shapiro;

POSTDOCTORAL FELLOWSHIPS AVAILABLE

Applications are invited for postdoctoral positions at Brock University, involving the use of our new Bruker WP60 FT nmr spectrometer which we expect to have installed in August equipped for ^1H , ^{13}C , ^{19}F & ^{31}P . Preferred starting date, September, 1974.

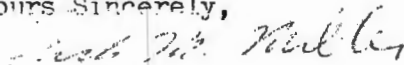
Candidates should have a background in high-resolution nmr.

Experience in vacuum line techniques and moisture free synthesis would also be an asset.

i.) with J.S. Hartman: Work will include studies of redistribution reactions about tetrahedral boron, in particular, those involving exchange of ions for neutral molecules. (see J.S. Hartman & G.J. Schrobilgen, Inorg. Chem., May or June 1974), e.g. D_2BF_2^+ studied by ^{19}F nmr.

ii). with J.M. Miller: Work will include studies of ^{13}C nmr of adducts of the boron trihalides, and pairwise additivity about tetrahedral boron, or ^{13}C , ^{19}F and ^{31}P studies of a series of C_6F_5 -organometallic derivatives.

Yours Sincerely,



Jack M. Miller
Associate Professor.

COLORADO SEMINARY

UNIVERSITY OF DENVER

UNIVERSITY PARK • DENVER, COLORADO 80210

DEPARTMENT OF CHEMISTRY/303.753-2436

May 15, 1974

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

Dear Barry:

Title: Phenyl Ring Rotation in Metal Complexes of Tetraphenylporphyrin Derivatives.

Recently we reported the temperature dependent pmr spectra of indium porphyrins with chloride in one axial position.¹ The nonequivalence of the two ortho protons and two meta protons of each phenyl ring in indium tetra-(p-trifluoromethylphenyl)porphyrin chloride, $\text{In}(\text{p-CF}_3\text{-TPP})\text{Cl}$, was observed to average on the nmr time scale between 30° and 120° by a concentration independent pathway. Averaging could be attributed to phenyl rotation or chloride exchange.¹

Papers reporting x-ray diffraction results on tetraphenylporphyrin complexes commonly emphasize the role of steric repulsion between the phenyl and pyrrole hydrogens in preventing the phenyl rings from becoming even approximately coplanar with the porphyrin ring.² Therefore, we have prepared an extensive series of compounds varying the ortho substituents on the phenyl rings, the metal, and the axial ligands on the metal to distinguish between the possible mechanisms for the observed averaging in the nmr spectra.

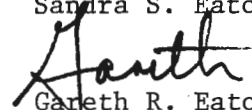
Indium tetraphenylporphyrin chloride complexes have been prepared with methyl and fluorine substituents in the ortho positions of the phenyl rings. No averaging of non-equivalent ortho-methyls in indium tetra(o-tolyl)porphyrin chloride or indium tetramesitylporphyrin chloride in 1,1,2,2-tetrachloroethane has been observed up to 140°C. The 56MHz ^{19}F spectra of indium tetra-(pentafluorophenyl)porphyrin chloride, $\text{In}(\text{F}_5\text{-TPP})\text{Cl}$, and tetra(pentafluorophenyl)porphyrin, $\text{H}_2(\text{F}_5\text{-TPP})$, are shown in the Figure.³ Chemical shifts are given in ppm downfield of external neat hexafluorobenzene. Assignments of resonances are based on analogy with substituted pentafluorobenzenes.⁴ The spin-spin coupled patterns observed for the ortho and meta fluorines in the free porphyrin (A) are approximately doubled in the complex (C) indicating non-equivalence of the two sides of the phenyl rings. The signals for the para-fluorine are about the same in the ligand and complex. Averaging of the nonequivalent fluorines is not observed up to 130° in 1,1,2,2-tetrachloroethane. Rapid chloride exchange can be achieved by addition of excess Bu_4NCl to $\text{In}(\text{F}_5\text{-TPP})\text{Cl}$ and a spectrum (B) similar to $\text{H}_2(\text{F}_5\text{-TPP})$ is obtained.

We have also looked at titanyl and ruthenium carbonyl complexes of tetra-(p-trifluoromethylphenyl)porphyrin, tetra(o-tolyl)porphyrin, and tetramesitylporphyrin. The variable temperature pmr spectra are very similar to those obtained for the indium chloride complexes. The averaging process occurs over the same temperature range for the indium chloride, titanyl, and ruthenium carbonyl porphyrins in which the ortho substituents of the phenyl rings are hydrogen. Averaging does not occur for any of the metal porphyrin complexes when the ortho substituents are methyl except for the case of indium in the presence of excess chloride. The similarity of activation energies would not be expected for a concentration independent ligand exchange, but is fully consistent with phenyl ring rotation. Since many nmr studies on metalloporphyrins involve derivatives of tetraphenylporphyrin, the dynamic behavior discussed above should be considered in interpreting the spectra. We will be submitting further details for publication shortly.

Sincerely,



Sandra S. Eaton



Gareth R. Eaton

References

1. TAMUNMR 180, 50 (1973)
2. e.g., E.B. Fleischer, Accts. Chem. Res. 3, 105 (1970).
3. A JEOL C-60HL spectrometer was used to obtain the spectra.
4. E.F. Mooney, ed., Annual Reports on NMR Spectroscopy 5A, 156-158 (1972).

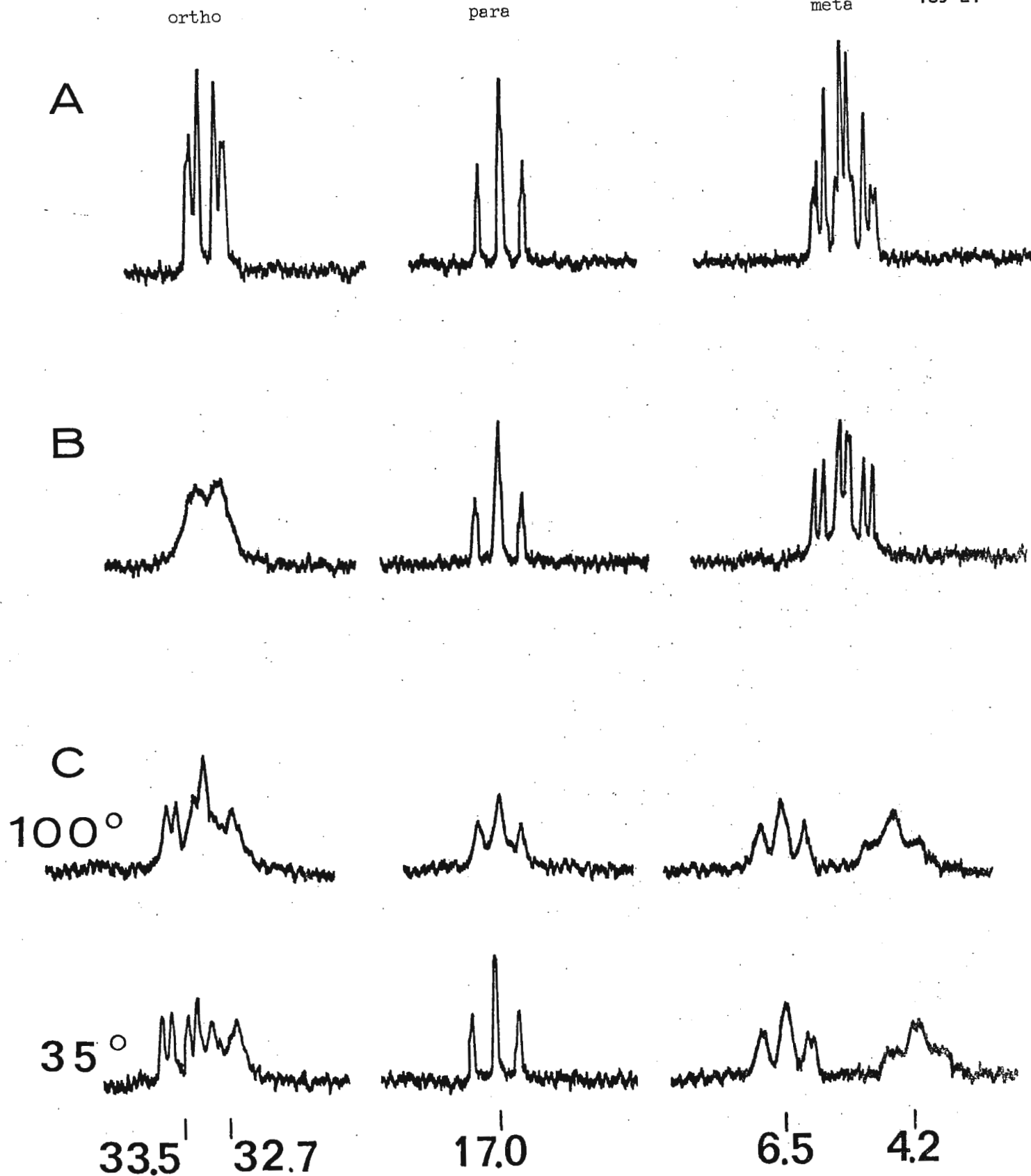


Figure Caption: ^{19}F NMR (56 MHz) spectra of 1,1,2,2-tetrachloroethane solutions of: A. $\text{H}_2(\text{F}_5\text{-TPP})$ at 30° , B. $\text{In}(\text{F}_5\text{-TPP})\text{Cl}$ in the presence of excess Bu_4NCl at 35° , C. $\text{In}(\text{F}_5\text{-TPP})\text{Cl}$ at 35° and 100° . Chemical shifts are in ppm downfield of external neat C_6F_6 .



University
of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building,
295 Cathedral Street, Glasgow G1 1XL Tel: 041-552 4400

13th May, 1974

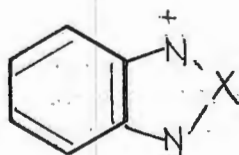
Professor B. L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station,
Texas, 77843.

Dear Barry,

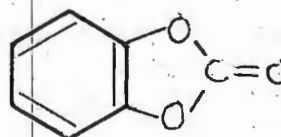
In my last contribution¹ I wrote about the nematic phase (E.B.B.A.) spectrum of benzo-2,1,3-thiadiazole (I, X = S) unaware that a publication existed² on this compound (albeit examined in a different nematic solvent). In contrast to this published work analysis of our spectrum gives impossible molecular dimensions (see table - note that r_B/r_A should be ~ 2.0 r/r_A should be ~ 1.0). The same applies to the oxygen analogue (I, X = O). However, benzo-2,1,3-selenadiazole (I, X = Se) and catechol carbonate (II) both give reasonable molecular dimensions. The discrepancies can be partially attributed to the poorer line separation in the case of the former two compounds, and they emphasize the need to choose a suitable nematic solvent in each individual case, particularly with solutes such as the present ones where there are few spins (cf³). In the cases of solutes without axial symmetry changes in solvent will be expected to lead to small but significant changes in orientation leading to different relative line separation. This is indeed apparent on comparing the literature² spectrum of (I, X = S) with ours¹.

Yours sincerely,

Peter Bladen



I



II

Compound	Ref	Solvent	D_A^*	D_B	D	D^1	r_B/r_A	r/r_A	r^1/r_A
I, X = O		EBBA	-54.8	-31.8	-581.25	-25.9	1.20	0.42	1.17
I, X = S		EBBA	-95.3	-7.5	-597.2	-54.7	2.34	1.14	1.91
I, X = S	2	Mixture	-193.1	-24.8	-898.5	-82.0	1.98	0.99	1.72
I, X = Se		EBBA	-112.1	-12.7	-424.0	-40.7	2.07	1.01	1.76
II		EBBA	-294.6	32.3	-1233.3	-45.4	2.08	1.03	1.77

EBBA \equiv p-ethoxybenzylidene-p-n-butylaniline

Mixture \equiv 70:30 p-methoxybenzylidene-p-amino α -methyl cinnamic acid n-propyl ester

+ anisole p-azophenyl n-capronate

* Frequencies in Hz. Indirect coupling constants for I, X = O, S, Se taken from the literature; for II estimated values were used. The values of direct coupling constants were computed using the program LAOCOONLC ⁵

References

- ¹ P. Bladon TAMUNMRN 1973, 179, 35.
- ² C. H. Khetrapal and A. C. Kunwar Mol. Crystals and Liq. Crystals 1972, 15, 363
- ³ P. Diehl and C. H. Khetrapal NMR Basic Principles and Progress, 1969, 1, 51
- ⁴ N. M. D. Brown and P. Bladon, Spectrochimica Acta, 1967, 24A, 1869.
- ⁵ A Library of Computer Programs for N.M.R. Spectroscopy. R. K. Harris and J. Stokes, S.R.C. 1971.



National Research Council . Conseil national de recherches
Canada Canada

Division of Biological
Sciences

Division des sciences
biologiques

File Référence

16 May 1974

DEUTERIUM NMR AS A PROBE OF BIOLOGICAL MEMBRANES.

WIDE SWEEPS ON THE XL-100?

Dear Barry:

During the past year ^2H has been very kind to us in reporting the degree of order and mobility in model membrane systems (1,2). Joachim Seelig's group in Basel has also pursued this approach with great success (3,4). Our approach is to deuterate at specific positions in a fatty acid or phospholipid (see figure), incorporate these into model membranes and use the T_1 and T_2 , and/or time-averaged quadrupole splitting, of ^2H as parameters. Those involved in NMR studies of membrane systems know that the data are easier to obtain than they are to interpret. The dominant quadrupole mechanism for ^2H relaxation gives us an opportunity to approach the problems encountered with ^1H and ^{13}C from a different point of view. The quadrupole splittings give us an insight into molecular order parameters which have been largely neglected by the ^1H and ^{13}C adherents.

As an example of the type of data obtainable, we show the ^2H spectra of a phosphatidyl choline probe labelled at the head group methyl position. In unsonicated dispersions of the lipid, which consist of very large arrays of bilayers, the quadrupole splitting has an averaged value due to intralamellar motion and ordering (upper figure). This leads to an estimate of 0.008 for the molecular order parameter. On sonication to spherical single bilayer vesicles of diameter approximately 250 Å, the rotational correlation time for overall motion of the model membrane becomes significantly shorter (ca. 10^{-6}), and the quadrupole splitting is averaged to zero (lower figure). Measurement of

T_1 and T_2 for this high-resolution resonance leads to estimates of correlation times for the various motions available to the probe. We are at present developing the theory to include order as well as molecular rotations in the expressions for T_1 and T_2 , and the lineshapes.

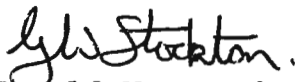
A severe limitation we have encountered in spectra of the former type is the difficulty in using spectral windows of greater than 15 KHz on our XL-100. The problem is due to various filters in the instrument and a software-controlled sampling time. We would like to know if any readers have made modifications to their instrument to circumvent this problem. The necessity for wider windows will increase as more interest in NMR of quadrupolar nuclei develops.

Our review on ^2H NMR for "Progress in NMR Spectroscopy" is nearing completion but we will be happy to include any further reprints or preprints that arrive soon.

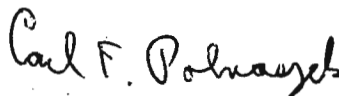
Best regards,



Ian C.P. Smith,

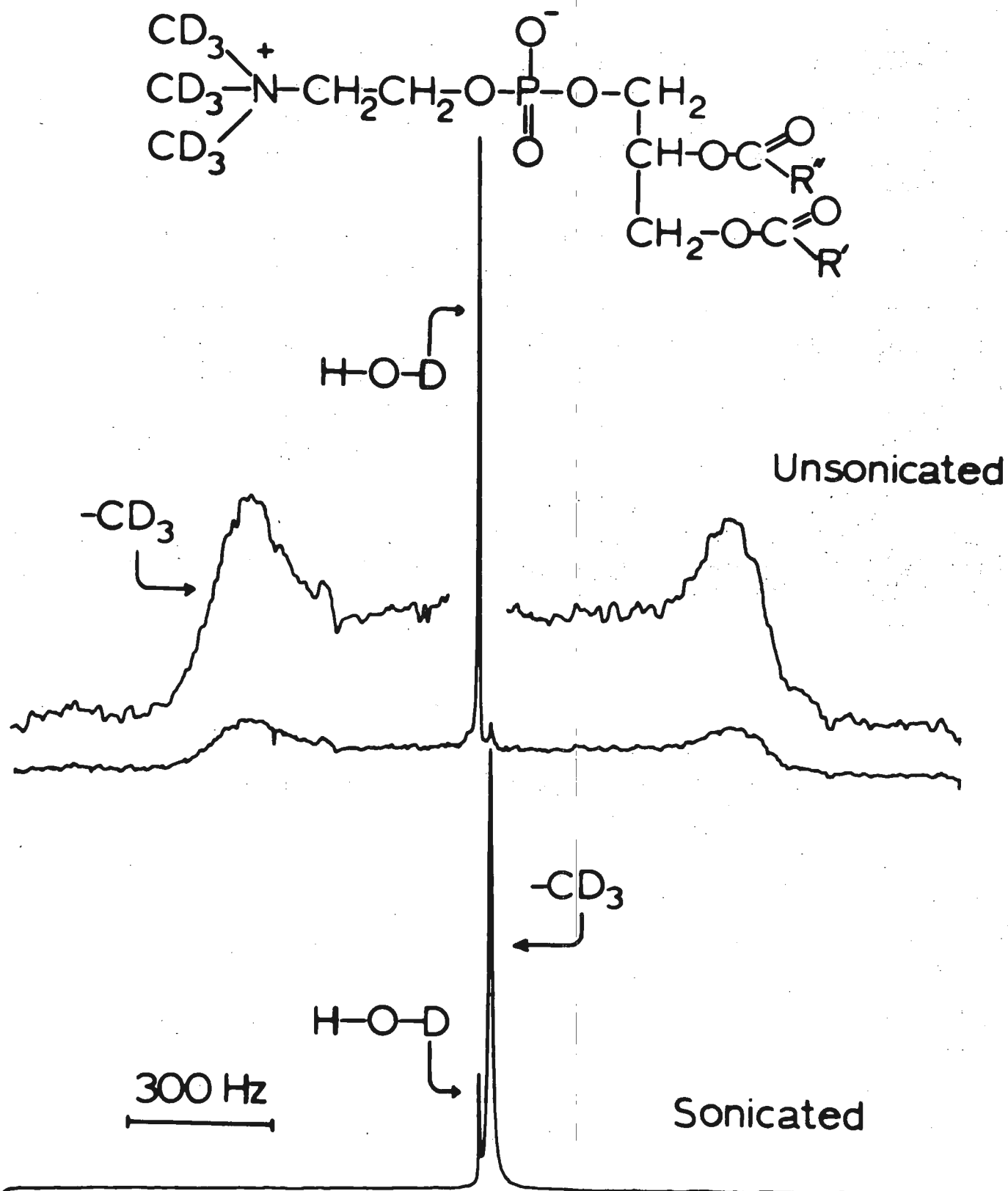


Gerald W. Stockton,



Carl F. Polnaszek

1. I.C.P. Smith, H. Saitô, and S. Schreier-Muccillo, TAMU NMR 178, 1 (1973).
2. H. Saitô, S. Schreier-Muccillo, and I.C.P. Smith, FEBS Letters 33, 281 (1973).
3. J. Seelig and W. Niederberger, J. Amer. Chem. Soc. 96, 2069 (1974).
4. J. Seelig and A. Seelig, Biochem. Biophys. Res. Comm. 57, 406 (1974).



^2H NMR spectra at 15 MHz (XL-100) of aqueous dispersions of the deuterated probe, 32 mg/ml (Upper) Unsonicated, 11,000 accumulations (Lower) Sonicated, 1,000 accumulations. Both spectra were obtained in Fourier transform mode.



UNIVERSITY OF SASKATCHEWAN, REGINA CAMPUS

REGINA, CANADA

S4S 0A2

DEPARTMENT OF CHEMISTRY

16 May 1974

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

RECENT RAMBLINGS
from REGINA

Dear Dr. Shapiro:

Our fairly new HX-90 spectrometer has now been working well for eight months or so, and I should like to mention a few of the interesting tasks upon which it has been set to work.

Proton NMR, which is finding itself somewhat neglected these days in the wave of enthusiasm for carbon-13, is by no means obsolete. For example, the vast increase in available sensitivity with the FT computer facility has enabled us to attempt the qualitative and quantitative characterisation of a number of basic drugs of the amphetamine and morphine families. Some early results hold out considerable promise, even in the face of problems such as proton-containing impurities in solvents, which become a nuisance at parts-per-million concentrations.

Our efforts with ^{13}C spectroscopy have included quantitative measurements of C-13 scrambling in the course of organic reactions. We find that, with suitable care, results of accuracy and precision comparable to those of H-1 NMR or C-14 tracing are attainable.

At the moment, we are awaiting the arrival of further equipment to extend our capability to F-19, P-31 and He3(!). Among other possibilities, we would like to explore the chances of measuring trace quantities of fluorine and phosphorus-containing substances in various applications such as water pollution.

Would you please credit this contribution to Frans Rummens who is presently enjoying a sabbatical year in Paris.

Yours truly,

R.D. Green

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:

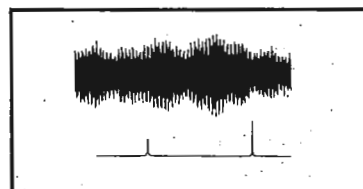
STOCHASTIC RESONANCE — This technique involves random noise modulation of the rf excitation frequency, leading to a broadband excitation whose response is measured and Fourier transformed much as in conventional pulsed-FT nmr. Its principal advantage lies in the fact that much less rf power is needed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

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.

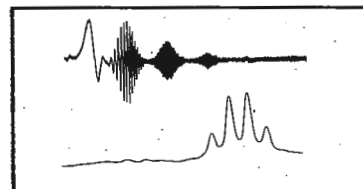
HOMOSPOIL T_1 SEQUENCE — This sequence allows the rapid measurement of long T_1 's without the long $5xT_1$ waiting period needed by the inversion-recovery sequence. It is accomplished by a $-(90\text{-spoils}\tau\text{-}90\text{-sample-spoil})$ - sequence.

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 a single frequency domain spectrum.

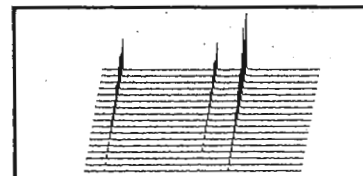
Please phone or write for details on these applications or to discuss how the versatile NMR-80 data system may be used for your experiments. Complete systems start at \$20,000. If you are already a Nicolet data system user, you may order free software for the above techniques from our Nicolet Users Society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



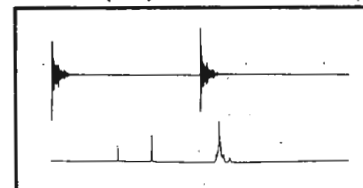
R. R. Ernst, *J. Mag. Res.* 3 10-27 (1970); R. Kalsner, *J. Mag. Res.* 3 28-40, (1970); J. Cooper and R. Addleman, 13th Experimental Nmr Conference (1972); E. Lippmaa, private communication.



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



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).



J. Schaeffer and E. O. Stejskal, 15th Experimental Nmr Conference (1974), and *J. Mag. Res.* March (1974) (in press). J. D. Elliott, et al. *Adv. Mag. Res.* 5 117 (1971)

NICOLET INSTRUMENT CORPORATION



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

Department of Chemistry

The Florida State University
Tallahassee, Florida 32306

May 17, 1974



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

Title: "Position Available: NMR Instrumentation, Research Associate

Dear Barry:

We have a unique opportunity for a bright, nmr instrumentation-oriented Ph.D. to spend two years at Florida State University as a postdoctoral research associate. The position (available on September 1, 1974) will consist primarily of two activities: (1) development of new Fourier transform nmr instrumental capabilities for our Bruker HX-270 and HFX-90 spectrometers and (2) research in ^{13}C , ^1H , or other nuclei FT nmr. Other activities will include supervision of instrumentation maintenance; however, the research associate will not generally be required to run samples for members of the department.

Our current instrumentation at FSU is quite versatile, having two field (21 and 63 kilogauss) capability for ^{13}C and ^1H Fourier transform or cw nmr. Each instrument is interfaced to a versatile Nicolet 1080 series computer with a disc-augmented memory. Equipment is being purchased and assembled to change over the HFX-90 to a frequency-synthesizer based multi-nuclei FT spectrometer. Our instrument development program will be supported by excellent machine and glass shops, etc.

The research programs in my group at present are largely in the area of molecular dynamics and ^{13}C relaxation. New efforts are starting in the areas of interactions between small molecules and complex biological systems; in electron-nuclear relaxation, and in studies of liquid structure. The choice of a specific research area for this position will be highly flexible.

Our group at present consists of two postdoctoral research associates, two graduate students, and a student-assistant. (A third research associate is scheduled to arrive this summer.)

I would very much appreciate your bringing this position to the attention of qualified candidates. The annual salary will be \$8000-9000 depending on qualifications.

Sincerely,

George C. Levy
Associate Professor

GCL/lrt

STATE UNIVERSITY OF GENT
ORGANIC CHEMISTRY DEPT.
LAB. FOR NMR SPECTROSCOPY



LABORATORIUM
VOOR
ORGANISCHE CHEMIE

Prof. M. ANTEUNIS
Krijgslaan 211 — GENT — 9000
BELGIUM

B-9000 GENT, May 21, 1974

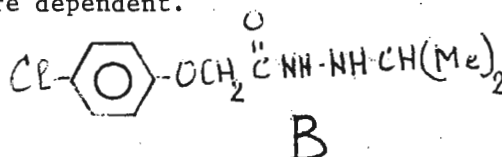
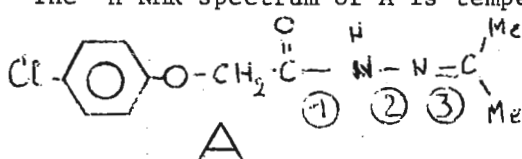
KRIJGSLAAN 271 - S 4 Tel. 22 57 15
(België-Europa)

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

Title: Rate Process in an Acylhydrazone

Dear Dr. Shapiro,

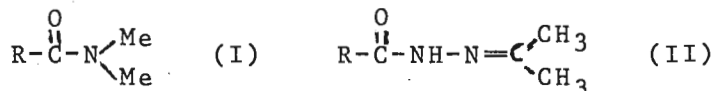
The $^1\text{H-NMR}$ spectrum of A is temperature dependent.



At room temp (CDCl_3 sol) the spectrum is indicative of two conformers, in a population ratio 4:6. There are 4 Me singlets, 2 CH_2 signals and 2 AA'BB' patterns for the aromatic moiety. At higher temp (DMSO sol) the signals coalesce to give two Me singlets, 1 CH_2 signal and AA'XX' pattern. ΔG^\ddagger_{338} is 17 kcal/mole (calc. from CH_2 signals). On the other hand compound B does not show exchange phenomena in the same temp (1 CH_2 peak, one AA'BB' pattern).

What rate process is responsible for these observations ?

There are two plausible hypotheses: (i) rotation around the amide bond $\text{O}=\text{C}-\text{NH}$ ① or (ii) rotation around the $\text{N}-\text{N}=\text{C}$ bond ② (Inversion/rotation around the $\text{N}=\text{C}$ bond ③ remains slow even at 90°C , as the anisochronism of the $\text{N}-\text{Me}$ groups persists at that temperature). A definite conclusion has not yet been reached. The room temperature shift difference of the CH_2 signals is large (0.34 ppm). This is a, perhaps tenuous, argument in favor of rotation around the amide bond being the culprit. This hypothesis could be tested by comparing the sensitivity of the exchange process to the nature of the R groups in the following series of compounds.



A close parallel between the two series for different R groups would be indicative of slow rotation around the amide bond being involved in II (and A)

But perhaps one of the newsletter-readers has the answer to this question. Comments and suggestions are invited.

Please could you credit this contribution to the laboratory of NMR Spectroscopy (Prof. M. Anteunis).

Yours sincerely,

D. Tavernier.

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

189-31

- A. Measuring line positions in FT mode .
B. Programs LAOCOON and LASS .

Ihr Zeichen

Ihre Nachricht vom

Unser Zeichen
DNL/VW/UH

Tel. Durchwahl:
7008363/364

Datum
May 21st, 1974

Dear Barry,

A. Santini and Grutzner have recently reported⁽¹⁾ on line-position errors in CW ¹³C-experiments. We wish to offer our experience with (preferable) FT measurements.

Our XL-100 is equipped with a disk and complementary software which permits long data lengths, up to 32 K. The peak listing routine, with an appropriate "fix"⁽²⁾ interpolates between channels to a precision greatly exceeding the Hz/channel resolution previously obtainable. In a typical high-resolution experiment (100 Hz width, 32 K data points) the line positions in a symmetrical spectrum were reproducible between experiments with an average deviation of less than 0.003 Hz; the symmetry about the centre of the spectrum also agreed to the same degree of precision. The maximum digital resolution under these conditions is 0.063 Hz/channel. Since no errors arise from a finite sweep rate and phase errors can be avoided by the use of the power spectrum, we consider the FT measurements to be inherently more accurate as well as more precise than high-precision line measurements.

As a check, we ran the same sample on our HA-100 at the temperature of the XL-100 probe. Within experimental error, line positions agreed here with those obtained on the XL-100. However, in spite of most careful work, the reproducibility of measurements (ca. 0.02 Hz) is, at best, one order of magnitude lower than on the XL-100.

B. At present, we are using a home-made version of LAOCOON (non-iterative, six-spin; eigenvectors, basis functions, levels and plotting on the console are optional), to run in core on any 16K 620 computer. We also developed a little program LASS (Lindeman - Adams Shift Simulation) which calculates a ¹³C-spectrum with a list of "connections" as input. The parameters developed by Lindeman and Adams⁽³⁾ are used with some crude corrections for substituents. Copies of either of these programs, as source (FORTRAN) or binary paper tapes, may be obtained on request.

Best wishes,

Sincerely yours,

.....
D. N. Lincoln
Abteilung II/16

V. Wray
.....
V. Wray

Wilbrand Hackmann, Stöckheim

(1) TAMU 187,48

(2) To be obtained from R. Stillman, Varian, Palo

Alto; we too will be glad to supply a copy.

(3) L. P. Lindeman and J. Q. Adams, Anal. Chem.

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY
REVELLE COLLEGEPOST OFFICE BOX 109
LA JOLLA, CALIFORNIA 92037

May 22, 1974

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

TITLE: Nuclear Transverse Cross Relaxation

Dear Barry,

We would like to tell you about another example of " T_2 " longer than " T_1 ". Cross relaxation is a well established mechanism for spin-lattice relaxation but has been ignored as a transverse relaxation mechanism until recently.¹ We measured the transverse relaxation rates of a 3:1 mixture of 2,5-dibromothiophene and benzene as part of a more complete study on molecular motions in this system. Partially relaxed Fourier transform spectra were obtained from the last half echo in a Carr-Purcell train. T_2 's were obtained by plotting the measured intensities of each line versus delay time. Single exponential plots were obtained through at least one full decade of decay for a range of pulse spacings from $2\tau = 500 \mu\text{s}$ to 90 msec. T_1 's were measured by 180- τ -90-FT inversion recovery method. The results of the pulse spacing dependence are shown in the figure. The solid line was calculated from theory using a modified relaxation matrix similar to that of Vold and Chan.¹ The parameters were varied until a best fit was obtained. The "self-relaxation" rate of benzene was $.0523 \text{ sec}^{-1}$ and for 2,5-DBT $.077 \text{ sec}^{-1}$. The experimental measurements were accurate to about $\pm 2\%$. These values predict an intermolecular NOE of 10.5% for benzene and 7% for 2,5-DBT. We have as yet been unable to measure these effects by conventional double resonance techniques on an HR-220. The chemical shift at 220 MHz is 145 Hz (36.3 Hz at 55 MHz for T_2 experiments). We would be very interested in knowing if anyone has measured NOE's with chemical shifts ≤ 150 Hz by a standard field sweep HR-220 spectrometer.

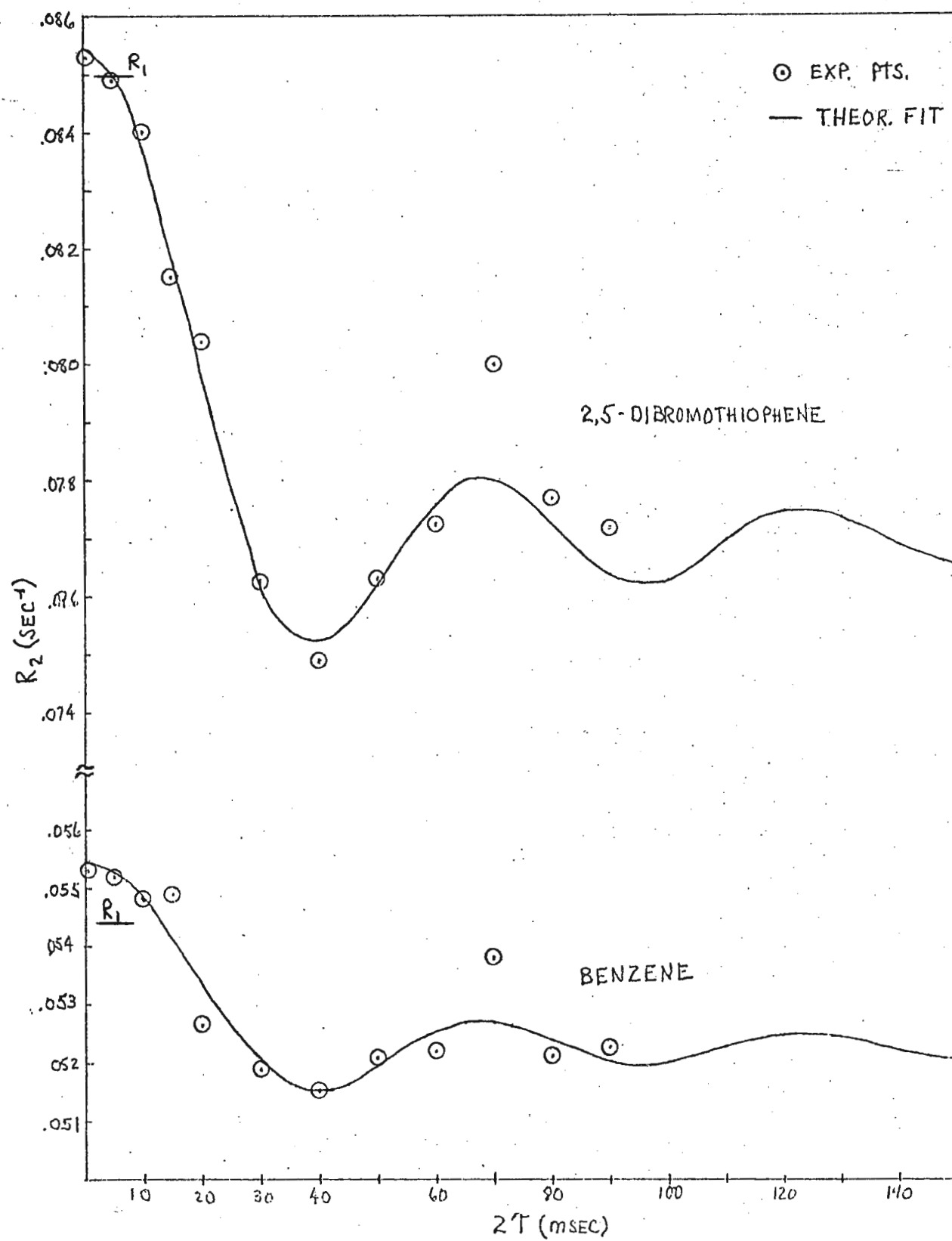
In doing our " T_2 " measurements, the spectrometer requirements for this type of measurement are exceedingly stringent and extreme care must be taken to obtain accurate results, especially when the relaxation times are around 20 seconds or longer. This type of measurement can be very useful in certain cases as it can yield much information from a single concentration, single temperature study.

Sincerely,

Howard E. Simon

P. S. Please credit this contribution to Dr. Robert L. Vold.

1. R. L. Vold and S. O. Chan, J. Chem. Phys. 56, 28 (1972).



STATE UNIVERSITY OF NEW YORK
AT STONY BROOK

DEPARTMENT OF CHEMISTRY

STONY BROOK, N.Y. 11790

May 24, 1974

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

Dear Barry:

Title: IN VIVO NMR ZEUGMATOGRAPHY

Since my preliminary description of "NMR Zeugmatography" in TAMUNMRN No. 175 (April, 1973), we have considerably improved our techniques and branched out in several directions. Although perfection continues to elude us, we have succeeded in generating a picture of the interior of a living mammal from its proton NMR signals. The attached figure is the result of an experiment done under the following conditions:

Sample: Adult female live mouse.

Spectrometer: Modified DA-60 operating at 8.13 MHz with 7 kHz time-sharing.

Gradient: Fixed Z-gradient of 0.3 gauss/cm, sample reoriented about X-axis.

Probe: Homemade cross-coil with 3 cm sample space. The receiver coil was located in the YZ plane and surrounded the thoracic cavity of the mouse.

Scans: Twelve 15-second scans at 15° intervals.


Digital Data Processing: Multiplicative ART-type reconstruction algorithm on a 32 x 32 array with 8 iterations.

Display: Overprinting of standard characters on line printer to generate 16 gray levels, followed by photographic optical filtering and contrast enhancement.

The picture has several imperfections, including the bright artifact in the center, but the outline of the body and the locations of the lungs are clearly visible. Because the receiver coil is most sensitive to signals emanating from regions near its plane, the image shown corresponds to a kind of thick section of the animal as viewed in the direction of its long axis.

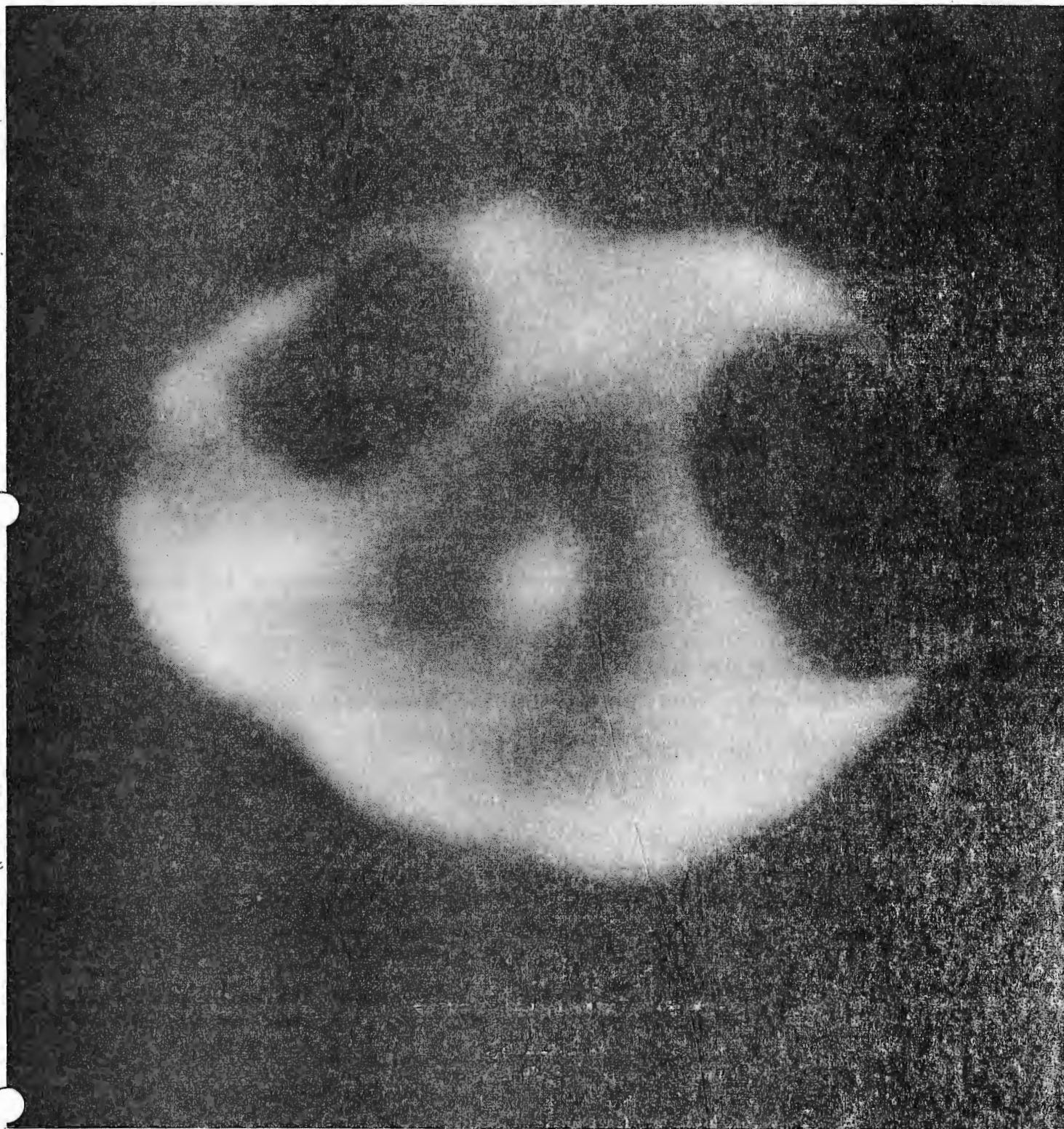
Keep TAMUNMRN coming!

Yours truly,



Paul C. Lauterbur
Professor of Chemistry

PCL:ab
Enc.



University of Waterloo



Waterloo, Ontario, Canada
N2L 3G1

Faculty of Science
Department of Chemistry
519/885-1211

May 14, 1974.

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

Dear Barry,

A short note about distortion of tetrahedral ions which are oriented in an electrical double layer. Fred Fujiwara has been investigating the acidified decylammonium tetrafluoroborate/ammonium tetrafluoroborate/water system in the middle soap regions. The tetrafluoroborate ion is oriented and the B-11 spectrum is a typical 3:4:3 arrangement derived from first order quadrupole splitting of the $3/2$ nuclear spin levels. More interesting at certain concentrations the direct dipole-dipole couplings between fluorine nuclei are resolved in the form of 1:3:3:1 quartets. For the sake of those used to the BF_4^- - F-19 spectrum as mainly (81% abundant B-11) a 1:1:1:1 quadruplet the spectrum shown has a dipole-dipole effect splitting between fluorines of 1.05 ± 0.05 Hz giving a $|D_{\text{FF}}| = 0.7$ Hz, superimposed upon this. The splitting of the 1:1:1:1 quadruplet is much larger than that in an isotropic micellar solution. The value $J_{\text{B-F}} = 0.61$ Hz in isotropic micellar solution gives $D_{\text{B-F}} = 5.75 \pm 0.6$ Hz for the oriented ion admitting both signs for J_{BF} from the $|J_{\text{BF}} + D_{\text{BF}}|$. Assuming all distortions are in C_{3v} symmetry (a gross untruth) angles (180 - tetrahedral) become 71.6° or 69.4° to the C_3 axis.

The NH_4^+ ion is oriented and almost as much so as in an anionic detergent middle phase. The positive surface of detergent cations produces a structured electrical double layer therefore and cations such as NH_4^+ can penetrate and become part of the structured double layer region. Studies have been made on degrees of order in $-\text{ND}_3^+$ head groups, water (as D_2O) and several other things as functions of concentrations and temperature. Some work is in press, some being refereed. This might give some idea of our latest lines at Waterloo and in São Paulo.

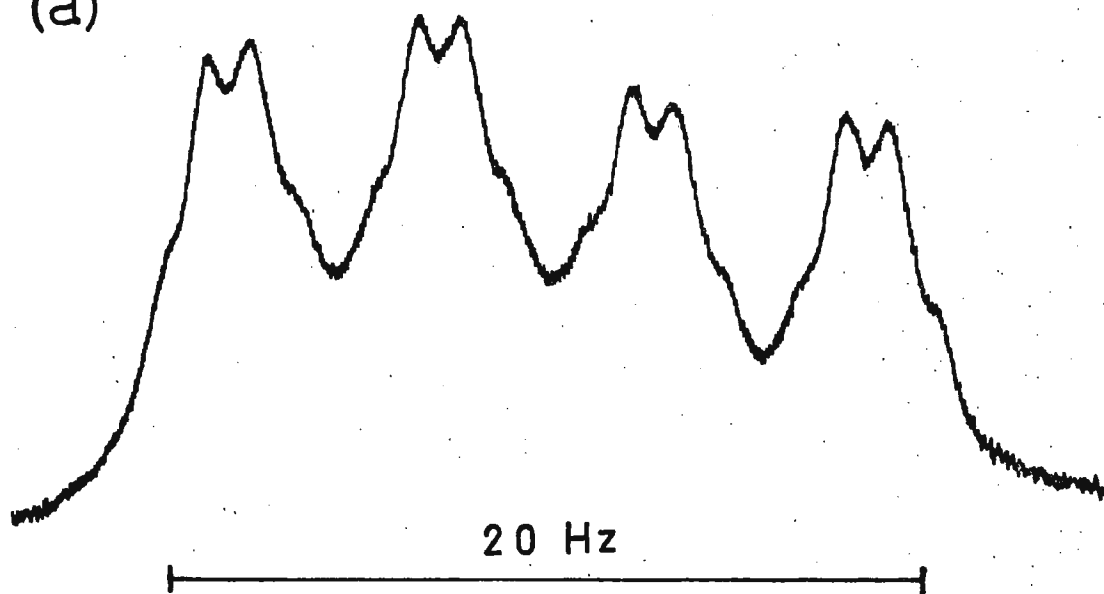
With Kind Regards,

Len Reeves

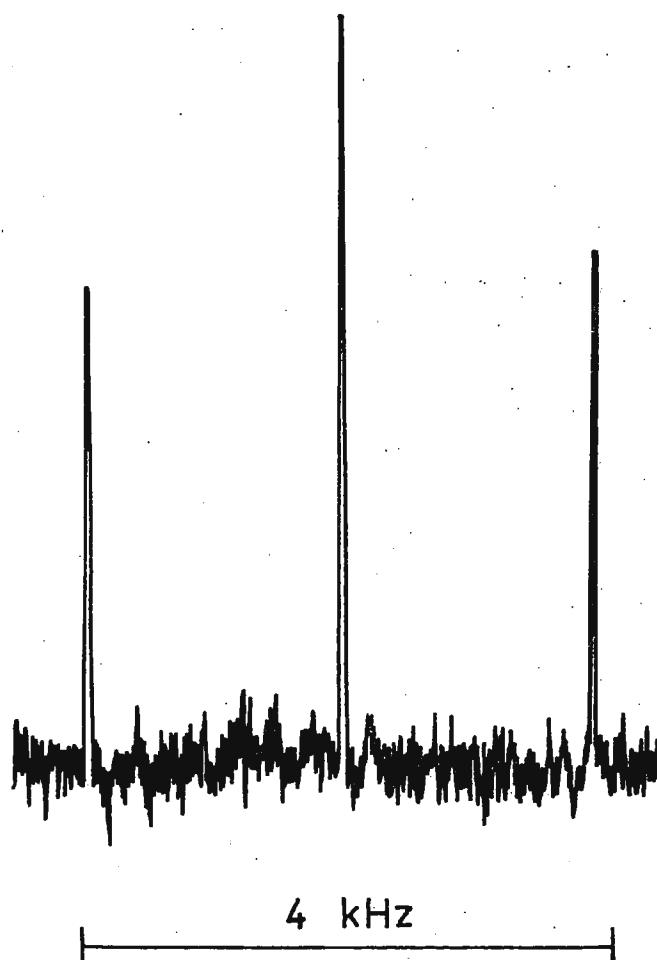
Dr. L.W. Reeves.

LWR/ta

(a)



(b)





Laboratorium
für anorganische Chemie
Eidg. Technische Hochschule
Zürich

8006 Zürich, May 28, 1974
Universitätstrasse 6

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

The Concentration Dependence of the ^{195}Pt chemical
shift in the PtCl_4^{2-} ion.

Dear Prof. Shapiro,

Our NMR facility at the Inorganic Chemistry Institute of E.T.H. is now established and we hope to keep our HX-90 quite busy.

We are continuing our studies of ^{195}Pt ($I = 1/2$, natural abundance $\approx 33\%$) using "conventional" FT techniques and a sampling of these results is shown in the table.

The concentration dependence of the ^{195}Pt chemical shift in the PtCl_4^{2-} specie is in contrast to that observed for the PtCl_6^{2-} specie. This may well be related to the fact that water is not an "innocent" solvent for PtCl_4^{2-} . Indeed we observe a 2nd ^{195}Pt resonance in all of these spectra which may be the $[\text{PtCl}_3(\text{OH}_2)]^-$ specie.

Compound	Solvent	Concentration (1)	$\delta^{195}\text{Pt}$ (2)
$\text{Na}_2[\text{PtCl}_6]$	H_2O	0.33	0
$\text{Na}_2[\text{PtCl}_6]$	H_2O	0.03	0
$\text{Na}_2[\text{PtCl}_4]$	H_2O	2.63	- 1671
$\text{Na}_2[\text{PtCl}_4]$	H_2O	0.66	- 1654
$\text{Na}_2[\text{PtCl}_4]$	H_2O	0.33	- 1652
$\text{Na}_2[\text{PtCl}_4]$	H_2O	0.22	- 1650
$\text{Na}_2[\text{PtCl}_4]$	H_2O	0.13	- 1647

(1) In mol/litre. (2) Values are in p.p.m. upfield from the resonance position of $\text{Na}_2[\text{PtCl}_6]$ and are estimated to be correct to ± 2 p.p.m.

Best wishes,

P. S. Pregosin
L. M. Venanzi

Paul S. Pregosin
L. M. Venanzi

Postdoctoral Research Assistant

An SRC funded research assistantship is available for two years from September 1974 (salary up to £2058 x 165) to work on the chemical applications of Heteronuclear INDOR Spectroscopy mainly of ^{195}Pt but also $^{111}/^{113}\text{Cd}$ and ^{199}Hg (cf. newsletter articles, 169, 43; 179, 6 and 187, 34). The project will involve some preparative work as well as the spectroscopy. For further details, please write to Dr. R.J. Goodfellow, Department of Inorganic Chemistry, University of Bristol, Bristol, BS8 1TS, England.

TEXAS A&M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

28 May 1974

Re: Drawings and Figures in the TAMU NMR Newsletter

1. Newsletter contributors are once again urged to take greater pains with the quality of the figures, graphs, etc. submitted for the Newsletter. We return poor drawings only in really desperate cases, but it would certainly improve the readability of otherwise excellent contributions if you would send originals or high contrast black on white drawings only. Please avoid fuzzy photocopies, blue ink, etc.

2. Please help us save space by making your drawings as small as possible, commensurate with adequate readability for the amount of data included. Because of our previously announced need to keep each Newsletter contribution down to a maximum of three pages, keeping figures and drawings small in size will be a considerable help.

B. L. Shapiro



GENERAL ELECTRIC COMPANY, RESEARCH AND DEVELOPMENT CENTER, P.O. BOX 8
SCHENECTADY, NEW YORK 12301, Phone (518) 346-8771

CORPORATE
RESEARCH AND
DEVELOPMENT

21 May 1974

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

TITLE: A High-Low Power Switching System for a TT 1020
High Power RF Pulse Amplifier Incorporated into
an XL-100 Spectrometer

Dear Barry:

We recently modified our XL-100 to incorporate a Transform Technology, Inc. TT 1020 high power RF pulse amplifier in the system. In order to be able to observe a nucleus at low power, or observe a nucleus for which the high power amplifier is not equipped, the spectrometer must be returned to its original configuration. Since we use the TT 1020 to observe ^{13}C and ^{29}Si only, and are equipped for ^1H , ^{31}P and ^{19}F as well, this became time consuming. Bill has designed a switching system which enables the instrument to be changed from high power to low power without changing any wires or shutting down the spectrometer.

The switching system (shown below) consists of two SPDT coaxial relays. A normal CW experiment is performed with the TT 1020 in CW and the XL-100 FT control module off. In this mode, relay 2 directs the output of the XL-100 transmitter module to the CW input of the TT 1020 and out to the probe through its internal relay. A low power FT experiment is performed with the TT 1020 in CW and the FT control module turned on as usual. In this mode relay 1 directs the FT output from the XL-100 transmitter module to the input of the XL-100 power amplifier. Relay 2 directs the output of the XL-100 power amplifier to the CW input of the TT 1020 and out to the probe. A high power experiment is performed with the TT 1020 in the FT mode and the FT control module on. In this mode relay 1 directs the FT output from the XL-100 transmitter to the FT input of the TT 1020. The internal relay directs the output of the TT 1020 power amplifier out to the probe.

Providing that the appropriate TT 1020 power amps and standard XL-100 power amps are available, either high or low power FT experiments may be carried out. We feel that this is a very useful device which can be incorporated in very little time at very low cost.

Sincerely,

Liz Williams

E.A. Williams
Materials Characterization Operation
Building K-1, Room 2A22

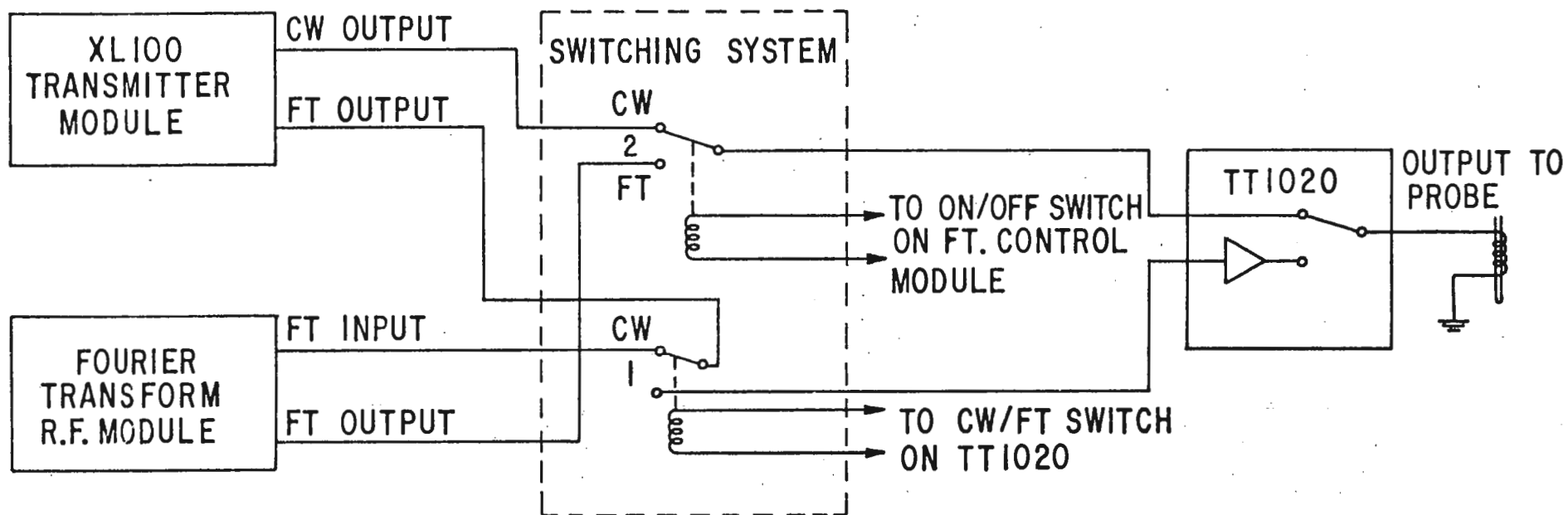
J.D. Cargioli

J.D. Cargioli
Materials Characterization Operation
Building K-1, Room 2A22

Bill Hatfield

W.T. Hatfield
Materials Characterization Operation
Building K-1, Room 2C22

bp



ACADEMIC/PROFESSIONAL OPENING
School of Chemical Sciences at Urbana-Champaign
May, 1974

SPECTROSCOPIST

We seek a person to be in charge of the Molecular Spectroscopy Laboratory of the School of Chemical Sciences (SCS). The academic/professional position is that of Spectroscopist. It has a broad range of professional, research and educational responsibilities. Minimum qualifications include an MS degree in a physical science or engineering, or the equivalent, plus two years of experience directly related to the responsibilities of the position.

The Spectroscopist is responsible for the supervision, training and evaluation of the 4.5 FTE research assistants who perform the day to day operations. He instructs students, post doctorates and faculty in the use of instruments when particular research is best accomplished in that manner. Also, he establishes policies so as to provide fair and general access of all SCS research personnel to the facility.

In general, the Spectroscopist is responsible for the proper operation of the laboratory as a research service facility in SCS, including maintenance of all instruments in good working order. He should have a good understanding of the physical principles underlying the operation of lab instruments, and an appreciation of their capabilities and limitations. Magnetic resonance spectroscopy is the major research function of the laboratory, which also includes infrared, ultraviolet and Raman capabilities. It is especially important that the spectroscopist have a strong background in nmr techniques, and be able to initiate and implement modifications and additions to existing instruments to keep them abreast of advances in the field.

The desired starting date is August 1, 1974. The position is permanent. The starting salary will be about \$14,000 or more per 12 months, depending upon qualifications and experience, with a month's vacation/year. Those interested should apply at once. The cut-off date for consideration of applications will be on or about July 1, 1974. Persons wishing to apply should send a curriculum vitae to the address given at the bottom of this announcement and arrange for three letters of recommendation to be sent there also.

The University of Illinois is an Affirmative Action/Equal Opportunity Employer and encourages applications from members of minority groups and women.

Inquiries should be addressed to:

Dr. H. S. Gutowsky, Director
School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

Phone: 217/333-0710

AUTHOR INDEX

Bladon, P.	22
Cargioli, J. D.	40
Ciampelli, F.	2
Cooper, J. W.	13
Davis, J. S.	8
Eaton, G. R.	19
Eaton, S. S.	19
Goodfellow, R. J.	39
Green, R. D.	27
Hatfield, W. T.	40
Highet, R. J.	16
Hilbers, C. W.	5
LaMar, G. N.	1
Lauterbur, P. C.	34
Levy, G. C.	29
Lincoln, D. N.	31
Miller, J. M.	18
Polnaszek, C. F.	24
Pregosin, P. S.	38
Reeves, L. W.	36
Rodrigues de Miranda, J. F.	5
Santoro, E.	2
Shapiro, B. L.	39
Simon, H. E.	32
Smith, I. C. P.	24
Stockton, G. W.	24
Tavernier, D.	30
Thomas, R. J.	8
Venanzi, L. M.	38
Williams, D. E.	10
Williams, E. A.	40
Williams, M. K.	8
Wray, V.	31



Your light touch to FT NMR Spectroscopy

The new JEOL **FX60**, a low-cost, routine FT NMR Instrument, adds a new dimension in simplicity of operation by replacing the standard keyboard with the **Light Pen Control System (LPCS)**. The **FX60** provides routine high performance and reliable data for both ^{13}C and ^1H studies. Sample tubes up to 10mm OD are standard. For complete information write to . . .

JEOL

Analytical Instruments, Inc.

235 Birchwood Ave., Cranford, NJ 07016

201-272-8820

The FX60 was recently previewed at the ENC Conference, Raleigh, North Carolina, April 28, 1974.

INSTRUMENTATION: NMR Spectrometers/Mass Spectrometers/ESR Spectrometers/Laboratory Computers/Scanning Electron Microscopes/Electron Microscopes/X-ray Microprobes/X-ray Diffractometers/Electron Beam Apparatus/Amino Acid Analyzers/Sequence Analyzers.

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

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 $+200^\circ\text{C}$. 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; Autosim™; 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 ^1H , ^{19}F , and ^2H , and external lock on ^1H 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



Brand names: ANASPECT™ • CARY® • MAT • VARIAN®
VARIAN AEROGRAPH® • VARIAN TECHTRON

CFT-20

