

Texas
A
M &
University
N - M - R
Newsletter

No. 200

May, 1974

<p>M. R. Willcott Hypothesis Testing and the Shift Reagent Problem: Queries! 1</p> <p>D. M. Wilson Deuterium Incorporation Sites by $^{13}\text{C}\{^2\text{H}, ^1\text{H}\}$ Difference Spectroscopy. 3</p> <p>G. W. Stockton, A. R. Quirt, L. Turner and I. C. P. Smith Increased Spectral Widths on the XL-100! . . . 6</p> <p>J. T. Gerig and D. C. Roe Multiple Forms of p-Trifluoromethylbenzene- sulfonylchymotrypsin 9</p> <p>W. B. Moniz, C. F. Poranski and S. A. Sojka Fixed Trap Capacitor in HA-100 Double-Tuned Probe. 12</p> <p>P. C. Lauterbur Postdoctoral Position Available. 13</p> <p>D. Ware and B. Hawkins Positions Available. 14</p> <p>W. C. Hutton, R. B. Martin and V. R. Miller Modifications to the JEOL PS-100P/EC-100 FT NMR System. 15</p> <p>S. A. Spearman and J. H. Goldstein NMR Studies of p-Dioxene 17</p> <p>P. A. Hart and J. Blackburn Pulse-Mode Proton Lock for Older Bruker HX90E'S. 20</p> <p>E. A. Williams and J. D. Cargioli Solvent Effects in ^{29}Si NMR. 21</p> <p>C. Gust Useful Old Equipment 23</p>	<p>F. M. Mourits and F. H. A. Rummens ^{13}C Medium Shifts of $^{13}\text{CH}_4$ in Natural Abundance 25</p> <p>A. A. Chalmers and K. G. R. Pachler Long-Range J(C,H) in Sulphur Containing 2-Pyrones 28</p> <p>W. B. Smith Chemical Shift Correlations of the Formyl and Acetyl Groups 29</p> <p>D. P. Kelly Large ^{13}C-^{19}F Coupling Constants in Cyclopropabenzonium Cations 31</p> <p>W. A. Thomas ^{13}C - ^1H Coupling in a Salicylaldehyde Derivative - XL-100 Recorder Problems 33</p> <p>C. L. Khetrapal and A. C. Kunwar Conformation of the Peptide Unit from Proton NMR Studies in Nematic Solvents. . . . 35</p> <p>Y. Kuroda Position Available. 36</p> <p>M. Cignitti, L. Guidoni, F. Podo, V. Viti, A. Brancati, F. Eusebi and A. DeSantis Proton NMR Studies on the State of Water in Aplysia Nerves and Squid Giant Axons . . . 38</p>
-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------

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.

YOU'LL ALWAYS FIND...

WILMAD[®]

**AT THE PEAK OF THE SPECTROSCOPIC
SUPPLY SPECTRUM**



WILMAD... the trade name with a history of absolute excellence in NMR and EPR Spectroscopy... is your assurance of unsurpassed quality in practically every item you need to carry on your spec-

troscopic investigations. Two decades of pioneering in the field have established us as the world's leading one-stop source for glassware, accessories, and supplies for spectroscopic research.

Whether you need...

- | | | |
|------------------------|------------------------------|---------------------------------|
| • SAMPLE TUBES | • SOLVENTS | • SPINNER TURBINES |
| • CHART PAPER | • RECORDING CHARTS | • MICROCELLS |
| • POST BINDERS | • DEWARs | • NEEDLES & SYRINGES |
| • COAXIAL CELLS | • INSERTS | • SAMPLE PIPETS |
| • QUARTZ CELLS | • REFERENCE MATERIALS | • TUBE HOLDERS |

... no matter what your requirements are... If they are involved in NMR or EPR spectroscopy... we can supply them... everything except the spectrometer.

**BE SURE YOU ARE ON OUR
MAILING LIST TO RECEIVE
NEW INFORMATION**

As the world's largest supplier of glassware, accessories, and consumables for spectroscopic research, we are continually publishing and distributing new catalogs, brochures, and miscellaneous information. To be sure that you receive our new literature as it is released, we suggest that you write and ask to have your name added to our mailing list.

*It Pays to Standardize
on WILMAD!*



WILMAD GLASS COMPANY, INC.

Route 40 & Oak Road, Buena, N.J. 08310 USA
(609) 697-3000 • TWX 510-687-8911

TAMU NMR NEWSLETTER - ADVERTISERS

Bruker Scientific, Inc.	- see p. 37
Electronic Navigation Industries	- see p. 27
Fisher Scientific Company	- see p. 11
JEOL Analytical Instruments, Inc.	- see outside back cover and (i)
Nicolet Instrument Corporation	- see p. 19
Varian Instrument Division	- see inside back cover
Wiley-Interscience	- see p. 5
Wilmad Glass Company, Inc.	- see inside front cover

TAMU NMR NEWSLETTER - SPONSORS

Abbott Laboratories
 Bruker Scientific, Inc.
 JEOL Analytical Instruments, Inc.
 Dr. R. Kosfeld, Abt. Kernres., Inst. f. Phys. Chem., TH Aachen (Germany)
 The Lilly Research Laboratories, Eli Lilly and Company
 The Monsanto Company
 Nicolet Technology Corp., Palo Alto, CA (formerly Transform Technology, Inc.)
 Unilever Research
 Varian, Analytical Instrument Division

TAMU NMR NEWSLETTER - CONTRIBUTORS

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

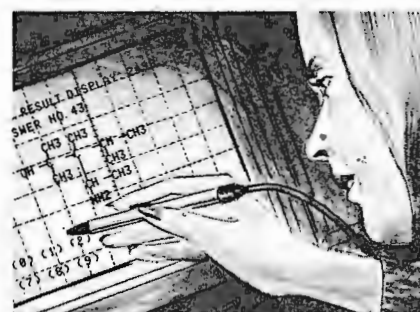
Deadline Dates: No. 201: 2 June 1975
 No. 202: 7 July 1975

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. 200

Blackbourn, J.	20	Moniz, W. B.	12
Brancati, A.	38	Mourits, F. M.	25
Cargioli, J. D.	21	Pachler, K. G. R.	28
Chalmers, A. A.	28	Podo, F.	38
Cignitti, M.	38	Poranski, C. F.	12
De Santis, A.	38	Quirt, A. R.	6
Eusebi, F.	38	Roe, D. C.	9
Gerig, J. T.	9	Rummen, F. H. A.	25
Goldstein, J. H.	17	Smith, I. C. P.	6
Guidoni, L.	38	Smith, W. B.	29
Gust, C.	23	Sojka, S. A.	12
Hart, P. A.	20	Spearman, S. A.	17
Hawkins, B.	14	Stockton, G. W.	6
Hutton, W. C.	15	Thomas, W. A.	33
Kelly, D. P.	31	Turner, L.	6
Khetrapal, C. L.	35	Viti, V.	38
Kunwar, A. C.	35	Ware, D.	14
Kuroda, Y.	36	Willcott, M. R.	1
Lauterbur, P. C.	13	Williams, E. A.	21
Martin, R. B.	15	Wilson, D. M.	3
Miller, V. R.	15		



We Challenge You to Light* On! in FT NMR Spectroscopy

We are so sure that you will be completely convinced that the **high performance** FX60, featuring the Light Pen Control System (LPCS), is as simple to operate as pointing a pen, **that we are extending the following challenge.**

We will let you run a demonstration on the JEOL FX60, utilizing the LPCS to "Light On". Then, why not directly compare our low cost FX60 against our competitors' systems by running a similar performance demonstration on the CFT-20, the WP-60 or any other comparable instrumentation? We challenge you not to be amazed at the total simplicity of the LPCS. We challenge you to deny, that while still maintaining the highest performance even when utilized by an unskilled operator, the FX60 has added a whole new dimension to FT NMR ease of operation. Don't take our word for it, make us prove it.

The FX60 story doesn't end there. Because of the LPCS technique, JEOL now introduces an optional **Structure Information Display (SID)** system which enables you to "Light On" to actually calculate and display molecular structures with CRT presentation.

Call or write for complete information or demonstration.

*Light Pen Control System (LPCS)



JEOL

Analytical Instruments, Inc.

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



University of Houston

HOUSTON, TEXAS 77004

Department of Chemistry
713/749-2612

April 3, 1975

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

Dear Barry:

HYPOTHESIS TESTING AND THE SHIFT REAGENT PROBLEM: QUERIES!

Bill Bearden and I have been concerned recently about hypothesis testing in the lanthanide shift reagents versus structure business. We have concluded there may be some pitfalls that have gone unrecognized. We are soliciting opinions from the Newsletter readers about the following possible points of contention.

In the event we compare two rather different arrays (such as the borneol-lanthanide and the isoborneol-lanthanide pairs) with a single set of shift data the hypothesis that "one substrate better represents the experimental one than the other substrate does" can be tested by the R-factor ratio using a level of hypothesis of one and entering the appropriate table provided by Walter Hamilton. In general we find that pairs of stereoisomers tested in this way usually lead to an unambiguous conclusion.

Now a second set hypothesis test involves the statistical differentiation between the lanthanide-substrate array reported by Worker A and the corresponding lanthanide-substrate array (for the same L-S pair) as reported by Worker B. In the ridiculous extreme, Worker A will have selected a different, but reasonable, set of internal coordinates for his substrate than Worker B and each of them will have used slightly different workups for the induced shift. This leaves us with the problem of comparing World War II battleships with 17th century chastity belts or its equivalent. We can get things on a common basis by assuring that both workers used the same internal coordinates for the substrate and permit different computational models for the matching of identical sets of shift data. In this event, the two workers might still get different lanthanide locations relative to the substrate because of differences in the computer code or in the assumptions from which the algorithm was built. When it happens that two L-S structures are reported, then we read that one structure is "better" than the other. In terms of hypothesis testing one can make the null hypothesis that the two lanthanide substrate arrays are indistinguishable. The level of this hypothesis would be four because we are saying that the X, Y, and Z coordinates for the lanthanide and the scale factor relating to the observed calculated have been adjusted, and one set of four parameters are

better than the other set of four parameters. Having recognized this we can then determine the degrees of freedom in the system, look in Walter Hamilton's¹ table under the appropriate dimensionality of the hypothesis and abstract a confidence level for the R-factor ratio as reported. This added worry about dimensionality makes most of the reported L-S arrays equivalent at confidence levels of 50-75 percent.²

We have also worried some about the degrees of freedom in a typical simulation of the pseudocontact shift by computation. In most cases there are at least four adjustable parameters involved in the problem. We feel that we should have eight or nine observable before even reasonably precise descriptions about the L-S array can be written. We will report on the pragmatic counting of the degrees of freedom at the ENC and hope to have a manuscript about the problem ready the next month or two.

In summary, we have found that external comparisons, that is, of two stereo isomers frequently indicates which one of that pair is the better description for the substrate being studied. In the internal comparison, that is, mapping the results obtained for the same lanthanide substrate pair by two different workers there is only a modest chance for a statistically significant difference in the two L-S arrays.

With best regards,

Sincerely yours,

MRW

M.R. Willcott
Professor of Chemistry

MRW:agr

1. W.C. Hamilton, Acta Crystallographica, **18**, 502 (1965).
2. W.C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y. 1964, pp. 157-162.

UNIVERSITY OF CALIFORNIA, BERKELEY

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



SANTA BARBARA • SANTA CRUZ

SPACE SCIENCES LABORATORY

BERKELEY, CALIFORNIA 94720

4 April 1975

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

Dear Professor Shapiro:

Deuterium Incorporation Sites by $^{13}\text{C}\{^2\text{H}, ^1\text{H}\}$ Difference Spectroscopy

As a continuation of an earlier study¹ in detecting and quantifying in vivo incorporation of ^2H from deuterated ethanol in bile acids of the rat, we have developed a form of difference spectroscopy which should be of widespread applicability in problems involving biosynthetic pathways or organic reaction mechanisms.

The method is simply to subtract $^{13}\text{C}\{^1\text{H}\}$ spectra from $^{13}\text{C}\{^2\text{H}, ^1\text{H}\}$ spectra of the same sample taken under otherwise identical conditions, where the brackets imply complete noise decoupling of the indicated nuclei. This is accomplished by alternately stepping a frequency synthesizer generating the ^2H frequency, between the center of the ^2H spectrum and 10 KHz away, and accumulating these spectra in different computer memory locations. After adequate S/N has been achieved, the two accumulations are subtracted and the result Fourier transformed. One of the two original spectra may be separately transformed, and the comparison of this spectrum with the difference spectrum affords very precise $^{13}\text{C} - ^2\text{H}$ isotope shifts.

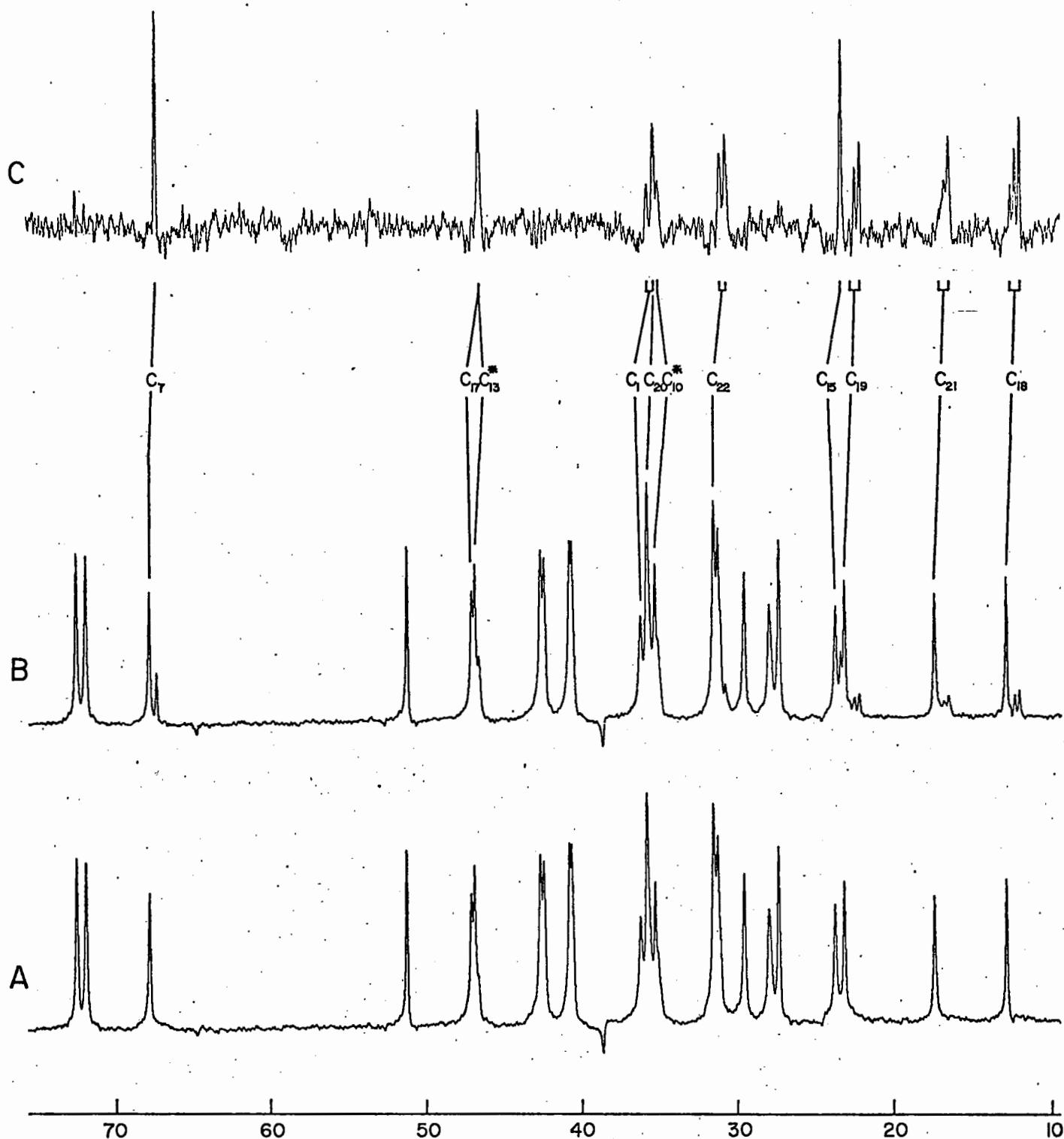
The results are typified by the accompanying spectra of methyl cholate isolated from rats which were administered $[2,2,2-^2\text{H}_3]$ ethanol. The particular sites and relative extent of ^2H incorporation along the steroid skeleton are quite evident. Also, since isotope shifts are approximately additive, the relative extent of mono- and di-deuterium incorporation in methylene groups C_1 and C_{22} , and mono-, di-, and tri-deuterium incorporation in methyl groups C_{18} , C_{19} and C_{21} are seen, although such comparisons must be considered cautiously since complete deuteration would cause substantial nuclear Overhauser and T_1 changes.

The spectrometer is a Varian XL-100 fitted with an external ^7Li lock and $^2\text{H}, ^{13}\text{C}$ - double tuning network, and quadrature detection and capillary sample bulb arrangement². The quadrature "glitch" at the spectrum center seems to arise from the use of non-deuterated solvents (in this case pyridine) for single-scan homogeneity tuning.

DM Wilson
 D. M. Wilson

References

1. D. M. Wilson, A. L. Burlingame, T. Cronholm and J. Sjövall, Biochem. Biophys. Res. Commun. **56**, 828 (1974).
2. D. M. Wilson, R. W. Olsen and A. L. Burlingame, Rev. Sci. Instrum. **45**, 1095 (1974)



Spectra of selectively ^2H -enriched methyl cholate (upfield region).
 A: $^{13}\text{C}\{^1\text{H}\}$ spectrum; B: $^{13}\text{C}\{^2\text{H}, ^1\text{H}\}$ spectrum; C: difference spectrum, with connections to assigned protonated peaks in the B spectrum. Asterisks denote carbon sites which are not deuterated, but appear because of geminal coupling to methyl deuterons. The abscissa is in ppm downfield from TMS.

F

WILEY-INTERSCIENCE... first with the finest books in your field!

1. TOPICS IN CARBON-13 NMR SPECTROSCOPY, Volume One

Edited by **George C. Levy**, *Florida State University*

The most comprehensive analysis of carbon-13 spectroscopy available. Topics include: an advanced treatment of carbon-13 chemical shifts; extensive coverage of new areas of carbon-13 nmr spectroscopy; an examination of carbon-13 reaction mechanisms; and authoritative predictions of future developments in nuclear magnetic resonance research.

1974 292 pages \$17.50

2. CARBON-13 NUCLEAR MAGNETIC RESONANCE FOR ORGANIC CHEMISTS

George C. Levy, *Florida State University*, and
Gordon L. Nelson, *General Electric Corporation*

Presents a new treatment of ^{13}C Fourier transform nmr data and principal experimental concepts and spectral characteristics. Other discussions show how to apply cmr methods, organic compound analysis, organic intermediates, and synthetic polymers and biopolymers.

1972 222 pages \$11.50

3. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF NUCLEI OTHER THAN PROTONS

Edited by **T. Axenrod**, *City College of the City University of New York*, and **G. A. Webb**, *University of Surrey*

This volume provides a comprehensive review of nmr spectra of nuclei other than protons. The book emphasizes both experimental and theoretical aspects of nmr spectra, focusing on nmr of paramagnetic systems, ft spectroscopy, and the theoretical treatment of nmr parameters.

1974 407 pages \$20.75

4. THE THEORY OF MAGNETIC RESONANCE

By **Charles P. Poole, Jr.**, and **Horacio A. Farach**, both of the *University of South Carolina*

Uses the direct product matrix expansion technique to underscore the essential similarities among the branches of magnetic resonance. Examines electron spin resonance, quadrupole spectroscopy, and the Mössbauer effect.

1972 452 pages \$23.00



WILEY-INTERSCIENCE

a division of John Wiley & Sons, Inc.
605 Third Avenue, New York, N.Y. 10016
In Canada: 22 Worcester Road, Rexdale, Ontario

Mail coupon to:

Wiley-Interscience, Dept. 737
P.O. 4569, Grand Central Station,
New York, N.Y. 10017

Gentlemen:

Please send me the book(s) I have checked to the right to read and use free for 10 days. At the end of that time, if I am satisfied with my order, I will send you the amount indicated for each book received plus postage and handling. Otherwise, I will return the order and owe nothing.

- ☐ 1 (1-53154-5) ☐ 3 (1-03847-4)
☐ 2 (1-53158-8) ☐ 4 (1-69383-9)
☐ Please send me a list of local bookstores carrying your titles.

Name _____

Affiliation _____

Address _____

City/State/Zip _____

Please add state and local taxes where applicable.

Prices subject to change without notice.

092-A5074-WI



National Research Council
Canada

Conseil national de recherches
Canada

Division of Biological
Sciences

Division des sciences
biologiques

File Référence

10 April 1975

INCREASED SPECTRAL WIDTHS ON THE XL-100!

Dear Barry,

In a previous letter (1), we announced our endeavours to study biological membranes using deuterium NMR of specifically labelled probe molecules and we mentioned experimental difficulty due to the limited spectral range of our XL-100 spectrometer in pulse Fourier transform mode. We have since carried out modifications to the instrument which have overcome many of the factors limiting the spectral width and other XL-100 owners may be interested in hearing about them. The following comments pertain to the XL-100-15 spectrometer and 620L computer with the Mk. I interface.

i) The software-controlled acquisition process imposes a maximum acquisition rate of about 24 KHz which limits the spectral width to 12 KHz. At faster acquisition rates, the digitized free induction decay will contain insufficient information and numerous "glitches" appear in the transformed spectrum. This difficulty was overcome by eliminating the software acquisition process and converting the computer to direct memory access (DMA) by the insertion of three circuit boards between the A/D converter and the computer memory, Fig. 1. The "active ingredient" is the buffer interlace controller (BIC) which routes the digitized FID from the A/D converter directly into the computer memory. The BIC is interfaced with the A/D converter and computer memory by the two DMA controller boards. The acquisition rate is then limited only by the maximum speed of the A/D converter, ca. 90 KHz for the Mk. I hardware. A new acquisition program was written to control the operation of the BIC and the signal averaging process. Simple wiring changes were made in the computer back plane to set the BIC device address and in the A/D converter to defeat the standard maximum speed free running mode and return control to the external clock frequency which is determined by the spectral width.

ii) The presence of hardware filters in the receiver chain also restricts the spectral window. The "audio" filter normally selected by the computer to match the spectral width must have greater bandwidth than the maximum of 10 KHz provided by the manufacturers. However, Varian has made provision for the connection of an external filter which may then be selected by the front-panel control. Frequency Device's four-pole Butterworth low-pass active filters were found to be satisfactory.

The 10.700 MHz crystal filter in the receiver i.f. strip has a normal bandwidth of 30 KHz. The r.f. carrier is normally centred in this window and the spectral width is thus limited to 15 KHz on either side of the carrier. This restriction may be overcome in two ways: the filter bandwidth may be increased to 60 KHz, or the centre frequency of the window

may be moved by 15 KHz whilst maintaining the 30 KHz bandwidth. We chose to use the latter method, which has the advantage of eliminating folded noise (with a gain of $\sqrt{2}$ in the signal-to-noise ratio) but with the possible disadvantage of restricting observation to one side of the carrier. We have installed a Tyco crystal filter with a centre frequency of 10.715 MHz and bandwidth of 30 KHz which provides a 30 KHz spectral window at the high-field side of the carrier and satisfies our requirements for the observation of the high-field half of a symmetrical spectrum containing large quadrupole splittings.

iii) The increased spectral width places a greater demand on the ability of the available r.f. power bandwidth to excite the spins. We have found that utilization of a Varian V-4420 High Power Pulse Amplifier tuned to 15.4 MHz for deuterium satisfies the power requirement for spectral widths up to (at least) our present maximum of 30 KHz.

Further improvement in spectral width would necessitate removal of the 40.96 KHz field modulation and utilization of a time-shared lock channel. A quadrature (dual-phase) detector could be used to advantage in the observation of wide but asymmetric spectra of, for example, liquid crystals, since both sides of the carrier would then be observed simultaneously (2,3).

As an example of the success of the above instrumental changes, Figure 2 illustrates the 20 KHz wide high-field half of the symmetric ^2H spectrum of perdeuteriodecanoic acid in a lyotropic liquid crystal (4) at 30°C. The narrow line at the arbitrary zero frequency is due to a small amount of isotropic phase and HOD. All other lines are due to decanoic acid in the homogeneously oriented liquid crystal phase. The spectrum is correctly phased and free of glitches across its entire span.

We wish to thank the scientific and engineering staff of Varian Associates for their invaluable help and advice with this project.

Best regards,

G.W. Stockton A.R. Quirt Leo Turner Ian
Gerald W. Stockton, Alan R. Quirt, Leo Turner, Ian C.P. Smith

1. I.C.P. Smith, G.W. Stockton and C.F. Polnaszek, TAMU NMR 189, 24 (1974).
2. E.O. Stejskal and J. Schaeffer, J. Mag. Res., 14, 160 (1974).
3. D.M. Wilson, R.W. Olsen and A.L. Burlingame, Rev. Sci. Instrum., 45, 1095 (1974).
4. R.C. Long, Jr., J. Mag. Res., 12, 216 (1973).

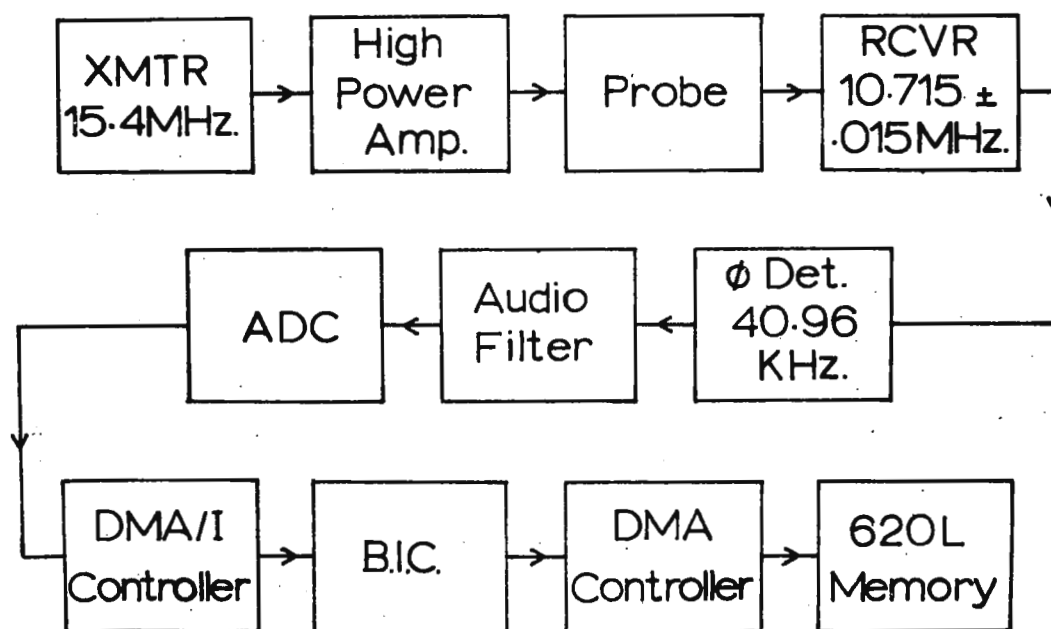


Figure 1. Block diagram of modified XL-100.

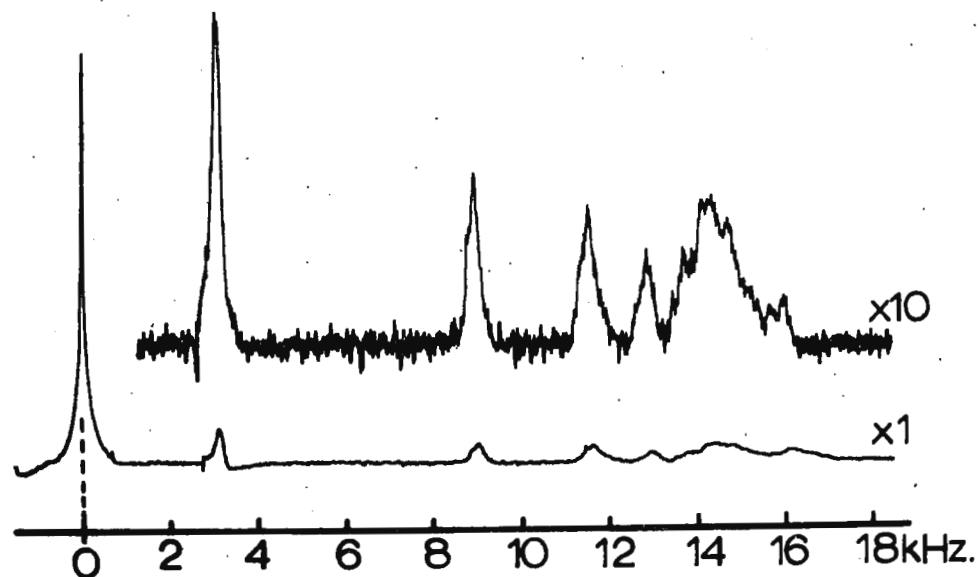


Figure 2. 15.4 MHz ^2H NMR spectrum of perdeuteriodecanoic acid (4.3%) in a lyotropic liquid crystal at 30°C; ca. 5000 transients.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

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



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA 93106

April 7, 1975

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

Dear Barry:

"Multiple Forms of p-Trifluoromethylbenzenesulfonylchymotrypsin"

We have previously shown that trifluoromethyl-substituted benzenesulfonyl fluorides inactivate the enzyme α -chymotrypsin, presumably by reaction with the serine-195 residue at the active site.¹ When the trifluoromethyl group is at the *para* position of the benzenesulfonyl moiety, the derivatized enzyme can be regarded as an analog of tosylchymotrypsin; an x-ray structure is available for the latter protein. We have been examining the fluorine-19 magnetic resonance spectra of the trifluoromethyl-containing enzymes hoping to obtain insight into the structure of these molecules in solution.

Through the kindness of Dr. Mike Maddox at Syntex we have obtained some preliminary high-resolution fluorine spectra using a Bruker WH-90. Some typical results are presented in Figure 1. At low pH there are present two types of trifluoromethyl signals, one much broader than the other. Above pH 5, the high-field signal is much sharper but it is not yet known that the broad high-field signal found at low pH titrates smoothly into this sharp resonance. The spectral changes observed are reversible with pH so that irreversible denaturation or the presence of impurities are not likely explanations of these observations. Moreover, when the enzyme is denatured either by treatment with 10% sodium dodecylsulfate or by heating above 40°, the two peaks in the spectrum of the modified enzyme are replaced by a single sharp peak at 12.7 ppm ($R_2 \approx 1.2 \text{ sec}^{-1}$).

Our results thus strongly suggest that at least two conformational isomers are present at the active site of this enzyme. There have been indications from studies of spin-labelled acylchymotrypsins that several conformers are present² but the congruence of these results to our own is not yet clear. Needless to say we are exploring these and related systems more fully, particularly with regard to the nature of the pH transition observed.

Sincerely yours,

A handwritten signature in cursive script, appearing to read "Tom", followed by a horizontal line.

J. T. Gerig

D. C. Roe

References

1. J. T. Gerig and D. C. Roe, J. Amer. Chem. Soc., 96, 233 (1974).
2. L. J. Berliner and S. S. Wong, J. Biol. Chem., 249, 1668 (1974).

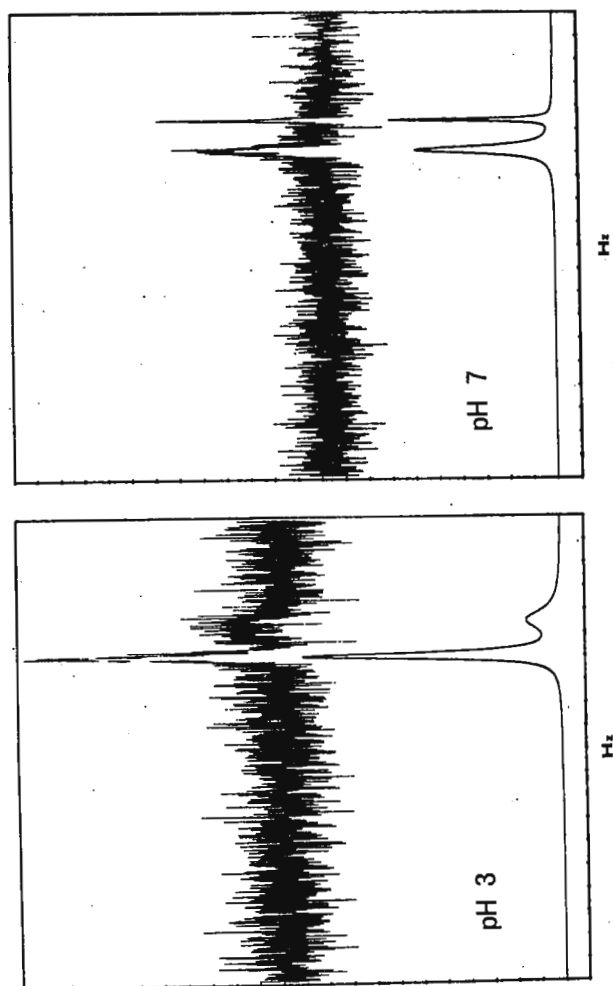
Caption for Figure 1

Observed and calculated high-resolution spectra of p-trifluoromethylbenzene-sulfonylchymotrypsin at 84.66 MHz. Each panel is 1000 Hz. wide. The computed lineshapes were obtained by summing Lorentzian bands characterized by the following parameters,

pH	Populations		Chemical Shifts, ppm ^a		R ₂ , sec ⁻¹	
	1	2	1	2	1	2
3	0.70	0.30	13.5	12.7	47	~160
7	0.75	0.25	13.6	12.8	55	16

^aChemical shifts downfield from 0.005 M internal trifluoroacetate

Samples were ~1.5 mM derivatized enzyme in 0.05 M KCl solution at ~23°. Instrumental resolution was 0.4 Hz.



Stingy

Fisher Deuterated Solvents have such outstanding isotopic and chemical purity, it's against their nature to make NMR spectrum contributions.

The stingiest Fisher Deuterated Solvents have an unsurpassed 100.0 atom % deuterium — ideal for critical NMR work. Not one atom of hydrogen is present to alter your spectrum. Seven commonly-used solvents are Fisher one-hundred-percenters: Acetone- d_6 , Benzene- d_6 , Chloroform- d , Deuterium Chloride (20% solution in D_2O), Deuterium Oxide, Methyl Sulfoxide- d_6 , and Pyridine- d_5 . Their exceptional purity eliminates masking even in the most sensitive Fourier Transform systems.

An additional 93 Fisher Deuterated Solvents are just a few atoms away from being the stingiest. Deuterium levels range from 99.9 to 98 atom %. Use them when the very highest level of sensitivity is unnecessary. Or, when economy is necessary.

Stringent Quality Control

All Fisher Deuterated Solvents pass a battery of stringent QC tests including infrared spectroscopy and NMR analyses, or else. Or else they never see a Fisher label.

Fisher Deuterated Solvents, the stingy ones, are available at your local Fisher branch. Delivery, within days.

Fisher Scientific Company





NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

IN REPLY REFER TO:
6120-113;WBM:hmk

16 April 1975

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

Fixed Trap Capacitor in HA-100 Double-Tuned Probe.

Dear Barry:

At the higher proton decoupling powers necessary to achieve complete decoupling of C-13 nuclei with short relaxation times, the trap capacitor in the double-tuned transmitter circuit of our HA-100 probe had a life-time of only two-three weeks. Typically, the standing wave ratio of the decoupling circuit drifts upward, accompanied by less efficient decoupling.

We have found what appears to be a long term solution in the substitution of a fixed capacitor for the variable trap capacitor. We use a Vitramon high current capacitor, type VY81, rated 2000 vac. Others may be suitable.

The variable trap capacitor is removed from a properly tuned trap circuit and its value measured. We use a Boonton R-X Meter tuned to 100 Mhz. A fixed capacitor having a similar measured capacitance is substituted in the circuit and the standing wave ratio measured. Some trial and error selection of values may be necessary due to lead capacitance, etc.

This modification has been in service for several weeks with no measurable drift in standing wave ratio, at a proton power level of 15-20 watts.

Sincerely,

A handwritten signature in cursive script, appearing to read "Bill Moniz".

W. B. Moniz
C. F. Poranski
S. A. Sojka

Stony Brook

State University of New York
at Stony Brook
Stony Brook, New York 11794

Department of Chemistry
telephone: (516) 246-5050 / 5051

April 14, 1975

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

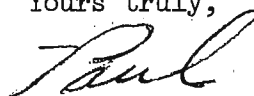
Post-Doctoral Position Available

Dear Barry:

It is very likely that a post-doctoral position will soon be available here for research on NMR zeugmatographic imaging and NMR studies of tissues and other organized biological systems. Applications are invited. We are an equal opportunity, affirmative action employer.

Best regards,

Yours truly,



Paul C. Lauterbur
Professor of Chemistry

PCL:eg

**Instruments, Inc.**

MANNING PARK
BILLERICA, MASSACHUSETTS 01821
(617) 272-9250

8 April 1975

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

Re: Positions Available

Dear Dr. Shapiro:

BRUKER has available at their new building in Billerica openings for two Post Doctoral Fellows/Junior scientists. These positions are in the following groups:

1. High Power Pulse

- physicist/chemist with strong instrumental background to work on research and development of new techniques and instrumentation in high power pulsed N.M.R.
- this person would work in close collaboration with Don Ware of BRUKER and Prof. John Waugh of M.I.T.

2. Classical High Resolution/Supercon

- chemist with strong instrumental and experimental background to work on problems in high resolution N.M.R.
- this person would work in close collaboration with Chris Tanzer and Bruce Hawkins of BRUKER

Both scientists will be expected to spend a part of their time solving general customer problems, running routine samples, etc.

Please send resumes to Don Ware.

BRUKER is an equal opportunity employer.

Regards,

Don Ware Bruce Hawkins

BH/DW:wz

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

April 16, 1975

Dr. Barry Shapiro
Chemistry Department
Texas A and M University
College Station, Texas 77843

Dear Barry:

We would like to describe briefly three relatively straight forward modifications to our JEOL PS-100P/EC-100 FT nmr system which may be of interest to other PS-100, FT users.

The simplest of these enables triple resonance studies to be performed using the JEOL homonuclear decoupling accessory in conjunction with the SD-HC heteronuclear decoupler. Instead of driving the heteronuclear decoupler in the usual fashion, one employs the PS-100 r.f. oscillator unit normally used for c.w. operation. The left hand oscillator's output can be conveniently picked-up at CN 2 on the connection box at the front of the magnet base. The level attenuator on the c.w. r.f. unit can be used to set the correct oscillator voltage. Homonuclear decoupling is done in the usual manner. We have successfully performed ^1H - $\{^{11}\text{B}\}$ - $\{^1\text{H}\}$ experiments using this set up. Any nucleus one has the hardware to do homonuclear decoupling with the JEOL system has the potential for triple resonance studies. We would like to thank JEOL for their cooperation.

Secondly we have modified the standard JEOL digital pulse programmer to do a 180° - t - 90° pulse sequence so that now t can be accurately set to a lower limit of 10^{-5} instead of the standard 10^{-3} sec. This modification was designed and modified by Mr. Chris Conte of Optimal Technology, Inc. It requires only the addition of a spst switch and minor rewiring of the standard JEOL "interval" PC board. After careful checking with a 100 MHz oscilloscope, no significant error could be detected in the t values as set by the digital pulse programmer. The use of the JEOL Auto T_1 program is not affected by this modification; but the T_1 value as determined by the computer is off by either one or two orders of magnitude! One must also set C35 and C100-C120 in the JEOL software either one or two orders of magnitude larger than the t values being used. This modification is necessary to accurately determine T_1 values less than 10 milliseconds.

Lastly Optimal Technology has designed and constructed a T_1 PC board for the digital pulse programmer which allows the generation of a T_1 sequence 180° -t- $90^\circ/x$ where $x = 6, 9, 12, 18$ or 36 . This board has been used in conjunction with eliminating "Ernst Effects"⁽¹⁾ which can cause non-linear T_1 plots. These studies are presently underway. Another possible application for this type of pulse sequence could be PRFT⁽²⁾ experiments in systems where conditions would allow a sampling pulse of less than 90° to yield more efficient signal averaging.

Bill Hutton would be glad to share the details of these modifications with any interested parties.

- 1./ R. Ernst, 15th Experimental NMR Conference, April, 1974;
R. Ernst et al., J. Mag. Res., 13, 196-216 (1974).
- 2./ D. Doddrell and A. Allerhand, Proc. Nat. Acad. Sci. U.S., 68 1083 (1971).

Sincerely,



William C. Hutton
Research Assistant
in NMR Spectroscopy
(804-924-3163)



R. Bruce Martin
Professor of Chemistry



Vernon R. Miller
Assistant Professor
of Chemistry

WCH/dhw

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

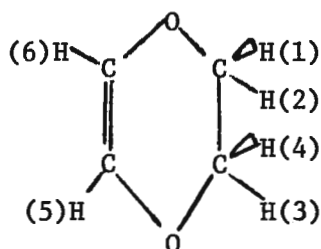
April 17, 1975

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

Dear Barry:

NMR Studies of p-Dioxene

We have recently completed NMR studies of p-dioxene



oriented in two different lyotropic mesophases, one being that based on sodium decyl sulfate and the other on potassium laurate. In addition, ^{13}C -H satellite and C-13 high-resolution spectra were also analyzed for the molecule in an isotropic medium.

The data in ordered media permit the determination of the interesting ring "twist" angle of this non-planar structure as 27.8° and 28.5° , respectively, for the two mesophases used. By comparison a low-temperature NMR value of 26.8° ⁽¹⁾, a microwave value of 29.9° ⁽²⁾ and a thermotropic value of 29.1° ⁽³⁾ have been reported elsewhere. Extended Huckel calculations carried out here predict the most stable form to correspond to a twist angle of 31° .

The accompanying table lists the liquid crystal parameters obtained by us in both of the phases used.

Sincerely,

Stephen A. Spearman
Stephen A. Spearman

J. H. Goldstein
J. H. Goldstein
Professor of Chemistry

1. R. H. Larkin and R. C. Lord, J. Amer. Chem. Soc., 96, 1643 (1974).
2. J. A. Willis and T. B. Malloy, Jr., J. Chem. Phys., 60(5), 2132 (1974).

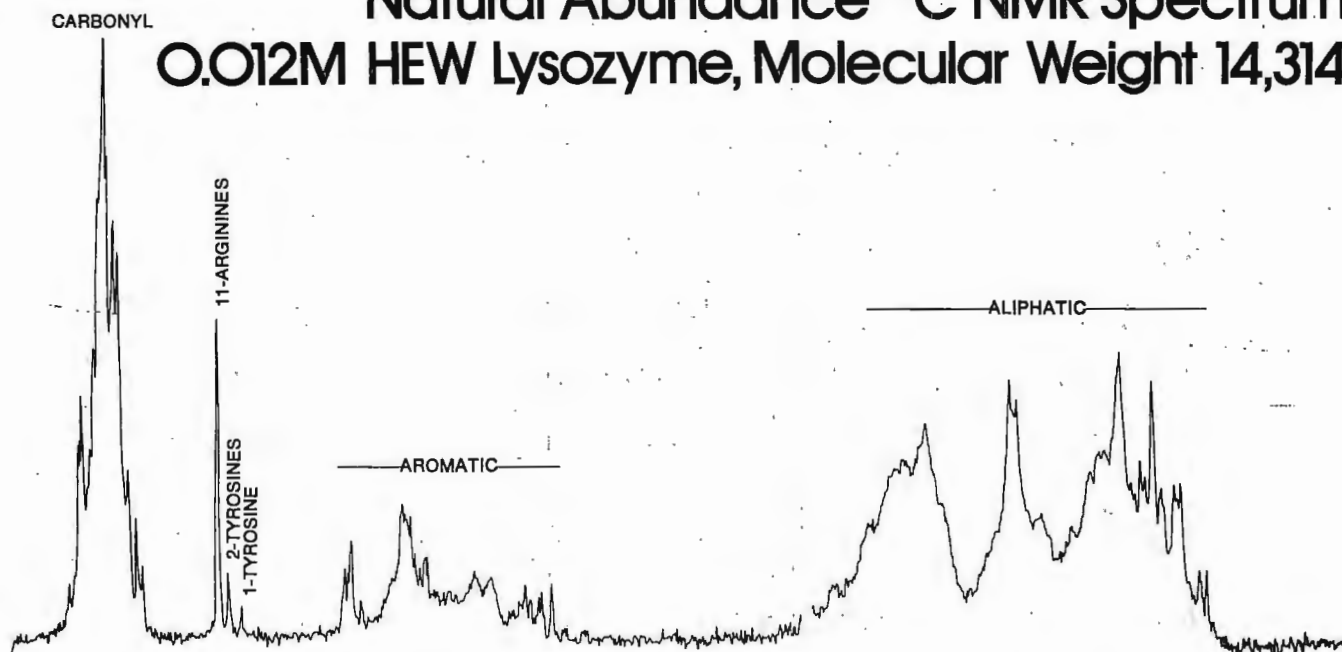
Liquid Crystal and Orientation Parameters for p-Dioxene

	KL		DS	
$\omega_1 - \omega_5^a$	173.82 \pm 0.08		172.36 \pm 0.11	
$J_{13} = J_{24}^b$	5.79 \pm 0.23		5.61 \pm 0.11	
$J_{14} = J_{23}$	2.09 \pm 0.14		2.20 \pm 0.02	
	Experimental Value	Calculated Value	Experimental Value	Calculated Value
$D_{12} = D_{34}$	-208.94 \pm 0.19	-208.80	-188.13 \pm 0.09	-187.98
$D_{13} = D_{24}$	20.56 \pm 0.09	21.93	5.76 \pm 0.03	7.16
$D_{14} = D_{23}$	- 41.56 \pm 0.14	- 41.53	- 61.54 \pm 0.05	- 61.48
$D_{15}=D_{25}=D_{36}=D_{46}$	16.93 \pm 0.38	15.69	18.08 \pm 0.10	16.90
$D_{16}=D_{26}=D_{35}=D_{45}$	16.91 \pm 0.36	19.51	23.14 \pm 0.10	25.82
D_{56}	215.01 \pm 0.08	214.89	193.21 \pm 0.11	193.06
	KL		DS	
$C_{3z^2-r^2}$	-0.014318 \pm 0.000031		-0.017608 \pm 0.000024	
$C_{x^2-y^2}$	0.043894 \pm 0.000026		0.042175 \pm 0.000025	
C_{xy}	-0.009222 \pm 0.000067		-0.012701 \pm 0.000037	

^a All values in Hz. Reported values are the averages and standard deviations of six spectra.

^b Other J_{ij} values were held constant during the final iterations.

Natural Abundance ^{13}C NMR Spectrum 0.012M HEW Lysozyme, Molecular Weight 14,314



Proton-decoupled natural abundance ^{13}C spectrum of hen egg white lysozyme in 0.15M NaCl in 9:1 $\text{H}_2\text{O}/\text{D}_2\text{O}$, pH 4.0, 45°C. Recorded with a TT-14 system¹ at 15.08 MHz using a 20 mm sample tube; 37,107 90° pulses; 4096 time-domain points; and 1.165 Hz digital line broadening. This spectrum demonstrates that in a small protein, single carbon resonances such as the one assigned above to C^β in a single tyrosine residue, can be observed after only five hours of signal averaging with use of the 20 mm sample technology developed at Indiana University by Dr. Adam Allerhand.^{2,3}

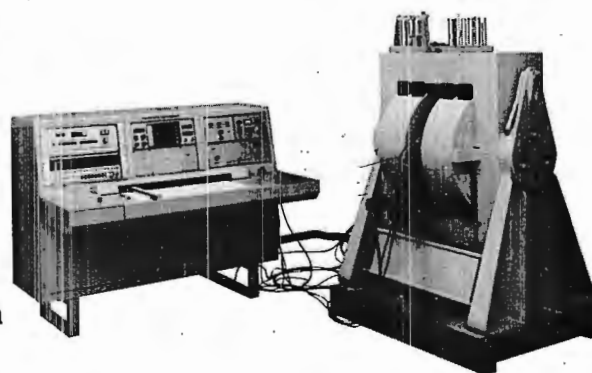
1. Sample run at the University of Chicago, courtesy of Dr. Philip Keim, Pritzker School of Medicine.
2. A. Allerhand, R.F. Childers, E. Oldfield, J. Magn. Resonance, 11, 272 (1973).
3. E. Oldfield and A. Allerhand, Proc. Nat. Acad. Sci. USA, 70, 3531 (1973).

HIGH SENSITIVITY CARBON-13 FT-NMR with a TT-14 System

The TT-14 FT NMR System combines a state-of-the-art solid state console, Nicolet NMR-80 computer, 20 mm sample probe developed by Dr. Adam Allerhand, and a time-proved Varian 14 kilogauss magnet into the highest sensitivity carbon-13 performance available today.

Features of this system are:

- internal deuterium lock;
- proton decoupler with pulse delay gating capability;
- observe, lock, and decoupler frequencies derived from a single master oscillator;
- 10 mm insert available for studies of limited sample quantities;
- readily convertible to other nuclei studies, e.g. ^{15}N , ^{31}P , or even ^1H ;
- multipulse capability, including automatic T_1 measurements;
- disk memory unit for program and data storage;
- excellent software package, including versatile quantitative measurement capability, automatic calculation of T_1 values with error limits, iterative 6-spin spectrum calculation, and new software as developed at no cost;
- available as an add-on for existing 14 kilogauss magnet system owners.



NTC NICOLET
TECHNOLOGY
CORPORATION

145 East Dana Street
Mountain View, California 94041
Phone: 415/969-2076
(formerly Transform Technology Inc.)

Please phone or write for additional information on the versatile TT-14 System.

CENTER FOR HEALTH SCIENCES



**School of Pharmacy
Pharmacy Building
425 North Charter Street
Madison, Wisconsin 53706
Telephone: 608/262-1415**



April 11, 1975

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

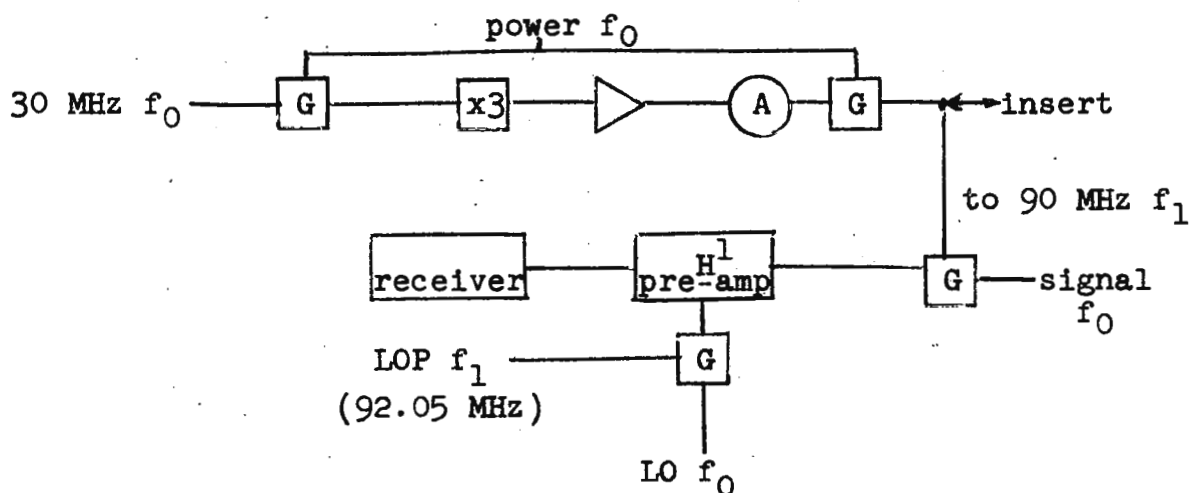
Dear Professor Shapiro:

PULSE-MODE PROTON LOCK FOR OLDER BRUKER HX90E'S

We have recently devised a simple means of operating our older Bruker HX90E in a pulse-mode, single coil, proton-locked configuration in order to observe deuterium. Only one piece of equipment is needed for the lock conversion, namely, a $H^1, F^{19}/X$ stabilization box.

The proton lock configuration is diagramed below. The gating frequencies are derived from the time sharing unit from the appropriate outputs as shown on the diagram.

It is desirable to use the regular deuterium lock relay network in the receiver section that is ordinarily energized by the H² switch on the transmitter panel. In order to allow that network to operate without getting interfering deuterium frequencies from the deuterium lock section it is necessary to inactivate the reference D and signal D relays of the relay board. That is accomplished by disconnecting pin 11 of the relay board and leading 20v from the adjacent power supply via the red lead formerly attached to pin 11 through existing connections to the remainder of the relay network. The 90 MHz button on the transmitter panel is depressed and lock is accomplished by shimming on the first upper side band (center band is still present) and locking in the usual way.



We would be happy to add further details for anyone interested in having them.

Sincerely yours

Phillip A. Hart

James Blackbourn



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

CORPORATE
RESEARCH AND
DEVELOPMENT

8 April 1975

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

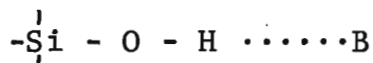
Solvent Effects in ^{29}Si NMR

Dear Barry:

We have found solvent shifts of up to 10ppm in the ^{29}Si nmr of silanols and some silylamines upon changing the solvent from chloroform to triethylamine. The upfield shift has been found to correlate with the electron pair donor ability of the solvent, as measured by Gutmann's "donor number".

The results for $\text{HO} \left[\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si-O} \\ | \\ \text{CH}_3 \end{array} \right]_6 \text{H}$ show the effect is greatest at the

terminal silicon, with the effect sharply decreasing at the D_2 units, and decreasing further for the central D_3 units. This is consistent with an interaction of the type



at the end of the chain leading to progressively smaller effects within the chain. The magnitude of the shift decreases for the less acidic silylamines; nonetheless, changes of 1.5-3ppm were observed for amines with protons available for hydrogen bonding to the basic solvent. A plot of $\delta^{29}\text{Si}$ vs donor number for a series of silanols and one silylamine is shown in Figure 1. The scale in parentheses (-28 to -38) corresponds to the shifts for $(\text{Ph})_2\text{Si}(\text{OH})_2$. In the titration of the D_6 -diol (neat sample) with DMSO (Figure 2), a plateau is reached at a mole ratio of 2:1 DMSO/ D_6 -diol, corresponding to the interaction of one solvent molecule at each end of the chain.

A complete discussion of these results will be reported shortly.

Sincerely,

E.A. Williams *J.D. Cargioli*

E.A. Williams J.D. Cargioli
MATERIALS CHARACTERIZATION OPERATION
Building K1, Room 2A22, Ext. 6153

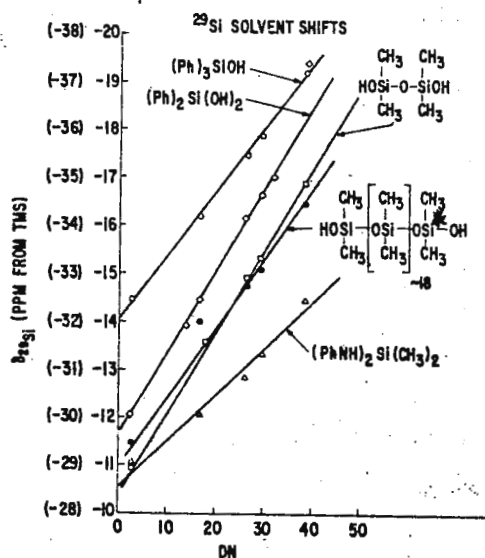


FIGURE 1

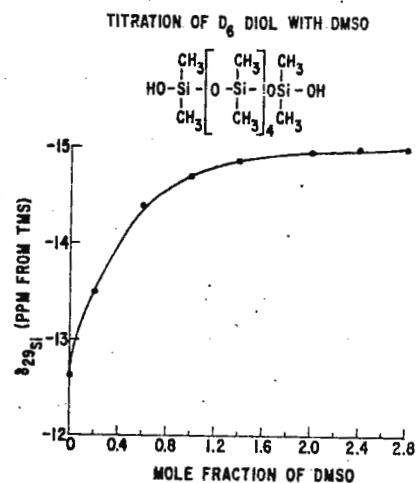


FIGURE 2

¹ V. Gutman, Chem. and Ind., 1971, 102.



April 29, 1975

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

Dear Barry:

Title: Useful Old Equipment

About a year ago we took inventory of what seemed to be obsolete NMR equipment in the department. Following is a list of the major items:

- 1 9 year old HA-60
- 1 3 year old V-4415 probe
- 1 V-4311 R.F. unit (F19)
- 1 V-4360 power supply
- 1 F.T. conversion for HA-100 (1970)
includes: 620I computer 8K
pulse unit
proton decoupler

The parts were assembled to produce a C^{13} F.T. system with F19 external lock. Since the V-4415 probe was available, we used it, but a V-4331 could also be used. The first decent spectrum was just run, and our 90% ethylbenzene is about 35 to 1. Our future plans include converting receiver to solid state and adding a decoupler filter, which should give us about 50 to 1 sensitivity.

The idea here is nothing new, but perhaps it will inspire some of our less fortunate colleagues to make use of what is available. In our case, we have an XL-100, but the time must be divided among 15 research groups. Our home-made system will be used to run preliminary samples as well as for training new students.

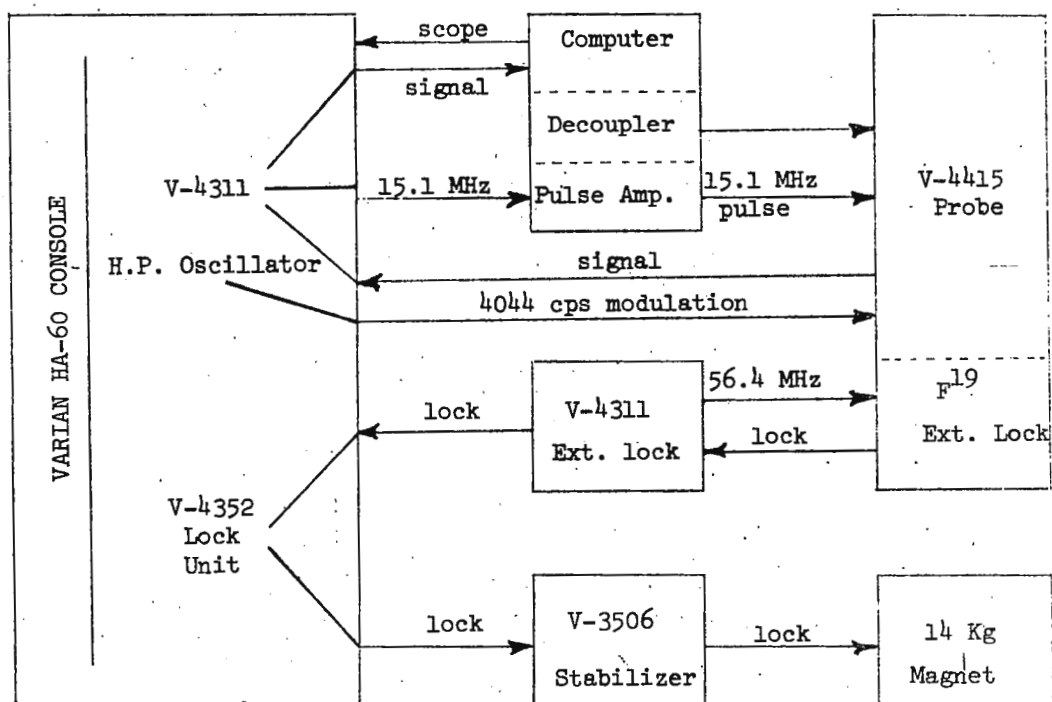
Attached is a block diagram and a copy of our spectrum.

Sincerely,

A handwritten signature in cursive script, appearing to read "Clarence Gust".

Clarence Gust
Instructor

CG:fs



SW(HZ)= 04044

AT(S)=00000.5

PD(S)=00009.5

PW(US)= 00045

TRANS=00016

PTS=04044

SE(S)=00000.2

HF

VRT=00010

INT=00100

BGN (HZ)= 04012

END (HZ)= 00000

HRZ=00000.3

DC BL

>PL

(HZ)= 02766 INT=00017

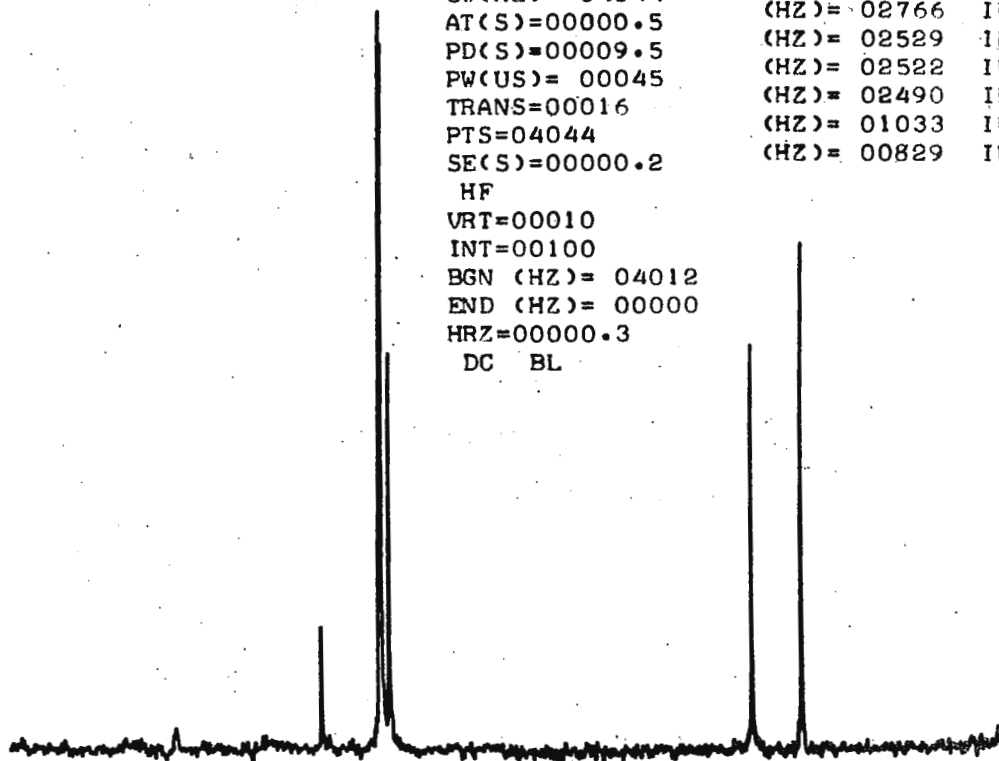
(HZ)= 02529 INT=00101

(HZ)= 02522 INT=00097

(HZ)= 02490 INT=00054

(HZ)= 01033 INT=00056

(HZ)= 00829 INT=00070





May 1, 1975

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

Dear Barry:

^{13}C medium shifts of $^{13}\text{CH}_4$ in natural abundance

We have recently completed a first series of measurements on the ^1H and ^{13}C of non-enriched CH_4 in the gas phase as function of density. Pressures of about 6 - 60 atm were used, the lower limit being set by the large accumulation times required (about 24 hrs for the 6 atm sample). The sample tube was 5 mm OD equipped with a Teflon valve (essentially the Mohanty-Bernstein design (1)). The sample tube contained a capillary with hexafluoroacetone 1.6 D_2O , allowing locking on ^{19}F and providing a ^{13}C reference at the same time. (In our HX-90 the ^{13}C and $^1\text{H}/^{19}\text{F}$ oscillators are independent so that there are long-term relative frequency drifts between ^{13}C and ^{19}F). The measured proton frequencies allowed us also to use selective proton decoupling in the ^{13}C spectra (without the decoupling a nice 1:4:6:4:1 quintet was observed, proving that the ^{13}C signal was due to CH_4). Due to the low decoupling power, no sample heating occurs; the probe temperature was constant at 22°C . Both the ^1H and the ^{13}C shifts were found to be proportional to ρ ; therefore, $\sigma_m = \sigma_1/V_m = \rho\sigma_1/M$. The medium shift in this case is composed of a bulk susceptibility term σ_b and a Van der Waals term σ_w . Using the binary collision model (2) one has

$$(\sigma_1)_w = \frac{-\pi N B \alpha_2 I_2 H_6(y)}{r_o^3 y^4}$$

which then allows the extraction of the B parameter. Based on $(\sigma_1)_b = -36.4$ ppm cm^3/mole , our results are as follows:

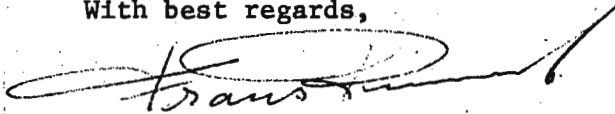
nucleus of CH_4	$(\sigma_1)_m$ ppm cm^3/mole	$(\sigma_1)_w$ ppm cm^3/mole	$B \times 10^{18}$ esu
^1H	-42.6 ± 1.6	-6.1 ± 1.6	0.57 ± 0.15
^{13}C	-275.6 ± 13.2	-239 ± 13	22.4 ± 1.2

The results for protons of CH_4 are very close to literature values (e.g. B values of 0.53 (1), 0.52 (2) and 0.71 (3)). The result indicates that Van der Waals shifts in ^{13}C are about 40x larger than in proton NMR. Gas-to-liquid medium shifts of ^{13}C of even non-polar solutes may therefore be expected to range between 2.5 and 30 ppm. If this prediction is borne out (such experiments are presently underway in our laboratory), it would mean that there is no — advantage left for internal referencing in ^{13}C NMR and that as a consequence ^{13}C shifts should be referenced externally.



Frank M. Mourits

With best regards,



Frans H. A. Rummens

FMM:
FHAR: jdy

- 1) Mohanty and Bernstein. J. Chem. Phys. 54, 2254 (1971).
- 2) Raynes, Buckingham and Bernstein. J. Chem. Phys. 36, 3481 (1962).
- 3) Gordon and Dailey. J. Chem. Phys. 36, 3096 (1962).

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 ultrasonics, 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 deflection 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.



NATIONAL CHEMICAL RESEARCH LABORATORY

OF THE SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

Telephone 74-8011 Telegrams NAVORSCHM

P. O. Box 395

PRETORIA

OUR FILE 60/6 - Pach
60/6 - Chal

YOUR FILE

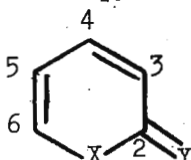
Prof. B.L. Shapiro
Texas A&M University
College of Science
College Station
TEXAS 77843
USA

22 APR 1975

Dear Prof. Shapiro,

LONG-RANGE J(C,H) IN SULPHUR CONTAINING 2-PYRONES

In our last contribution (TAMUNN 190-37) we reported a full set of long-range J(C,H) for 2-pyrone (I).¹



I	X = O	Y = O
II	X = O	Y = S
III	X = S	Y = S

We have now obtained single-resonance ¹³C spectra for the two related compounds II and III. These, unlike I, are solids and the enormous concentrations required for very high resolution work could not be achieved. Consequently couplings to C-2 were not studied and only couplings >2 Hz were observed. These are shown in the table with the relevant data for I.

	³ J(C ₅ H ₅)	³ J(C ₄ H ₆)	³ J(C ₅ H ₃)	² J(C ₅ H ₆)	³ J(C ₆ H ₄)	² J(C ₆ H ₅)
I	6.8	7.8	7.9	8.5	7.6	7.6
II	6.3	7.0	8.5	5.5	7.7	5.2
III	6.8	8.5	8.1	>2	7.5	4.0

The ³J(C,H) are fairly constant but do show some indication of a regular variation down the series - ³J(C₃H₅) and ³J(C₄H₆) decrease from I to II and then increase from II to III whereas the other two ³J(C,H) behave in the opposite fashion. ²J(C,H) are shown by only C₅ and C₆ in I and II, and by just C₆ in III. ²J(C₅H₆), therefore, shows the well documented variation with substituent electronegativity found for monosubstituted ethylenes and related compounds.² Variation in ²J(C₆H₅) can be compared with that of the analogous couplings in furan³ (11.0 Hz) and thiophen⁴ (4.7 Hz).

1 A.A. Chalmers and K.G.R. Pachler, Can.J.Chem., in Press.

2 D.M. McKinnon and T. Schaefer, Can.J.Chem., **49**, 89 (1971).

3 M. Hansen and H.J. Jakobsen, J.Magn. Resonance, **10**, 74 (1973).

4 F.J. Weigert and J.D. Roberts, J.Amer.Chem.Soc., **90**, 3543 (1968).

Yours sincerely,

A.A. Chalmers
A.A. Chalmers
SENIOR RESEARCH OFFICER

K.G.R. Pachler
K.G.R. Pachler
SENIOR CHIEF RESEARCH OFFICER
CHEMICAL PHYSICS GROUP



TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129
817-926-2461

Department of Chemistry

May 2, 1975

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

Dear Barry:

Recently Ben Shoulders mentioned to me that formyl and acetyl groups were bad actors with regard to substituent additivity rules and C-13 chemical shifts in aromatic systems. It seemed of interest to see how they would perform in the \mathcal{F} , \mathcal{R} , and Q regression equations with which we have had some success previously (see J. Phys. Chem., 74, 812 (1970) and J. Magn. Resonance, 7, 364 (1972)). The \mathcal{F} and \mathcal{R} in this case are the field and inductive parameters of Swain and Lupton.

Unfortunately none of these three parameters had been determined for the formyl group. By using the regression equations for each of three carbons in a series of monosubstituted benzenes and the chemical shift data for the comparable carbons in benzaldehyde one can write three equations in three unknowns et voila $\mathcal{F} = 0.759$, $\mathcal{R} = 0.279$ and $Q = 2.40$. Since \mathcal{F} and \mathcal{R} are known for acetyl it is simple to take the C-13 data for acetophenone and get $Q = 2.34$. These numbers have now been tested in several systems and seem to work well.

For instance applied to the data for ten vinyl compounds (Org. Magn. Resonance, 6, 413 (1974)) one obtains a three parameter multiple regression equation for each carbon with correlation coefficients and average deviations, as shown.

	C_α	C_β
r	.983	.994
Aver. dev (ppm)	3.2	1.4
Shift range (ppm)	68	57

The predicated and (experimental) values are:

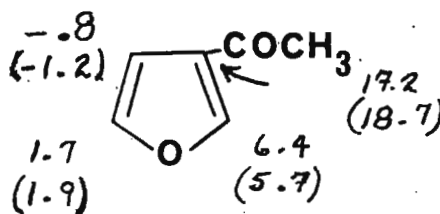
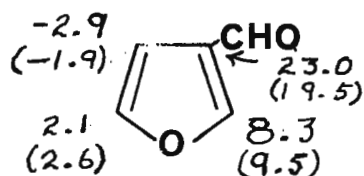
$CH_2 = CHCHO$	$CH_2 = CHCOCH_3$
59.3 56.7	62.2 58.9
(56.1) (55.1)	(64.2) (56.0)

ref. CS_2

Of course, this is a little unfair since the regression equations included these points. However, the eight point regression equations such as one would have used to predict the shifts above give almost the same numbers.

Another case - just to make the point - is offered by the 3-X-furans (Gronowitz, et al., *Chemica Scripta*, 1974). Substituent chemical shifts were used here to fit nine compounds.

	C-2	C-3	C-4	C-5
r	0.995	0.991	0.965	0.923
Aver. dev. (ppm)	0.6	2.8	0.9	0.4
Shift range (ppm)	29	87	13	4



The above correlations are much better than with \mathcal{F} and \mathcal{R} or with Q alone. In these plus several other systems the formyl and acetyl groups appear "well behaved." I'll leave the other systems for another time so as to avoid treading upon the two page rule.

Yours sincerely,

Bill

W. B. Smith
Chairman
Department of Chemistry

WBS/dc

TELEPHONE
34 0484

TELEGRAMS
UNI MELB PARKVILLE



University of Melbourne
DEPARTMENT OF ORGANIC CHEMISTRY

Parkville, Victoria 3052

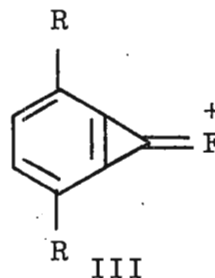
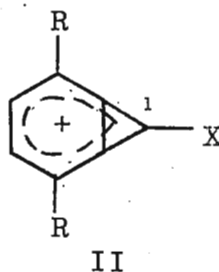
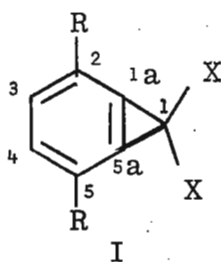
16th May, 1975.

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

Dear Dr. Shapiro,
Large ^{13}C - ^{19}F Coupling Constants
in Cyclopropabenzenium Cations

Our HA-60-DIGILAB-PDP-15 spectrometer (TAMU 191-2) has continued to run well with very little 'down-time'. We (with U. Flego and R.C. Westcott) have modified the software and the pulse programmer to allow 8K/4K transforms and gated decoupling experiments.

Together with Dr. B. Halton (Victoria University of Wellington, New Zealand) and Drs. P. Müller and U. Burger (University of Geneva, Switzerland) we (with H. Hügel) have obtained both ^1H and ^{13}C spectra of three cyclopropabenzenium cations (II). Although these ions have been postulated as fragments in mass spectrometers and reactive intermediates in solution, it is only recently that their presence has been confirmed by direct observation^{1,2}.



- a, R=H, X=F
b, R=Ø, X=F
c, R=Ø, X=Cl

Ionisation of the dihalogeno-precursors (I) in fluorosulphonic acid at low temperature, yields clear orange solutions of the cations, II. The ^{13}C - ^{19}F coupling constants of Ia, b increase from 303, 300 Hz to 474, 461 Hz respectively, which to our knowledge are the largest values of $^1J_{\text{CF}}$ yet observed.

^{13}C NMR Parameters*

	1	1a(5a)	2(5)	3(4)	$^1J_{\text{CF}}$	$^2J_{\text{CF}}$	$^3J_{\text{CF}}$	$^4J_{\text{CF}}$
IIa	148.1	141.1	119.8	158.3	474	2.6	3.8	8.3
IIb	147.2	134.7	130.8	148.7	461	<2	5	9
IIc	131.2	150.4	146.4	147.5				

*Chemical shifts from external TMS

The large increase in the magnitude of $^1J_{\text{CF}}$ on ionisation is probably due mainly to the increase in the s electron density at both carbon and fluorine atoms due to the positive charge. This is consistent with an increase in π bond character between carbon and fluorine.

We also observed a reduction in the total downfield shifts ($\Sigma\Delta\delta$) upon ionisation from the expected value of 160ppm³ to 103 (Ia) and 81ppm (Ib).

We have interpreted these results as indicative of a significant contribution of resonance structure III, to the hybrid configuration of the cations. This work is to be published in J.Chem.Soc., Perkin II and preprints are available on request.

Yours sincerely,


D. P. Kelly.

1. B. Halton, A.D. Woolhouse, H.M. Hügel and D.P. Kelly, J.C.S. Chem.Comm., 1974, 247.
2. U. Burger, P. Müller and L. Zuidema, Helv.Chim.Acta 1974, 57, 1881.
3. H. Spiesscke and W.G. Schneider, Tetrahedron Letters, 1961, 468.

TITLE: Large ^{13}C - ^{19}F Coupling Constants in Cyclopropabenzonium Cations.



2 May 1975

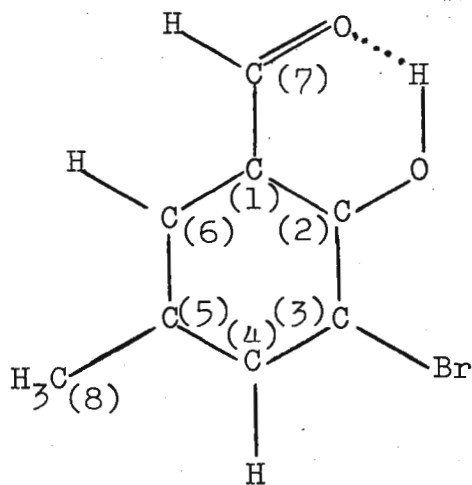
Dr B L Shapiro
 Department of Chemistry
 Texas A & M University
 College Station, TX 77843 USA

Roche Products Limited PO Box 8 Welwyn Garden City Hertfordshire AL7 3AY Telephone Welwyn Garden 28128

Title: ^{13}C - ^1H Coupling in a Salicylaldehyde
 Derivative - XL-100 Recorder Problems

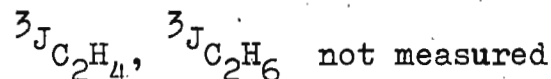
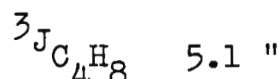
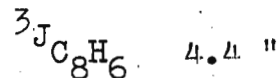
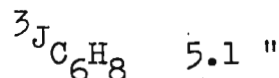
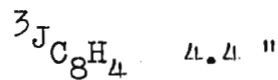
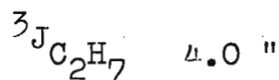
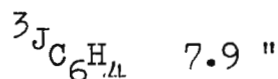
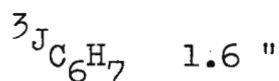
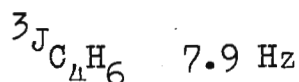
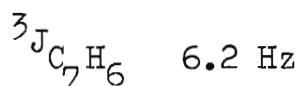
Dear Barry,

Following your blue reminder, I enclose some results from the analysis of the undecoupled ^{13}C spectrum of 3-bromo-5-methyl salicylaldehyde (I), as a model probe for the determination of the orientation of an aryl group about an Ar - CH bond, using 3-bond C-H couplings.



(ppm from TMS) CDCl_3 solution

C_1	110.2
C_2	155.3
C_3	120.6
C_4	140.1
C_5	130.3
C_6	132.7
C_7	195.6
C_8	19.8



Assignments were confirmed by selective proton decoupling experiments. It is clear that if the conformation is fixed as shown, trans ($\phi = 180^\circ$) couplings are significantly larger than cis ($\phi = 0^\circ$), although electronic factors may be important.

The failure of the bulb in the Gurley Incremental Encoder in the XL-100 recorder, controlling the CW recorder movements, led us to investigate the possibility of avoiding replacement of the whole thing (v £200) by dismantling this complex device and replacing the bulb with one from the tape recorder in our JEOL amino acid analyser (M I L 24367-683 ASI). This bulb was not quite powerful enough to provide the required signal, without increasing the amplifier gain in the next stage, but the procedure does work and saves considerable expense.

Finally, we have removed much of the noise emanating from our standard teletype by installation of a silencer cover (Exchange Telegraph Co Ltd, London), a worthwhile investment at £115 to keep the laboratory staff reasonably sane!

Yours sincerely

Jon

Dr W A Thomas

Professor C.L.Khetrapal
Dr. A. C. Kunwar

April 1, 1975

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

Title: Conformation of the peptide unit from
PMR studies in nematic solvents

I hope the following contribution retains us on the mailing list of the TAMU-NMR News Letter.

The technique of high resolution NMR spectroscopy of molecules dissolved in liquid crystal solvents can be conveniently applied to some systems of biological importance. We wish to apply the method to find out whether the three bonds meeting at the nitrogen atom in a peptide unit lie in a plane or there are non-planar deformations around it. For such a purpose, it is convenient to investigate first monosubstituted amides which are simplest structures containing such a unit. N-methyl formamide and N-methyl acetamide have been investigated.

The spectrum of N-methyl formamide shows separate lines due to the cis and the trans conformations such that the abundance of the trans form is larger than 90%. In this case 4 different inter-proton dipolar couplings are obtained from the proton spectrum. If the peptide unit is planar these 4 coupling constants by a suitable least square fit provide the 3 independent order parameters required to define the problem when known molecular geometry is used. A self-consistency of the results indicates planarity of the unit. In the present case, it was found that the results critically depend upon whether the methyl group rotates freely about the C-C bond or its rotation is hindered. In this case, the results are consistent with the planar conformation only if the methyl group rotates freely.

We also considered the possibility of an inversion about nitrogen such that the N-H and the N-C_α bonds are bent below or above the planar conformation by an angle (θ) with equal probability. In such a case also there is an 'effective plane of symmetry' due to rapid inter-conversion between the two conformations. Such calculations indicate that θ should be between 6 to 10° depending upon the mode of rotation of the methyl group.

Yours sincerely,

C.L. Khetrapal A.C. Kunwar

C.L. Khetrapal A.C. Kunwar

JEOL

ANALYTICAL INSTRUMENTS, INC. • 235 BIRCHWOOD AVENUE • CRANFORD, NEW JERSEY 07016
INSTRUMENTS and APPLICATIONS CENTER • (201) 272-8820
TELEX NO. 13-8840

April 28, 1975

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

Dear Professor Shapiro,


To our readers, I would like to notify you that JEOL has an opening for a field service engineer, who should have practical knowledge and experience with analog and digital concepts including RF circuitry.

The instrumentation to be covered in NMR and Mass Spectrometers and the responsible area is the Mid-Atlantic states.

Accordingly, applicants should live in or be willing to re-locate to the area.

Interested individuals should contact me at our Cranford, New Jersey address.

Sincerely,


Yukio Kuroda
AID Service Manager

YK/ah

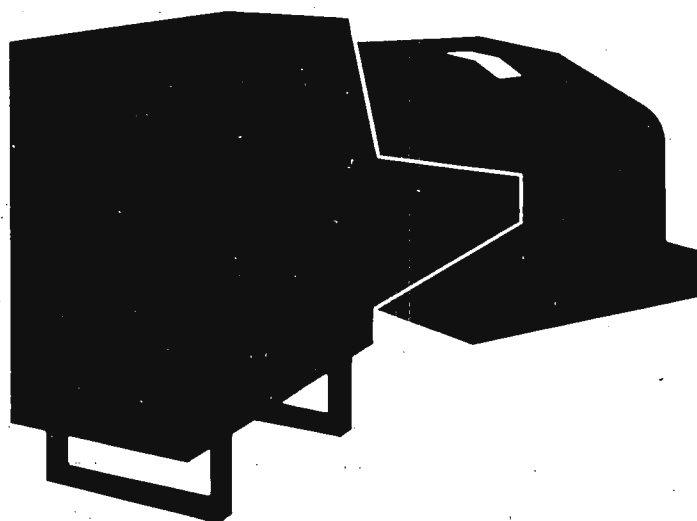
JEOL

"Bringing the Scientist Tomorrow's Capabilities Today."



WP 60

The ultimate in low-cost
FT NMR Spectroscopy...



- Full multinuclear capability
- High resolution magnet for proton FT
- 10 mm variable temp for C¹³
- Superior sensitivity

FOR DETAILS, PLEASE CONTACT YOUR NEAREST BRUKER REPRESENTATIVE.

USA

Bruker Scientific Inc.
One Westchester Plaza
Elmsford, N. Y. 10523
Tel. (914) 592-5470
Tlx. 13-1524

Bruker Magnetics Inc.
1 Vine Brook Park
Burlington, Mass. 01803
Tel. (617) 272-9250
Tlx. 94-9493

Bruker Research
1548 Page Mill Road
Palo Alto, Calif. 94305
Tel. (415) 493-3173
Tlx. 34-5533

CANADA

Bruker Spectrospin Ltd.
84 Orchard View Blvd., Suite 101
Toronto, Canada
Tel. (416) 486-7907
Tlx. 02-2771



ISTITUTO SUPERIORE DI SANITÀ

VIALE REGINA ELENA, 299 - 00161 ROMA

May 2nd, 1975

TELEGRAMMI: ISTISAN - ROMA
TELEX: RMOTI ISTISAN

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

PMR studies on the state of water in Aplysia
nerves and squid giant axons.

Dear Prof. Shapiro,

in collaboration with the Institute of Human Physiology (II C.) - University of Rome and with the Stazione Zoologica (Neurobiology Dept.) - Naples, we have measured proton magnetic resonance linewidths on the water signals of nerves and axons, previously treated with different saline solutions. The measurements were respectively performed on nervous tracts dissected from Aplysia Limacina abdominal ganglia and on giant axons of Loligo Vulgaris.

Nerves or axons, soaked for at least one hour in either the standard or modified Ringer solution, were carefully sucked in teflon tubes of barely larger diameter. The tubes were then tightly inserted in glass capillaries, held by teflon spacers along the axis of a 5-mm NMR cell. Spectra were recorded on a Bruker HF-90 spectrometer; external lock signal was either provided by toluene or hexamethyldisiloxane.

Fritz and Swift (1) as well as Silvini and Easton (2) have shown that either soaking with Ringer solutions enriched with KCl or electric depolarization, both induced significant line-broadenings on the water signal of different nerves.

In substantial agreement with these Authors, we have observed that the water signal appears actually broadened by more than 50% in Aplysia nerves, and by about 40% in squid giant axons, when the KCl concentration in the Ringer is increased up to 30 times with respect to the standard level. However we have observed that signal line-broadenings can be also induced in the Aplysia nerves by Ca^{++} excess (CaCl_2 20 to 40 mM), as well as by K^+ - free or Na^+ - free (LiCl substituted to NaCl) Ringer solutions. Addition of LiCl caused instead a significant (about 25%) narrowing of the water signal. This effect, also induced by CaCl_2 , failed to be found in RbCl -containing solutions. Conspicuous line-broadenings were also produced by addition of ouabain and tetrodotoxin to soaking Ringer. Analogous studies are in progress also on the squid giant axons.

These preliminary results suggest that linewidth changes of the water resonance are not simply related to the resting membrane potential value. Moreover a considerable contribution to line-broadenings seems to be due to decreased Na^+ effluxes, associated with ATPase partial or total inhibition.

In an attempt to discriminate among the various mechanisms responsi-

ble of the observed water linewidth changes, we are also carrying out parallel studies on various model systems.

Yours sincerely,

M. Cignitti⁺
(M. Cignitti)

L. Guidoni⁺
(L. Guidoni)

Francesco Podo⁺
(F. Podo)

Vincenzo Viti⁺
(V. Viti)

(A. Brancati)⁺⁺

F. Eusebi⁺⁺
(F. Eusebi)

(A. De Santis)^o

- 1) Fritz, O.G., Jr., and Swift, T.J. (1967), Biophys. J. 7, 675
- 2) Silvidi, A.A., and Easton, D.M. (1971), J. Applied Phys. 42, 5168

+ Istituto Superiore di Sanità, Rome, Italy. (Physics Lab. and Chemistry Lab.).

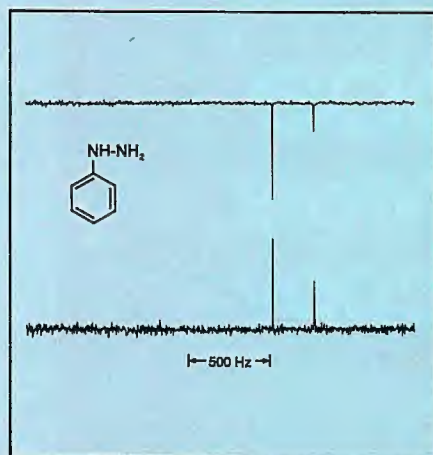
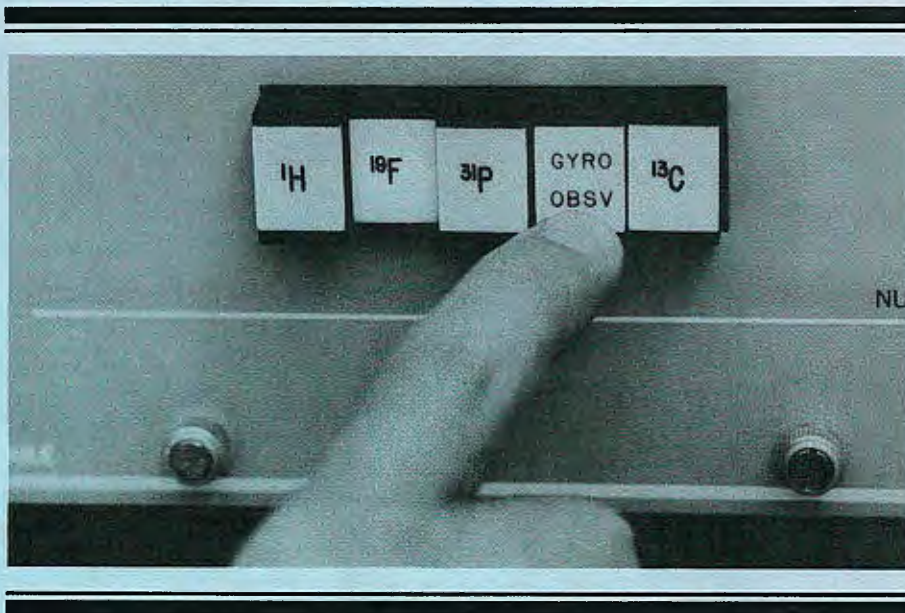
++ Institute of Human Physiology (II C.) - University of Rome.

o Stazione Zoologica, Neurobiology Department, Naples.

Varian's Special Offer: Over 30 Additional Nuclei

If you own an XL-100 NMR Spectrometer, Varian now offers you an opportunity to add a list of more than 30 nuclei to your experimental repertoire. The new GyroCode™ Observe Accessory makes it possible to observe ^{15}N , ^{17}O , ^2H , ^{29}Si , ^{13}C , and ^{11}B and many other nuclei in the XL-100's frequency range of 9.65 to 32.5 MHz — most of them at little or no extra cost per nucleus.

The GyroCode Observe Accessory expands the capabilities of the XL-100 significantly. And it is the first time this

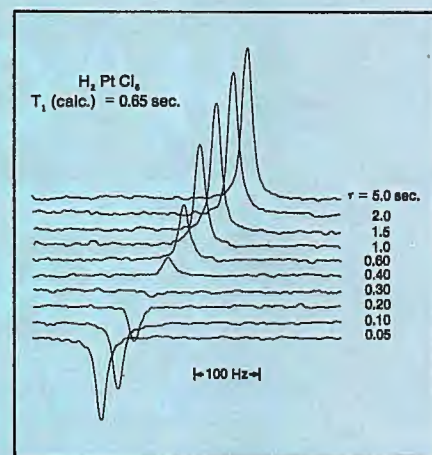


The nucleus observed for this spectrum is ^{15}N , at 10.1 MHz. The upper trace shows 500 transients ($\alpha = 90^\circ$) of a proton noise-decoupled spectrum of phenylhydrazine in C_6D_6 . The negative magnetogyric ratio of ^{15}N produces negative NOE, hence the inverted lines in the trace. The lower trace shows 2000 transients of phenylhydrazine ($\alpha = 90^\circ$); the decoupler was on during acquisition and off during the pulse delay. This technique makes it possible to measure NOE while retaining the advantages of a ^1H noise-decoupled spectrum.

degree of experimental freedom is offered for an NMR Spectrometer that combines state-of-the-art performance and ease of operation. At present, we cannot begin to assess the impact the new-found experimental scope might have on the direction of future investigations. But we expect that a lot of new ground will be broken.

The inorganic chemist, for example, will be able to work with unexplored nuclei whose usefulness as NMR probes or ability to solve real chemical problems is still a matter of speculation. The list of nuclei he will be working with will include ^{23}Na , ^{27}Al , ^{59}Co , ^{77}Se , ^{113}Cd , ^{199}Hg , and ^{195}Pt . And he will enjoy this opportunity without having to commit large sums of research monies.

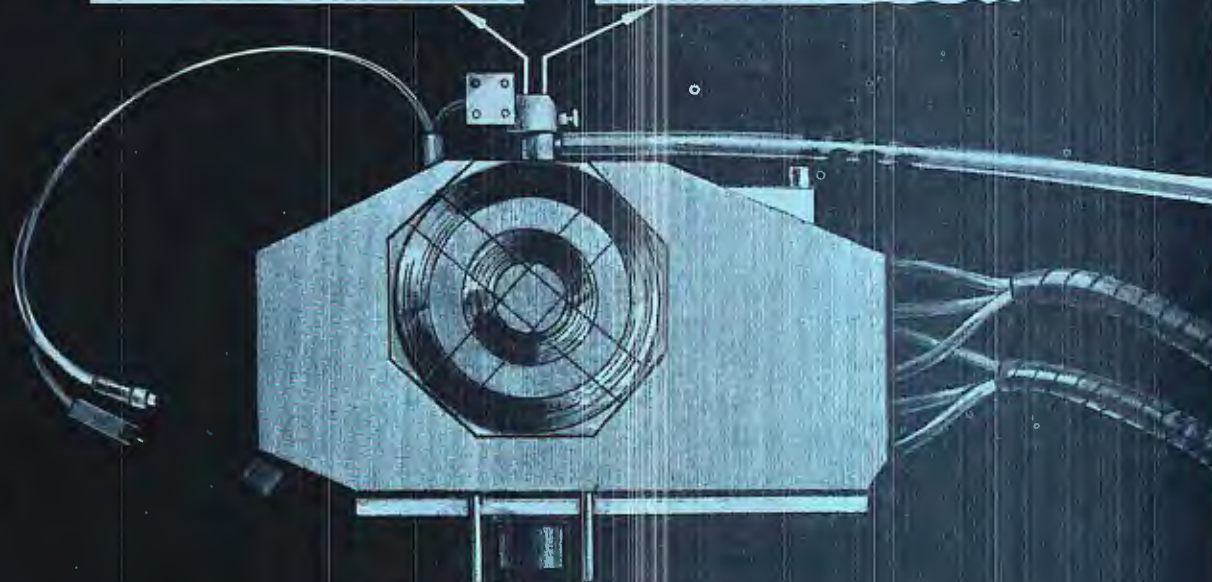
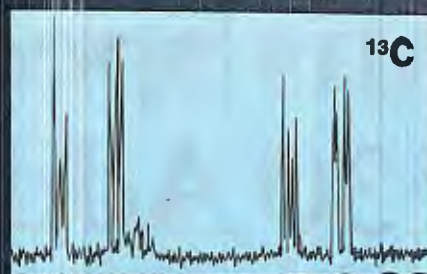
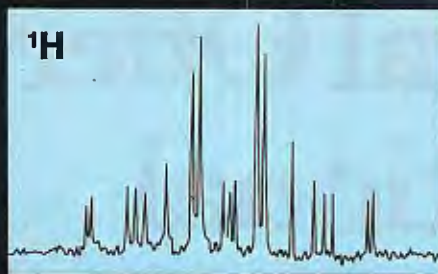
Let us send you our brochure on the GyroCode Observe Accessory. If, on the other hand, you do not own an XL-100 — this may be the time to reconsider. Write Varian Instrument Division, Box D-070, 611 Hansen Way, Palo Alto, California 94303.



In this spectrum, the new accessory allows the observation of ^{195}Pt at 21.5 MHz; the sample was aqueous hexachloroplatinic acid. An inversion recovery (180° - τ - 90°) pulse sequence was used in the automatic measurement of the spin-lattice relaxation time (T_1) for the ^{195}Pt nucleide.

We wish to acknowledge the cooperation of Professor Paul Ellis, of the University of South Carolina, whose early experimental work contributed to development of this capability of the XL-100.

varian
instrument division



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

Now with the FX60 you can change frequencies from ^{13}C to ^1H 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.*

JEOL

Analytical Instruments, Inc.

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