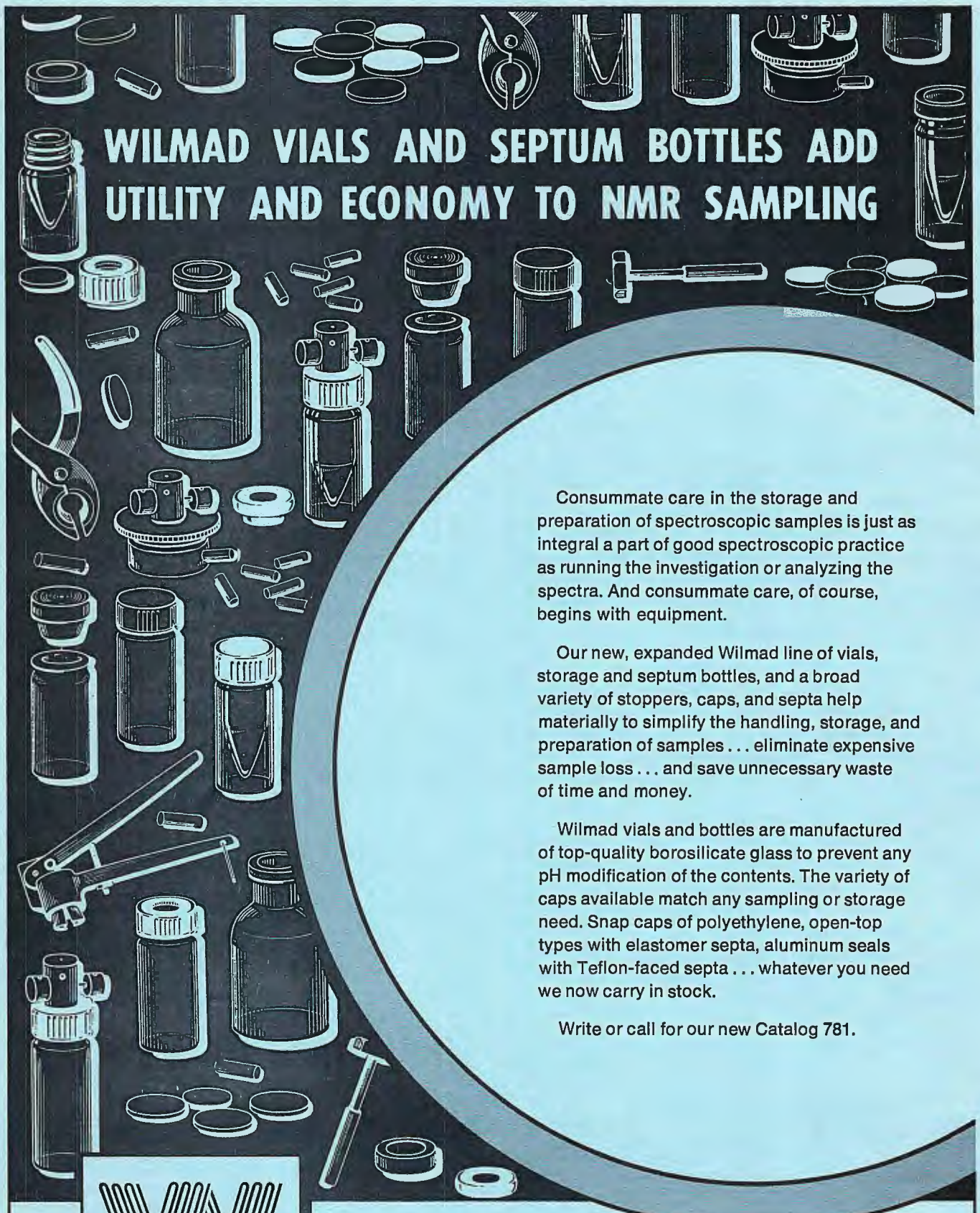
Texas A&M University N-M-R Newsletter

No. 237

June, 1978



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DEADLINE DATES: No. 238: 3 July 1978
No. 239: 7 August 1978

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.

A U T H O R I N D E X - TAMU NMR NEWSLETTER NO. 237

The University of Western Ontario

Department of Chemistry
Chemistry Building
London, Canada
N6A 5B7

^{13}C NMR OF SOME B-NOR and A-HOMO-B-NOR STEROIDS

May 12, 1978.

Dear Barry:

Although literally hundreds of steroids have been examined by ^{13}C nmr, there seems to be a dearth of ^{13}C results for A-homo-B-nor and B-nor steroid skeletons. Recently, I have had the opportunity to examine a few of the latter in connection with one of Ed Warnhoff's projects and some of these results may be of interest to some Newsletter readers. At the same time, I can perhaps settle the issue raised by your pink letter.

Acid-catalyzed opening of the oxide ring in 3α,5α-oxido-A-homo-B-norcholestane (1) with $BF_3 \cdot Et_2O$ at room temperature gave a single alcohol containing a fully substituted double bond. Clearly, a back-bone rearrangement had occurred, the extent of which was of some interest. The ^{13}C spectrum revealed the 18-methyl carbon at 11.0 ppm and signals corresponding to those for C-13 and C-15 to C-27 in many cholestanes (1) were evident. Further, in the presence of $Eu(fod)_3$, the olefinic signals were more strongly affected than any of the methine signals except for that from the carbinyl carbon. It follows that a Westphalen-type of rearrangement had occurred to produce 2. The aforementioned shieldings agreed well with those for a variety of 5-methyl-19-nor-5β-cholesten-9(10)-enes (2). At lower temperatures, the oxide opening gave the Δ^4- and Δ^5-unsaturated alcohols 3 and 4 as well as 2. Not unexpectedly, half of their signals correspond closely with those found for many cholestanes while the remainder could be assigned to specific carbons in the usual way; these results are listed in the Table for 2-4. Interestingly, the carbinyl carbons in 2 and 4 are equivalent as are the carbinyl protons. However, the half-widths of the proton absorptions were 20 and 11 Hz, respectively, from which the favored conformation of the A ring can be deduced as sketched in A and B below. Three examples in the B-nor series were also available (5, 6 and 7) for which the corresponding results are included in the Table. A comparison of these data with those for the corresponding cholestane derivatives showed that pronounced differences (up to 14 ppm) occur for the B-ring carbons. In general, the shieldings for C-11,-12, and C-15 to C-27 are similar in both series. This is also true for C-1,-2 and -3 in the unsaturated cases but significant differences for these centres are found for the saturated ketone 7. This is not surprising because of the appreciable geometrical differences between 5β-cholestan-3-one and its B-nor analog 7. The preparation and characterization of these compounds will appear in ref. 3. The complete results together with those for several additional examples in the A-homo-B-nor series will be submitted for publication shortly.

I trust this will satisfy the ~~demand~~ * of the pink letter.

Jake

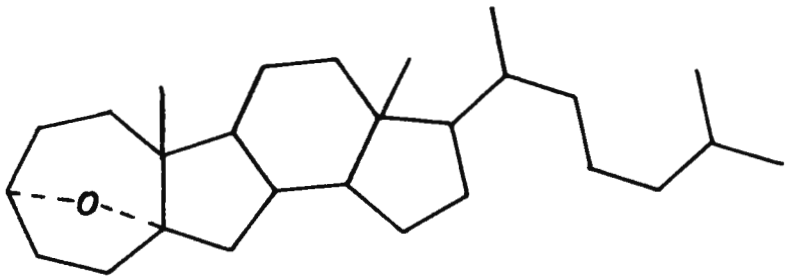
J. B. Stothers

1. Org. Mag. Reson. 9, 439 (1977).
2. J.M. Coxon, P.R. Hoskins and T.K. Ridley. Aust. J. Chem. 30, 1735 (1977).
3. V. Dave and E.W. Warnhoff. J. Org. Chem. submitted for publication.

* invitation !!

^{13}C shieldings (ppm from TMS, $CDCl_3$ solutions) for 2-7

	C-1	C-2	C-3	C-4	C-4a	C-5	C-6	C-8	C-9	C-10	C-18	C-19
2	19.6	39.8	75.9	33.5	35.3	49.2	43.8	43.0	136.7	140.0	11.0	26.7
4	32.4	33.2	75.9	40.6	23.5	153.9	127.0	45.0	56.5	48.9	12.4	18.7
3	34.2	30.8	67.0	32.4	113.7	156.9	38.5	38.9	59.8	46.4	12.4	16.2
5	37.3	32.0	71.6	36.6		149.0	125.4	46.2	62.5	44.8	12.3	15.0
6	35.4	33.7	199.3	122.5		179.0	34.7	38.4	58.1	44.1	12.4	17.4
7	32.4	35.3	214.7	44.4		44.3	38.4	40.1	55.1	39.8	12.3	24.9



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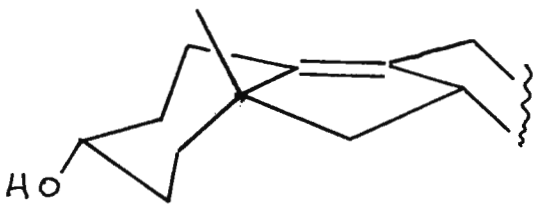
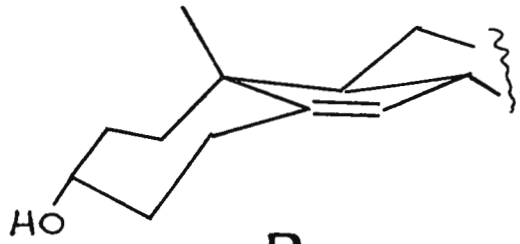


A



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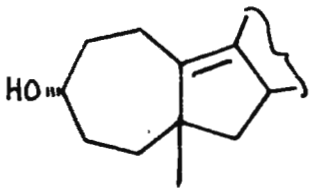

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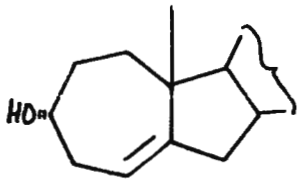

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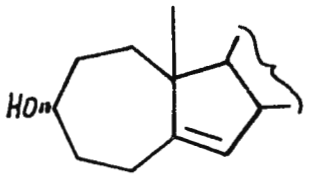

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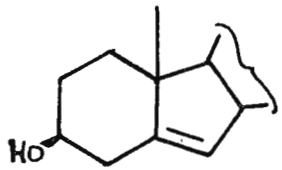

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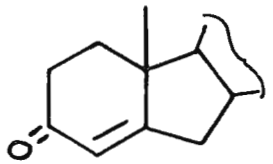

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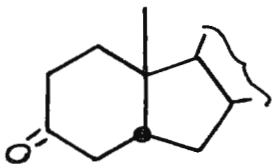

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Department of Chemistry

YORK UNIVERSITY

FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW, ONTARIO M3J 1P3

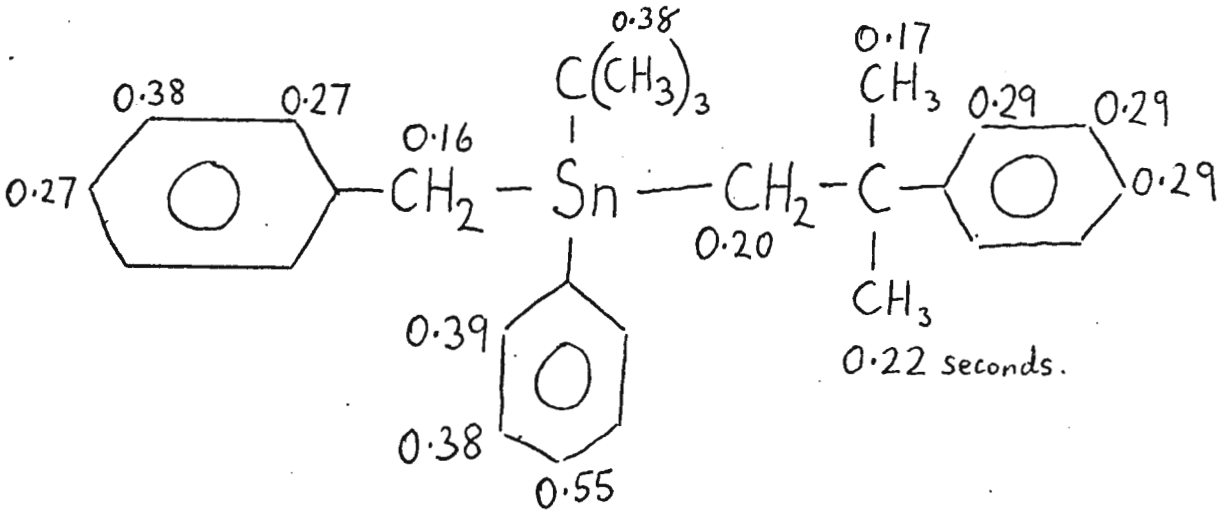
April 25, 1978

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

Dear Professor Shaprio:

T_1 Studies of Sterically Crowded Organotin Derivatives

We have been examining the applicability of T_1 studies for identifying and characterising barriers to internal rotation (eg. Axelson & Holloway, Can.J.Chem. 54 2820 (1976)) in a number of sterically crowded molecules. Where overall isotropic rotational reorientation can be assumed, the analytical procedure is a relatively simple one bearing in mind of course, the structural effects pointed out by Blunt and Stothers(J.Magn.Res.27,515(1977)) We decided to examine some organotin compounds lying around the lab, which were originally designed to be as sterically hindered as possible with a view to isolating optical enantiomers. In some of these a ligand bears an anisochronous pair of methyl groups, which give rise to two methyl resonances. The question could be asked whether they do so because of the intrinsic asymmetry of the molecule or because they are locked in specific sites. In the latter case, each site could also differ with respect to the rotational barrier of each individual methyl group. A fairly typical example is shown in the figure below for tertiarybutylbenzylneophylphenyltin run as a pure liquid with an external D_2O lock, at 35°C on a CFT 20.



Assuming isotropic reorientation of this relatively heavy molecule, the shortest NT_1 value representing the most rigid parts of the system is about 0.3. The phenyl group on the tin has a slightly longer NT_1 which may be due to some residual motion whereas the benzyl and neophyl phenyl rings appear to have the shortest NT_1, perhaps due to intermolecular dipolar relaxation (all nOe values are maximum). The τ-butyl methyl groups are probably spinning, but not fast enough to be called free rotors (which would require their T_1 values to be about $3(NT_1)$). The neophyl anisochronous methyls seem to be in more restricted environments than the τ-butyl methyls, and also each have slightly different rotational barriers.

We are currently looking for systematic trends in a series of these compounds, the chemistry and nmr of which have been previously reported (Kandil & Holloway, J.C.S. Dalton 1421 (1973) and Axelson, Kandil & Holloway, Can.J.Chem. 52, 2968 (1974)).

Sincerely yours,

Clive E. Holloway

CEH/kl

C.E. Holloway
Associate Professor
Chemistry Department

JACKSON STATE UNIVERSITY
JACKSON, MISSISSIPPI 39217

DEPARTMENT OF CHEMISTRY
601-968-2171

May 31, 1978

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

TITLE: A-60A or A-56/60A wanted

Dear Professor Shapiro:

We are interested in purchasing a Varian A-60A or A-56/60A spectrometer. An audio oscillator, frequency counter, variable temperature accessory and CAT are also needed for use with the spectrometer. Anyone interested in selling the above should write to me or call at (601) 968-2171.

Sincerely,

Eric Noe

Eric A. Noe

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

May 2, 1978

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

Dear Dr. Shapiro:

We thought Newsletter readers would be interested in a variable frequency pulsed spectrometer which we have built here at Virginia. This instrument will be used mainly for water proton relaxation measurements on enzyme and membrane systems, but we have already observed lithium-7 resonances and feel that this machine has the sensitivity to be useful with a variety of nuclei.

As you know, magnets suitable for such a system are hard to come by. New ones are of course expensive, and good used magnets are hard to find. After writing to all the major chemistry departments in the U.S. and Canada, we finally bought a very well preserved magnet and power supply from a Varian DA-60 spectrometer in the lab of Ted Schaefer at the University of Manitoba. To circumvent the problems of frequent replacement (at high cost!) of the 304 TL tubes in the 2100B magnet power supply, we had Rolf Tschudin install his solid state pass bank, which has been operating since August, 1977 with no problems. This cleverly designed unit of Rolf's consists of 34 high voltage power transitors, each on its own plug-in heat sink, which, along with several other circuit boards, fit on one large rack in the space vacated by the 304 TL's.

The probes, r.f. circuitry and pulse programmer for this unit were designed and built for us by Don Vickers and Tom Hill at SEIMCO, New Kensington, Pennsylvania. Their elegantly-designed consoles are now in use in various labs around the country, but we have their first set of broad band, cross-coil probes installed now in our unit. The two probes cover the ranges of 4-15 MHz and 15-60 MHz and are equipped for temperature control via a standard Varian V-4343 Temperature Controller. With a 50 Vpp signal at the transmitter coils, the pulse widths required for a 90° pulse are

Low Frequency Probe	4 MHz	9.5 μsec
	6 MHz	10.4 μsec
	8 MHz	13.0 μsec
	11 MHz	17.0 μsec
	15 MHz	16.0 μsec
High Frequency Probe	15 MHz	23.0 μsec
	22 MHz	25.0 μsec
	30 MHz	25.0 μsec
	42 MHz	24.0 μsec
	60 MHz	28.0 μsec

Since we run this instrument unlocked, using only the V-3508 solid state superstabilizer, titrations of a sample are rapid and convenient. Frequency changes are also quite easy and take only a few minutes, since the magnet and power supply, with Tschudin's modification, stabilize quickly.

We are presently using this spectrometer to examine the binding of CrATP and other nucleotide analogs to the $(Na^+ + K^+)$-ATPase and other similar enzymes. Most of our measurements are of T_1 and T_2, but the versatile pulse programmer from SEIMCO allows choice of other pulse sequences. For example, $T_{1\rho}$'s can be easily measured on this instrument. We will be happy to provide more information on this instrument and modifications to interested parties.

Please credit this contribution to Dr. Bruce Martin's "account".

Sincerely,

Charles M. Grisham

Charles M. Grisham
Assistant Professor of Chemistry

CMG:ltt

P.S. The ENI Model 310 L Power Amplifier is ideal for this system, since it has a frequency range of 250 kHz - 110 MHz. The frequency counter we use is a Data Precision Model 585 and it is impressive for its range (250 MHz), precision (8 digits), small size (5 1/2" x 1 3/4" x 3 1/2") and best of all, its small price (~ $300.00)!

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Institut für Molekularbiologie und Biophysik
Prof. Dr. K. Wüthrich

HPM-Gebäude
Telefon 01 57 57 70

Postadresse:
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und Biophysik
ETH - Hönggerberg
CH - 8093 Zürich

Prof. B.L. Shapiro
Department of Chemistry
Texas A and M University

College Station, Texas 77843

USA

Zurich, 22nd May 1978

Positive Results from Negative NOE's

Dear Barry:

The negative proton-proton NOE's that occur in protein NMR spectra at high fields offer an attractive means for obtaining protein structural information. [1,2] This is because the enhancements are largely determined by intramolecular dipole-dipole interactions. The interpretation of these NOE's, however, is often complicated by large cross-relaxation terms involving spins other than the irradiated and observed nuclei. [3] In order to obtain NOE difference spectra which are more easily interpreted, we have been using the transient NOE technique, introduced by Solomon in his classic study of HF. [4] We apply a selective inversion pulse on an individual line of the ^1H NMR spectrum, and monitor the resulting NOE difference spectrum as a function of time. The intensity of each line in the transient NOE spectrum builds up by spin diffusion at a characteristic rate. After reaching a maximum, the lines decay to zero via spin lattice relaxation. The initial rate of intensity increase depends only on the cross-relaxation coefficients between the irradiated and observed nuclei, and is simply related to proton-proton distances in the three-dimensional structure of the protein. In Figure 1, we show some experimental results for horse ferrocytochrome c, a heme protein of molecular weight 12,500. The positions of the Met 80 resonances

$$-C^{\alpha}H-C^{\beta}H_2-C^{\gamma}H_2-S-C^{\varepsilon}H_3$$

are indicated at the top of the figure. Notice that each Met 80 methylene proton has a different resonance frequency. The bottom trace is the steady state NOE difference spectrum [5] which results

from irradiation of the γ resonance at -1.8 ppm, with negative Overhauser enhancements appearing as positive peaks. The upper traces are transient NOE difference spectra for different delay times τ after inversion of the γ resonance. At τ=0, the large signal at -1.8 ppm corresponds to the inverted line while the smaller signal at -3.7 ppm corresponds to the geminal methylene proton. The latter signal is the result of spin diffusion during the 15 msec inversion pulse. For increasing values of τ, the pulsed line decreases in intensity, while the other lines grow with initial rates which are in agreement with what we expect from the proton-proton distances of the Met 80 residue. A more detailed account of these experiments will be presented in a forthcoming publication.

With best wishes,

Yours sincerely,

Sid

Sidney L. Gordon
Visiting Professor

Kurt

Kurt Wüthrich

References:

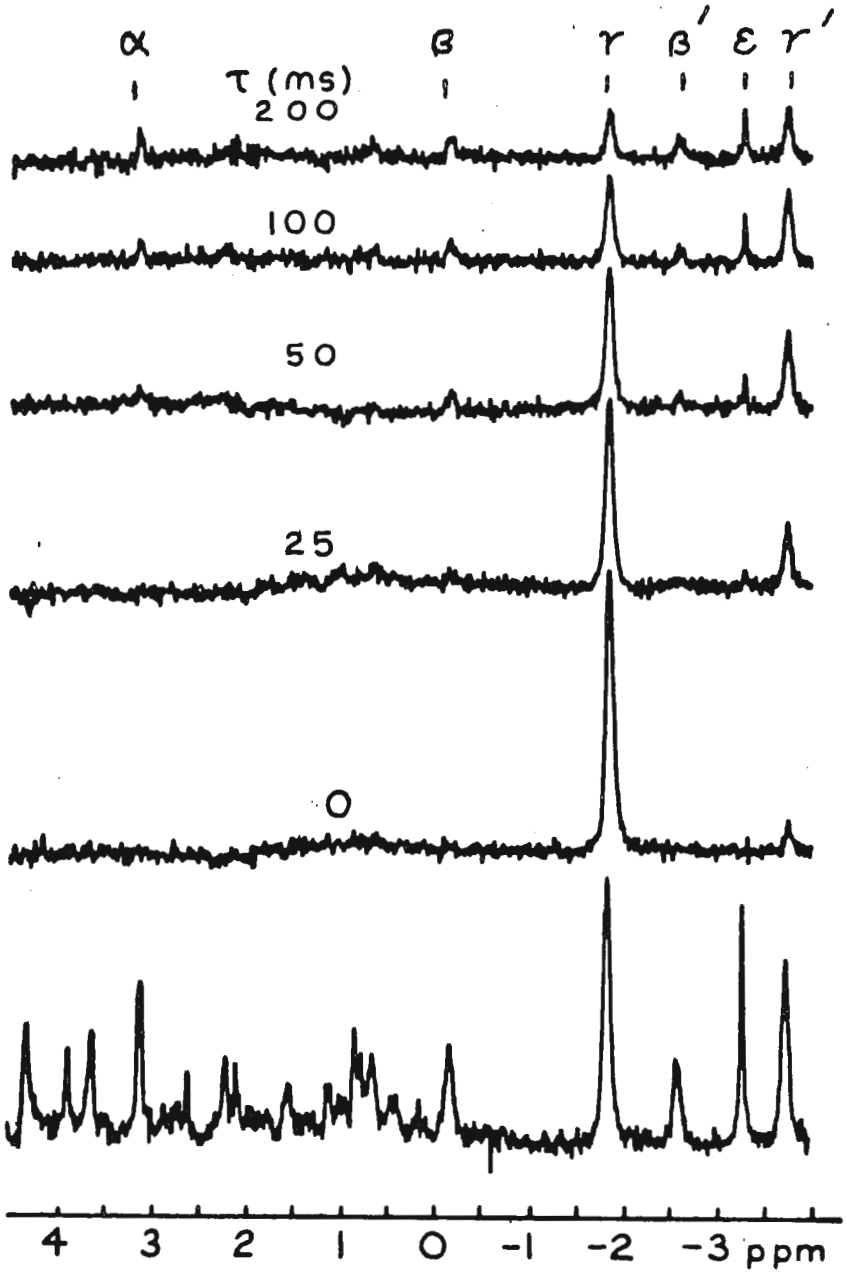
1) J.D. Glickson, S.L. Gordon, T.P. Pitner, D.G. Agresti & R. Walter, Biochemistry 15, 5721 (1976).

2) R.M. Keller & K. Wüthrich, Biochim. Biophys. Acta 533, 195 (1978).

3) A. Kalk & H.J.C. Berendsen, J. Magn. Reson. 24, 343 (1976).

4) I. Solomon, Phys. Rev. 99, 559 (1955).

5) R. Richarz & K. Wüthrich, J. Magn. Reson., in press.



360 MHz Fourier transform ^{1}H steady state and transient NOE difference spectra of a 0.008 M solution of horse heart ferrocytochrome c in 0.05 M deuterated phosphate buffer, pD = 6.8, T = 49°. The steady state NOE difference spectrum is the result of 2000 accumulations and the transient NOE difference spectra are each the result of 1000 accumulations. The steady state NOE's were obtained by applying a 2s low power saturating pulse followed by a 90° observation pulse. The transient NOE's were obtained by applying a 15 ms inversion pulse followed, after a delay time τ, by a 90° observation pulse. The difference spectra were obtained by subtracting the spectra with NOE's from reference spectra obtained by offsetting the irradiation pulse to -5 ppm.

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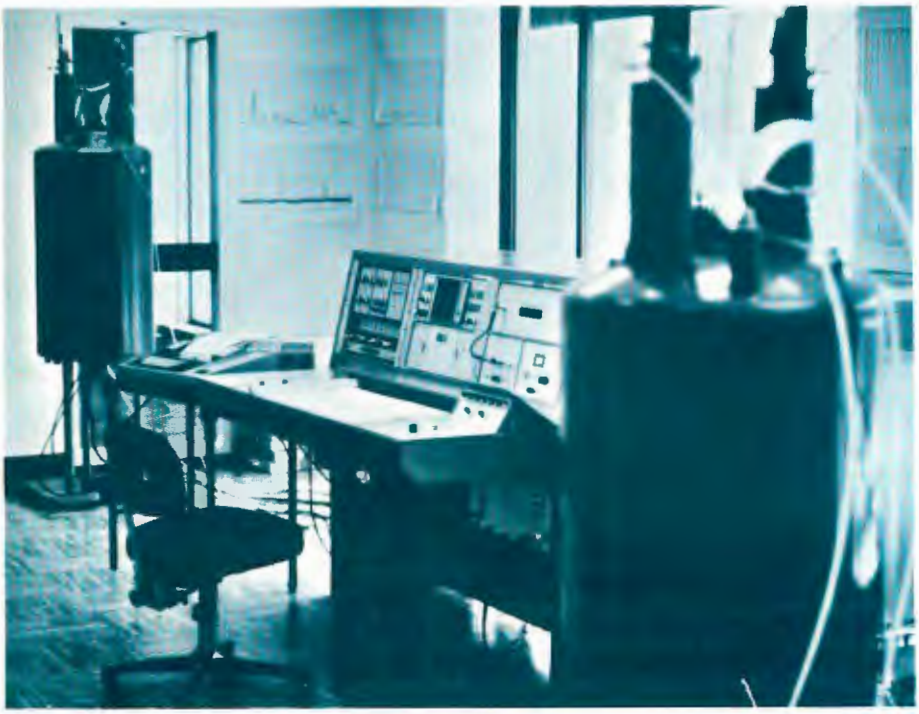

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SAN FRANCISCO, CALIFORNIA 94143

May 3, 1978

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

Re: Post-doctoral Position

Dear Barry:

A post-doctoral position is available for an individual interested in studying mobility in proteins and membranes. In particular, the $T_{1\rho}$ method for studying translational motion (1) and the off-resonance $T_{1\rho}$ technique we have been developing for examining rotational motions (2,3) will be utilized. A background in the area of molecular motions or in specific labeling of proteins and phospholipids would be useful but not essential.

Interested applicants should forward their curriculum vita and arrange for three letters of recommendation to be sent. Salary for the position is twelve to thirteen kilobucks per annum. The University of California is an Equal Opportunity/Affirmative Action employer.

Yours truly,

Tom

Thomas L. James
Assistant Professor of Chemistry
and Pharmaceutical Chemistry

TLJ:bw

(1) Fisher, R.W., and James, T.L., Biochemistry, 17, 1177 (1978).

(2) James, T.L., and Matson, G.B., TAMU NMR NEWSLETTER, 233, 29 (1978).

(3) James, T.L., Matson, G.B., Kuntz, I.D., Fisher, R.W., and Buttlaire, D.H., J. Magn. Reson., 28, 417 (1977).

DEPARTMENT OF CHEMISTRY
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T6G 2G2

May 16, 1978

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

Re: Decitek - Nova Interface

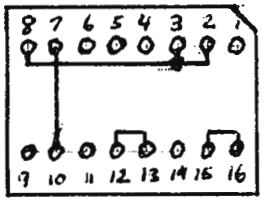
Dear Barry,

As any Digilab owner will tell you, the time required for loading the Digilab DPNMR program via the teletype reader makes a bed a necessary item of laboratory furniture. Failing to convince our purchasing department of this evident fact, we did the next best thing and acquired a WP-60 with a Decitek High Speed Reader. Interfacing the Decitek to the Nova computer cut our loading time from about 5 hours to 15 minutes. Perhaps some of your readers can make use of this interface.

The first thing to do is to determine whether or not your Nova Teletype Board has a 4011 Paper Tape Reader Option (IC's U50-55,67,68,70,71,U83-U88). If not, a schematic and kit containing the necessary IC's and small parts may be obtained from Datagen and soldered onto the board. (We'll be happy to supply more information.) That done, note that on the lower edge of the Nova back plane are pins for five 20-pin connectors. The one labelled P-7 is factory wired to the HSR portion of the I/O board. A 20-pin socket (A-MP86148-1) and harness must be made up to connect P-7 to a 25 pin Cinch socket (DB-25S) mounted on the computer rear panel with the other I/O connectors.

A length of 20 conductor ribbon cable and two 25-pin Cinch plugs (DB-25P) connect the computer and HSR. Alternate conductors should be grounded at the computer end of the cable to minimize cross-talk and noise pick-up.

Finally, a Mode Selector plug (see diagram) must be wired and plugged into the 16-pin DIP socket in the Decitek.



MODE SELECTOR

Nova - Decitek Interconnection Diagram

Back Plane	Nova Signal Name	P7	Nova Cannon Connector	Decitek Cannon Connector	Decitek Signal Name
	Gnd	1			
A59	CH6	2	11	11	DATA6
A61	CH5	3	10	10	DATA5
A63	CH4	4	9	9	DATA4
A65	CH3	5	7	7	DATA3
A67	CH2	6	6	6	DATA2
A69	CH1	7	5	5	DATA1
	+5V	8			
A71	STOP	9	3	3	PULSE
				1	RESET
	Gnd	10	25	25	Gnd
	Gnd	11			
A57	CH7	12	12	12	DATA7
A49	CH8	13	13	13	DATA8
A47	GO	14			
		15			
A77	SPKT	16	2	2	FLAG
A75	$\overline{\text{RDRDY}}$	17			
	+5V	18			
A73	FWD+STOP CONTR	19			
	Gnd	20			

Please credit this to Dr. Nakashima's account.

Sincerely,

Glen Bigam

GB/ss

Yale University *New Haven, Connecticut 06510*

DEPARTMENT OF MOLECULAR BIOPHYSICS
AND BIOCHEMISTRY

Sterling Hall of Medicine, 333 Cedar Street
(203) 436-8100

May 18, 1978

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

TITLE: ^{31}P Saturation Transfer on a Bruker HFX-90; Postdoctoral Position Available

Dear Professor Shapiro:

For the past couple years we have been using ^{31}P NMR to monitor the enzyme-phosphate intermediates which lie along the reaction pathway of E. coli alkaline phosphatase. We have shown that the covalent (E-P) and noncovalent (E·P) complexes give rise to resonances which are well resolved from that of the product of the reaction, inorganic phosphate (P) (Fig. 1a). Spurred by the recent interest in using magnetization transfer to extract kinetic information from enzymatically catalyzed reactions, we decided to test the feasibility of performing saturation transfer experiments on the alkaline phosphatase system using our modified Bruker HFX-90.

The frequency for the homonuclear decoupling pulse was selected digitally from a General Radio GR 1061 frequency synthesizer with the usual array of in line mixers to attenuate the off resonance (several KHz) frequency and reduce saturation effects during acquisition. Unique perhaps to our old system (Bruker HFX-90) was the availability of an extra set of fixed orthogonal coils in the probe arm which we found to be ideally suited for the introduction of the saturating pulse. This procedure provided much better isolation than could be obtained from a directional coupler. ^{1}H decoupling was also employed in these experiments using the Helmholtz coils on the insert.

For the experiment shown in Fig. 1, saturating pulses of 1.0 sec. (indicated by the arrows) were positioned off resonance (1a) or on E-P, E·P and P_i, respectively. Each spectrum (22,500 transients) was of 2.4 mM enzyme plus 9.6 mM phosphate, pH 5.5 contained in 0.8 ml in a 10 mm tube. The data clearly show that the intensities of the nonsaturated species are reduced upon saturation of the species with which they are in slow exchange. The magnitude of these intensity losses allows one to calculate the rate constants k_1, k_{-1}, k_2, and k_{-2} using a simple 3-site exchange formalism. In fact, if all three species are sequentially saturated as in Fig. 1 the system is overdetermined, allowing checks to be made on the reliability of the experimental data as well as the proposed enzyme mechanism.

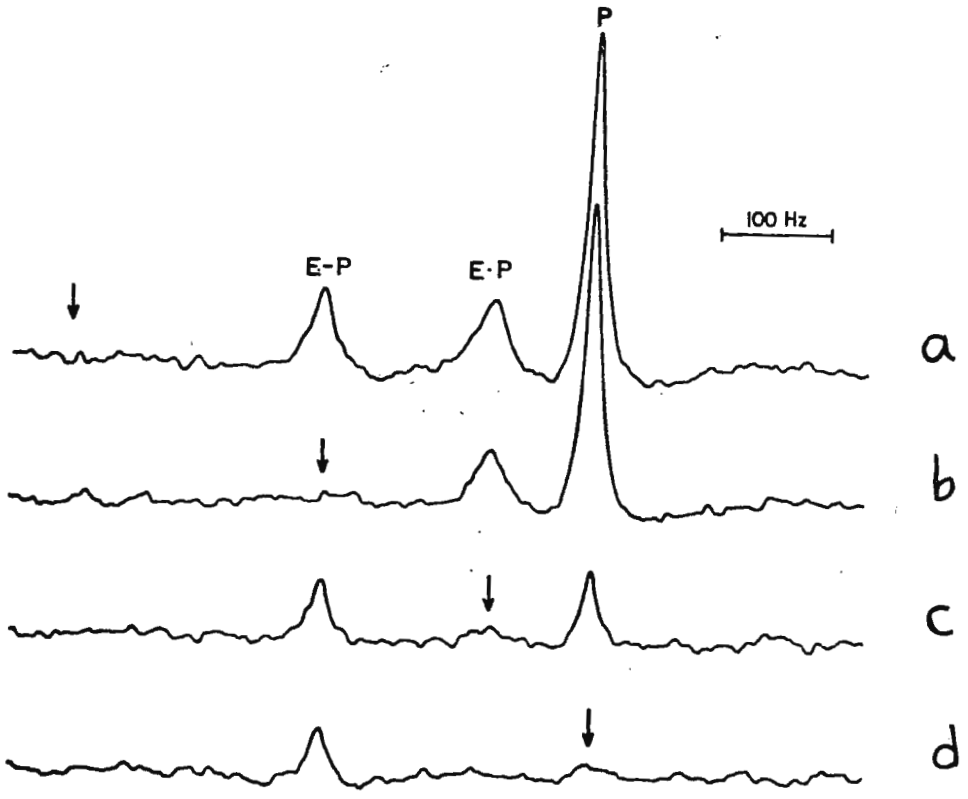
One of us (IMA) has a postdoctoral position available for 1 year. Applicants with experience in applying multinuclear NMR techniques to biological systems would be preferred.

Sincerely,

J.R. Alger — Ian M. Armitage — J.D. Otvos

1. J.F. Chlebowski, I.M. Armitage, P.P. Tusa and J.E. Coleman, J. Biol. Chem., 251, 1207 (1976).

2. T.R. Brown and S. Ogawa, PNAS (USA), 74, 3627 (1977); T.R. Brown, K. Ugurbil, and R.G. Shulman, PNAS (USA), 74, 5551 (1977).



$$E\text{-}P \underset{K_2}{\overset{K_{-2}}{\rightleftharpoons}} E\cdot P \underset{K_1}{\overset{K_{-1}}{\rightleftharpoons}} E + P_i$$

Figure 1

UNIVERSITY OF BRADFORD

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

DWJ/JB

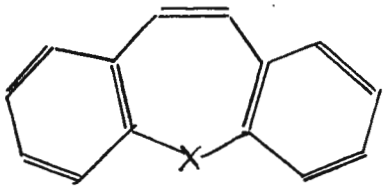
22nd May 1978

Dear Professor Shapiro,

COUPLING-CONSTANT ERRORS WITH LAOCOON III CALCULATIONS IN HETEROCYCLIC COMPOUNDS

If some of the transition frequencies overlap, errors in the observed line frequencies of a high-resolution n.m.r. spectrum can lead to doubts about the uniqueness, and uncertainties in the magnitudes, of the computed transition parameters (1,2). When these are refined iteratively by a program such as LAOCOON III, so that r.m.s. discrepancies between observed and calculated line frequencies are minimized, examination of the residual errors between observed and calculated frequencies can lead to a misleadingly optimistic impression of the parameter accuracy achieved. Thus Ewing (3) concluded that 2.5 is a realistic figure for the underestimation of such errors.

Recently J.A.G.D. has had occasion to make around 20 independent determinations (separate iterative analyses from independently measured 220 MHz ^{1}H spectra) each for several closely-coupled four-spin systems. Provided inter-ring coupling can be neglected, these ABCD systems are characterized by four aromatic chemical shifts and six coupling constants. The data on 5H-dibenzo[a,d]cyclohepten-5-one (I) and related compounds (II,III) and on fluoren-9-one (IV) [TAMUNMR Newsletter 221-16 (Feb. 1977)], which have close chemical shifts (spread over narrow ranges of 0.4 p.p.m.



I X = C = O

II X = CHOH

III X = O

or less for II, III, and IV), provide an interesting comparison between LAOCOON-calculated probable errors in coupling constants, J, (assumed independent of the conditions) and the deviations (assumed normally distributed) derived from separate analyses of spectra recorded under different conditions of solvent ($CDCl_3$ or CS_2), concentration and temperature.

For each of the six coupling constants in the four compounds, the Table shows the mean J(from 22 analyses of I, 12 of II, 16 of III, and 21 of IV), the mean LAOCOON probable error (PE), the r.m.s. deviation σ_e from the set of replicate analyses, and the ratio σ_e/PE between these. The mean LAOCOON r.m.s. errors for I-IV are 0.04, 0.04, 0.03, and 0.04 Hz respectively. If $2\sigma_e$ is taken as an acceptable indicator of the error in J, then the present data (σ_e/PE average is 3.6) suggest that the individual LAOCOON probable errors in J be multiplied by a factor of 7.

With apologies for being so late with this contribution.

Yours sincerely,

J.A.G. Drake Dewy Jones Hooshang Pakdel

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

TABLE: Mean H-H coupling constants and their LAOCOON probable errors (PE/Hz) and experimental e.s.d.s (σ_e/Hz) for ABCD systems in aromatic regions of I, II, III, and IV.

	I				II				III				IV			
Coupling	J/Hz	PE	σ_e	σ_e/PE	J/Hz	PE	σ_e	σ_e/PE	J/Hz	PE	σ_e	σ_e/PE	J/Hz	PE	σ_e	σ_e/PE
$J_{1,2}$	7.79	0.02	0.11	5.5	7.58	0.02	0.10	5.0	7.60	0.02	0.06	3.0	7.40	0.02	0.08	4.0
$J_{1,3}$	1.24	0.02	0.07	3.5	1.25	0.02	0.05	2.5	1.70	0.02	0.04	2.0	1.14	0.02	0.05	2.5
$J_{1,4}$	0.47	0.02	0.09	4.5	0.38	0.02	0.10	5.0	0.33	0.02	0.06	3.0	0.74	0.02	0.03	1.5
$J_{2,3}$	7.30	0.02	0.07	3.5	7.41	0.02	0.07	3.5	7.39	0.02	0.06	3.0	7.52	0.05	0.23	4.6
$J_{2,4}$	1.42	0.02	0.05	2.5	1.18	0.02	0.04	2.0	1.20	0.02	0.06	3.0	1.01	0.05	0.24	4.8
$J_{3,4}$	7.79	0.02	0.10	5.0	7.82	0.02	0.10	5.0	8.08	0.02	0.07	3.5	7.50	0.02	0.07	3.5

References

1. R.J. Abraham and S. Castellano, J. Chem. Soc. B., 49 (1970).
2. D.W. Jones, R.S. Matthews, and K.D. Bartle, Spectrochim. Acta, 30 A, 489 (1974).
3. D.F. Ewing, Org. Magn. Resonance, 7, 520 (1975).

Oklahoma State University

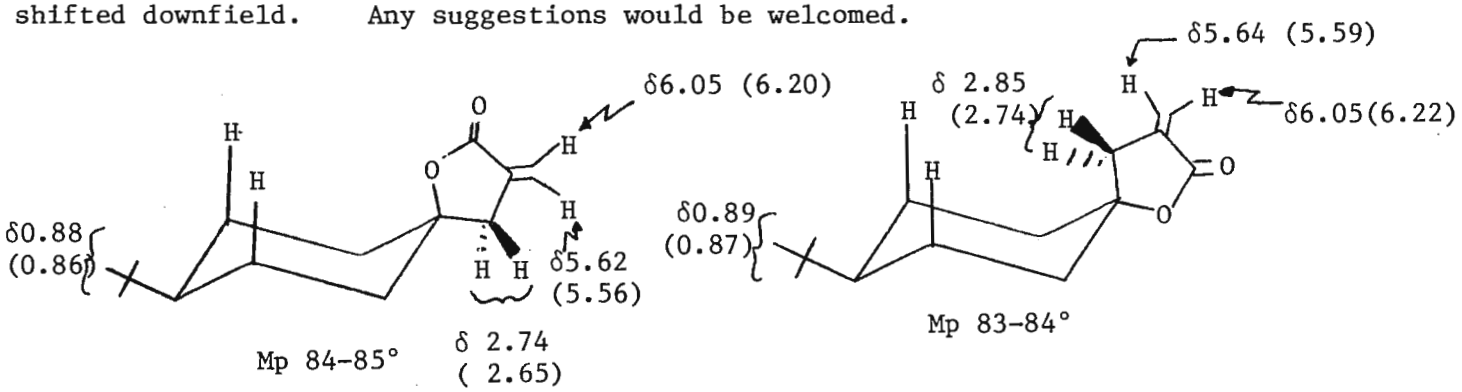
Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74074

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

Short Title: Novel solvent induced shifts in α-methylene-γ-butyrolactones attached to rigid systems.

Dear Barry:

I am sorry for the delay in getting in our contribution. We have been examining some alpha methylene-γ-butyrolactones of late. The two isomers show the dramatic effect of polar versus nonpolar solvents on the shifts in rigid systems. At the moment we have no explanation for the upfield shift of the vinyllic proton,which is anti to the carbonyl group, when the solvent changes from hexadeuterioacetone to $DCCl_3$. In contrast, the syn proton is shifted downfield. Any suggestions would be welcomed.



^1H shift in $D_3C-\overset{O}{\overset{\|}{C}}-CD_3$ from TMS (In $DCCl_3$)

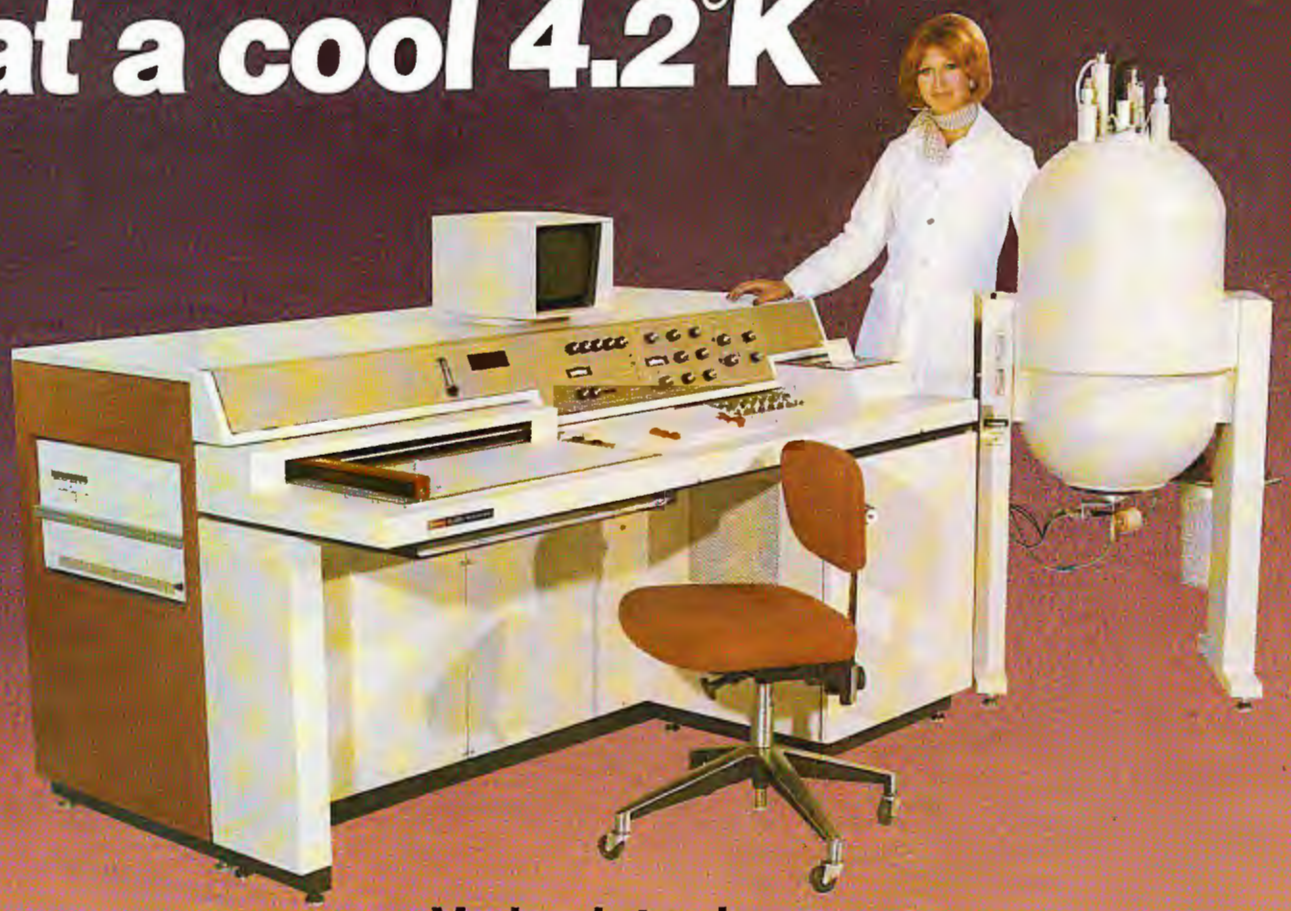
I shall try not to be so late next time with this letter but the lab has loaded with sample requests of late.

Sincerely yours,

Darrell

K. D. Berlin
Regents Professor

A hot performer at a cool 4.2°K



Varian introduces:
The XL-200 superconducting FT NMR spectrometer

In a cost- and resource-conscious world, the new XL-200 with 47-kG superconducting magnet makes a lot of sense. To begin with, its high-field performance and advanced design come in a truly affordable package. And economy characterizes the XL-200 spectrometer in other ways, too—such as the low-loss dewar unit, which lets the system operate over three months on only 25 liters of liquid helium!

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DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

May 26, 1978

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

Dear Dr. Shapiro:

The University of California, Davis, will have an opening for an NMR spectroscopist for our new Biological Magnetic Resonance Facility, as described below. We would appreciate it if this notice can be made available to all potential candidates in your Department.

NMR Spectroscopist Position Open

Assistant Research NMR Spectroscopist to supervise new Biological Magnetic Resonance Laboratory consisting of 200 MHz and 360 MHz Multinuclear FTNMR Spectrometers. Candidate must show strong evidence for productive research, as position involves advising and collaborating with biological science faculty as well as pursuing independent research. Responsibilities also include spectrometer maintenance and development, supervising one or more technicians as well as training and scheduling users. Ph.D. in Chemistry or equivalent degree, thorough background in FTNMR and hardware/software experience essential; some experience in biological FTNMR applications highly desirable. Salary $17,500 - $20,500, depending upon qualifications and experience. Send curriculum vitae, bibliography and three letters of reference to Professor G.N. La Mar, Department of Chemistry, University of California, Davis, CA 95616. The final date of application for the position will be July 17, 1978.

In compliance with federal and state laws and University policy, the University of California does not discriminate on the basis of race, color, national origin, religion, sex, handicap, age, or against disabled veterans or Veterans of the Vietnam era. The University of California is an affirmative action/equal opportunity employer.

Sincerely yours,

Gerd

Gerd N. La Mar
Professor of Chemistry
Co-director, UCD Biological
Magnetic Resonance Facility

GNL:jkg

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DEPARTMENT OF CHEMISTRY
TAMPA, FLORIDA 33620

813:974-2144
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May 22, 1978

Dear Barry:

Often in handling multiple-step equilibria by fast-exchange NMR, problems are encountered in doing statistics on the resultant shift vs. concentration curves. A rigorous treatment requires highly accurate first and second derivatives of concentrations and concentration-dependent functions. These, in turn, are best facilitated by exact, closed-form, solutions for concentrations. We give below a solution for two-step equilibria which is totally unambiguous and fool-proof. Previously published solutions, although correct, were too general to be of use when statistical applications of a rigorous nature were carried out (i.e., solutions including standard errors of equilbrium constants and/or bound shifts). In the results below, things which can be deduced by simple algebra are omitted; only the more difficult things are shown in detail.

The following system is solved for [AB]:

$$A + B = AB \quad \text{and} \quad AB + B = AB_2$$

This has respective equilibrium constants of K_1 and K_2. $[AB_2]$ may be obtained from simple algebraic manipulation after [AB] has been found. Now, let $\rho = A_o/B_o$ (the relative formalities of A and B) and let $k = K_1/K_2$. Then, if we let $x = [AB]$ for notational convenience, solution of the following cubic equation will give us the desired concentration:

$$x^3 + a_2x^2 + a_1x + a_0 = 0$$

Here,

$$a_0 = \rho k^2 B_o^{\,2}/[K_1(k - 4)],$$

$$a_1 = \{B_o^{\,2}\, k(1 - 2\rho) + k^2[B_o(1 + \rho) + 1/K_1](1/K_1)\}/(4 - k),$$

and,

$$a_2 = k[(1/K_1) + 2\rho B_o/(4 - k)].$$

If $k = 4$, these equations are not used and are replaced by a simple quadratic form not shown. For the more common occurrence ($k \neq 4$), we write the complete solution. First, we let

$$q = (3a_1 - a_2^{\,2})/9,$$

$$r = [(a_1a_2 - 3a_0)/6] - (a_2/3)^3,$$

and

$$D = q^3 + r^2.$$

Now, if $D > 0$, we have the relatively simple solution

$$[AB] = x = s_+ + s_- - a_2/3$$

where

$$s_\pm = (r \pm \sqrt{D})^{1/3}$$

and we use the real cube roots (positive or negative). This first case is totally unambiguous since there is only one real root with $D > 0$. However, if $D \leq 0$, there are three real roots; the physically relevant root is determined by whether $k < 4$ or $k > 4$. Below are given the "recipes" for these two possibilities.

$k < 4$ case:

Let $t = (r^2 + |D|)^{1/2}$

and $\Omega = [\text{arc cos}(r/t)]/3.$

Then, $[AB] = x = 2t^{1/3} \cos(\Omega) - a_2/3.$

$k > 4$ case:

Use the x as obtained immediately above (for $k < 4$) and go a little further by letting

$Q = a_2 + x$ and

$R = -a_0/x.$

Then, $[AB] = [-Q + \sqrt{Q^2 - 4R}\,]/2.$

The above solutions are totally unambiguous and represent the fastest way to calculate [AB] and, hence, $[AB_2]$. Needed derivatives can be obtained from these equations (with an appropriate amount of suffering).

Hopefully, some papers applying these--and derivations for more complicated systems--will appear as papers in the near future.

Sincerely yours,

Milt

Milton D. Johnston, Jr.
Assistant Professor of Chemistry

SUGGESTED TITLE: Two-step equilibria the fastest way

GORLAEUS LABORATORIA DER RIJKSUNIVERSITEIT TE LEIDEN
SUB-FACULTEIT - SCHEIKUNDE

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Postbus 75

Telefoon 48333
toestel: 3921

Afdeling: Dr. J.Lugtenburg

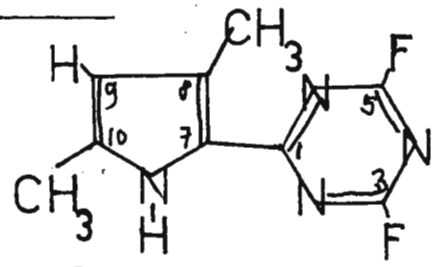
Onderwerp:

LEIDEN. 23th May 1978

Dear Professor Shapiro;

^{13}C NMR spectrum of a pyrryl-s-triazine

Recently we prepared



Its ^{1}H noise decoupled ^{13}C NMR spectrum shows the following features (solvent: hexadeuteroacetone, 30°C, chemical shifts relative to T.M.S.)

chemical shift δ		assignment	coupling constant	
13.0		8 CH_3		
14.4		10 CH_3		
115.2		9 C		
123.0	t	7 C	2.3 Herz	J_7-^{19}F
135.7		8 C		
140.1		10 C		
170.2	t	1 C	14.5 Herz	J_1-^{19}F
171.5	dd	3 C = 5 C	225.5 Herz	19.6 Herz
			J_3-^{19}F	J_3-^{19}F
			J_5-^{19}F	J_5-^{19}F

The ^{13}C NMR spectrum at -10°C shows additional splitting in the signals corresponding to 3C and 5C (all other features are the same within experimental error).

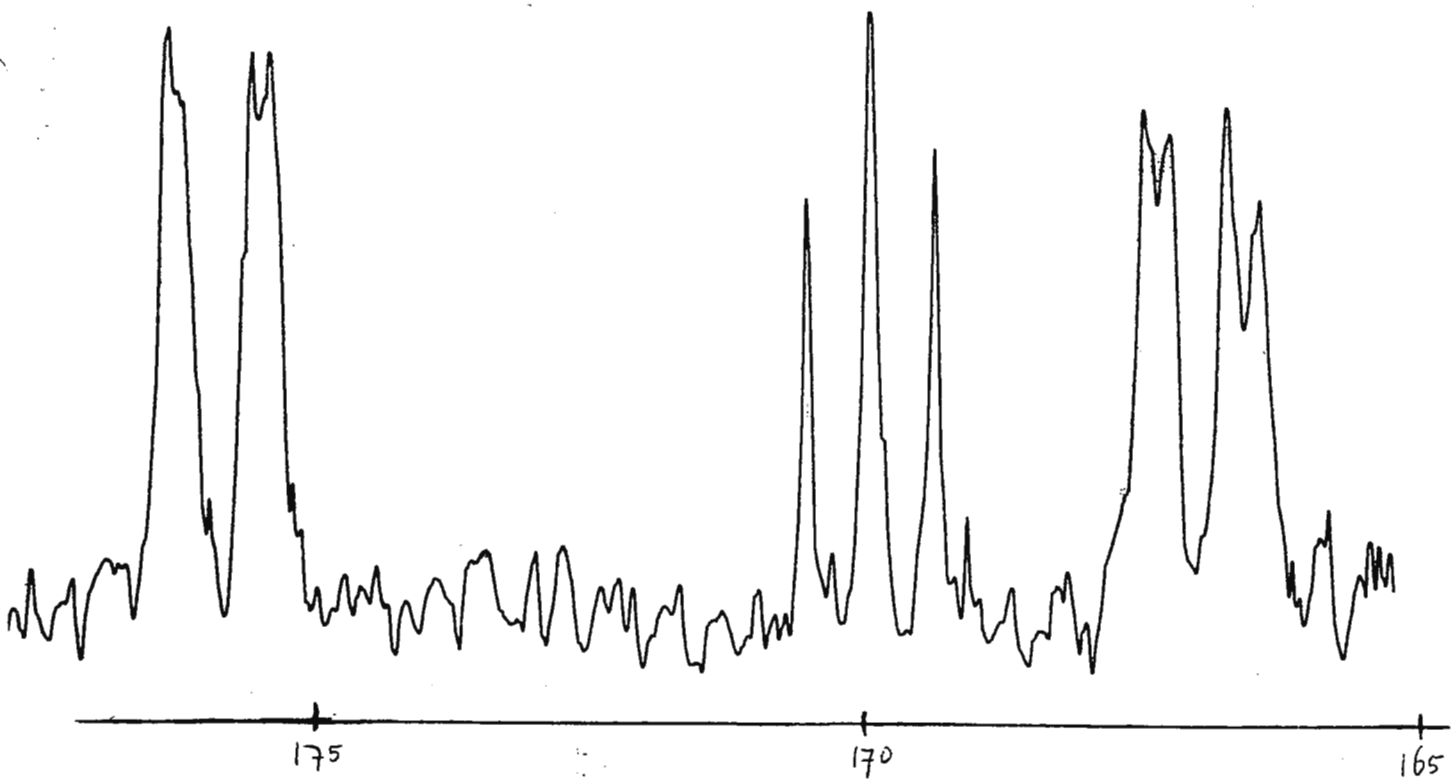
These facts can be understood by assuming that rotation around the 1-7 bond at -10°C is slow on the NMR time scale giving an observable

chemical shift difference between C3 and C5 of 0.2 ppm.
At 30°C the rotation is that rapid that only the averaged chemical shift of C3 and C5 can be observed.

The compound lacking the 8 and 10 methyl groups does not show a difference between the C3 and C5 signals at -10°C or 30°C. Clearly showing that the 8 CH_3 has a profound influence on the rotation barrier between the two ringsystems. Its ^{13}C NMR spectra at -10°C and 30°C are identical and very similar to the 30°C ^{13}C NMR spectrum of the dimethylderivative.

Sincerely Yours,

Jeroen Jacob Duijfjes Cees Erkelens Johan Lugtenburg



Signals of C_1, C_3 and C_5 in the ^{13}C NMR spectrum of the dimethyl-pyrryl-s-triazine. ('H noise decoupled, solvent hexadeutero-acetone, temperature: -10°C).

CONSIGLIO NAZIONALE DELLE RICERCHE

ISTITUTO DI CHIMICA DELLE MACROMOLECOLE

20133 MILANO, May 23, 1978
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29.52.78 - 29.54.82 - 29.60.71 - 28.53.10

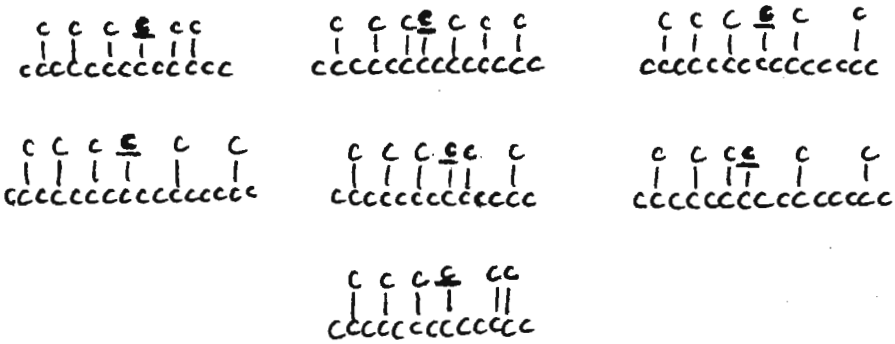
NS. RIF. PROT. N.

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

The ^{13}C methyl shift in models of regioirregular polypropylene

Dear Dr. Shapiro,

in a work on the structural characterization of models of regio-irregular polypropylene we have measured the ^{13}C chemical shift of the methyl groups (underlined position) in the following hydrocarbons:



The observed methyls can be present in the possible arrangements of irregular polypropylene.
The obtained data suggest that it may be possible to estimate the chemical shift of a methyl in a paraffinic chain trough an additivity scheme of the kind introduced by Grant and Paul and making allowance for configurational effects.

Thus the methyl shift is given by the relation

$$\nu = 17.99 + \Sigma N_i P_i + \Sigma R_{ij}$$

where N_i ia the number of methyl groups having a definite distance from and a steric relation with the observed methyl, P is the additivity parameter characterizing both the distance ($\gamma,\delta,\varepsilon,\zeta$) and the steric relationship (erithro or treo) and R_{ij} is a parameter which describes the effect of the proximity of two methyl substituents and depends on their steric relation.

The values of the parameters we have found are the following:

P_i	P_γ	P_δ	P_ε	P_ζ
erithro	-3.05	0.77	0.16	0.05
threo	-4.83	0.22	0.06	-0.03

R_{ij}	$R_{\delta\zeta}$	$R_{\delta\varepsilon}$	$R_{\gamma\varepsilon}$
e e	0.02	0.17	-0.12
e t	-0.10	-0.06	-0.40
t e	-0.15	-0.33	-0.14
t t	-0.20	-0.39	-0.52

These parameters can be used in the study of the spectra of irregular polypropylene and of copolymers of ethylene with propylene.

A detailed report is in press on Macromolecules.

Best regards

G. Gatti

G. Gatti

ISTITUTO SUPERIORE DI SANITA'
ROMA

Viale Regina Elena, 299
Tel 4990
Telegr : ISTISAN-ROMA

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

Proton Magnetic Relaxation Studies of Dextran Derivatives

Dear Prof. Shapiro,

NMR spectroscopy has been indicated as a powerful tool for the structural determination of polysaccharides. Chemical shifts and coupling constants from either ^{1}H or ^{13}C spectra have been used for identifying the anomeric configuration of glycosidic linkages, as well as the location of substituents on the carbohydrate moieties. In particular, a comparison of NMR and other chemical methods (e.g. methylation followed by the use of combined gas liquid chromatography-mass spectrometry (glc-ms)), has been carried out on native dextrans isolated from various bacterial strains. Although methylation data provide more precise values for the degree of branching, NMR spectroscopy has been shown to provide more specific information on the nature of anomeric linkages (1). Moreover NMR has the additional advantages of being a nondestructive technique and allowing the identification of non-carbohydrate organic material possibly present in the preparation.
Another advantage of NMR lies in the possibility of providing insight into the nature of molecular motions of these polysaccharides, through the study of spin- lattice and spin-spin relaxation times, determined at the level of the individual chemical groups. ^{13}C T_1 relaxation measurements, carried out by Benesi and Gerig (2) on linear, $\alpha(1\rightarrow6)$-linked dextrans of different molecular weight (T 40, MW$\simeq 4\cdot10^4$; T 250, MW$\simeq 2.3\cdot10^5$; T 2000, MW$\simeq 2\cdot10^6$; Pharmacia Fine Chemicals), as well as on a cross-linked dextran, Sephadex G-75, have shown that a) the relaxation of all carbon atoms in these polymers is overwhelmingly dominated by dipolar interactions; b) the small segments of the polymer are able to execute rapid local motions that are relatively independent of the overall conformation of the polymer in solution; c) all relaxation data (T_1, T_2, NOE) can be consistently analysed in terms of anisotropic reorientation of the monomeric units (considered as ellipsoids of revolution) in which "the molecular motion of the glucose residues about the axis roughly defined by the polymer chain directions is about 16 times easier than reorientation normal to the chain direction" (2).

In an attempt to make use of the potentiality of NMR relaxation methods for assessing the structure and mobility of these polysaccharides in relation to their immunochemical properties, we have carried out proton magnetic relaxation measurements (100 MHz, 37°C, c= 2 mg/ml, in D_2O saline solution) on O-stearoyl dextrans (OSD) prepared by reacting increasing amounts of stearoyl groups (esterified at the C-3 position) with dextran T 70 (MW$\simeq 7\cdot10^4$) (3). Immunochemical studies on dextran T 70 and its O-stearoyl derivatives (stearoyl contents ca. 0.4, 1.4, 2.7, 3.9 % w/w respectively) had shown that, although all these compounds precipitate with a rabbit anti-dextran serum, the two derivatives with higher stearoyl contents (2.7 and 3.9 %)

exhibit some loss of specificity (3). Our NMR studies are aimed at assessing whether the observed changes in immunochemical properties can be related to changes of chain flexibility possibly induced by increasing stearoyl contents. ^{1}H peak assignments on dextrans were based on a) a comparison of the spectral features of oligosaccharides of the isomaltose series; b) peak assignments worked out at 300 MHz by De Bruyn et al. (4) for the α-D-glucopyranosyl-α-D-glucopyranose and "shift-increments" determined vs. α-D-glucopyranose; c) double resonance experiments. Although at 100 MHz the signals arising from the saccharide rings are strongly coupled and partially overlapping to each other, a careful analysis of the partially relaxed spectra and double resonance experiments allowed us to assign the bands arising from H3-H2-H4 and to H5-H6A-H6B respectively. As a comparison, ^{1}H T_1 studies have also been carried out on linear dextrans of different molecular weight (MW $\simeq 2 \cdot 10^4$; $7 \cdot 10^4$; $2 \cdot 10^6$) and on the above mentioned stearoyl derivatives. Our results have shown that: 1) in agreement with the ^{13}C T_1 results by Benesi and Gerig (2), the T_1 values of all proton groups are maintained practically constant (within ± 5%) in the dextrans of the various sizes tested; 2) by increasing the stearoyl content of dextran T 70 the α (1→6)-linked anomeric proton shows slight but reproducible decreases in ^{1}H T_1 from 270 ms (T 70, OSD 0.4%) to 250 ms (OSD 1.4%) to 235 ms (OSD 2.7% and 3.9%). The ^{1}H T_1 values of H3, H2 and H4 are practically kept constant at a value of 320 ± 10 ms up to a stearoyl content of 2.7% whereas they drop to 270 ± 10 ms in OSD 3.9%. T_1 values of H5 and H6 are kept constant within experimental errors, for all samples tested.

The selective changes observed for the various groups, at the level of H3 H2 and H4, as well as -although to a minor extent- at the level of the anomeric proton, would suggest that, rather than to simple micelle-like aggregation, these changes should be attributed to a modified mobility of the monomeric units induced by an increase in the stearoyl content. ^{13}C NMR measurements are now in progress for further testing these tentative conclusions, in terms of rotational diffusion and segmental flexibility of the chains. If our preliminary conclusions are confirmed these studies would point to a possible conformational role of the antigenic determinants in the immunochemical specificity of polysaccharides and to the potentiality of NMR relaxation techniques in further elucidating the molecular mechanisms governing the interaction of these antigens with specific antibodies.

Franca Podo Carlo Ramoni Giuseppe Vicari

(Franca Podo) (Carlo Ramoni) (Giuseppe Vicari)
Laboratorio di Biologia Cellulare e Immunologia, Istituto Superiore di Sanita', Roma

1) Seymour, F.R. Knapp, R.D. and Bishop, S.H., Carbohydrate Research, 51 179--194 (1976).
2) Benesi, A.J. and Gerig J.T., Carbohydrate Research, 53, 278-283 (1977).
3) Svensson, S. Vicari, G. and Wilkinson S., J. Immunol. Methods, 9 315-321(1976).
4) De Bruyn A. Anteunis M. and Verhegge, G., Bull. Soc. Chim. Belg. 84 721-734 (1975).

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StonyBrook

May 25, 1978

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

"T_1scendental Manganization, or
How to Relax Your Dogs and Rats"

Dear Barry:

As a prelude to zeugmatographic imaging experiments with Relaxation Contrast Reagents, we have been carrying out a number of experiments on the effect of Mn^{++} on water proton relaxation times in tissues. The first measurements were on rat plasma and on samples of myocardium (heart muscle) from pigs and dogs (don't you long for the good old days when the standard test sample was potable?). Now, however, we are shooting manganous solutions into the veins of dogs and rats, and then looking at the water proton T_1 values and the Mn contents of various normal organs and of normal and ischemic myocardium. To make a long (and still very incomplete) story short, the table below shows the 4 MHz T_1 changes produced after 1 hour in some rat organs by non-lethal Mn^{++} doses of 0.1 mmol/kg body weight, and the sketch shows the relaxation rates in pieces of a dog's heart in which an ischemic region was produced by tying off coronary arteries at the points indicated, injecting the same dose of Mn^{++} in saline solution an hour later, and then sacrificing the animal after another half hour. Not only are different organs differently affected, probably largely because of differences in Mn^{++} uptake, but the poorly perfused region of the heart shows a much smaller effect than the regions still supplied with a normal flow of blood. It may be that such enhanced T_1 contrast will be useful in NMR zeugmatographic imaging in living animals and humans, and we hope to test that idea soon.

This work has been done in collaboration with a visitor, M. Helena Mendonça Dias, of the Instituto Superior Tecnico, Lisbon, and with A.M. Rudin and M.J. Glucksman, with funding from the NIH and from a V.A. Grant to M.J. Jacobson at the Northport VA Hospital and the SUNY/SB Department of Surgery.

Best regards.

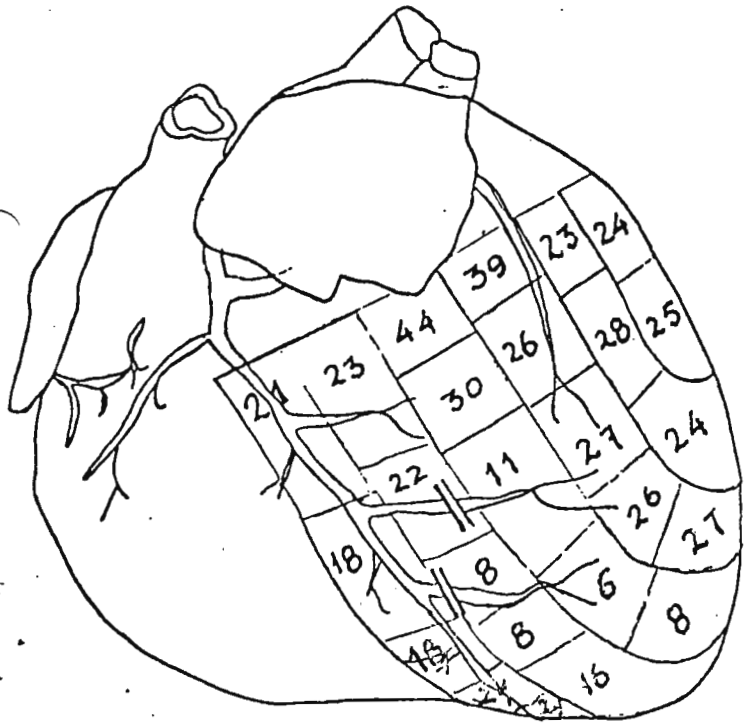
Yours truly,

Paul C. Lauterbur
Professor of Chemistry

PCL:eg

T_1 (msec)

	control	0.1 mmol/kg Mn^{++}
blood	656	465
heart	363	47
lung	404	221
liver	123	29
spleen	244	186
muscle	278	262



$(T_1)^{-1}$ values (in sec^{-1}) for dog myocardium after injection of Mn^{++} at 0.1 mmol/kg. The $(T_1)^{-1}$ value for myocardium without Mn^{++} injection is about 3. Note the region of decreased relaxation enhancement distal to the ligations.

237-35

Laboratorium
für anorganische Chemie
Eidg. Technische Hochschule
Zürich

8006 Zürich, Universitätstrasse 6

10. 5. 1978

Multinuclear NMR Studies on the Pt-Sn System

Postdoctoral Position Available

Dear Prof. Shapiro,

Catalytic systems containing magnetically active metals and ligands provide fruitful ground for multinuclear studies, and the system cis-$^{195}PtCl_2(^{31}PR_3)_2$ + $^{117,119}SnCl_2$ represents one such example. The product resulting from the interaction of these two molecules (see equation) can be readily identified using a combination of ^{195}Pt, ^{119}Sn, ^{31}P and ^{1}H methods.

$$cis\text{-}PtCl_2(PR_3)_3 + SnCl_2 \longrightarrow trans\text{-}PtCl(SnCl_3)(PR_3)_2$$

The appearance of a two-bond tin-phosphorus coupling (^{31}P spectrum) as well as the chemical shift of the coordinated tin prove that the two metals lie within one coordination sphere. The one-bond platinum-phosphorus coupling (^{195}Pt and ^{31}P spectra) and the nature of the second order ^{1}H spectrum support a trans configuration of the phosphorus atoms, although the starting material may be seen to have cis geometry. Finally, the number of phosphorus atoms attached to the metal (good catalysts are, by definition, labile) is confirmed by the ^{195}Pt spectrum. NMR and transition metal chemistry continue to enjoy a profitable partnership.

There will be a position for a postdocotral student in our lab beginning September of this year. The work will involve the nmr of catalytic systems and interested parties may write to me directly.

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

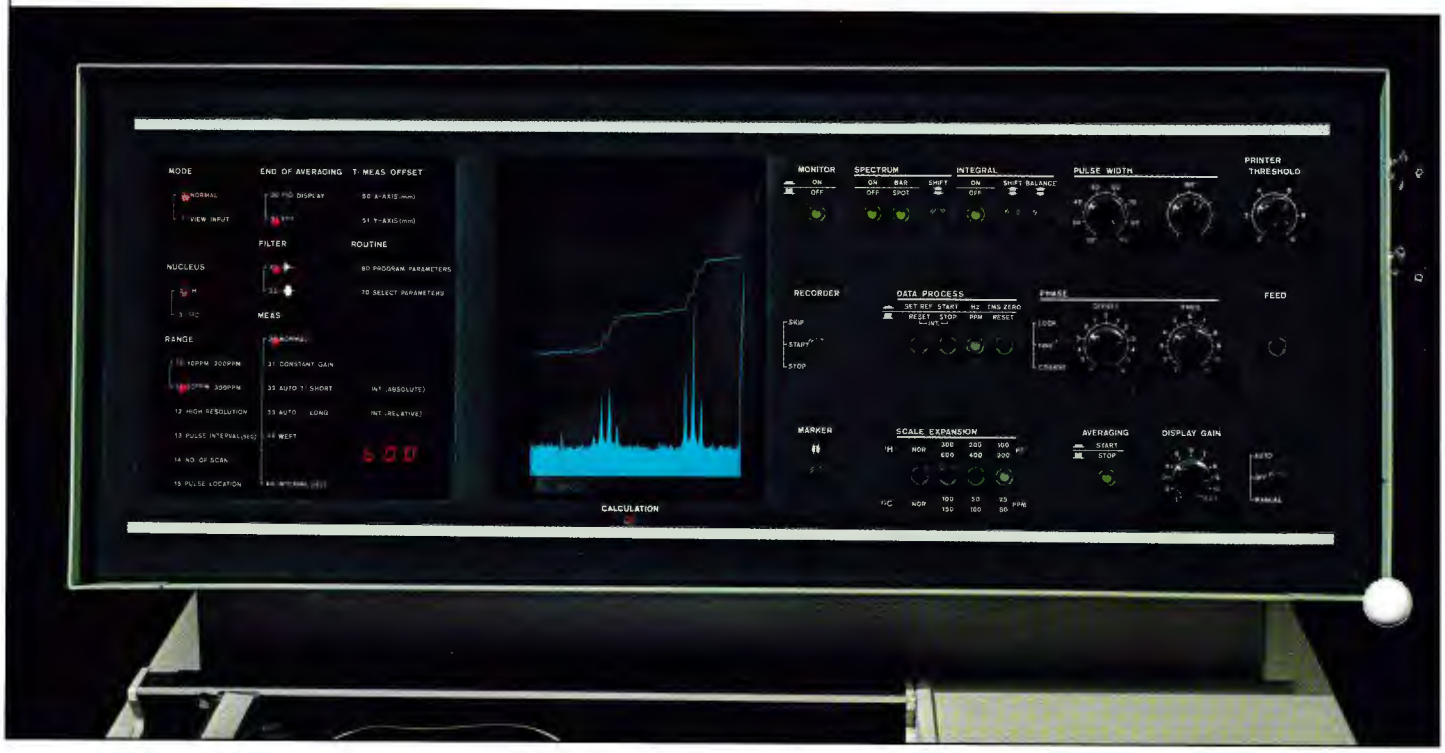
Sincerely yours,

Paul S. Pregosin

Dr. P. S. Pregosin

NUCLEAR MAGNETIC RESONANCE

The R-600 control panel is simple to operate, easy to understand.



NOW... EFFORTLESS FT NMR

Perkin-Elmer's Model R-600 is a high-performance, low-cost instrument for routine proton observation at 60 MHz. It's the first commercially available NMR spectrometer with a dedicated digital microcomputer that doesn't require a computer expert. The R-600 utilizes the proven R-24 Series magnet system. And because it's a permanent magnet NMR, there are no special requirements for water or power. Just plug it in.

So it's easy to operate, easy to install. And with an extremely low price tag and operating cost, it's also easy on your budget.

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All you need are microgram samples to get routine spectra from the Model R-600. Consequently, you can apply NMR in many new areas. You can get unequivocal identification of many LC and GC fractions. You can use NMR to analyze trace amounts of impurity or isolated natural product when these are all you have available.

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Even if you have a complex FT NMR spectrometer now, you still need the Model R-600. Your large unit is usually tied up with time-consuming ^{13}C experiments. Besides, adapting it to proton capability would be tedious or costly. Adding a Model R-600 will give you the extra NMR you need, save money, and get your work done on time.

With superb sensitivity, the R-600 lets you run routine experiments on a small scale. Your sample requirements drop from milligram sizes to 500 micrograms or less. But you'll still get the same quality spectra.

SIMPLE OPERATION

Not only is the microcomputer easy to operate, it also does most of the work. And the R-600 is the first FT NMR with controls arranged for operation like a conventional continuous wave instrument. Programming was designed by an NMR spectroscopist, so operational parameters and commands are user oriented. With just ten keys, the control panel simplifies setting the operating conditions and readout of the measurements.

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The Model R-600 has other advantages. For instance, its two Auto-T_1 modes enable you to run a complete T_1 experiment while specifying the fewest parameters. There's also a solvent suppression mode to minimize interfering peaks such as water.

GET ALL THE FACTS

Learn how the Model R-600 can simplify your NMR life. Request our literature describing its long list of benefits. Ask for a demonstration. Write Perkin-Elmer Corp., Main Ave., MS-12, Norwalk, CT 06856. Or call Tom Proulx or Jim Hannon at 203-762-1778.

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NANTES, le 31 Mai 1978

Professor B.L. SHAPIRO
T - M University
College Statron
TEXAS

IS ^{15}N SPECTROSCOPY A GOOD WAY FOR EVALUATING NITROGEN LONE-PAIR DELOCALISATION ?

Cher Barry,

Je vous prie de nous excuser pour le retard mis à vous envoyer notre contribution qui concerne l'utilisation de la spectroscopie ^{15}N à la prévision de la délocalisation électronique dans différentes séries de composés N-X.

Nous avons établi plusieurs corrélations entre les énergies d'activation Ea ou les valeurs d'enthalpies libres d'activation $\Delta G_T^{\ddagger}$ de processus de rotation gênée monomoléculaire , autour d'une liaison N-X et le déplacement chimique $\delta^{15}N$. Lorsque la barrière est essentiellement d'origine π et que les phénomènes intermoléculaires ou stériques ont une importance relative négligeable dans une série de composés, la corrélation présente une très bonne linéarité (cf. figure).

Nous avons ainsi étudié :

- des thioamides $(CH_3)_2N\text{-}CSR$
- des amides $(CH_3)_2N\text{-}COR$, $(CH_3CH_2)_2NCOR$, $H_2N\text{-}COR$, $CH_3HN\text{-}COR$
- des anilines et énamines : $-C{=}C\text{-}N(CH_3)_2$, $-C{=}C\text{-}N(CH_2CH_3)_2$
  $C_6H_5\text{-}N(CH_3)_2$, $C_6H_5N(CH_2CH_3)_2$, $C_6H_5NH_2$
- des composés diazotés : $(CH_3)_2N\text{-}N = A$ $A \equiv CRR'$, O, O_2, N-Ar

et avons observé que les valeurs des pentes (b) des corrélations sont comprises entre 0,1 et 0,3 kcal/ppm.

Plusieurs remarques peuvent alors être faites :

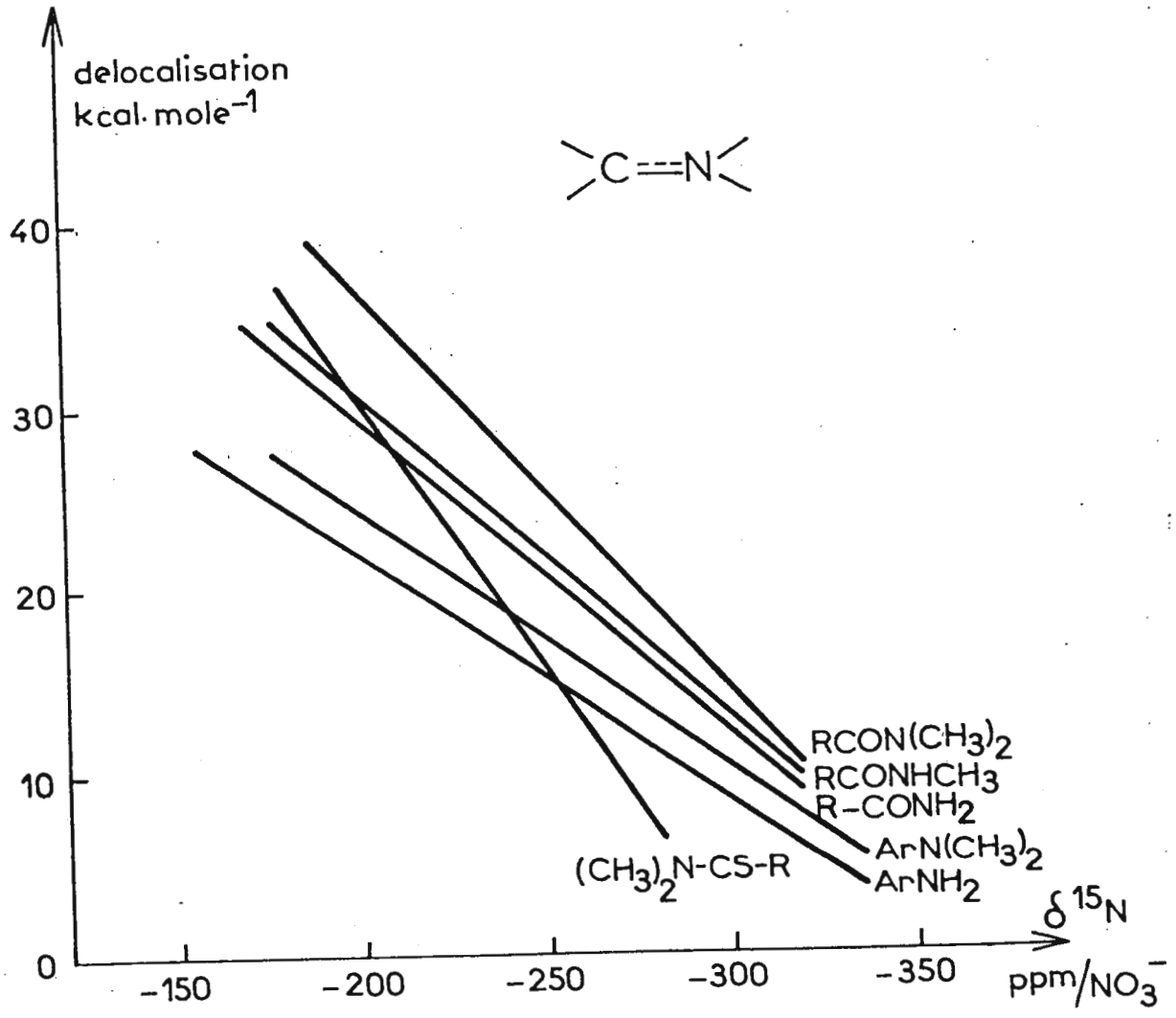
i) La RMN de l'azote ^{15}N est une méthode très précise et très sensible pour obtenir des valeurs de délocalisation en terme de hauteur de barrière. En effet, une valeur $\delta^{15}N$ peut être mesurée d'une façon reproductible à ± 0,1 ppm et la délocalisation électronique peut être calculée avec une précision supérieure à 0,05 kcal.mole^{-1}.

ii) La RMN de l'azote ^{15}N est une méthode juste (accurate) lorsque des renseignements relatifs sont recherchés : comparaison des valeurs de délocalisation d'un composé à l'autre dans une série, variation en fonction du solvant ou de la concentration etc ... La méthode est moins juste lorsque les hauteurs absolues des barrières sont calculées au moyen des corrélations car l'erreur sur l'ordonnée à l'origine peut être importante (elle n'est d'ailleurs pas plus grande que les erreurs systématiques liées aux mesures de RMN dynamique).

iii) La RMN de l'azote ^{15}N est aussi une méthode prospective car elle permet de prévoir des valeurs de barrières qui n'avaient pas pu être mesurées antérieurement. Le dernier exemple exploité au laboratoire est particulièrement

illustratif : la tétraméthyl urée $(CH_3)_2N\text{-}CO\text{-}N(CH_3)_2$ (TMU) a été abondamment étudiée par les techniques de RMN dynamique mais aucun phénomène de coalescence n'a pu être mis en évidence jusqu'à ce jour tant en résonance ^1H que ^{13}C. La valeur du déplacement chimique $\delta^{15}N$ = - 315,3 ppm permet cependant de prévoir une barrière de 11,6 Kcal.mole^{-1} qui devrait correspondre à un phénomène de coalescence aux alentours de 210/230°K . Incités par cette constatation, nous avons pu effectivement faire apparaître deux signaux $^{13}CH_3$ à basse température en utilisant une solution de TMU et de $Eu(FOD)_3$ dans CD_2Cl_2 ; $\Delta G^{\neq}$ = 11,1 Kcal.mole^{-1}.

G.J. MARTIN, M.L. MARTIN, M.L. FILLEUX.



CASE WESTERN RESERVE UNIVERSITY • CLEVELAND, OHIO 44106

June 1, 1978

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

SALE ON NMR AND EPR INSTRUMENTATION

Dear Professor Shapiro:

We are having a sale here at Case Western Reserve on some of our NMR spectrometers, and one EPR, and thought some of the readers might know of someone starting on low-budget NMR/EPR, or could use these instruments for back-up parts, or could make use of their associated magnets (all Varian):

HA 100 with Fourier Transform, ^{1}H and ^{13}C observe
HA 60 with high impedance magnet
HA 60 with low impedance magnet
A 60A with spin decoupler and V.T. S:N = 22:1
A 60 with V.T. S:N = 15:1
V 4502-14 EPR with X-band bridge, and 12 inch wide gap (2.625 in.) low impedance magnet

We're not going out of the NMR/EPR business, but rather making room and raising runds toward some newer instrumentation. Those interested may write, or call us at (216) 368-3589 or 3658.

Sincerely,

William Ritchey

Alan Olson

AO:fs
cc: W. Ritchey

THE UNIVERSITY OF NORTH CAROLINA
AT
CHAPEL HILL

Department of Chemistry

The University of North Carolina at Chapel Hill
Venable and Kenan Laboratories 045 A
Chapel Hill, N.C. 27514

May 26, 1978

Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas
7 7 8 4 3

Dear Professor Shapiro:

Metal Ion NMR For The Study of The pH Dependence of Metal Ion Binding to Macromolecules.

Traditional methods of investigation of the interactions between metal ions and macromolecules, such as equilibrium dialysis, are cumbersome. In a fast-exchanging system it is possible to probe the pH-dependence of metal ion binding rapidly and with small expenditure of protein (a few milligrams) by the monitoring of linewidth (and, thereby, transverse relaxation) changes in the NMR signal of the metal ion upon association/dissociation of the complex.

The protein involved in this study was a calcium ion-binding fragment, Fragment-1, of a blood coagulation protein, prothrombin. At the La^{3+} concentration employed, it has been established in other studies that not only are the high affinity ion-binding sites occupied, but also an undetermined number of relatively non-specific, lower affinity sites. Effects seen are therefore an average of those characterizing the various individual sites.

The general dependence of the linewidth of the $^{139}La^{3+}$ resonance, with and without added protein, on pH is illustrated in the accompanying figure. Total Fragment-1 concentration was 4.48×10^{-5} M in 0.15 M sodium chloride, 50 mM MES buffer pH initially 6.0 (adjusted with triethylamine). The symbol o refers to runs carried out in the presence of a total lanthanum ion concentration of 6 mM. pH was varied by addition of microliter amounts of 1 N hydrochloric acid slowly added to the vigorously stirred protein:lanthanum sample. Sample volume was 6.0 ml. Sweep width was 5,000 Hz. Approximately 200,000 transients were accumulated per spectrum. Lanthanum ion linewidth controls were run under exactly the same conditions, but in the absence of fragment-1. The symbol refers to an experiment organized as follows: the pH of a sample containing fragment-1 (4.77×10^{-5} M) in 6 mM Lanthanum chloride, 5 mM calcium chloride, 0.15 M sodium chloride 50 mM MES buffer, pH initially 6.0 (adjusted with triethylamine). The symbol corresponds to lanthanum controls run under the same conditions, including ion concentration, but in the absence of fragment-1. In all cases adjustment was from high to low pH values.

A small decrease in $^{139}La^{3+}$ linewidth occurs on decreasing the pH from 6.0 to 5.2. Below pH 5.0 a broad titration process, typical of protein carboxyl groups, is indicated until a pH value of 3.4 is reached. Below this value the linewidth plateaus prior to falling off below pH 2.5 to approach that of unbound $^{139}La^{3+}$. Studies designed to allow more detailed interpretation of these observations are ongoing.

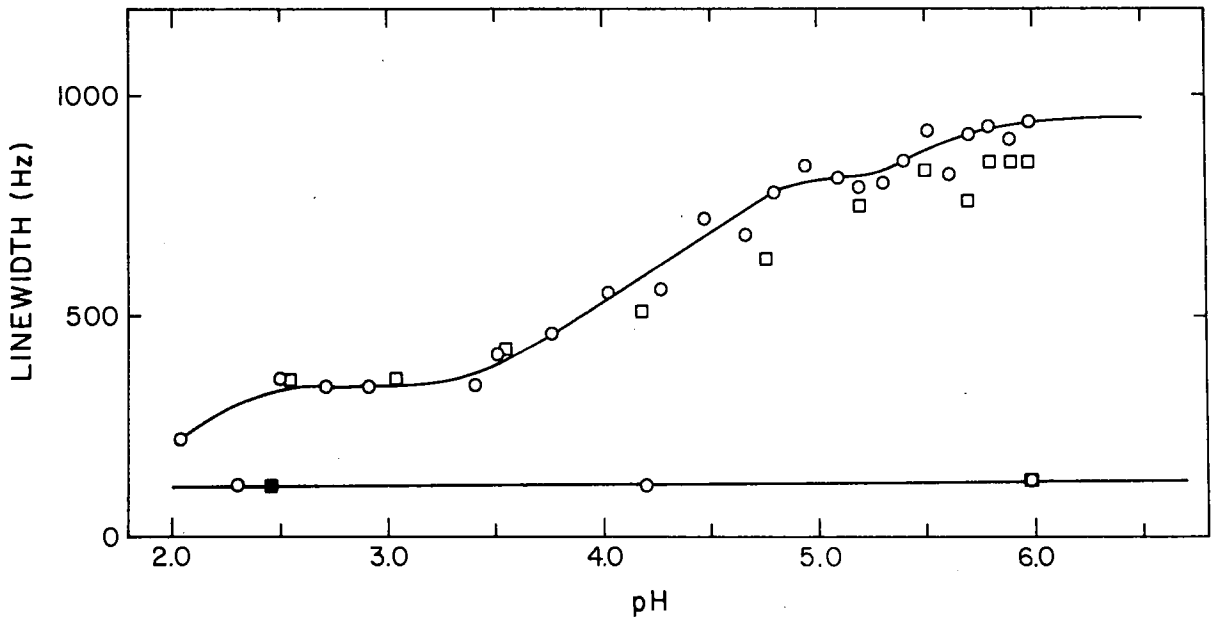
Spectra were recorded at 14.13 MHz on a Varian XL100 FT spectrometer in 18mm spinning tubes with vortex plugs. The instrument was modified for multinuclear operation in the manner described by Marshall et al. (Marshall, A.G., Hall, L.D., Hutton, M., and Sallos, J., J. Mag. Res., 13, 392 (1974). The 18mm probe was made by Nicolet Technology, Inc.

Yours sincerely,

David L. Harris
Department of Chemistry

Karl A. Koehler
Department of Pathology

DLH:KAK:dcm



237-45

UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND 20742

DEPARTMENT OF CHEMISTRY

June 1, 1978

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

Dear Barry:

Interfacing a Clock to an XL-100

When making T_1 or other measurements requiring long delays between pulses, a spectrometer operator frequently loses track of the time since the last pulse. This could be useful information: if the spectrometer should lose lock between pulses, one might have time to reestablish lock before the next pulse, without having to delay or abort the experiment. More commonly one might wish to touch up the homogeneity prior to each pulse. Or, when using a new data acquisition program one might wish to time the pulse delays, to ensure they are what they should be.

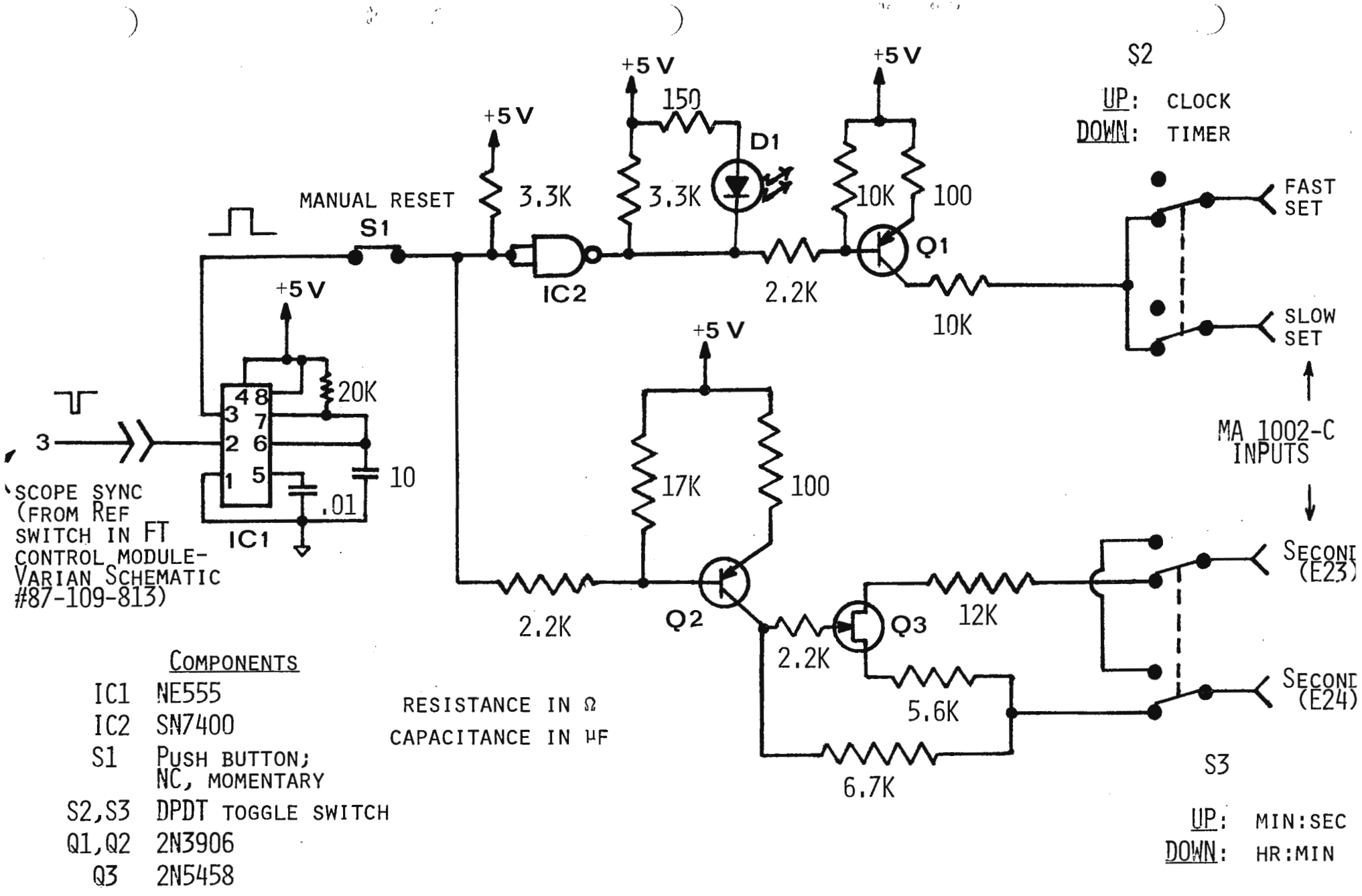
To solve these problems we have been using a National Semiconductor Corporation MA 1002-C clock chip, which is a 24-hour clock with LED display. Using the schematic shown in Figure 1, we interface the clock to our XL-100 spectrometer. The clock resets on each pulse (or manually), and displays either minutes:seconds (up to 9:59) or hours: minutes (up to 23:59) since the last pulse. When not in use for timing pulse delays, the clock can be used to display the time of day.

Sincerely yours,

Mark Mattingly Bob Rowan

Mark Mattingly Robert Rowan, III

MM/RR/ssc



Components	
IC1	NE555
IC2	SN7400
S1	Push button; NC, momentary
S2,S3	DPDT toggle switch
Q1,Q2	2N3906
Q3	2N5458

Figure 1. MA 1002-C/XL-100 INTERFACE

237-46

237-47
INDEPENDENCE MALL WEST PHILADELPHIA, PA. 19105, U.S.A. TELEPHONE (215) 592-3000
CABLE ADDRESS: ROHMHAAS TELEX 845-247

REPLY TO:
RESEARCH LABORATORIES
SPRING HOUSE, PA. 19477
(215) MI 3-0200
(215) CH 2-0400

ROHM AND HAAS COMPANY

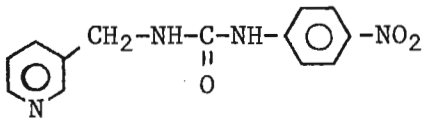
June 2, 1978

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

SUBJECT: In the Trenches with a Rodenticide Metabolite

Dear Professor Shapiro,

Recently, I was involved in identifying a series of metabolites of the rodenticide Vacor^{R}, which has the structure:



One metabolite which was formed in dog liver had been isolated by column chromatography on XAD-2 and Bio Sil A, preparative TLC, and reverse-phase HPLC. The sample of 34 µg of metabolite obtained was run with a 1 mm microinsert on a Varion XL-100 and gave the spectrum shown in Figure 1. Although we have never had contamination problems before, the spectrum was strongly reminiscent of unwanted paramagnetic ions! The sample was treated by passage over a microcolumn of Chelex 100 and 20 µg of the metabolite reisolated and examined again by NMR, giving the spectrum shown in Figure 2. From these data the metabolite was identified as nicotinamide. Re-examination of Figure 1 shows that the H2 and H6 peaks were preferentially broadened and shifted compared to H4 and H5, which implies specific rather than nonspecific broadening has occurred due to complex formation involving the pyridine nitrogen. I attempted to duplicate the spectrum of Figure 1 by adding various paramagnetic ions to pure nicotinamide, but could not get a spectrum which matched well. Thus the exact nature of the problem remains a mystery, although the Chelex 100 treatment is recommended for anyone who encounters a similar situation.

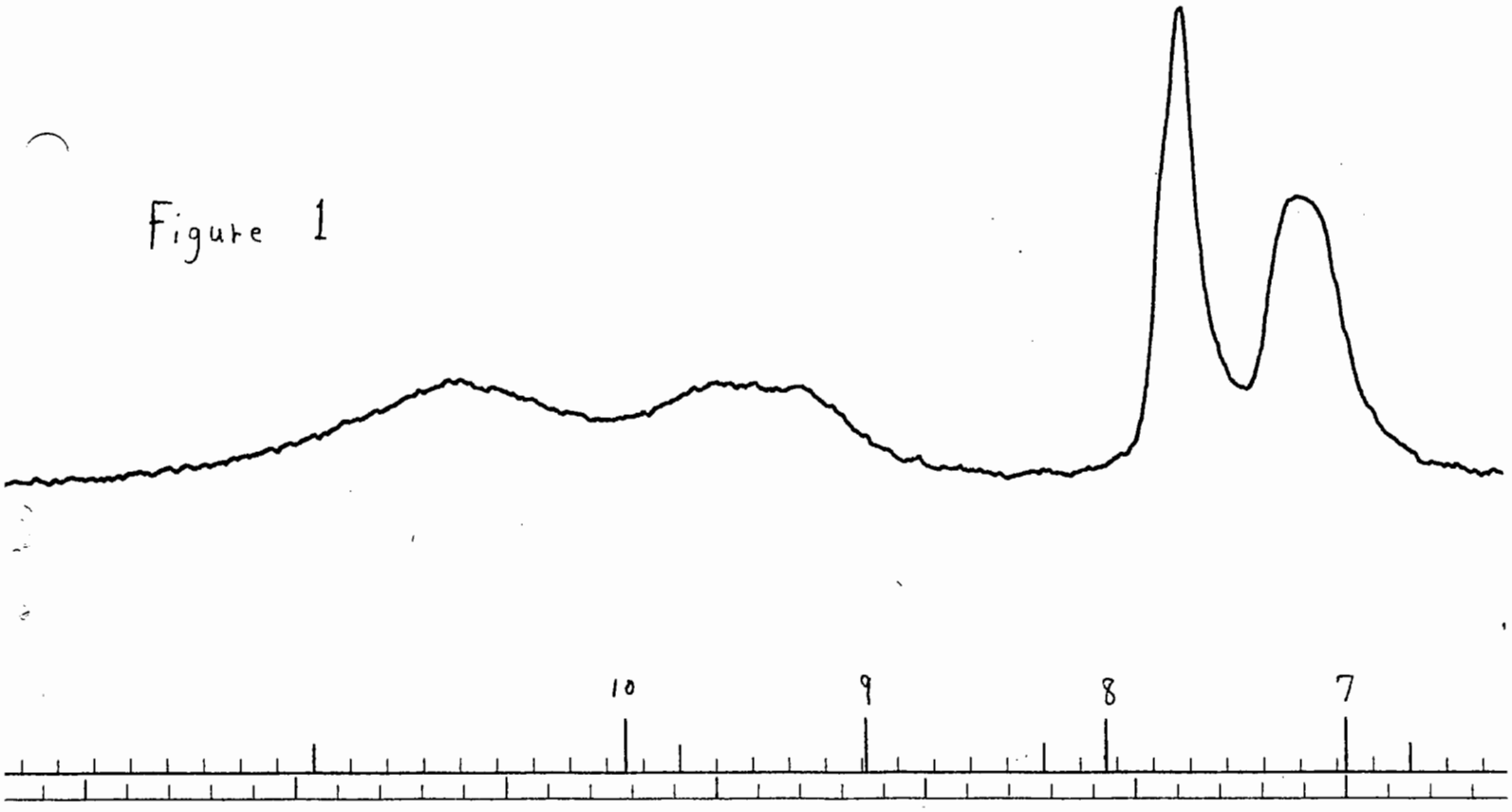
Yours truly,

David G. Westmoreland

David G. Westmoreland

DGW:pt

Figure 1



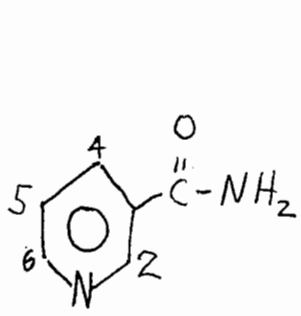
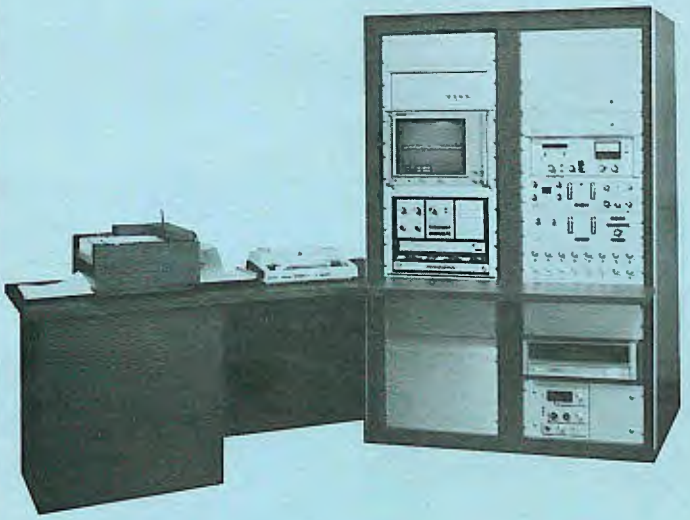


Figure 2

NT-150 A WIDE-BORE, FT-NMR SYSTEM FROM NICOLET



For routine NMR and state-of-the-art techniques such as:

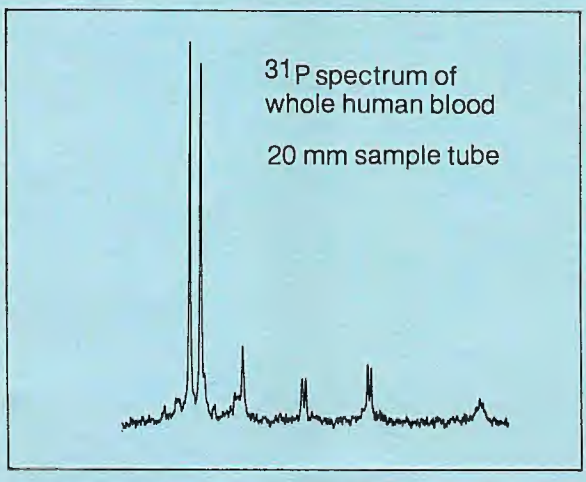
- ^{31}P experiments on living organs.
- Cross-polarization studies on solids.
- ^{13}C studies of high molecular weight polymers.
- Two-dimensional FT-NMR.

FEATURES INCLUDE:

- 3.5T superconducting magnet with 10 cm room-temperature bore.
- Straight-through access to sample area.
- Quick-disconnect probes for rapid changeover.
- 5, 12 and 20 mm sample tubes as standard, 30 mm optional.
- Quadrature phase detection as standard.
- Computer-controlled audio filter from 100 Hz to 51,100 Hz in 100 Hz steps.
- Nicolet 1180 data system with simultaneous acquisition, processing and plotting.
- Digital plotter with plot lengths selectable from 1 cm to 900 cm.

OPTIONS INCLUDE:

- NT-150 MF: broad-band multi-nuclei observe for 4 to 60 MHz.
- NT-150 CP: optimized system for Waugh-Pines cross-polarization studies.



For more information or to discuss your applications, please telephone or write.

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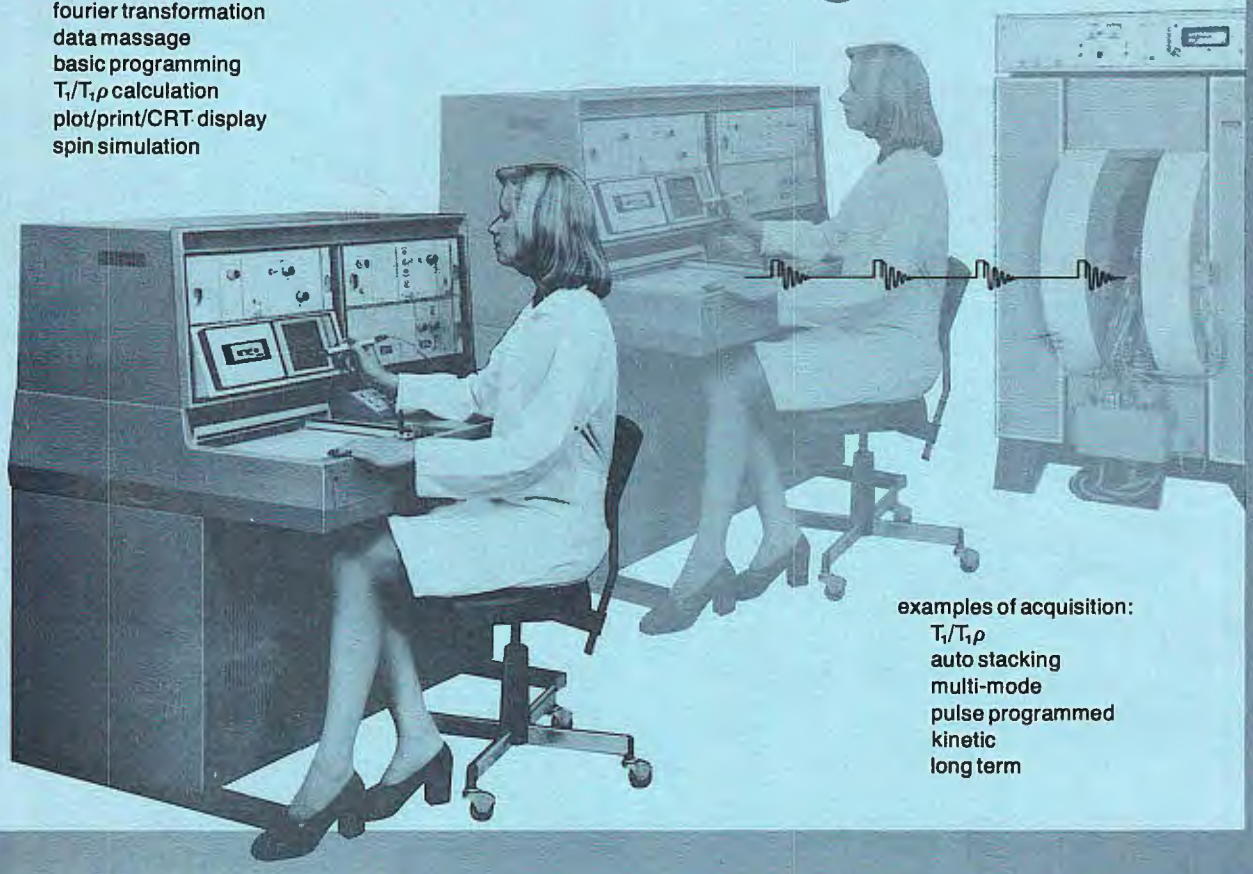
Mountain View, California 94041
Phone: 415/969-2076

While you're working in the foreground*...your FX is working in the background*

examples:
- fourier transformation
- data massage
- basic programming
- $T_1/T_1\rho$ calculation
- plot/print/CRT display
- spin simulation



examples of acquisition:
- $T_1/T_1\rho$
- auto stacking
- multi-mode
- pulse programmed
- kinetic
- long term

* Foreground/Background system

The FX60Q, FX90Q & FX100 features:

- (DQD) DIGITAL Quadrature Detection System
- Multi-Frequency TUNEABLE Probe observation
- Dual Frequency probes
- 4-channel DIGITAL phase shifters (DPS)
- Comprehensive auto-stacking system
- * **Foreground/Background system**
- Computer based pulse programmer with Multiple Pulse Sequence Generator
- CPU Expandable to 65K words (MOS)
- 2-channel 12 bit AD/DA
- $T_1\rho$/spin locking system
- Disc storage systems
- Multi-Mode HOMO/HETERO decoupling capabilities
- Programmable Variable Temperature Unit
- Simplex Y/Curvature gradient controller

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