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Newsletter

No. 183

December, 1973

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Deadline Dates: No. 184: 7 January 1974 No. 185: 4 February 1974
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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.

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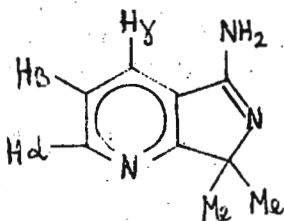
October 26, 1973  
204/3175/Schr

Prof. B. L. SHAPIRO  
Texas A & M University  
COLLEGE STATION  
Texas 77843, USA

Title: NOE & LIS Simultaneously

Dear Professor Shapiro:

Using NOE experiments and  $\text{Eu}(\text{FOD})_3$  induced shifts separately, we have recently determined that the structure of a reaction product was (I)



I

Having (I) in a solution with the shift reagent and having the NOE technique at hand, we played with NOE on this solution<sup>x</sup> to get 18% enhancement of the total intensity of alpha proton lines with those

of beta proton being saturated to 50-80%. (Approximately the same enhancement was observed in the absence of the reagent.)

On the other hand the reagent broadens the gamma proton lines and the NOE from beta to gamma proton is zero. (This NOE experiment cannot, however, be performed at all at 60 MHz in the absence of the reagent owing to the proximity of the lines.)

Our results, similar to the independent observations of Tori et al. (J.C.S.Chem.Comm. 1973, 620), show that it is possible to apply simultaneously the two techniques. In some cases this combination might make the observation of NOE more feasible or possible in the first place.

Sincerely yours,

*J. Dédina*  
J. Dédina

*J. Schraml*  
J. Schraml

<sup>x</sup> 0.3 M solution of (I) in  $\text{CDCl}_3$  with  $\text{Eu}(\text{FOD})_3$  in mol. ratio to (I) 1:12.5. LIS at this concentration are 0.18, 0.25, and 0.50 ppm downfield for shifts of protons alpha, beta, and gamma, resp.



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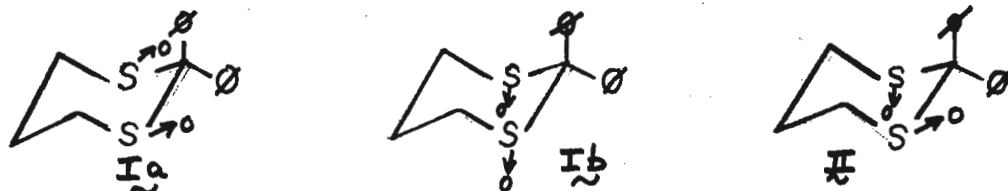
GENT, November 6, 1973  
KRIJGSLAAN 145 Tel. (09) ~~222222~~  
(België - Europa)

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

CONCERNING: Identification of cis-, and trans-2,2-diphenyl-1,3-dithiane-1,3-dioxide

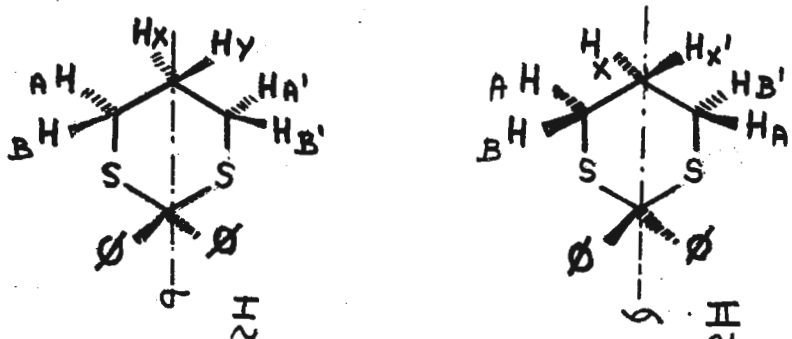
Dear Barry,

During our continuing investigation of the conformational properties of substituted 1,3-diheterocyclohexanes we recently have started studying the oxidation products of 1,3-dithianes. In literature is, for some time now, a discussion going on concerning the position (eq. or ax.) of the oxygen atoms of the sulfoxide functions in cis-2,2-diphenyl-1,3-dithiane-1,3-dioxide (I).



Based on infrared studies, Otting and Neugebauer<sup>1</sup> claimed a diequatorial cis-isomer (Ia), whereas de la Mare et al.<sup>2</sup> concluded for a diaxial structure (Ib). Recently Arbuzov and Arshinova<sup>3</sup> carried out some dipole-moment and energy calculations, and they have shown quite convincingly that the cis-form cannot exist in a diaxial chair form. Furthermore they suggested that the earlier cis-trans assignments should be inversed. Because the dipole calculations left some doubt in differentiating both isomers, we have decided to check this by <sup>1</sup>H-NMR spectroscopy.

Indeed, in view of the great influence of the molecular symmetry on the appearance of the NMR-spectra, the two compounds may readily be distinguished.





Indeed under conditions of rapid exchange, the trans-form possesses a twofold symmetry-axis, (isochronous 5-protons) and we expect an AA'BB'XX'-system wherein  $J_{AA'}$  and  $J_{AB'}$  are nearly zero. On the other hand, the cis-isomer holds a symmetry plane, and the chemical shifts of the two 5-protons are not averaged out. Consequently, we expect an AA'BB'XY'-system with two separated multiplets for the 5-protons. The relevant chemical shifts of the pertinent compounds are gathered in Tabel I

Table I. Chemical shift of A and B (CCl<sub>4</sub> 5% w/v, vs TMS int.)

	H <sub>4a</sub>	H <sub>4e</sub>	H <sub>5a</sub>	H <sub>5e</sub>	mp. <sup>1</sup>	IR <sup>1</sup>
A	3.40	3.20	1.94	2.89	177°	1058 and 1085 cm <sup>-1</sup>
B	3.19*	3.26*		2.68	189°	1058 cm <sup>-1</sup>

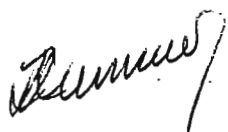
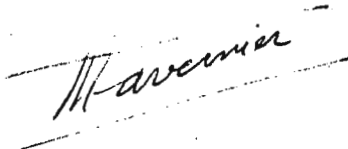
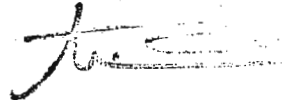
The compound A, attributed by Otting and Neugebauer<sup>1</sup> and de la Mare et al<sup>2</sup> to the trans-structure, clearly is the cis-compound, whereas B is the corresponding trans-isomer. This corroborates the findings of the russian authors<sup>3</sup>, although the measured coupling constants do indicate the presence of some boatform.

We further wish to point out that also the phenyl-proton-resonances may be used as an internal probe for the molecular symmetry.

D. Danneels

D. Tavernier

M. Anteunis

#### Ref.

1. W.Otting, F.A.Neugebauer, Chem.Ber. 95, 540 (1962).
2. P.D.B.de la Mare, D.J.Miller, J.G.Tillet, D.Watson, J.Chem.Soc., 1619 (1963).
3. B.A.Arbusov, R.P.Arshinova, Zhur.Strukt.Khimii, 12, 1103 (1971).

## INDIANA UNIVERSITY

Department of Chemistry

CHEMISTRY BUILDING

BLOOMINGTON, INDIANA 47401

November 5, 1973

TEL. NO. 812—

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

Dear Barry:

The "pink threat" prompts me to write the following:

Observation of Resonances from Some Minor Bases in the Natural-Abundance  $^{13}\text{C}$  NMR Spectrum of Unfractionated Yeast tRNA.

The development of a probe for sample tubes of 20-mm outside diameter has increased the sensitivity of natural-abundance  $^{13}\text{C}$  Fourier transform nmr to the point that resonances of some minor-base carbons of tRNA in concentrated solutions can be studied. In order to facilitate the identification of minor base resonances of tRNA, we first recorded and assigned the  $^{13}\text{C}$  spectra of some minor-base mononucleosides. We then obtained the proton decoupled natural-abundance  $^{13}\text{C}$  Fourier transform nmr spectrum (at 15.18 MHz) of aqueous (150 mg/ml) unfractionated tRNA from baker's yeast in the presence of  $\text{Mg}^{+2}$  (about 8 ions per tRNA molecule) at  $41^\circ\text{C}$ . On the basis of  $^{13}\text{C}$  chemical shifts of mononucleosides and mononucleotides, some ring carbons of dihydrouridine, pseudouridine, inosine, and ribosylthymine residues, as well as all methyl carbons, should resonate in regions of the spectrum free of interference from ribose and major base resonances. The  $^{13}\text{C}$  spectrum of tRNA (Fig. 1, 14 hr. signal accumulation time) yields resonances of carbons 4, 6, and 5 of dihydrouridine residues (peaks 1, 20, and 22, respectively). Peak 20 also contains a methyl carbon component. There is also evidence of other methyl carbon resonances, and of a peak arising from carbon 5 of pseudouridine and/or ribosylthymine residues. In addition, we show that dihydrouracil rings of folded tRNA undergo fast internal motion (with a correlation time  $\leq 2 \times 10^{-10}$  sec), a result that suggests a lack of direct participation of dihydrouridine residues in the determination of the secondary and tertiary structure of tRNA. Further details are available in preprint form (R. A. Komoroski and A. Allerhand, Biochemistry, in press).

Sincerely yours,



Adam Allerhand  
Professor of Chemistry

AA/dcw  
encl.



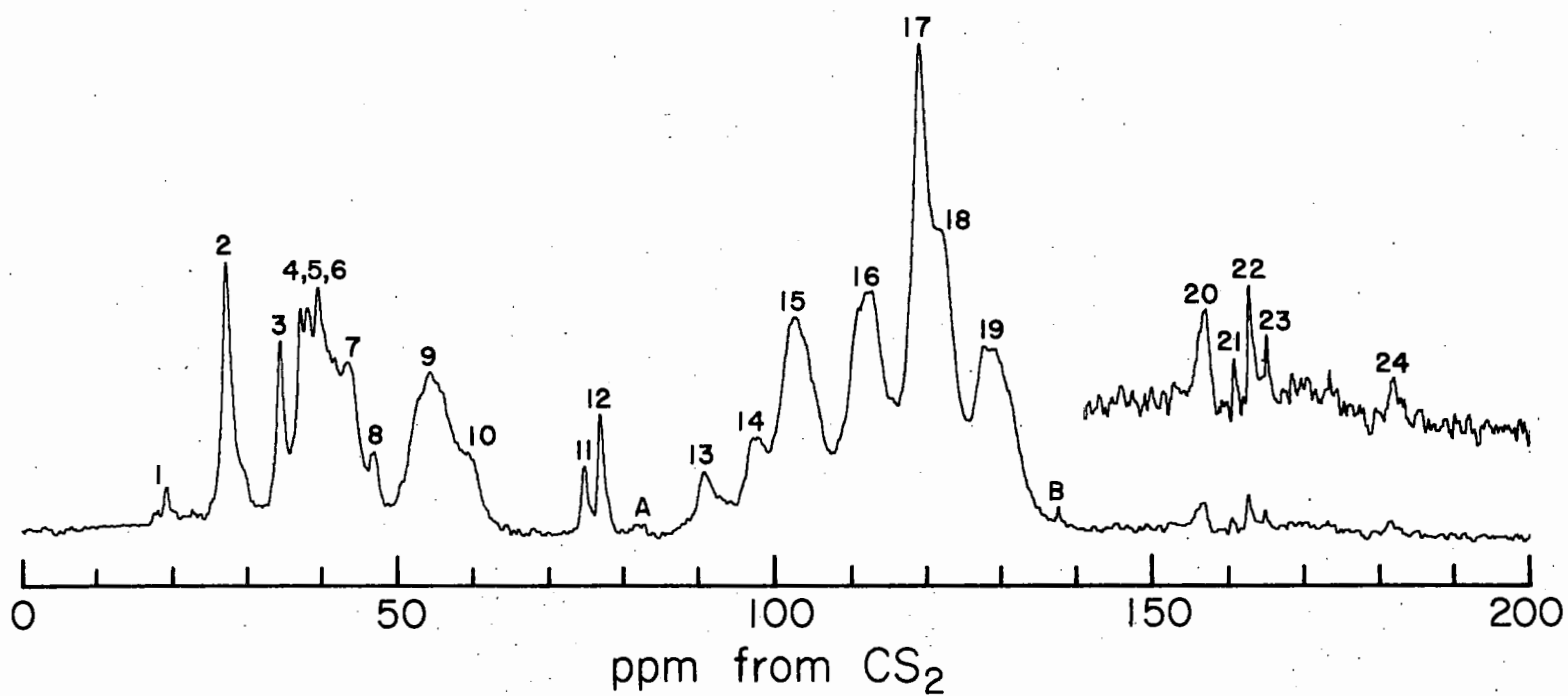


Fig. 1

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DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

November 5, 1973

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

Quantitative Use of Lanthanide Relaxation Reagents

Dear Barry,

We have become interested recently in the potential use of relative nuclear relaxation times and linewidth as a technique for extending the capabilities of lanthanide reagents for effecting solution structural determinations. After completing a preliminary investigation on a series of model compounds, we have concluded that relative relaxation rates or linewidths are useful only when magnetically isotropic lanthanides (i.e.,  $\text{Eu}^{+2}$ ,  $\text{Gd}^{+3}$ ) are used.

The basis for our conclusions is as follows. Using the dipolar relaxation equations for an axially anisotropic paramagnet,<sup>1</sup> the relative linewidths,  $\delta$ , for two non-equivalent protons in a rigid lanthanide reagent-substrate complex ( $\text{Ln}(\text{DPM})_3\text{-S}_2$ ) are given by

$$\frac{\delta_i}{\delta_j} = \frac{r_i^{-6}}{r_j^{-6}} \frac{[\bar{\chi} + \chi_{||} \cos^2\theta_i + \chi_{\perp} \sin^2\theta_i]}{[\bar{\chi} + \chi_{||} \cos^2\theta_j + \chi_{\perp} \sin^2\theta_j]},$$

where  $r$  is the Ln-H, distance,  $\theta$  the angle between the  $r$  vector and the unique axis,  $\bar{\chi}$  the average susceptibility and  $\chi_{||}$  and  $\chi_{\perp}$  the two components of the susceptibility tensor. In a pyridine-type substrate, the known molecular structure yields

$$\frac{\delta_o(\text{o-H})}{\delta_p(\text{p-H})} = \frac{r_o^{-6}}{r_p^{-6}} \frac{[\bar{\chi} + 0.67 \chi_{||} + 0.33 \chi_{\perp}]}{[\bar{\chi} + \chi_{||}]}$$

This equation predicts that for lanthanide reagents which cause upfield shifts ( $\chi_{\perp} > \chi_{||}$ ),

$$\frac{\delta_o}{\delta_p} > \frac{r_o^{-6}}{r_p^{-6}},$$

while for downfield shift reagents ( $\chi_{||} > \chi_{\perp}$ ),

$$\frac{\delta_o}{\delta_p} < \frac{r_o^{-6}}{r_p^{-6}},$$

Since  $\chi_{||} = \chi_{\perp}$  for  $Gd^{+3}$ , we expect

$$\frac{\delta_o}{\delta_p} = \frac{r_o^{-6}}{r_p^{-6}},$$

which is in agreement with experiment.<sup>2</sup> However, we find, for example, that for the downfield reagent  $Er(dpm)_3$ ,

$$\frac{\delta_o}{\delta_p} \approx 23,$$

while for the upfield reagent,  $Dy(dpm)_3$ ,

$$\frac{\delta_o}{\delta_p} \approx 13.$$

In general, there is no relationship between the sign of the dipolar shift (anisotropy) and the direction of the deviation of the linewidth ratio from that for  $Gd(dpm)_3$ .

Preliminary theoretical considerations indicate that the difficulty arises from the assumed axial symmetry. The shift reagent complexes are known to exhibit rhombic anisotropy. Though the rhombic anisotropy averages to axial anisotropy as far as the shift is concerned,<sup>3</sup> the effect of rhombic anisotropy is retained in the relaxation terms. This suggests that linewidth analyses using anisotropic lanthanide ions are not likely to be useful unless the susceptibility tensor for the complex is known in detail. More experimental data will be available in a preliminary note which has been submitted for publication.

Sincerely yours,



Gerd N. La Mar  
Associate Professor of Chemistry

1. H. Sternlicht, J. Chem. Phys., 42, 2250 (1965).
2. G. N. La Mar and J. W. Faller, J. Amer. Chem. Soc., 95, 3817 (1973).
3. J. Briggs and E. W. Randall, Chem. Commun., 1180 (1972).



DEPARTMENT OF CHEMISTRY

RIVERSIDE, CALIFORNIA 92502

November 12, 1973

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

Title: An Inexpensive Solid-State 50 Watt 60 MHz Tuned Power Amplifier

Dear Professor Shapiro:

We would like to submit the accompanying circuit diagram of an inexpensive solid-state 50 watt, 60 MHz tuned power amplifier as our tardy contribution to TAMUNMR. We have used this amplifier for several months for proton noise decoupling with essentially no trouble.

The heart of the amplifier is the 2N3375 medium power transistor (Motorola, 8-10 watts) and the 2N3950 high power transistor (Motorola, ~50 watts). The first three amplifier stages are constructed using three conventional low power, high frequency transistors. As designed, an approximately 50 mv 60 MHz input is sufficient to drive the output to 50 watts (nominal).

Inductors L1, L2, L3, and L4 were constructed of 4 turns of #28 wire with 1/8" diameter slug tunable cores. Inductors L5 and L7 are 4 or 5 turns of #12 wire with 1/4" radii; air core. Inductor L6 is essentially a section of connecting wire with an inductance of less than 1  $\mu$ H.

The three low-power amplifier stages are built in individual small chassis boxes with minimum length feed-through connectors to minimize pick-up of the output radiation. The input to 2N3375 and coil L5 are shielded from the output of 2N3950 by means of a metal partition.

The medium and high-power transistors are mounted directly on a 1/8" thick copper plate (which serves as the front panel of the amplifier) for maximum heat dissipation. All other elements are mounted on this copper plate. The tuning and gain controls are accessible from the front of the amplifier. Output impedance is 50 ohms. No provision is made for overload protection so it is suggested that a SWR meter be placed in the output line to monitor matching to the load.

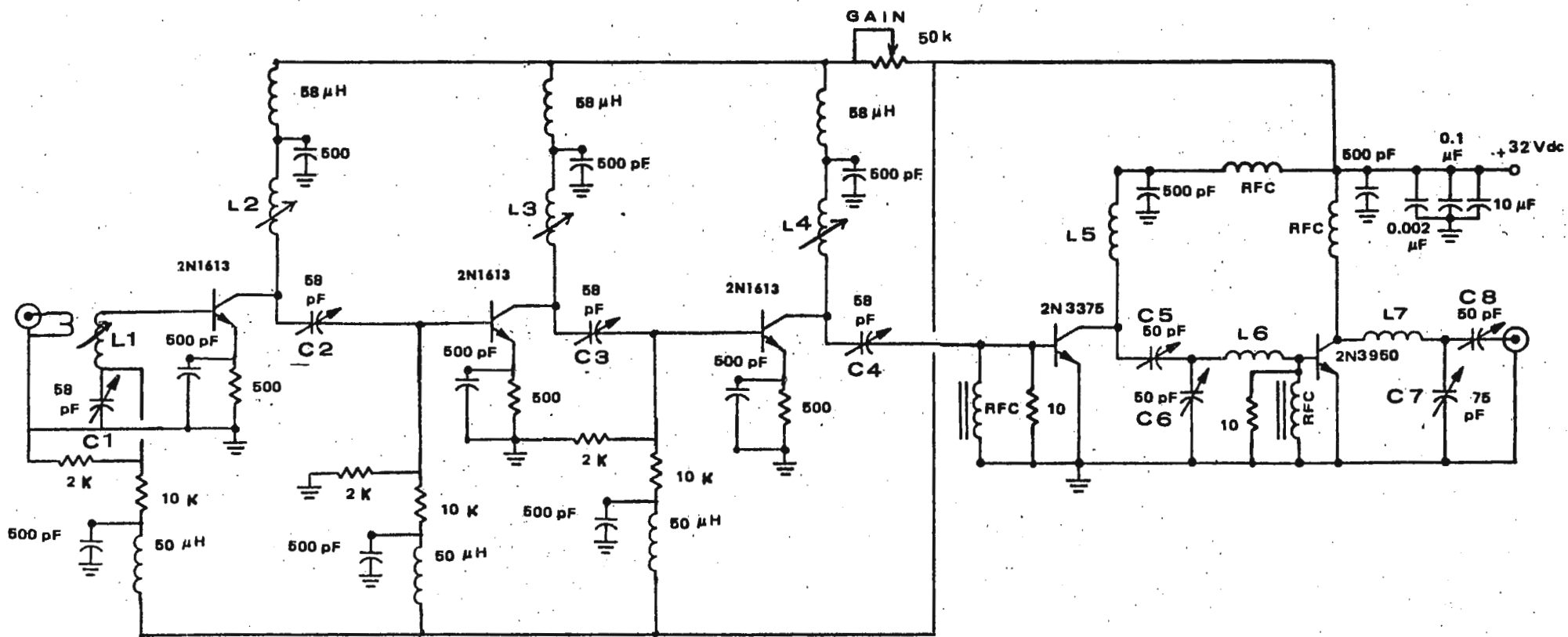
Please credit this contribution to Professor Janes L. Sudmeier, University of California, Riverside.

Sincerely,

Phillip D. Curb

William Hagstrum





# THE PENNSYLVANIA STATE UNIVERSITY

152 DAVEY LABORATORY  
UNIVERSITY PARK, PENNSYLVANIA 16802

College of Science  
Department of Chemistry

November 13, 1973

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

Dear Professor Shapiro,

Effect of Saccharides on the  $H_2O$  Proton  
Relaxation Rates of Mn(II)-Concanavalin A

I have been studying solvent interactions in solutions of the Mn(II) containing protein Concanavalin A (which binds saccharides) at a variety of frequencies (6-100MHz) and temperatures (1-50°). The purpose of these studies is to understand the underlying physical mechanisms which lead to the observed paramagnetic effect of the protein bound Mn(II) on the solvent proton relaxation rates ( $T_1$  and  $T_2$ ).

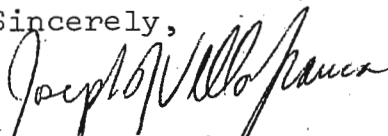
I have observed that the life time of solvent molecules ( $\tau_m = 1.9 \mu\text{sec}$ ) from the primary coordination sphere of Mn(II) is the dominant relaxation process at low frequencies (6-24MHz) but at 100 MHz this contribution is equal to about one half of the observed paramagnetic effect of the longitudinal relaxation rate ( $1/pT_{1p}$ ).

From some of my other  $^{13}\text{C}$  studies, the distance between the "ring" of  $\alpha$ -methyl glucoside and the concanavalin A bound Mn(II) is  $\sim 10\text{\AA}$ . This means that the bound saccharide is clearly not in the primary coordination sphere of Mn(II). However, when the solvent proton relaxation rates are measured in the presence of a variety of saccharides, the values of  $1/pT_{1p}$  are lower (up to 30%). A correlation has been found between the %, decrease in  $1/pT_{1p}$  and the dissociation constant of various saccharides, with the more strongly bound saccharides giving the largest effect. No correlation was obtained between length of saccharide (mono, di or trisaccharide) and decrease in  $1/pT_{1p}$  with the same decrease being found with mono- and trisaccharides which have the same  $K_D$  value.

From a frequency and temperature dependence study, the decrease in the relaxation rate is due to a change in  $q/\tau_m$  where  $q$  is the number of water molecules. These results suggest to us that a saccharide can bind  $\sim 10\text{\AA}$  from a metal ion and induce a change in the protein

conformation which results (in this case) in a lengthening of the residence time or a decrease in the "effective" number of water molecules interacting with the metal ion. We are pursuing these studies solvent relaxation rate studies along with more  $^{13}\text{C}$  studies on this very interesting Mn(II) containing protein.

Sincerely,



Joseph J. Villafranca  
Assistant Professor  
Department of Chemistry  
152 Davey Laboratory  
The Pennsylvania State University  
University Park, Pa. 16802

JJV/mlb

P.S. Preprints available upon request.

DEPARTMENT OF THE AIR FORCE  
 AIR FORCE MATERIALS LABORATORY (AFSC)  
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REPLY TO  
 ATTN OF: AFML/LPH (R. E. Rondeau/513-255-2280)

13 Nov 1973

SUBJECT: Liquid Crystals & Shift Reagents

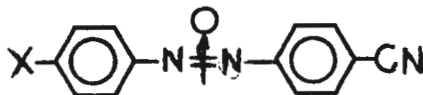
TO: Dr. Bernard L. Shapiro  
 Department of Chemistry  
 College of Science  
 Texas A & M University  
 College Station, Texas 77843

Dear Dr. Shapiro:

Here is my belated contribution to the Newsletter.

We have been restricting our NMR work to liquid crystals in general and to nematic materials with a positive dielectric anisotropy in particular. Nematic PDA systems can be pre-aligned in a sandwich cell and thus can be operated in a field effect mode. This type of operation makes for lower voltage threshold, better contrast and improved response times.

The systems we've been looking at are the type:



where X = R, RO, RCOO, ROCOO and R is varied from C<sub>1</sub> to C<sub>7</sub>.

In addition to obtaining their crystal → nematic and nematic → isotropic transition points, lanthanide shift reagents have been used before with azoxybenzene liquid crystals with a negative dielectric anisotropy (JACS, 94, 1096 (72)).

In the course of this work, we didn't stick to one particular LSR but used several until we found the best one for a class of compounds. For instance, for the X = CH<sub>3</sub>OCO - and X = CH<sub>3</sub>COO - compounds, Dy(fod)<sub>3</sub> is much, much more effective than Eu(fod)<sub>3</sub> in separating the methyl resonance of the two isomers.

In the case of X = alkyl, however, neither the Eu(fod)<sub>3</sub> nor the Dy(fod)<sub>3</sub> worked. For this substrate we synthesized a new shift reagent, tris (1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptenedionato) europium (III), which worked like a charm.

Sincerely,

*Roger E. Rondeau*

ROGER E. RONDEAU  
 Chemical-Physics Branch  
 Electromagnetic Materials Division



# Oklahoma State University

Department of Chemistry / (405) 372-6211, Ext. 7215 / Stillwater, Oklahoma 74074

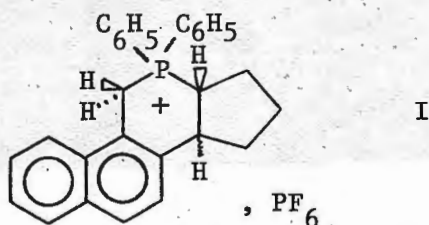
November 13, 1973

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

Title:  $^1\text{H}$  Spectrum of a Phosphasteroid System

Dear Dr. Shapiro:

We have recently prepared the first 12-substituted phosphasteroid compound I,



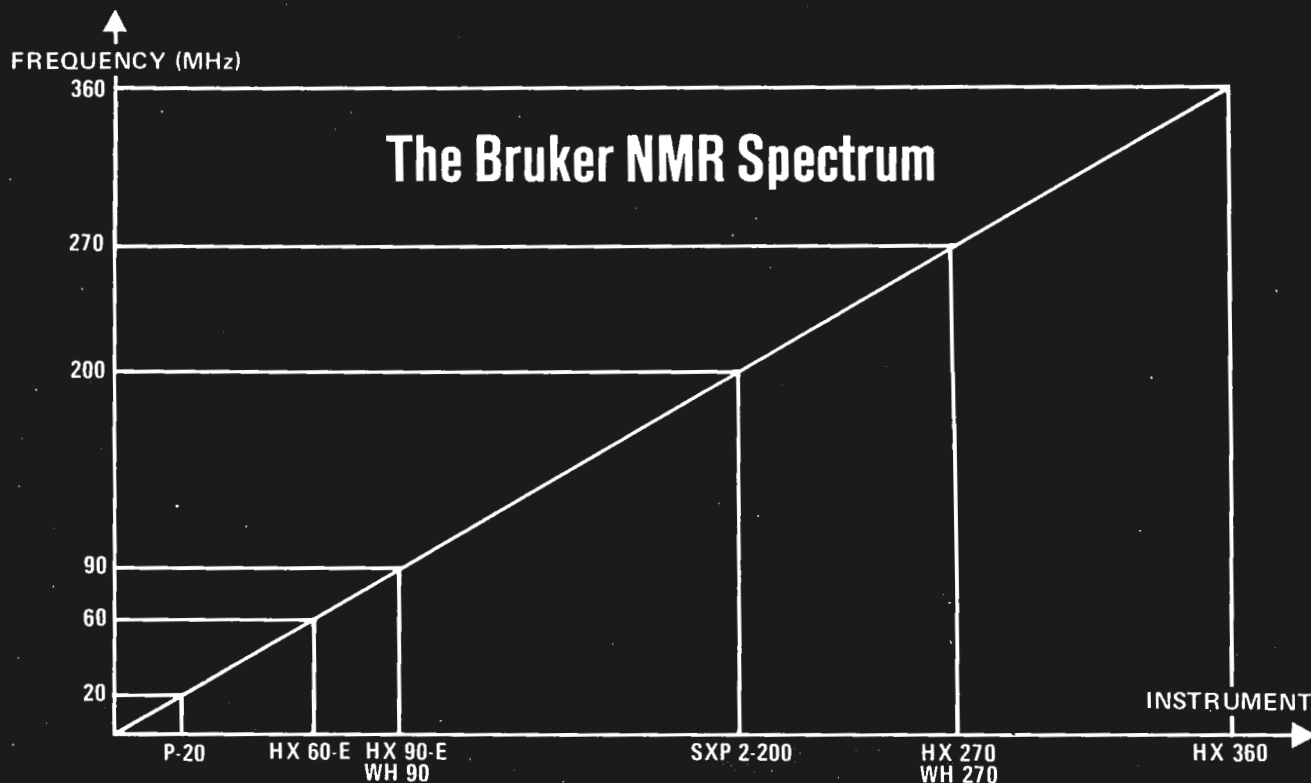
a very rare class of C-P heterocycles. Although crystalline and sharp melting, extensive  $^1\text{H}$ - $^1\text{H}$  and  $^1\text{H}$ - $^{31}\text{P}$  coupling has prevented determination of the geometric relationship of the bridgehead protons. In pyridine- $d_5$  the spectrum is reasonable:  $\delta$  2.04-3.00 (m, 6H,  $\text{CH}_2$  protons in cyclopentyl ring); 3.80 (bm, 1H, Ar- $\text{CH}$ ); 4.26 (bm, 1H, P- $\text{CH}$ ); 5.00 (t, 1H,  $J_{\text{PCH}} = 15.5$  Hz, Ar $\text{CH}_2\text{P}$ ); 5.62 (t, 1H,  $J_{\text{PCH}} = 17$  Hz, Ar $\text{CH}_2\text{P}$ ); and 7.12-8.96 (m, 16H, arH). Heteronuclear  $^{31}\text{P}$  decoupling caused a collapse of the triplets at  $\delta$  5.00 and 5.62 to give two doublets ( $J_{\text{PCH}} = 17$  Hz). Homonuclear  $^1\text{H}$ - $^1\text{H}$  homonuclear decoupling gave  $J_{\text{PCH}} = 16$  Hz. Work is continuing in this area.

Sincerely yours,

*K D Berlin*

K. D. Berlin  
Regents Professor

# NMR



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Department of Chemistry

The Florida State University  
Tallahassee, Florida 32306

November 6, 1973

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

SUBJECTS: NMR SPECTROSCOPY AT FLORIDA STATE UNIVERSITY  
BRUKER HX-270 SPECTROMETER; SPIN-LATTICE  
RELAXATION MEASUREMENTS ON SINGLE COIL SPECTROMETERS

Dear Barry:

This, my first, contribution from Florida State University (along with a suitable cash payment) should bribe you into sending issues for another year. A few observations follow from my first months at FSU.

## NMR SPECTROSCOPY AT FLORIDA STATE UNIVERSITY

Our nmr facilities consist of (a) Brüker HFX-90, (b) Brüker HX-270—just installed, and (c) Varian A-60 spectrometers. The two Brüker spectrometers have dedicated Nicolet 1080 series computer systems. The HX-270 has the super 1089 with 36K core and 600K disc. The larger Nicolet computer system has proven versatile in  $^{13}\text{C}$  and  $^1\text{H}$  usage. Both Brüker spectrometers are operated in FT and CW modes.

## THE BRÜKER HX-270 SPECTROMETER

After initial teething troubles the first complete U. S. Brüker FT HX-270 has indicated some of its tremendous capabilities. Resolution for  $^1\text{H}$  and  $^{13}\text{C}$  are both excellent. We have observed 0.11 Hz in 5mm tubes at 270 MHz ( $^1\text{H}$ ) and better than 0.5 Hz with 10mm tubes at 67.9 MHz ( $^{13}\text{C}$ ). The pulsed  $^2\text{H}$  lock system works superbly. Our  $^{13}\text{C}$  and  $^1\text{H}$  probes have not incorporated all new advances but we are getting good sensitivity. A 37 minute accumulation for 0.04 M sucrose in a 10mm tube is shown below. The S:N of this spectrum is ca. 35% lower than reported by Allerhand, *et al.* (see November 1972 *American Laboratory*) for a 20mm tube. We reckon that our present sensitivity should be ca. 30-50% higher after appropriate modifications of our probe design are made (but we are already doing pretty well!).

Proton operation on the HX-270 is also excellent. We have been using the various modes of  $^1\text{H}$  homonuclear decoupling (in CW and FT nmr); the pulse mode is very convenient.

# SPIN-LATTICE RELAXATION MEASUREMENTS ON SINGLE COIL SPECTROMETERS

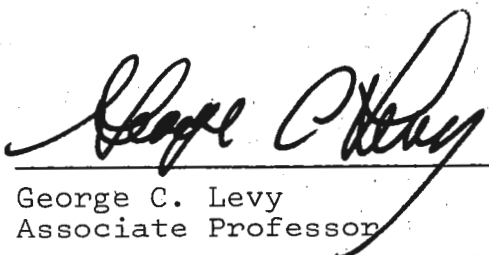
-(Finally some real science)

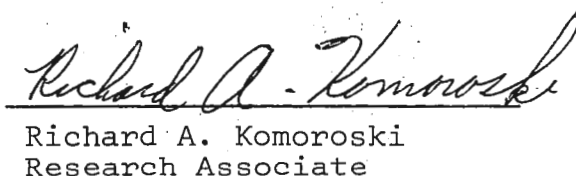
For those of you initiating forays into the world of  $T_1$ 's—some advice on sample geometry. It is important that the sample not extend too far outside the effective coil height since diffusion effects can result in anomalously low  $T_1$ 's for carbons determined by inversion-recovery pulse sequences (The same could be true for other sequences also). The effect will be most significant for nuclei with long  $T_1$ 's when measurements are done on single coil instruments (small coil). Frank Anet has observed an apparent  $T_1$  of as short as 65 sec for the C-1 carbon of toluene (degassed) in a normal sample configuration. That observed  $T_1$  was  $\sim 85$  sec for a small sized sample kept inside the coil (F. A. L. Anet and O. Yamamoto, unpublished results).

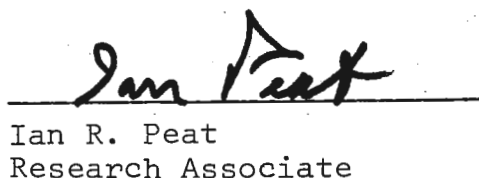
Below we report  $T_1$ 's for toluene (10% acetone- $d_6$ , undegassed) samples of different heights obtained on our HX-270 at  $\approx 40^\circ$  and 67.9 MHz (The coil height is ca. 16mm). For calibration, the expected values (G. C. Levy, Chem. Comm., 1972, 47) are also shown:

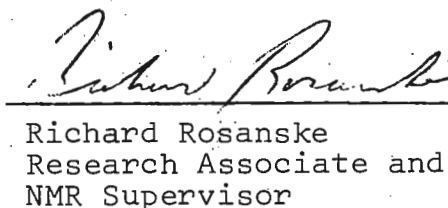
CARBON	CROSS COIL, 25 MHz	$T_1$ (sec, 67.9 MHz)[ $\pm 5\%$ ]						Sample height(mm)
		M*	14	19	24	29	45	
C-1	55	52.5	51.0	48.0	51.0	49.0	43.0	
C-2, C-3	22	19.1	23.0	21.8	22.0	22.2	20.8	
C-4	17	16.7	17.5	18.0	19.0	18.5	18.5	

\*microcell, 9.5mm,  $T_1$ 's  $\pm 10-15\%$

  
George C. Levy  
Associate Professor

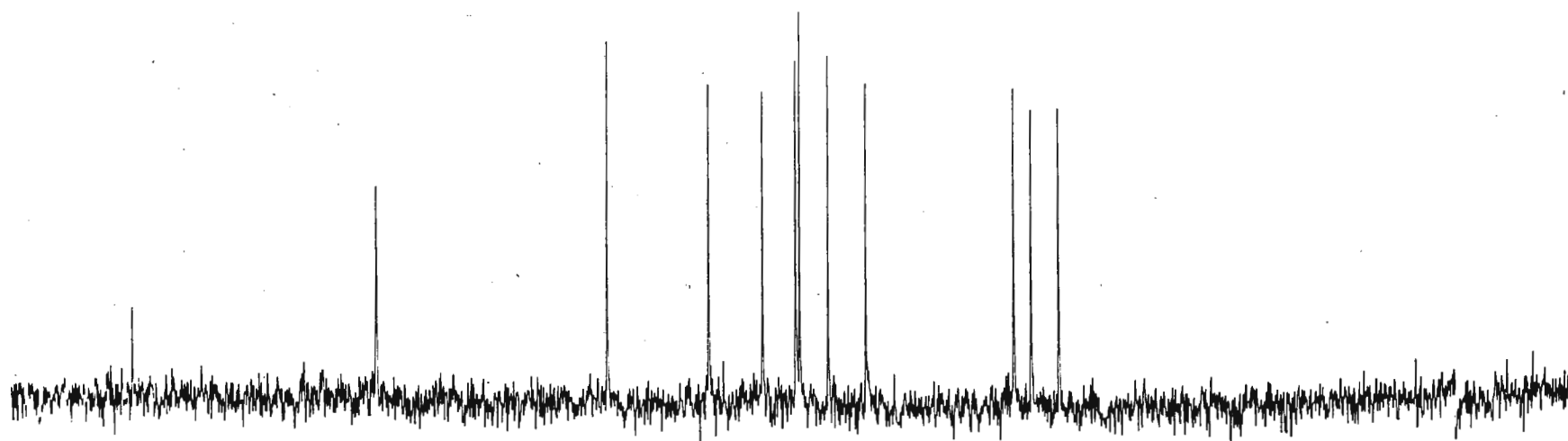
  
Richard A. Komoroski  
Research Associate

  
Ian R. Peat  
Research Associate

  
Richard Rosanske  
Research Associate and  
NMR Supervisor



0.04 MOLAR SUCROSE 1024 SCANS; 37 MINUTES  
SPECTRAL WIDTH 5,000 Hz (74 PPM) 16K TRANSFORM



# UNIVERSITY of PENNSYLVANIA

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## *The School of Medicine*

JOHNSON RESEARCH FOUNDATION  
DEPARTMENT OF  
BIOPHYSICS AND PHYSICAL BIOCHEMISTRY

November 16, 1973

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

### Conversion of DP-60 to FT

Dear Barry:

We wish to describe the modification of an old Varian DP-60 NMR spectrometer to a pulsed (FT) spectrometer. For data acquisition and processing we selected a Varian 620L computer equipped with 12k words of memory, a dual 10/14 bit Digital to Analog converter (DAC) and a 14 bit analog to digital converter (ADC) with an 8 channel multiplexer and a digital I/O module. This configuration provides 8 sense and 8 one bit logic output lines for controlling the various operations of the spectrometer.

The modification proceeded along three lines:

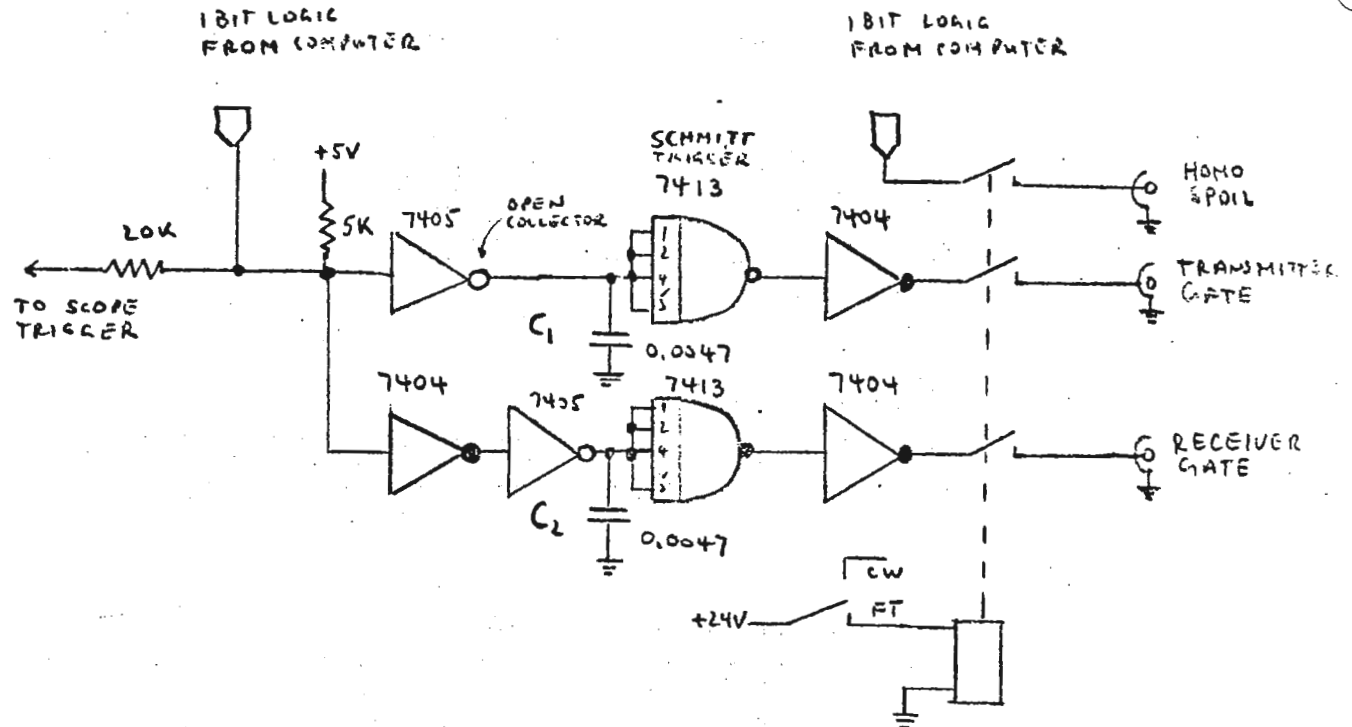
- a) the conversion of the 4311 transmitter/receiver unit for pulsed operation and the development of a "hi-power", solid state RF amplifier.
- b) construction of an interface between the computer and the spectrometer.
- c) development of software.

The V-4311 transceivers were modified by gating both the transmitter and receiver. (see the accompanying diagram). The gate inputs are TTL compatible and are arranged so that with an open input the transmitter and receiver are both turned on permitting normal CW operation when the unit is disconnected from the computer. 60 MHz RF is derived ahead of the transmitter gate and supplied through a buffer amplifier to the lock transmitter to permit the use of the Varian V-4357 external reference proton stabilization controller during both pulsed and CW operation. The external lock was found to operate satisfactorily during pulsed operation. At best the V4311 transmitter develops 6 volts peak to peak across a 50 ohm load. In order to get a reasonable rf field level we made a solid state amplifier which produces 70 volt pulses across 50 ohms. This results in a 90° pulse length of 82  $\mu$  sec.

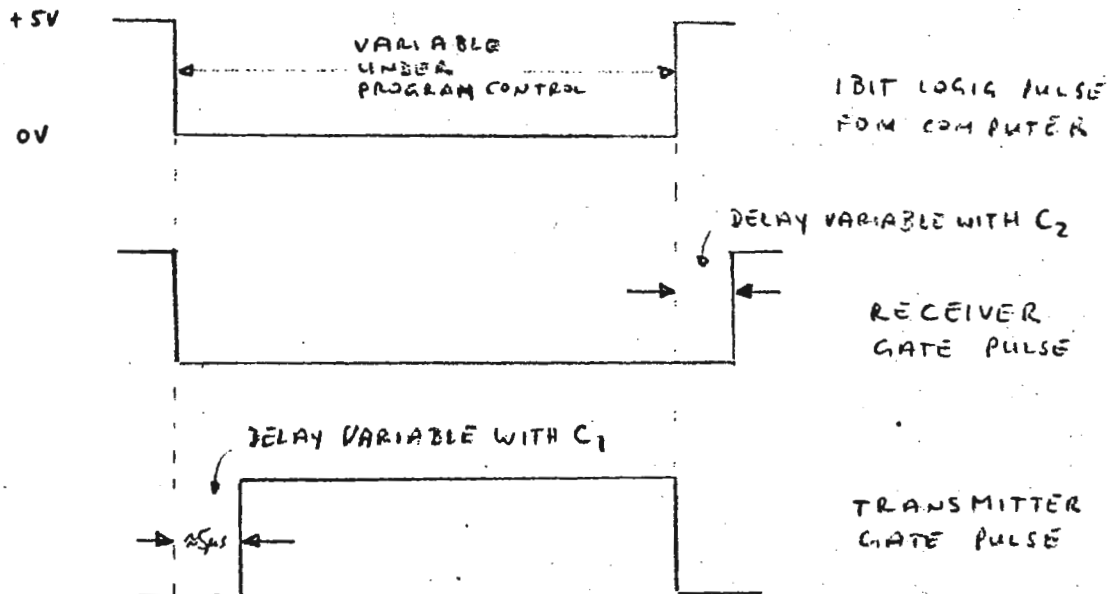
The computer-spectrometer interface involved conditioning the signal from the receiver before passing it to the ADC. The output from the receiver cathode follower output rides at +26 volts. The signal which may range from several



## LOGIC CIRCUIT FOR GATE SIGNALS



## TIMING DIAGRAM FOR GATE SIGNALS





millivolts to several volts must be DC coupled to the ADC. The interface contains an operational amplifier with adjustable offset and gain controls. An RC filter provides an enhancement of the signal to noise ratio.

In order to avoid using two external control lines from the computer to gate the transmitter and receiver TTL logic was used to provide both pulses with one input. The transmitter remains on and the receiver off until the computer line is turned off at which time the transmitter is shut off first and then the receiver is turned on.

The interface provides one switch conversion from CW to FT operation with the following automatic operations:

- it connects the hi-power amplifier in line between the probe and the transmitter.
- it switches the transceiver to the pulsed mode of operation.
- it disables the 2 KHz field modulation, the linear field sweep unit and the recorder field sweep.

Another switch overrides all except the computer scope input, routing the free induction decay signal and a trigger pulse to the scope.

A standard 10000 step Varian MARS recorder replaced the old synchronous motor driven recorder. The MARS recorder requires four inputs for remote operation: a remote override, a right or left movement enable, a clock pulse and a pen-down enable. To make efficient use of the eight computer external control lines, hardware logic was provided so that setting either the left or right line would also set the remote override line. One line is used to transfer the scope inputs from the spectrometer to the DACs, however when the recorder is enabled, the y axis signal is diverted to the recorder and the scope spot is deflected off the screen.

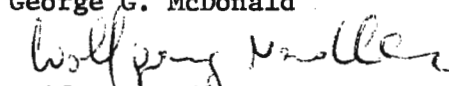
The computer program was prepared by modifying an existing Varian FT program designed to work in a 16k computer. The modification includes reducing the data table size, changing the fast fourier transform routine to operate on a smaller data table and changing the device codes to conform with the new equipment configuration.

This obviously is not the only way one might update an old instrument but it does represent a viable approach to the problem.

Details for any of the modifications will be supplied upon request.

Sincerely,

  
George G. McDonald

  
Wolfgang Nadler

GM:jtc

Credit this contribution to the account of Mildred Cohn



## UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

Department of Chemistry  
(803) 777-5263

November 19, 1973

Professor Barry Shapiro  
1101 Merry Oaks  
College Station  
Texas 77840

Title: Homo-Spoil  $T_1$  Measurements on an XL-100

Dear Barry:

Hopefully this will stop the pink letter barrage. We would like to describe another method to measure  $T_1$ 's on an XL-100. This sequence is a Homo-Spoil modification to the standard Varian  $T_1$  software package, i.e.

old pulse sequence:  $\{PD-P1-\tau-P2-AT\}_n$

new pulse sequence:  $\{PD-P1-HS-\tau-P2-AT-HS\}_n$ .

Here P1 and P2 denote the various rf pulses and HS represents a Homo-Spoil pulse given to the Z-axis shim coils, the remaining symbols have their usual meanings.

If  $P1 = 180^\circ$  pulse and  $P2 = 90^\circ$  pulse, the new sequence can be used as a spin echo suppressed  $180^\circ-\tau-90^\circ$  pulse sequence. If, on the other hand, we have  $P1 = P2 = 90^\circ$  pulses and  $PD = 0.0$ , then the resulting pulse sequence,  $90^\circ-\tau-90^\circ$ , is a version of the sequence introduced by Markley, Horsley and Klien.<sup>1</sup> The "new" sequence is identical to that reported by McDonald and Leigh.<sup>2</sup> The relative benefits of this new sequence compared to the  $180-\tau-90$  sequence has been discussed by both groups, but in a somewhat contradictory style (with regard to the relative timing advantages). However, we would like to show the interested readers how to do the experiment and answer some potential questions about this method.

In Figure 1 is a schematic diagram of the necessary modifications to do the Homo-Spoil sequence described by McDonald and Leigh. Please note that EXC 235 and EXC 335 commands are computer dependent neumonics. Furthermore, the length of the Homo-Spoil pulse may vary depending on the particular spectrometer.

For this pulse sequence to work properly (give the "correct" value of  $T_1$ ) the induced value of  $T_2^*$  must be sort of compared to  $T_1$ , i.e.  $T_2^* \ll T_1$ . This condition can not be fulfilled with just any Homo-Spoil timer word. We have found that on our system a timer word of approximately 20 msec is sufficient to measure a  $T_1$  of

1 sec or longer. It is necessary to point out that this timer word length is not sufficient for a  $T_1$  of approximately 0.4 sec. That is, one would get excellent  $T_1$  plots with just the wrong slope (compared to the value obtained by 180- $\tau$ -90 sequence). It is therefore essential for each user of this sequence to determine his own correct value of the timer word for his system.

Another point of interest is: What happens to the homogeneity after the Homo-Spoil pulse? This can be answered by examining a narrow resonance ( $\approx 1$  Hz) shortly after the Homo-Spoil pulse ( $\tau = .1$  sec). Figure 2 shows two superimposed spectra of TMS. The first trace is the result of an 180- $\tau$ -90 experiment with  $\tau = 0.1$  sec (sweep width: 25 Hz). Superimposed on this trace is the Homo-Spoil version of the 180- $\tau$ -90 sequence. They are essentially the same, and hence there is no apparent degradation of the homogeneity after waiting a 0.1 sec after the application of the Homo-Spoil pulse. It should be pointed out that this experiment (or its equivalent) should be attempted by any interested user. The main reason being that the "center of gravity" of the Z-axis Homo coils may not correspond to the center of the receiver coil, and hence there may be a field shift and a subsequent field splitting after the Homo-Spoil pulse.

Details as to an error analysis and the level of agreement of this method vs the standard methods, and timing considerations will be given at a later time.

With regards,

Sincerely yours,



Charles S. Peters  
Varian Associates



Paul D. Ellis  
Assistant Professor of Chemistry

PDE/bc

#### References

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

# HOMO-SPOIL MODIFICATION FOR A VARIAN 620I/XL-100-15

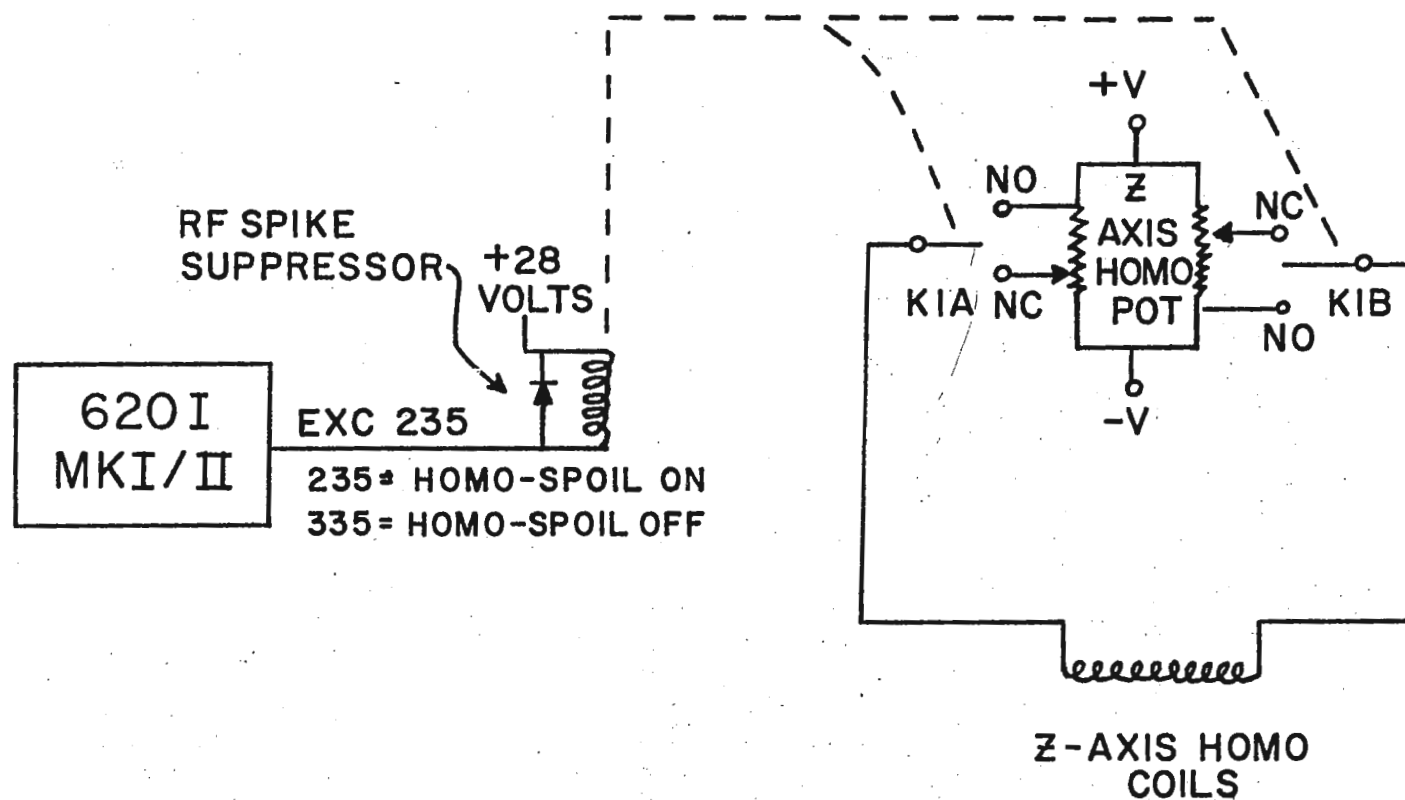


FIGURE I

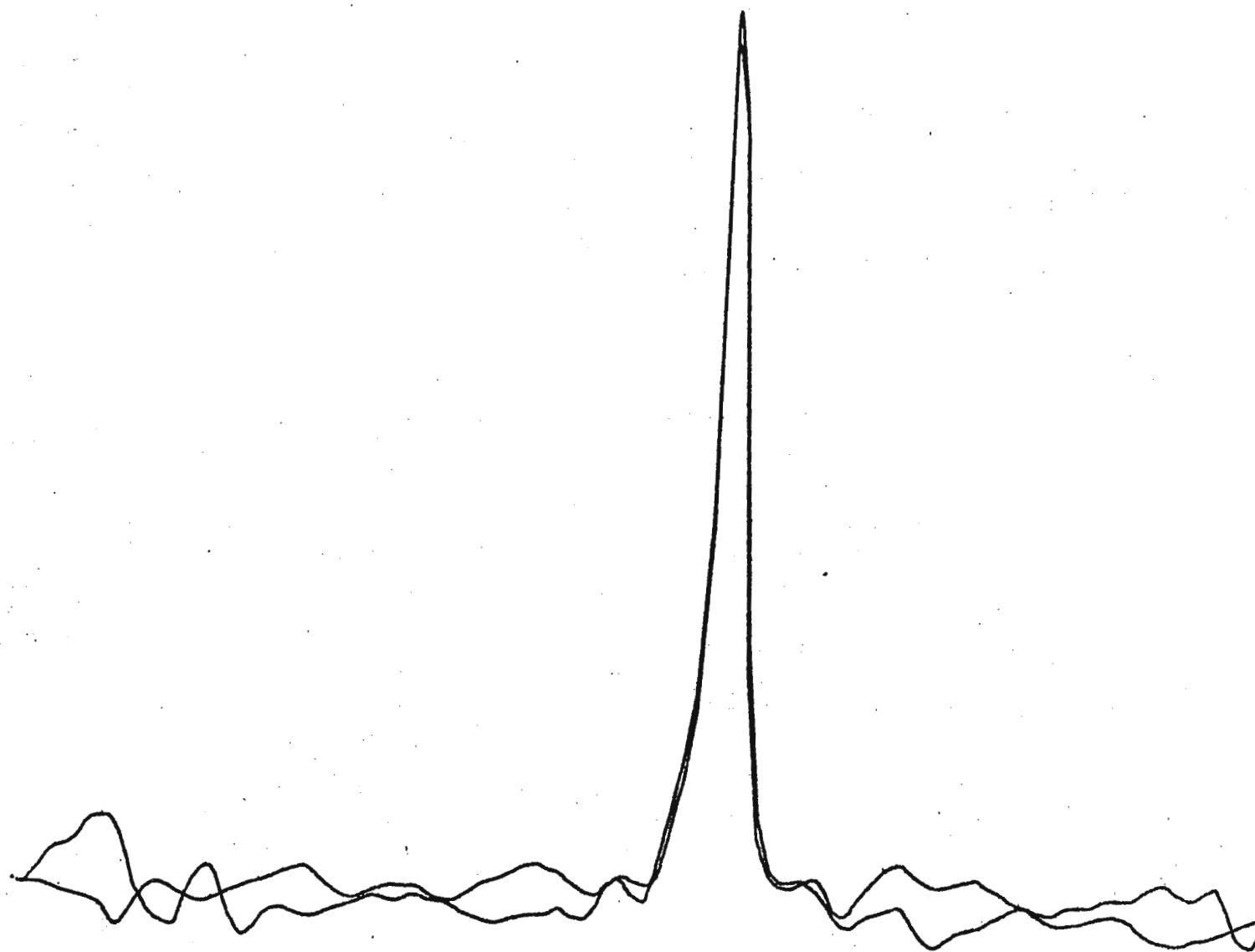


FIGURE II

# the Nicolet 1020A is a time averaging system for magnetic resonance spectrometers that gives you results like these:

The Nicolet 1020A is an easy-to-use time averaging system combining unique data processing capabilities with extremely useful display and readout routines.

Using a normalized signal averaging method, the 1020A presents a true average on its built-in 5" CRT display. The complete spectrum (or any expanded portion of it) is continuously displayed throughout the averaging process.

Thumbwheel switches select sweep times from 60 milliseconds to 1,999 seconds for a 2048-word sweep with 4-digit accuracy. The 1020A can provide sweep current to the spectrometer and can compensate for spectrometer field drift when using the Field Stabilization mode. The calibrated sweep widths are front panel selected and can be matched to any spectrometer.

The analog-to-digital converter (ADC) resolution is 12 bits (one part in 4096) for sweep times over 1 second and 9 bits (one part in 512) for sweep times less than 1 second.

Total memory capacity is 2048 words, 24 bits long. The upper 12 bits store the final average while the lower 12 may be used to store the integral. Averaged spectra may be stored in halves of memory and added to or subtracted from one another.

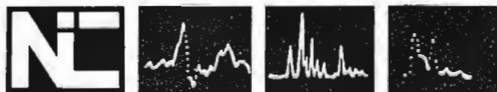
Digital integration is built-in and does not destroy the original spectrum thus allowing simultaneous display of spectrum and integral. Baseline correction can be accomplished during display of the integral to assure optimal results.

Another unique display feature is the ability to expand the displayed spectrum in both the X and Y axes by factors of 2 up to a total expansion of 64 times. (Typical expansion examples are shown to the right). In addition to this analog display a simultaneous numerical display shows the amplitude and address values of any data point selected by a moveable electronic cursor.

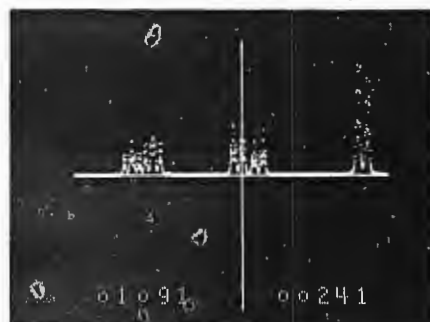
Write or call collect for complete details or to arrange a demonstration in your laboratory.



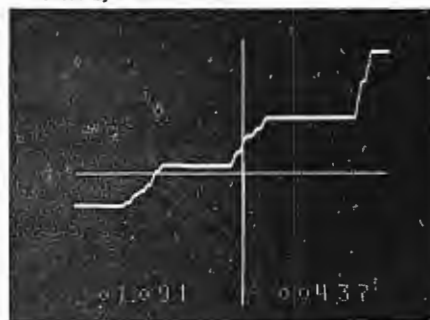
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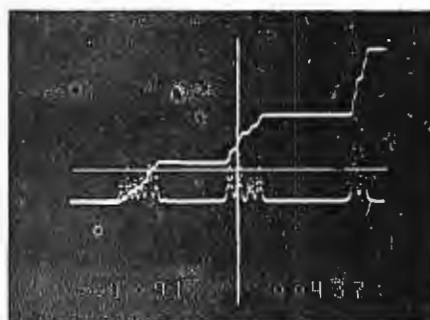
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Phone 608/271-3333 TWX: 910-286-2713



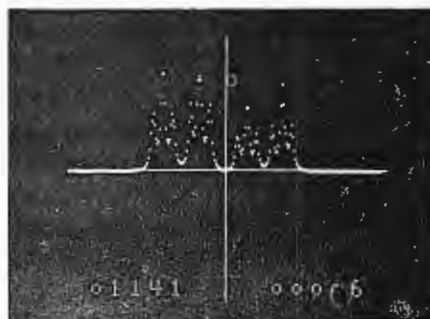
1. Averaged spectrum of 2-butyl-1, 2-dihydropyridene with spectrum expanded on amplitude scale by a factor of 2.



2. Integral of Figure 1 averaged spectrum.



3. Figure 1 spectrum and Figure 2 Integral displayed simultaneously.



4. Averaged spectrum expanded by a factor of 4 on both the amplitude scale and the frequency scale.



5. Integral of Figure 4 averaged spectrum.

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November 21, 1973

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

Dear Barry:

Bound Radicals on Coenzyme-B<sub>12</sub>  
Enzymes Detected by ESR and T<sub>1</sub>  
of Water Protons

In collaboration with Professor Robert H. Abeles and his colleagues at Brandeis University (1, 2), I have been studying the role of radical intermediates in the mechanism of diol dehydrase, an enzyme which utilizes a derivative of vitamin B<sub>12</sub> as a coenzyme. Within 40 msec after mixing the substrate analog chloroacetaldehyde with the enzyme-coenzyme B<sub>12</sub> complex, strong ESR signals, equivalent to 2.0 unpaired electrons per bound coenzyme appear at g values of 2.2 and 2.0 (1). The former were assigned to low spin Co(II) from the coenzyme and the latter to organic radicals derived from the substrate analog and/or the coenzyme (1).

Deuterium substitution in chloroacetaldehyde causes a 5 gauss narrowing and <sup>13</sup>C enrichment causes a 10 gauss broadening of the ESR signals at g = 2.0, but has no effect on the signal at g = 2.2, establishing the presence of spin density on the hydrogen and carbon atoms of the bound substrate analog (2). These results suggest that enzymes which utilize vitamin B<sub>12</sub> coenzymes function by radical mechanisms.

The enzyme-bound radicals exert a detectable but very weak effect on 1/T<sub>1</sub> of water protons at 24.3 MHz amounting to 1% of the effect produced by enzyme-bound spin labels, suggesting that the former are occluded from the solvent. An order of magnitude calculation using the outer sphere equation of Luz and Meiboom (3) indicates a distance of closest approach of ~10Å between water protons and these enzyme bound radicals (1).

Sincerely yours,

*Albert S. Mildvan*

ASM/bh

Albert S. Mildvan

1. Finlay, T. H., Valinsky, J., Mildvan, A. S. and Abeles, R. H. J. Biol. Chem. 248, 1285 (1973).
2. Valinsky, J., Abeles, R. H., and Mildvan, A. S. J. Biol. Chem., in press.
3. Luz, Z. and Meiboom S. J. Chem. Phys. 40, 2686 (1964).



## UNIVERSITY OF CALIFORNIA, BERKELEY

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SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY &amp;

Lawrence Berkeley Laboratory

BERKELEY, CALIFORNIA 94720

November 20, 1973

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

Dear Barry:

Re: Carbon-13 NMR in Organic Single Crystals

High sensitivity, high resolution  $^{13}\text{C}$  nmr in solids is now more or less routine in our laboratory; the main problems are the preparation and orientation of single crystals and the analysis of data. We have determined the  $^{13}\text{C}$  chemical shielding tensors in a number of organic solids, employing both multiple-contact and total cross-polarization versions of proton-enhanced nmr. One series of compounds, containing carboxyl groups, was looked at by Dr. Robert Griffin, visiting us from the National Magnet Laboratory and Dr. James Chang, a postdoctoral fellow in my laboratory. Some interesting trends are beginning to emerge, and these will be discussed in print in the near future. Here I should like to describe an example of the work, to show you the type of spectra we observe and the information extracted.

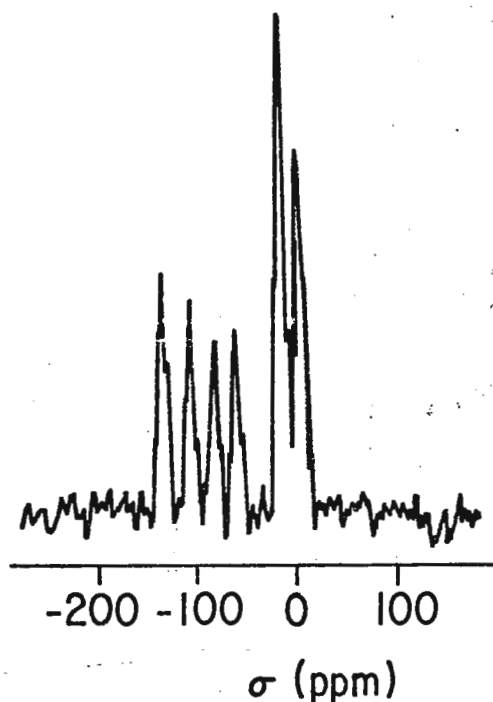
Figure 1 shows a  $^{13}\text{C}$  spectrum obtained by our method from a small single crystal of ammonium tartrate in an orientation with several magnetically inequivalent carbon nuclei; in contrast, only two lines are observed by conventional nmr in isotropic solution. In our case, eight tensors are extracted, by a crystal rotation analysis, from the two molecules in the unit cell, of which only two have different principal values. The others differ only in orientation and can of course be derived from these two by the symmetry operations of the crystal. It is clear that a substantial amount of structural information is available from such studies.

Of particular interest is the manner in which the principal axes of the shielding tensors "sit" on the carbon nuclei. This is shown in figure 2 for the carboxyl carbon of the tartrate ion; it is gratifying that they clearly reflect the local symmetry in the molecule, as we have observed in several other cases, so that crystal effects are small. The shielding values are also interesting and will be reported later.

I challenge my theoretically inclined friends to guess these values before they are published (formate ion might be the simplest prototype).

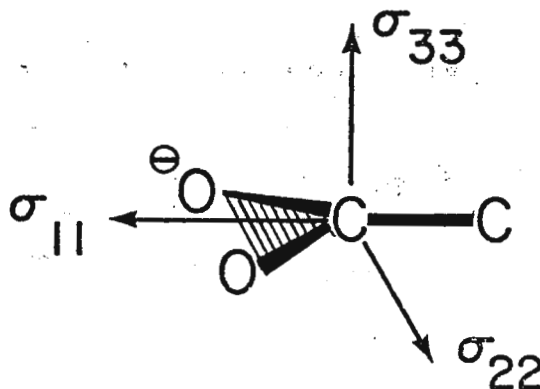
Best regards,

Alex Pines  
Assistant Professor



XBL 7311-6635

Figure 1: Nmr spectrum of single crystal of (D)-ammonium tartrate obtained by Fourier-transformation of proton-enhanced and decoupled  $^{13}\text{C}$  free induction decay. Scale is referenced to liquid methanol.



XBL 7311-6636

Figure 2: Orientation of principal axes of  $^{13}\text{C}$  chemical shielding tensors for carboxyl carbons in tartrate ion of solid ammonium tartrate. The  $^{13}\text{C}$  nucleus is most shielded when  $H_0$  is perpendicular to the  $\text{COO}^-$  plane and least shielded when  $H_0$  is along the C-C bond.

CHEMISCHE LABORATORIA  
DER RIJKS-UNIVERSITEIT

Afd.: Theor. Org. Chemistry  
Wassenaarseweg P.O.Box 75  
Leiden  
Telefoon 4 83 33

Drs. J.A. den Hollander.

LEIDEN, November 19th 1973.

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

Subject: Controlling the Varian FT100 by a PDP-11.

Dear Professor Shapiro,

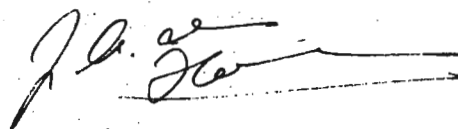
Recently we started using a DEC PDP-11 computer for Fourier Transform NMR on our HA100, equipped with a Varian FT100 pulse unit.

In order to increase the possibilities of this system it is desirable to control both pulsewidth and pulse interval by the computer. We therefore built an interface for the FT-100 which is already operating to our satisfaction. The pulsewidth is generated by a 12 bit counter counting at 2MHz, the pulse interval by a 16 bit counter at 100Hz. Both frequencies are derived from a 2MHz crystal controlled oscillator. At the start of each pulse-interval sequence both counters are loaded from preset-buffers and a processor interrupt can be generated at the end of the r.f. pulse. Both preset-buffers can be loaded by a program. E.g. the interrupt service routine can load the preset buffers without affecting the current sequence. The interface was built by Mr. A. Petersen of the Centraal Reken Instituut of this University.

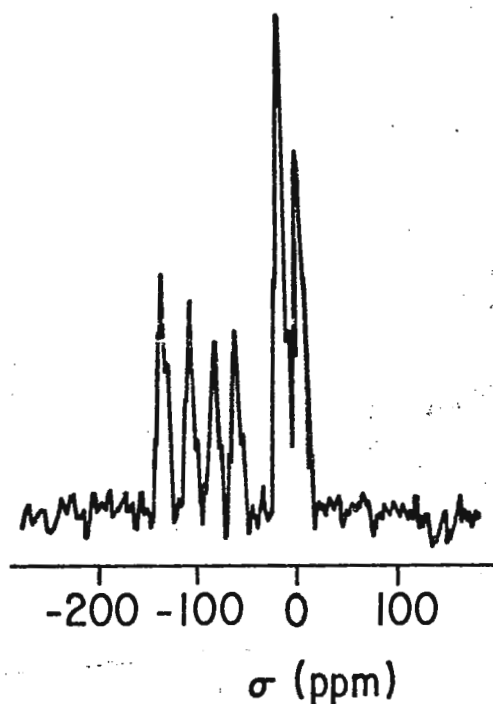
Yours Sincerely,



P.C.M. van Rossum,

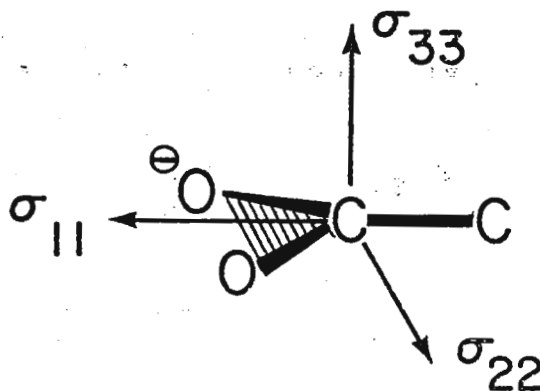


J.A. den Hollander.



XBL 7311-6635

Figure 1: Nmr spectrum of single crystal of (D)-ammonium tartrate obtained by Fourier-transformation of proton-enhanced and decoupled  $^{13}\text{C}$  free induction decay. Scale is referenced to liquid methanol.



XBL 7311-6636

Figure 2: Orientation of principal axes of  $^{13}\text{C}$  chemical shielding tensors for carboxyl carbons in tartrate ion of solid ammonium tartrate. The  $^{13}\text{C}$  nucleus is most shielded when  $H_0$  is perpendicular to the  $\text{COO}^-$  plane and least shielded when  $H_0$  is along the  $\text{C-C}$  bond.

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Afd.: Theor. Org. Chemistry  
Wassenaarseweg P.O.Box 75  
Leiden  
Telefoon 48333

Drs. J.A. den Hollander.

LEIDEN, November 19th 1973.

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

Subject: Controlling the Varian FT100 by a PDP-11.

Dear Professor Shapiro,

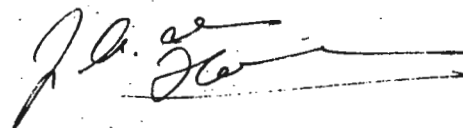
Recently we started using a DEC PDP-11 computer for Fourier Transform NMR on our HA100, equipped with a Varian FT100 pulse unit.

In order to increase the possibilities of this system it is desirable to control both pulsewidth and pulse interval by the computer. We therefore built an interface for the FT-100 which is already operating to our satisfaction. The pulsewidth is generated by a 12 bit counter counting at 2MHz, the pulse interval by a 16 bit counter at 100Hz. Both frequencies are derived from a 2MHz crystal controlled oscillator. At the start of each pulse-interval sequence both counters are loaded from preset-buffers and a processor interrupt can be generated at the end of the r.f. pulse. Both preset-buffers can be loaded by a program. E.g. the interrupt service routine can load the preset buffers without affecting the current sequence. The interface was built by Mr. A. Petersen of the Centraal Reken Instituut of this University.

Yours Sincerely,






P.C.M. van Rossum,



J.A. den Hollander.

Table

No	Compound	$T_c (^{\circ}\text{K})$		$\Delta G_{298.2}^{\ddagger}$ (kcal/mol)	
		ref.1	our data	ref.1	our data
<u>1</u>	 -CONMe <sub>2</sub>	319	320	$17.9 \pm 0.5$	$17.4 \pm 0.2$
<u>2</u>	 -CONMe <sub>2</sub>	298	301	$15.9 \pm 0.5$	$16.3 \pm 0.2$
<u>3</u>	 -CONMe <sub>2</sub>	318	322	$16.6 \pm 0.5$	$16.4 \pm 0.2$

We are still exploring the influence of various factors and error sources on the  $\Delta H^{\ddagger}$ - and  $\Delta S^{\ddagger}$ -values. However, this example proves once more the importance of the  $\Delta G^{\ddagger}$ -values as a only reliable measure of the rotational barrier in amides.

Sincerely yours,

*Stefan Spassov*

S.L.Spassov

V.Dimitrov

M.Agova

I.Kantschowska-Dimicoli

- 1) F.G.Riddell, D.A.R.Williams, J.Chem.Soc.(Perkin II), 587(1973).
- 2) S.L.Spassov, V.S.Dimitrov, M.Agova, I.Kantschowska, R.Todorowa, Organic Magnetic Resonance 2, 551 (1971).

PHYSIKALISCHES INSTITUT  
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Prof.Dr.P.Diehl

Basel, November 20, 1973/ho

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

The structure of trimethylphosphate by "oriented NMR".

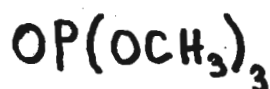
Dear Barry,

Here is a case of a beautiful spectrum, 10-spin system ( $A_3A_3'A_3''X$ ) with total spin, symmetry and lots of subspectra.

Fig. Trimethylphosphate, 12% in EBBA

A. observed

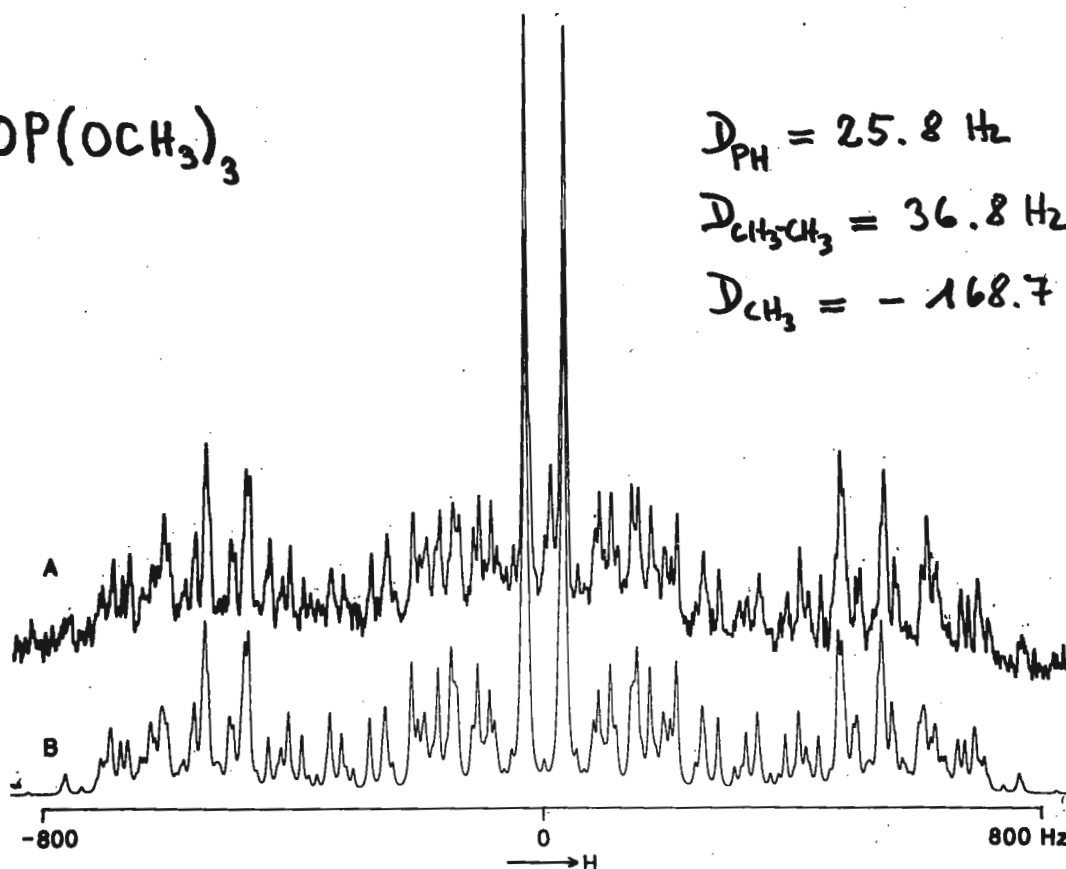
B. calculated



$$D_{PH} = 25.8 \text{ Hz}$$

$$D_{CH_3CH_3} = 36.8 \text{ Hz}$$

$$D_{CH_3} = -168.7 \text{ Hz}$$



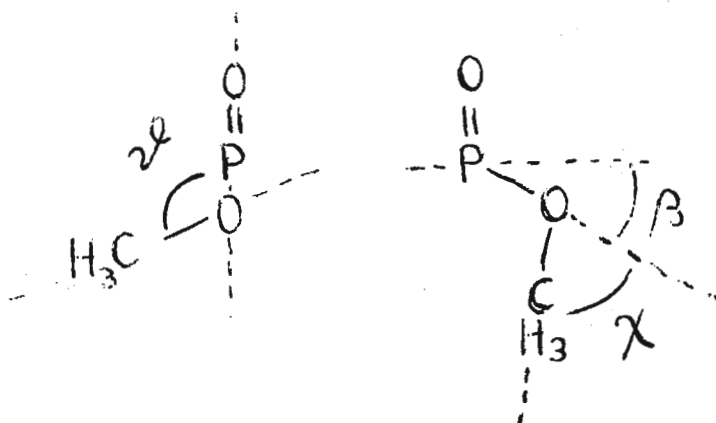


Unfortunately the spectrum does not carry very much information. First of all there are only 3 direct couplings of which one defines the molecular orientation. Secondly the  $\text{OCH}_3$ -groups may perform very complex motion so that only averages are observed.

On the basis of the following assumptions:

$$r_{\text{PO}} = 1.57\text{\AA} ; \quad r_{\text{CH}} = 1.09\text{\AA} ; \quad \chi = 66^\circ$$

$$r_{\text{OC}} = 1.43\text{\AA} ; \quad \beta = 22^\circ ;$$



(only one  $\text{OCH}_3$ -group shown)

we find that there are only two relatively save results. The first is the average angle <sup>$\nu$</sup>  of tilt between the  $\text{P} = \text{O}$  axis and the  $\text{C} - \text{O}$  axis as defined in the figure.

It turns out to be  $105^\circ$  and it lies between  $100^\circ$  and  $110^\circ$  if the assumptions are varied within a reasonable range. The second result is the degree of order of the  $\text{P} = \text{O}$  axis which is found positive ( + 0.05), i.e. the axis is parallel to the liquid crystal optical axis.

Yours sincerely

Diehl

J. Vogt

P. Diehl

J. Vogt

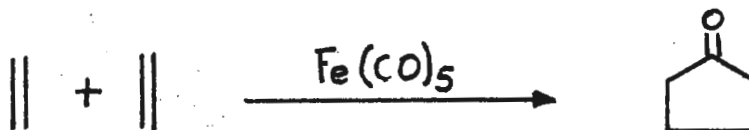
Professor B.L. Shapiro  
 Department of Chemistry  
 Texas A & M University  
 College Station, Texas 77843, USA

November 23, 1973

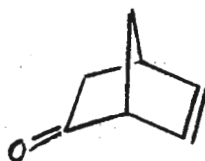
Elucidation of a stereochemical maze: Accuracy, fairness  
 and Frans Rummen.

Dear Barry,

We have been studying the coupling of olefins effected by carbonyls to yield cyclopentanones :



Our efforts have been focussed mainly on the reaction of norbornene derivatives. When dehydronorcamphor (1) is used as a substrate, as the racemic mixture,



1

one could anticipate (1) a variety of stereoisomeric coupling products, listed below in matrix form according to whether the norbornanone carbonyl is syn (S) or anti (A) with respect to the central cyclopentanone carbonyl in the adduct; exo-exo (X) or endo-endo (N) substitution of the norbornane skeleton by the central cyclopentanone; and a cis (C) or trans (T) substitution pattern of the central ring :

cis series : four meso stereoisomers + six pairs of enantiomers

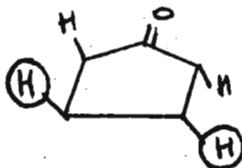
<u>SNCNS</u>	SNCNA	SNCXS	SNCXA
<u>ANCNS</u>	<u>ANCNA</u>	ANCXS	ANCXA
SXCNS	SXCNA	<u>SXCXS</u>	SXCXA
AXCNS	AXCNA	<u>AXCXS</u>	<u>AXCXA</u>

trans series : four pairs of enantiomers with a  $C_2$  axis + six pairs of enantiomers.

<u>SNTNS</u>	SNTNA	SNTXS	SNTXA
<u>ANTNS</u>	<u>ANTNA</u>	ANTXS	ANTXA
SXTNS	SXTNA	<u>SXTXS</u>	SXTXA
AXTNS	AXTNA	<u>AXTXS</u>	<u>AXTXA</u>

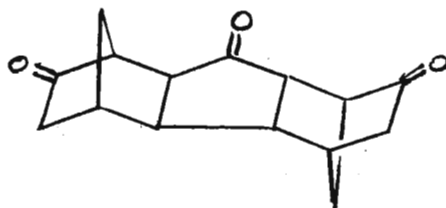
A single triketonic adduct  $C_{15}H_{16}O_3$  is obtained. Its structure is distinguished, from the 19 other diastereomeric structures, as follows :

1. all the off-diagonal elements are ruled out by the observation in the 300 MHz  $^1H$  spectrum of eight multiplets integrated for two protons each; and (better) observation in the  $^{13}C$  spectrum of only eight distinct resonances.
2. a trans-substituted cyclopentanone is indicated :

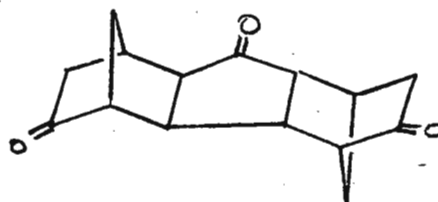


$$^3J_{H,H} \leq 2\text{Hz}$$

3. exo-exo substitution is derived from the absence of substantial coupling between the (endo) protons on the central ring and the bridgehead protons.
4. finally, a choice can be made between the two remaining structures,



$$\text{SXTXS } \mu_{\text{calc}} = 4.7 \pm 0.7\text{D}$$



$$\text{AXTXA } \mu_{\text{calc}} = 1.5 \pm 0.5\text{D}$$

simply by a dipole moment determination :  $\mu = 4.6 \pm 0.3\text{ D}$ .

This work was done in collaboration with Dr. Jean Grandjean and Mr. Armel Stockis.

- (1) A. Speert, J. Gelan, M. Anteunis, A.P. Marchand and P. Laszlo, Tetrahedron Letters, 2271 (1973).

\* \* \* \*

Now to go to the elucidation of a rhetorical maze [re Dr. Rummens' letter TAMU-NMR 178-17, hereafter referred to as R73]; lest readers get conned by it, I am forced to restate again that denigrating statements made by Rummens [TAMU-NMR 163-14; R73] are blatant misrepresentations of the experimental procedure we had followed in our JACS article with Ed Engler. Let us examine a few of Dr. Rummens' categoric statements :

1. "it is simply impossible to obtain any reference-free ASIS until one determines experimentally the medium shifts (gas-to-liquid) of the reference compound" (R73)

Wrong. What about the elegant technique pioneered by Becconsall [JACS, 92, 430 (1970)] involving joint use of spectrometers with samples spinning parallel and perpendicular to the field ?

2. "Laszlo in his work uses the C10 signal of camphor to reference the C9 and C8 signals. What he is in fact discussing and plotting are ( $\Delta C10 - \Delta C9$ ) and ( $\Delta C10 - \Delta C8$ ) values, free of TMS influence, but not free from the medium effects of C10. All he has done is replacing one internal reference (TMS) by another (C10 of camphor), but that does not improve the situation one iota" (R73).

"It does not matter whether one starts from C10 or TMS-reference  $\Delta$  data; after the corrections are made, the  $\Delta$  data are the same for any solvent pair" (R73).

3. "For solutes with two (or more) proton signals the difference of the ASIS's is free from internal reference problems, but the ratio [E.M. Engler and P. Laszlo, JACS, 93, 1317 (1971)] is not". [Rummens, TAMU-NMR 163-14]

Wrong again. We did not base any conclusions on anything but ASIS obtained by the  $\Delta$ -difference method.

4. "So again, Engler and Laszlo's  $\Delta C9$  vs.  $\Delta C8$  plots prove the opposite of what they claim. Since it does not matter whether TMS or C10 of camphor is chosen as reference this seems to indicate, if anything, that there are no specific interactions" (R73).

"Specific complexation is not necessary to explain the large shifts observed for (such) polar solutes in aromatic solvents. These solvent shifts arise from general solvation" [E.M. Engler and P. Laszlo, JACS, 93, 1317 (1971)].

5. "Hopefully, that will settle this issue once and forever" (R73).

"Philosophers of science have repeatedly demonstrated that more than one theoretical construction can always be placed upon a given collection of data"; "The claim to have solved the crisis-provoking problems is, however, rarely sufficient by itself. Nor can it always legitimately be made" .

[T.S. Kuhn, The Structure of Scientific Revolutions, University of Chicago Press, 1962, p. 76 and p. 153].

The truth (and the point) of the matter is that in my work with Ed Engler, we pointed out the inadequacy of a 1:1 complex with a well defined, time-independent geometry, as a model for the ASIS. Our TMS-independent data were entirely sufficient for this purpose. I am delighted that Rummens has come up with refinements which do improve the data, and may therefore help to augment our knowledge of these interactions.\*

I now consider this rather petty exchange as closed, at least from my end.

With warmest regards,  
Sincerely yours,



Pierre Laszlo

PL:nd

\*I am looking for trouble : I am bound to be misquoted on this one too ! Some of the credit belongs to Messrs. Hallam and Bellamy.

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TELEX NO. 13-8840

November 14, 1973

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

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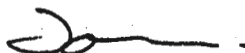
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All inquiries should be addressed to Mr. W. Wakefield who is also at the above address.

Very truly yours,



Thomas C. Farrar  
Director of R & D

TCF/rmz

cc: Dr. T. Maruyama  
Mr. H. Christle  
Mr. W. Wakefield

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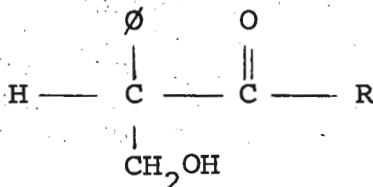
reference

27 November 1973

Professor B L Shapiro  
Texas A&M University  
College of Science  
College Station  
TEXAS 77843

Dear Barry

Recently when examining the  $^1\text{H}$  and  $^{13}\text{C}$  spectra of atropine hydrobromide and some of its analogues we encountered an interesting ABC spectrum for the fragment.

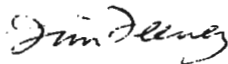


If an ABX subspectral analysis of the 220 MHz  $^1\text{H}$  spectrum is carried out it can be seen that one of the ab(ABX) subspectra falls within the second ab subspectrum indicating that  $J_{\text{AX}}$  and  $J_{\text{BX}}$  have opposite signs: a detailed iterative ABC analysis to fit the 220 MHz and 100 MHz spectra gives the coupling constants

$$J_{\text{AB}} = 6.45 \quad J_{\text{AC}} = -11.03 \quad J_{\text{BC}} = 8.20 \text{ Hz}$$

Clearly the observed relative signs indicate that the low field proton is one of the methylene protons. We have not encountered a  $^1\text{H}$  spectrum of this type before but maybe some of your readers might let us hear if they have seen such cases.

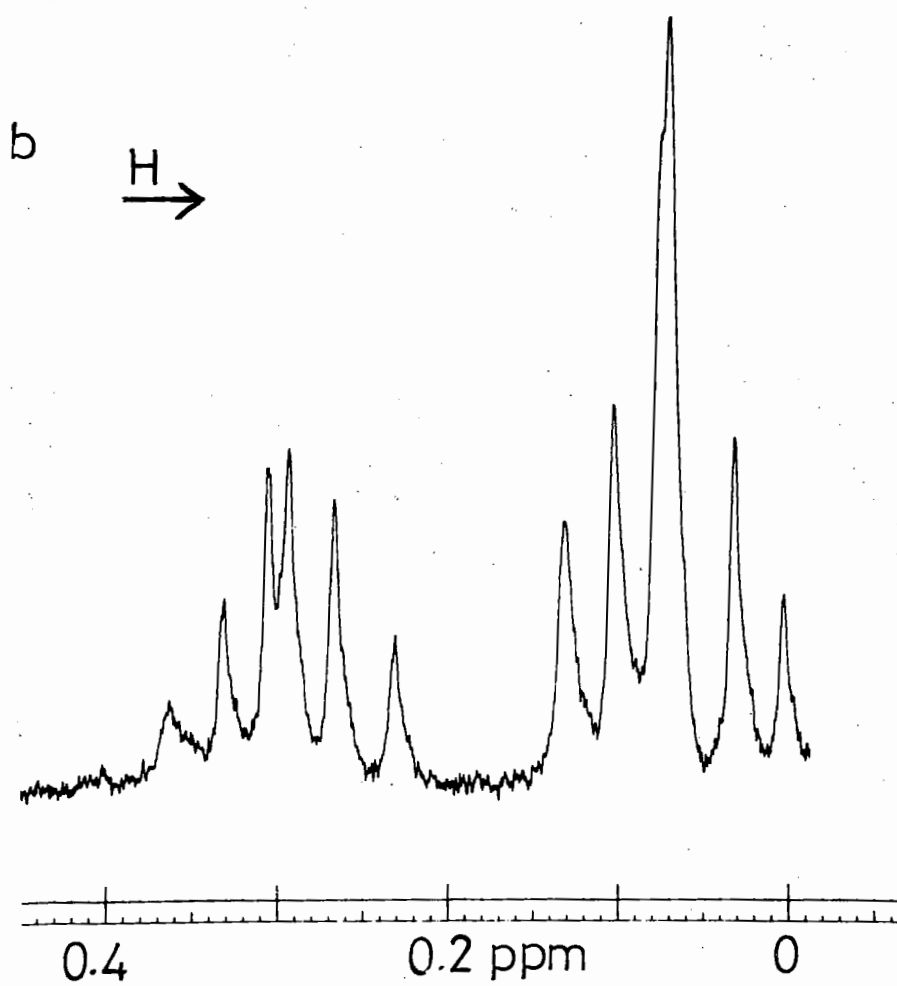
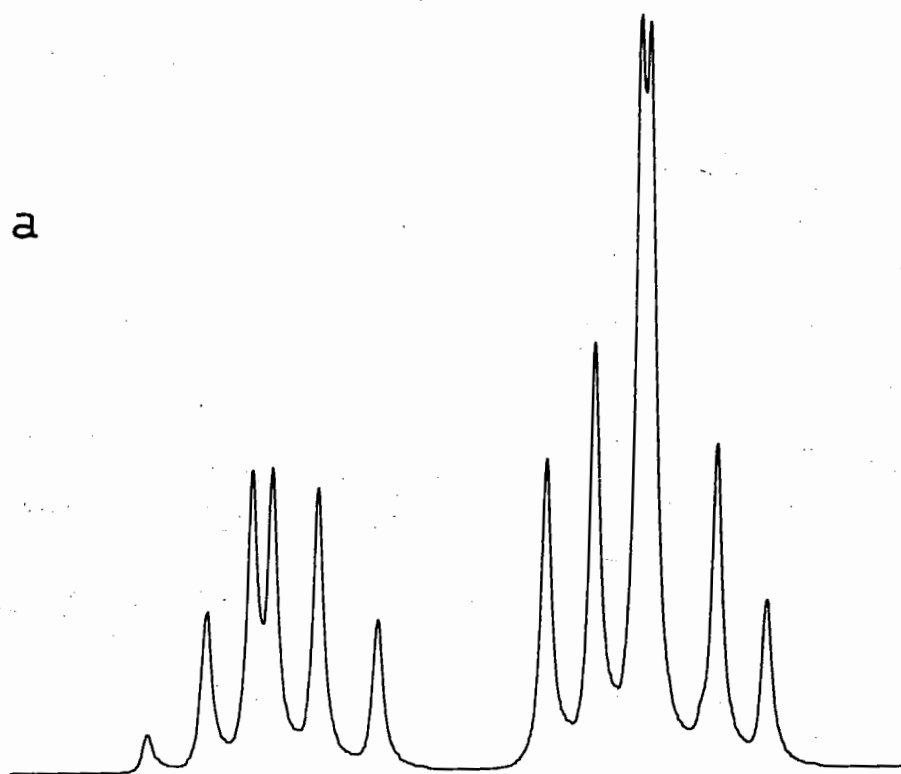
Yours sincerely



J FEENEY, P PARTINGTON and R FOSTER

Figure (a) The calculated  $^1\text{H}$  resonance spectrum of the  $-\text{CH}_2\text{CH}$  fragment of atropine hydrobromide.

Figure (b) The observed  $^1\text{H}$  resonance spectrum at 220 MHz of the  $-\text{CH}_2\text{CH}$  fragment of atropine hydrobromide.



## TEXAS A&amp;M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

December 3, 1973

Department of  
CHEMISTRY

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

Title: Request for  $^{13}\text{C}$  Data on Macromolecular Systems

Dear Barry:

We are currently compiling data for a review on high resolution  $^{13}\text{C}$  nmr spectra of macrocyclic and macromolecular systems of biological importance to be published in Vol. 12 of Advances in Physical Organic Chemistry. The contents include the following:

- A. Carbohydrates and Derivatives: Monosacharides; Di-, tri-, and polysaccharides
- B. Nucleic Acids and Constituents: Nucleosides, Nucleotides, and Nucleic acids
- C. Proteins and their Residues: Simple peptides, oligopeptides, and polypeptides; Native and denatured proteins; helix coil transformations, e.g., gelatin, ribonuclease, modified myoglobin, lysosyme, and other proteins
- D. Lipids: Phospholipids; Bile salts and other lipids
- E. Macromolecular Model Systems: Micellar Surfactants; Macrocyclic compounds such as synthetic crown-ethers and naturally occurring macrocyclic compounds

In order to be as comprehensive and up-to-date as possible, we would greatly appreciate preprints and/or correspondence regarding unpublished data on or related to the above. Any unpublished data will be kept strictly confidential until released by the author(s) if so desired. The deadline for inclusion is Feb. 1, 1974; however, a limited amount of material may be added at or immediately prior to the galley proofs. For this work to be of maximum utility to everyone, we earnestly solicit your assistance.

Sincerely,

*Steven Rosenthal*

S. N. Rosenthal

*James*

J. H. Fendler

*Ellie*

E. J. Fendler

## TEXAS A&amp;M UNIVERSITY

## COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

December 3, 1973

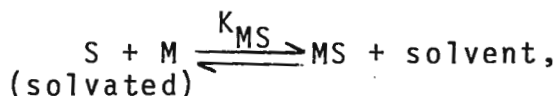
Department of  
CHEMISTRY

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

Dear Barry:

Title: Solubilization Behavior in Non-aqueous Surfactant Systems,  
 or More Soap

We have been using  $^1\text{H}$  nmr to investigate the qualitative and quantitative aspects of solubilization of different substrates by dodecylammonium propionate (DAP) in benzene, chloroform and dichloromethane. An understanding of the factors which affect the binding and specific orientation of substrates in reversed or "inverted" micelles is of prime importance in elucidating the factors responsible for the up to  $5 \times 10^6$ -fold rate enhancements elicited by these systems for diverse types of reactions. We were particularly interested in determining the relative importance of the DAP head group interactions, H-bonding, dipole-dipole interactions as well as electrostatic interactions using DMSO, imidazole, methanol, pyrazole, 2-pyridone and tetrabutyl ammonium perchlorate as solubilizates. The micelle-solubilize binding constant  $K_{MS}$  in the equation

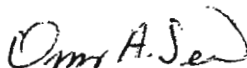


where (S) is substrate, M micelle and MS is micelle-substrate complex, has been determined from the observed chemical shift values of the solubilizates at different DAP concentrations. The results indicate that hydrogen-bonding superceeds dipole-dipole interactions. The determined  $K_{MS}$  values are a function of the structure of the solubilize and the nature of the solvent. The latter affects  $K_{MS}$  by affecting the degree of solubilize aggregation. Times of residence,  $\tau_M$ , for some of the solubilizates in micellar DAP systems indicate that the lifetime in the micellar phase is dependent upon both hydrogen-bonding interactions and solubilize volume. These results will be fully reported in the literature.

Sincerely yours,



E. J. Fendler



Omar El Seoud

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# Varian has an NMR system for every application...

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

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

### EM-300X

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

### EM-360

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

### T-60A

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

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

### CFT-20

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

### XL-100

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

### SC-300 and SC-360

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

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

**varian instruments** 

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

CFT-20

