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Newsletter

*Princ. H. Lykes*  
**No. 162**  
**MARCH, 1972**

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Flanagan, P. W.  
Job Wanted

30

Stothers, J. B.  
Position Available

31

Deadline dates: No. 162: 3 April 1972  
No. 163: 1 May 1972

All Newsletter correspondence, etc. should be addressed to:

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

БЪЛГАРСКА  
АКАДЕМИЯ НА НАУКИТЕ  
ИНСТИТУТ ПО ОРГАНИЧНА ХИМИЯ

Sofia, the February 4th 1972

BULGARIAN  
ACADEMY OF SCIENCES  
INSTITUTE OF ORGANIC CHEMISTRY  
Sofia 13, Bulgaria

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

Rotational barriers in phthalic and acetylenic amides

Dear Professor Shapiro,

In answer to your blue letter, let us give the preliminary results for the rotational barriers about the C-N bond in some amides of phthalic and acetylenic acids.

Compound (CDCl <sub>3</sub> , 0.5 M)	$\Delta V_{\text{CH}_3\text{N}}$ (Hz at 60 MHz)	T <sub>c</sub> (°K)	$\Delta G_c^\ddagger$ (kcal/mole)
o-Me <sub>2</sub> NOC-C <sub>6</sub> H <sub>4</sub> -CONMe <sub>2</sub>	8.3	319	16.9
m-Me <sub>2</sub> NOC-C <sub>6</sub> H <sub>4</sub> -CONMe <sub>2</sub>	7.8	295	15.6
p-Me <sub>2</sub> NOC-C <sub>6</sub> H <sub>4</sub> -CONMe <sub>2</sub>	8.4	298	15.7
HC≡CONMe <sub>2</sub>	16.2	377	19.6
MeC≡CONMe <sub>2</sub>	15.0	363	18.9
PhC≡CONMe <sub>2</sub>	15.6	367	19.1

The determination of all activation parameters by the iterative total line-shape method is in progress.

Yours sincerely,

*S.S. Spassov* V. Dimitrov M. Agova I. Kantschowska  
S.L. Spassov V.S. Dimitrov M. Agova I. Kantschowska



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

Building 2, Room B2-02

February 8, 1972

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

Dear Dr. Shapiro:

Simplified Method of Adjusting Homogeneity  
Controls on Varian HR-220

It is often necessary to readjust the homogeneity controls of the Varian HR-220 spectrometer when changing samples, particularly if a solvent change is involved. Even though only  $z_1$ ,  $z_2$  and  $z_3$  need be adjusted, it is possible to waste considerable time in trying to optimize all three simultaneously. We felt that the use of a nuclear sideband oscillator system would give us something similar to the "adjust" position on the Varian A-60 in the sense that a meter indication or the recorder pen position on the spectrometer gives an indication of homogeneity settings. (Better settings give higher meter readings or a pen position more toward the top of the chart.)

The circuit of the nuclear sideband oscillator amplifier used in the T-60 was used with minor changes to raise the frequency from 5 kHz to 10 kHz and change the output and AGC-characteristic. The input to the NSBO amplifier is taken from J206, connected all the time. The output then feeds the field modulator through a switch that changes the  $B^+$  and the connection from the 10 kHz oscillator to the NSBO amplifier. The output amplitude is set to the nominal 10 Vpp at J212, M, the phase for optimum stability and amplitude when locked to a line. The NSBO circuit was built on a small circuit board and inserted into the V-3523 integrator audio unit. The switch that turns the inserted unit off and on was wired in such a manner that all power to the NSBO is turned off when the switch is in the "off" position.

We have used the sideband oscillator many times, usually tuning up on the TMS in the sample, or sometimes on a water peak or on the Varian standard water sample, which has a broadened peak. The recorder position or scope peak location has to be set so that the system is  $\pm 200$  Hz from the peak one wishes to use for tune up. The signal amplified and RF level are turned up sufficiently to get a detector level meter indication on the spectrometer. Then the  $z_1$ ,  $z_2$  and  $z_3$  control are rocked back and forth gently so that the maximum indication is observed. The improvement in peak height and ringing pattern on the scope corresponds very closely to the maximum deflection on the signal meter. We have installed a fine control on  $z_1$ , and after using

Professor B. L. Shapiro  
February 8, 1972  
Page 2

the sideband oscillator and maximizing  $z_1$ ,  $z_2$  and  $z_3$ , we find that all that is necessary to begin running a spectrum is to rock  $z_1$ -fine back and forth so as to obtain the best recorder presentation. This tuning system is particularly useful when recovering from widely different  $z_1$ ,  $z_2$  and  $z_3$  settings that had previously been used to optimize homogeneity in a highly conducting sample, one with very different susceptibility or one containing a magnetic particle.

We shall be glad to supply further information to anyone interested in this system.

Sincerely yours,

*Robert B. Bradley*

Robert B. Bradley  
Laboratory of Physical Biology  
National Institute of Arthritis  
and Metabolic Diseases

*R. Tschudin*

Rolf Tschudin  
Varian Associates  
4701 Lydell Drive  
Cheverly, Maryland 20785



# NATIONAL CHEMICAL RESEARCH LABORATORY

OF THE SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

Telephone 74-8011 Telegrams NAVORSHEM

AIR MAIL

P. O. Box 395

OUR FILE

YOUR FILE

PRETORIA

60/22/4221/1

Professor B.L. Shapiro,  
Texas A & M University,  
Department of Chemistry,  
College of Science,  
COLLEGE STATION,  
Texas 77843,  
United States of America.

9. FEB. 1972

Dear Professor Shapiro,

## Lanthanide-induced CMR Shifts of Quinoline

Opinions differ as to the presence of observable contact shift in the  $^1\text{H}$  spectrum of  $\text{Eu}(\text{dpm})_3$  .... Quinoline. Sanders and Williams have detected a decrease in the  $J_{231}$  coupling constant<sup>(1)</sup>, and in agreement with an investigation of the  $^1\text{H}$  shifts of pyridines in the presence of lanthanide cations<sup>(2)</sup> have suggested significant contact interaction. However, Huber and Pascual have produced statistical evidence that there is no contact contribution to the  $^1\text{H}$  shifts of quinoline in the presence of  $\text{Eu}(\text{dpm})_3$  and using the McConnell-Robertson equation define an  $\text{Eu}(\text{dpm})_3$  .... quinoline complex of reasonable geometry<sup>(3)</sup>, Eu atom positioned 4.0 Å from nitrogen and only slightly off the two-fold axis of the pyridine ring.

We have measured the shifts of the  $^{13}\text{C}$  lines of quinoline (4) in the presence of the most used shift reagents  $\text{Eu}(\text{dpm})_3$ ,  $\text{Eu}(\text{fod})_3$ ,  $\text{Pr}(\text{dpm})_3$ , and  $\text{Pr}(\text{fod})_3$ , and the results are shown on the accompanying diagram. In all cases the mole ratio of quinoline to shift reagent was 30 to 1. The spectrometer was locked on to the deuterium signal of the solvent  $\text{CDCl}_3$ . No shift in the solvent  $^{13}\text{C}$  line was observed and the quinoline lines in the presence of the same mole fraction of  $\text{La}(\text{dpm})_3$  were unshifted.

For examples I and II the large difference in the shifts of  $\text{C}_2$  and  $\text{C}_9$ , and  $\text{C}_3$  and  $\text{C}_{10}$ , the small and negative shifts of  $\text{C}_3$  and  $\text{C}_{10}$ , together with the fact  $\text{C}_8$  is shifted more than  $\text{C}_9$  show that a purely pseudocontact

interaction/ ....

- 2 -

interaction based on the above mentioned geometry is inadequate. This clear evidence for the presence of contact shifts in the CMR spectra is not so obvious in examples III and IV where the order of the observed shifts would allow a correct assignment of the resonances.

Yours sincerely,

*Klaus Pachler*

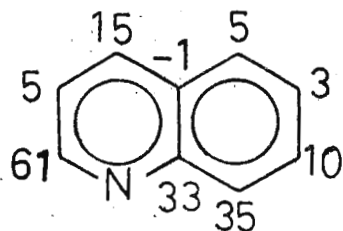
K. Pachler  
SENIOR CHIEF RESEARCH OFFICER  
CHEMICAL PHYSICS GROUP  
NATIONAL CHEMICAL RESEARCH LABORATORY

*A.A. Chalmers*

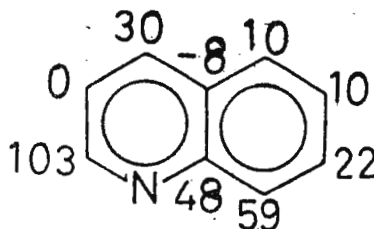
A.A. Chalmers  
SENIOR RESEARCH OFFICER  
NATIONAL CHEMICAL RESEARCH LABORATORY

#### REFERENCES

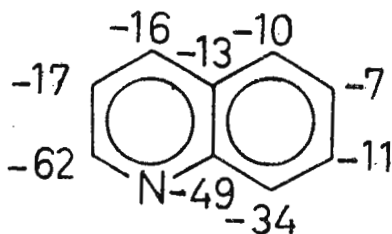
1. J.K.M. Sanders and D.H. Williams, J. Amer. Chem. Soc., 93, 641 (1971).
2. E.R. Birnbaum and T. Moeller, J. Amer. Chem. Soc., 91, 7274 (1969).
3. H. Huber and C. Pascual, Helv. Chim. Acta, 54, 913 (1971).
4. R.J. Pugmire and D.M. Grant, J. Amer. Chem. Soc., 91, 6381 (1969).



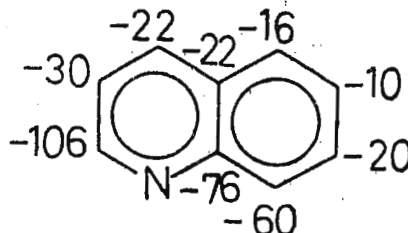
(I) Eu(dpm)<sub>3</sub>



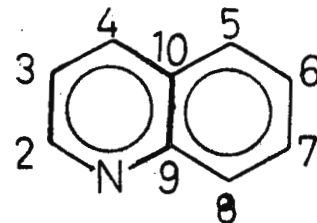
(II) Eu(fod)<sub>3</sub>



(III) Pr(dpm)<sub>3</sub>



(IV) Pr(fod)<sub>3</sub>



Shifts in Hz at 25.1 MHz positive downfield.

162-6

Prof. Dr. E.G. Hoffmann

# MAX-PLANCK-INSTITUT FÜR KOHLENFORSCHUNG

MPI für Kohlenforschung, 4330 Mülheim-Ruhr, Kaiser-Wilhelm-Platz 1

Prof. Dr. B.L. Shapiro  
Department of Chemistry  
Texas A and M University  
College Station  
Texas 77843  
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4330 Mülheim a. d. Ruhr  
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Telefon Sa.-Nr. ~~34921~~ 30 61  
Durchwahl: 306 .....

Ihr Zeichen

Ihre Nachricht vom

Unser Zeichen

Datum

Ho/Lk

12.2.1972

## FTS - NMR-Service with a Remote Large Time-Sharing Computer

Dear Dr. Shapiro,

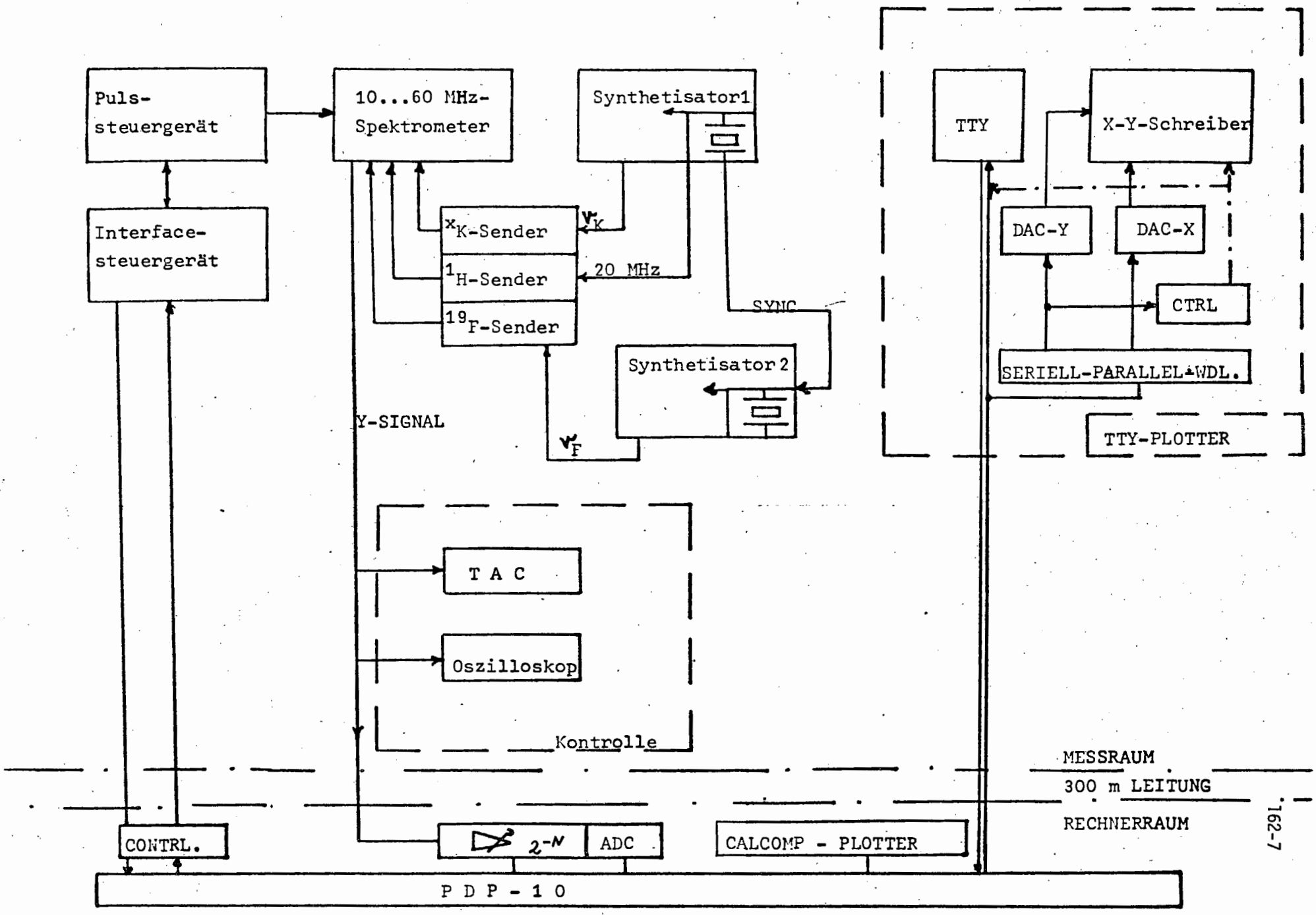
in TAMUNN-Letters 158 (1971) 32 I contributed a scheme of our way interfacing CW-spectrometers with a great time-sharing PDP10-computer. I promised to give a contribution about interfacing our multi-purpose pulse spectrometer (Fig. 1) cp. also TAMUNN-Letter 148 (1971) 4 and W. Stempfle and E.G. Hoffmann, Z. Naturforschung 25a, 2000 (1970)). A critical review of our experiences with the use of NMR-spectrometers on line with the PDP10/50-system will appear in the journal: Angewandte Chemie in the middle of this year. Our main problem is that only one fast ADC-unit can be monitored by the computer and therefore there exists a competition between the GC/MS-combination-analysis and our own FTS experiments, which frequently need a very great number of accumulations and short acquisition times. Therefore we plan to use our own ADC with a small computer bound to the large system via teletype lines. (At the moment, a direct connection to the I/O-bus of the PDP10 will be problematic because of the great distance between our labs and the main computer.

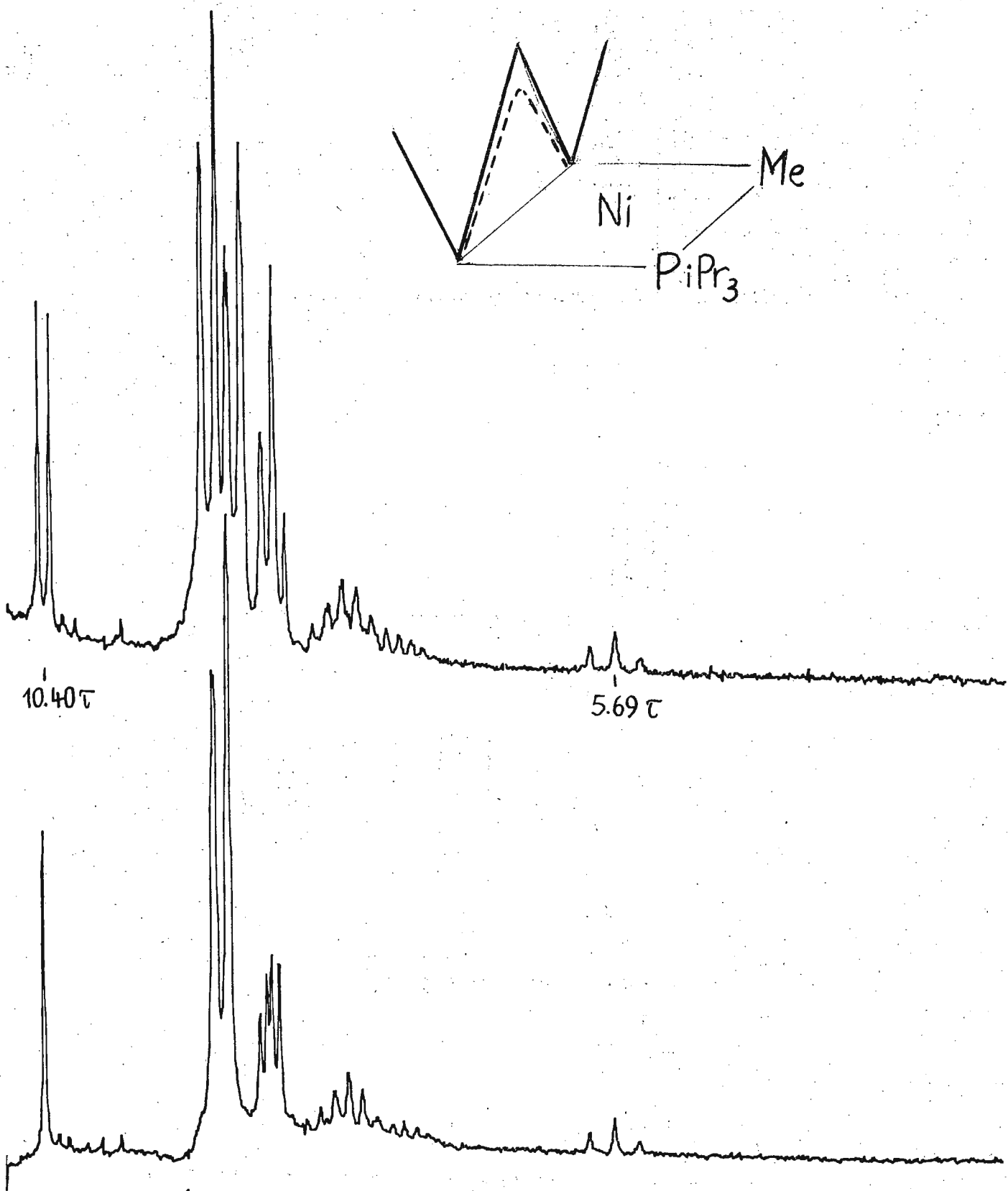
Fig. 2, as an example shows a  $^1\text{H}$ -FT-spectrum of a compound stable only at low temperatures. It is used as a model to assign the signals of similar compounds showing complex spectra by additional splitting due to induced chirality.

Sincerely yours,

*E. G. Hoffmann*





Fig. 2:  $^1\text{H-NMR-FT-Spectra}$ 

undecoupled (above)

 $^{31}\text{P}$ -noise decoupled (below)



BROWN UNIVERSITY Providence, Rhode Island • 02912

DEPARTMENT OF CHEMISTRY

17 February 1972

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

High Intensity UV Irradiation in an HA-60 Probe

Dear Professor Shapiro:

In view of recent interest in searching for chemically induced dynamic nuclear polarization (CIDNP) in photochemical reactions, I will describe briefly two experimental arrangements for photolysis inside of the modified probe of an HA-60 which have proven to be quite useful.

In an early configuration similar to those reported by others<sup>1</sup> the apparatus consisted of a 1000 watt Philips SP-1000 mercury arc lamp with its beam focused through the lower rear paddle hole in an HA-60 probe by a front-silvered mirror and a quartz lens. The path for admitting UV light to the sample was cleared by cutting a hole in the faraday shield and using a homemade detector coil wound on quartz instead of glass. It was also necessary to remove the bulky piggyback water sample at the rear of the probe and operate only in the unlocked mode. The sample could be cooled by a rapid flow of air through a bronze tube which replaced one of the front paddles. With this apparatus it was possible to obtain ca. 15% conversion of an acetone solution of benzoyl peroxide (ca. 0.1M) to benzene with 4 minutes of irradiation. Unfortunately, however, the sensitivity and stability of the spectrometer, while usable, were below standard and the CIDNP line from benzene, for example, could be detected only with difficulty.

In a more recent refinement the lens system was replaced by a light pipe consisting of a flat-ended 10 mm. diameter Suprasil rod 60 cm. in length which extended from the face of the cooling jacket of a GE AH6 lamp to the front edge of the hole in the faraday shield. The quartz insert was replaced by a free standing detector coil made of no. 22 enamelled copper wire. Furthermore, it was also possible to replace the piggyback water sample, and operate in the locked mode, by placing the electronic components in a slightly smaller aluminum case. Surprisingly, no apparent loss of sensitivity or resolution occurred when these modifications were made. This configuration also produces benzene by photolysis of benzoyl peroxide about 8 times faster than the earlier one and is consequently to be favored for photo CIDNP studies.

Please credit this contribution to R.G. Lawler's account.

Sincerely,

*Stuart Rosenfeld*  
 Stuart M. Rosenfeld

smr:e

1. G.L. Closs and L.E. Closs, J. Amer. Chem. Soc., 91, 4549 (1969); R. Kaptein, et. al., Chem. Commun., 1687 (1970); H. Shindo, TAMU NMR Newsletter, 153, 20 (1971).

à: Bernard L. Shapiro

date: February 17, 1972

sujet: Molecular dynamics of the camphor-benzene interaction.

Dear Barry,


Continuing our investigation of camphor in various solvents<sup>1</sup>, we are determining  $^{13}\text{C}$  relaxation times, with the "progressive saturation" method<sup>2</sup>. Comparison (Table) of the data for the three methyl carbons implies isotropic rotational reorientation of the quasi-spherical camphor molecule. Assumption of a dominant dipolar mechanism of relaxation with the bonded protons yields the correlation times also listed in the Table. Internal consistency is achieved in each solvent within the combined experimental errors<sup>3</sup>.

It is noteworthy that, despite the virtual equality of bulk viscosities, the correlation time is shorter in  $\text{C}_6\text{D}_6$  than in the  $\text{CCl}_4\text{-C}_6\text{D}_{12}$  mixture : a long-lived camphor-benzene complex would conversely be expected to bring about an increase in the correlation time for molecular motion.

We are currently attempting to obtain the correlation function from vibrational spectroscopy in order to glean additional information on the molecular dynamics of camphor in solution.

We acknowledge with thanks the help of Dr. F.W. WEHRLI, Varian Associates, Zug (Switzerland) in obtaining the above data.

Best regards,  
Sincerely



Jean GRANDJEAN

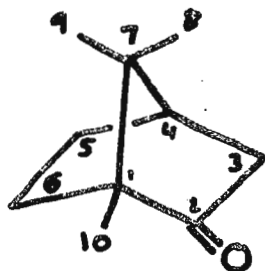


Pierre LASZLO

- (1) E.M. ENGLER et P. LASZLO, J. Am. Chem. Soc., 93, 1317 (1971)
- (2) R. FREEMAN et H.D.W. HILL, J. Chem. Phys., 54, 3367 (1971)
- (3) a limit of ca. 20% on each  $T_1$  value is estimated on the basis of a systematic error of three times the standard deviation.

TABLE

$^{13}\text{C}$  Relaxation Times (s) and Correlation Times ( $10^{-12}\text{s}$ ) for Camphor (at  $32^\circ\text{C}$ )



Solvent		$C_{10}$	$C_9$	$C_8$	$C_6$	$C_3$
$(\text{CD}_3)_2\text{CO}$	$T_1$	18,0	18,0	16,6	-	13,1
	$\tau_r$	0,8	0,8	0,8	-	1,6
$\text{CCl}_4\text{-C}_6\text{D}_{12}$ (60%-40% v/v)	$T_1$	4	5,4	3,6	3,4	9,4
	$\tau_r$	3,5	2,6	3,9	6,2	4,5
$\text{C}_6\text{D}_6$	$T_1$	12,6	11,7	11,4	12,3	-
	$\tau_r$	1,2	1,2	1,2	1,6	-

## NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

February 22, 1972

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

Dear Professor Shapiro,

Please credit this contribution to Joe Lambert's "account."

We have been investigating lanthanide shift reagents from an organometallic and inorganic standpoint. This work includes both the application of conventional shift reagents (tris  $\beta$ -diketonate complexes) to problems in non-organic areas, and the design of new kinds of shift reagents.

We find the conventional reagents to be tools of great utility in organometallic and inorganic chemistry for,

- 1) Spectral simplification.
- 2) Conformational and stereochemical mapping.
- 3) Chemical probing.

The first two applications are illustrated in the Figure, which records the effect of increasing amounts of  $(fod)_3Eu$  ( $A = 0.0M$ ,  $B = .08M$ ,  $C = .22M$ ) on the pmr spectrum of an iron acyl complex as a  $.33M$  solution in toluene- $d_8$ . Note that the coupling of the phosphorus to the protons on the cyclopentadienyl ring is observed in all spectra; this indicates that the Fe-P bond has remained intact. A variety of ligand groups (e.g., cyanides, chlorides, fluorides, azides, carbonyls, nitrosyls) possess sufficient basicity to interact. Indeed, the shift reagents are exceptionally useful for probing the basicity of unusual functionalities (application 3). For example, a number of metal bases (e.g.  $(C_5H_5)_2Sn$ ,  $(C_5H_5)_2WH_2$ ) interact. All evidence from the  $\beta$ -diketonate complexes indicates that they are very hard acids.

We have also been experimenting with lanthanide complexes of other ligand systems in an attempt to modify ("fine tuning" if you like) the acidity properties of the rare earth metals, hence their ability to interact as shift reagents with various kinds of bases. The lanthanide complexes,  $(C_5H_5)_3M$ , appear to be softer acids

Professor Bernard L. Shapiro  
February 22, 1972

Page Two

in that far larger shifts are induced in the pmr spectra of soft bases (e.g. phosphines) than can be induced by conventional shift reagents. Frequently, however, the conventional reagents do produce larger shifts in the spectra of hard bases. Thus the organometallic complexes have considerable practical potential as "soft shift reagents" in systems where the  $\beta$ -diketonate complexes are of scant utility. From the standpoint of coordination chemistry, it is remarkable that the nature of lanthanide acidities can be manipulated to such an extent by change in ligand system. We intend to publish these results in the near future.

Sincerely yours,



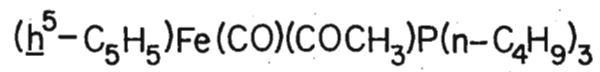
Tobin J. Marks  
Assistant Professor of Chemistry

TJM/as

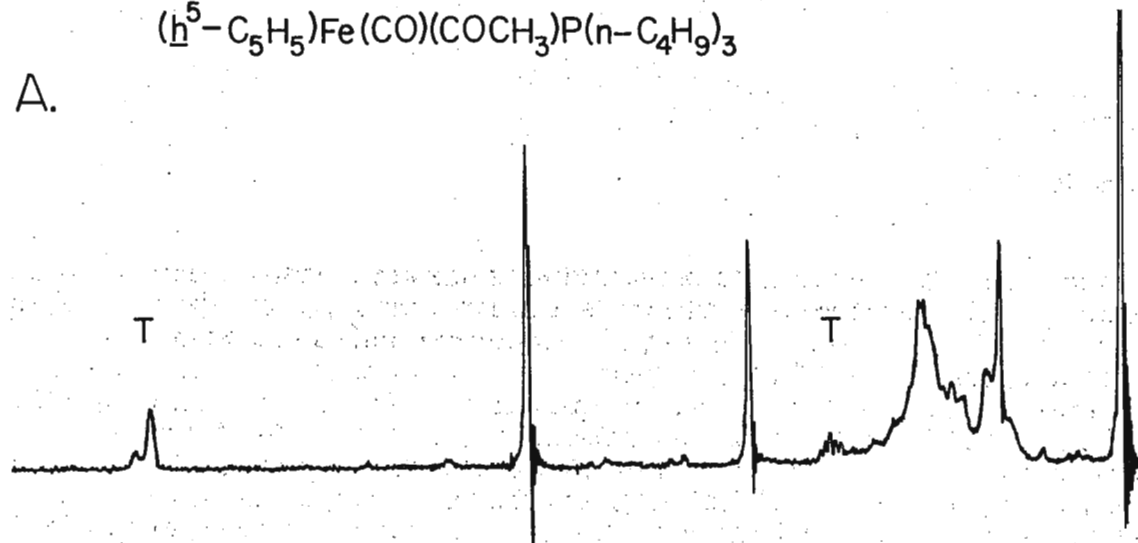
P.S. Would anyone have computer programs which:

- 1) Calculate the dependence of chemical shift on concentration for systems involving multi-step equilibria?
- 2) Simulate broadline spectra and do second moment calculations?

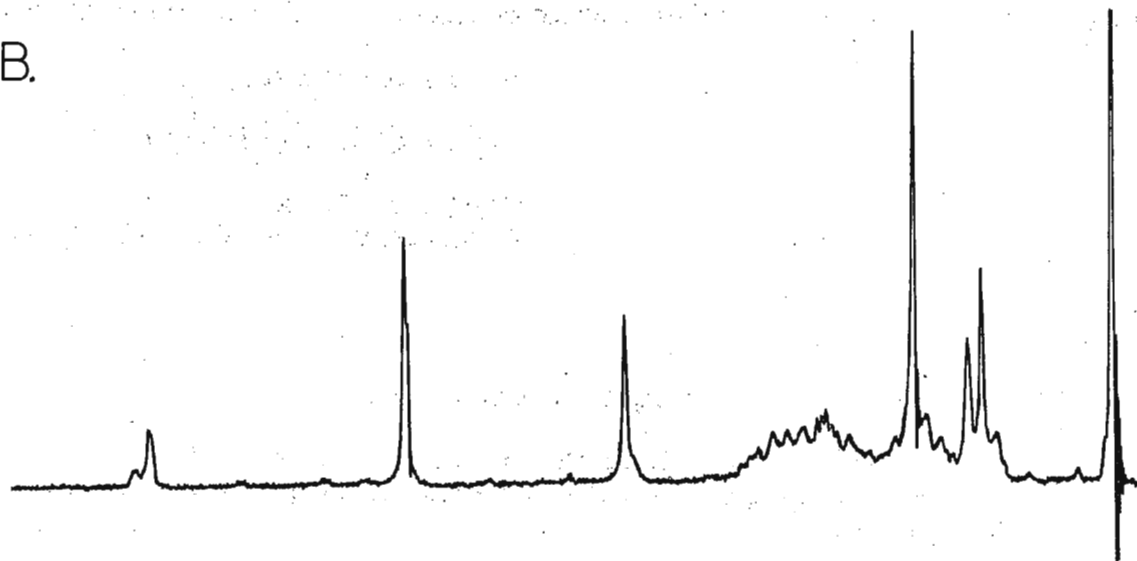
Title: New Shift Reagent Developments.



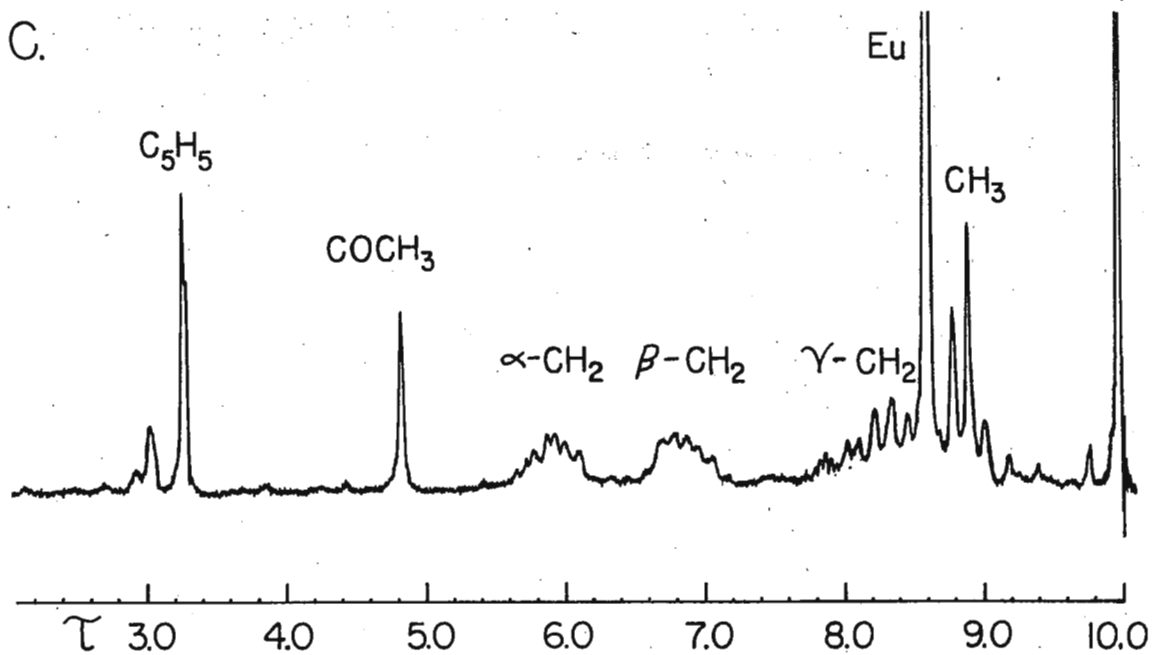
A.



B.



C.





The University of Manitoba  
Department of Chemistry  
Winnipeg 19, Manitoba, Canada



February 18, 1972.

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

Dear Barry:

Short title: Worked problems or micturated matrices.

In the May issue of the Newsletter I offered a planned compilation of worked problems from the book by Carrington and McLachlan. The reader response was encouraging and forced me to work (curses!) in the marvellous autumn weather in Oxford. The final, informal collection consists of 250 typewritten pages of 108 of the problems in the monograph. Some copies for lazy learners or busy bodies are still available at \$15.00 a copy.

Best wishes from,

Ted Schaefer,  
Professor.

TS/jf

## THE PENNSYLVANIA STATE UNIVERSITY

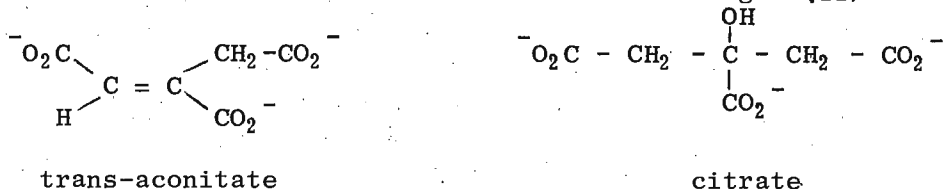
212 WHITMORE LABORATORY  
UNIVERSITY PARK, PENNSYLVANIA, 16802College of Science  
Department of Chemistry

February 21, 1972

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

Dear Dr. Shapiro:

Recently I have been investigating the interaction of Mn(II) with various tricarboxylic acids by CW NMR. The purpose of this work is to establish the role of metal ions in the mechanism of action of the enzyme aconitase. The progressive saturation technique was used to obtain  $1/T_1$  values of the protons of citrate and trans-aconitate as a function of increasing Mn(II) concentration.



In this technique the  $1/T_2$  values are measured and  $1/T_1$  calculated from the expression  $1/T_1 T_2 = \omega^2$ , where  $\omega$  is the precession frequency at saturation.

The proton NMR spectrum of tri-sodium trans-aconitate, pD 7.5, consists of a doublet 3.90 ppm downfield from TMS with  $J = 0.78$  Hz representing the methylene protons and a triplet 7.04 ppm downfield from TMS with  $J = 0.78$  Hz representing the methine proton.

When the  $\text{MnCl}_2$  concentration is varied from 1-10  $\mu\text{M}$  in a 125  $\text{mM}$  solution of trans-aconitate the resonance lines of the methylene protons and methine proton broaden and the apparent coupling constant decreases to  $\sim 0.3$  Hz for both the doublet and triplet lines. From 13-50  $\mu\text{M}$   $\text{MnCl}_2$  the doublet and triplet character of the resonance lines is no longer apparent and the broadening simply increases with added  $\text{MnCl}_2$ . No changes in chemical shift are observed.

In Fig. 1A the line width of the methylene and methine resonance is plotted as a function of  $\text{MnCl}_2$ . Three different regions are apparent which exhibit the phenomenon of chemical-exchange spin decoupling discussed by Frankel (1,2). This phenomenon can be observed in coupled proton spectra in which the effect of the paramagnetic metal is to shorten the longitudinal relaxation rate of one proton thereby decoupling it from another proton. Using Frankel's nomenclature, region A, in which the paramagnetic ion has no effect on the apparent  $J$  value is not detected. In region B of Fig. 1A the splitting of the resonance peaks begins to decrease and  $1/T_{2p} = 1/T_{2p}^{\text{CH}} + 1/T_{1p}^{\text{CH}_2}$  where  $1/T_{2p}^{\text{CH}}$  is the paramagnetic

contribution to the transverse relaxation rate of the methine proton and  $1/T_{1p}^{CH_2}$  is the paramagnetic contribution to the longitudinal relaxation rate of the methylene protons. The result is that the observed broadening of -CH- is greater than that due to  $1/T_{2p}^{CH}$  because -CH- and -CH<sub>2</sub>- are partially decoupled. The "excess" broadening is proportional to and may be used to estimate  $1/T_{1p}^{CH_2}$ . Conversely the "excess" broadening of the <sup>1</sup>-CH<sub>2</sub>- proton may be used to estimate  $1/T_{1p}^{CH}$ . The longitudinal relaxation rates of the -CH- and -CH<sub>2</sub>- protons calculated in this manner ( $1/pT_{1p} = 14,700 \text{ sec}^{-1}$  (CH) and  $15,400 \text{ sec}^{-1}$  (CH<sub>2</sub>)) show reasonable agreement with those obtained by power saturation in region D ( $1/pT_{1p} = 7,100 \text{ sec}^{-1}$  (CH) and  $14,200 \text{ sec}^{-1}$  (CH<sub>2</sub>)). In region C, Fig. 1A, the doublet and triplet are collapsed into single separate lines; however, -CH- and -CH<sub>2</sub>- are not completely decoupled. Complete decoupling has been achieved in region D where  $1/T_{2p} = 1/T_{2p}^{CH} = \pi\Delta\nu$  which means that the observed line broadening at half height ( $\Delta\nu$ ) no longer contains a contribution from  $1/T_{1p}$  of -CH<sub>2</sub>-.

Neglecting the decoupling contribution to the line broadening in region B would therefore yield values of  $1/T_{2p}$  for the methylene and methine protons too large by factors of 1.7 and 2.0, respectively and lead to incorrect values for  $1/T_1$ .

The proton NMR spectrum of tripotassium citrate, pD 7.5, is an AB pattern centered at 3.10 ppm downfield from TMS. At Mn(II) concentrations up to 200  $\mu\text{M}$  where the four lines can no longer be distinguished the line broadening is linear. The coupling constant  $J_{AB}$  remains 15 Hz up to the limit where it can be measured in the spectrum. The implication is that the line broadening measures the paramagnetic contribution to  $1/T_{2p}$  without a contribution due to decoupling.

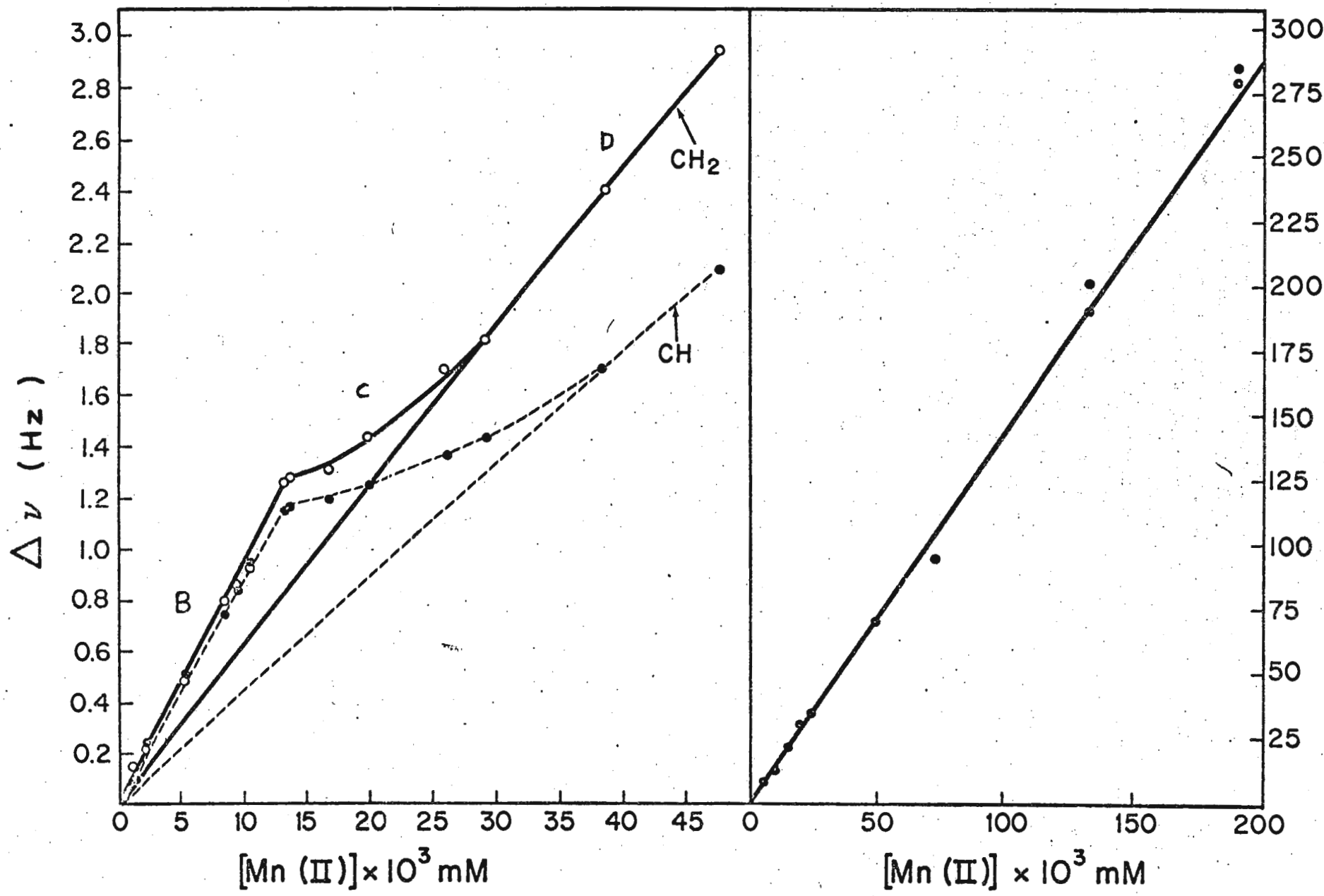
Sincerely,



Joseph J. Villafranca  
Assistant Professor of Chemistry

JJV/bhs

- 1) Frankel, L. S., J. Chem. Phys., 50, 943 (1969).
- 2) Frankel, L. S., J. Mol. Spec., 29, 273 (1969).



Duke University  
DURHAM  
NORTH CAROLINA  
27708

DEPARTMENT OF CHEMISTRY  
PAUL M. GROSS CHEMICAL LABORATORY

February 22, 1972

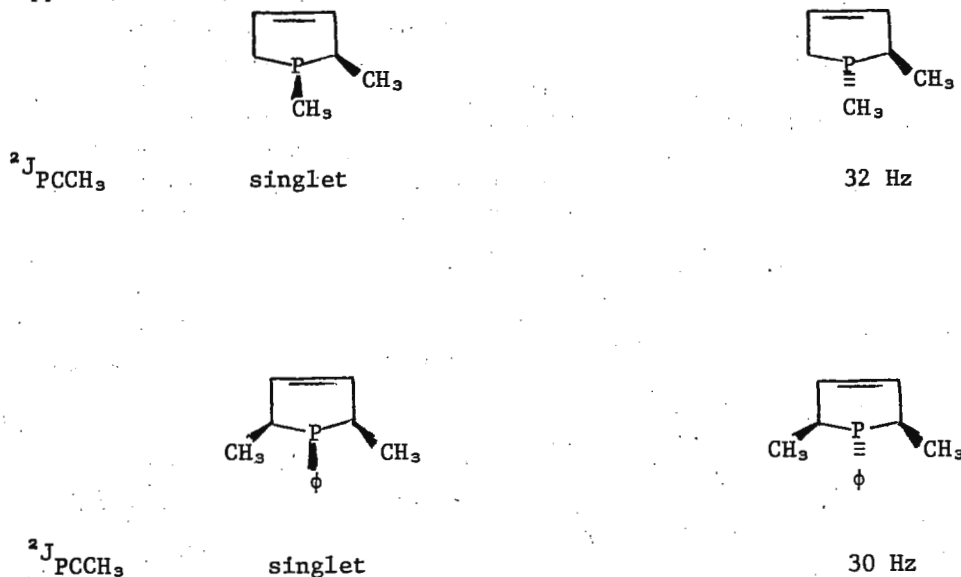
TELEPHONE 919-684-2414

Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A and M University  
College Station, Texas 77848

Dear Professor Shapiro:

Stereospecificity in One-Bond and Two-Bond P-C Coupling in Phosphines

Stereospecific  $^{13}\text{C}$ - $^{31}\text{P}$  couplings for the ring methyl signals are observed in the cis-trans isomers of 1,2-disubstituted and 1,2,5-trisubstituted-3-phospholenes. Although stereospecificity in  $^1\text{H}$ - $^{31}\text{P}$  coupling in cyclic phosphines is a well-known phenomenon, we think this is the first observation of its occurrence in  $^{13}\text{C}$  n.m.r. spectroscopy.



The corresponding phospholene oxides do not exhibit such stereospecificity, and this is true of  $^1\text{H}$ - $^{31}\text{P}$  coupling as well.

Steric effects also influence one-bond  $^{13}\text{C}$ - $^{31}\text{P}$  coupling for the P- $\text{CH}_3$  group above; the cis isomer has a value of 21.5 Hz, the trans 17.5. Gray and Cremer have recently [Tetrahedron Letters, 3061 (1971)] pointed out the uniqueness of this effect, discovering it in certain phosphetane oxides but not in phospholene oxides.

This report is to be credited to the account of P. W. Jeffs of this Department.

*L. D. Quin*

L. D. Quin  
J. J. Breen  
S. I. Featherman  
R. C. Stocks

LDQ/mc



# THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175  
CINCINNATI, OHIO 45239

February 28, 1972

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

Dear Professor Shapiro:

We have recently converted one of our Varian HA-100 spectrometers to observing phosphorus-31 in the centerband sweep mode. This scanning method is desirable because it provides a constant analytical channel phase, eliminates base line distortions and requires a minimum intensity lock signal. We are using a Hewlett-Packard 5105A/5110B frequency synthesizer/driver and a Boonton 230A RF power amplifier to provide the 40.5 MHz sweep and a Wavetek 111 VCG for the sideband sweep. The sweep voltage is obtained from a Fabri-tek 1064 computer. A phase control has been added to the internal reference stabilizer circuitry to adjust the analytical phase independent of the lock channel. A Varian 5 mm P-31 probe is used. A 1 mm ID capillary of  $P_4O_6$  provides the lock signal. The system affords a very stable lock signal (monitored at point "P" of J-1316 of the internal reference stabilizer V-4354A) in the 100 ppm sweep range at the sweep rate of 40.5 Hz/second.

We find this scanning technique superior to the fixed RF mode where we were limited to 25 ppm sweep range and the changes in the analytical phase made spectrum integration almost useless.

Enclosed is a spectrum of 5% dimethyl methyl phosphonate in  $CCl_4$ , averaged 80 times in the CB sweep mode.

Sincerely yours,

THE PROCTER & GAMBLE COMPANY  
Research & Development Department

*C. D. Sazavsky*

C. D. Sazavsky

lw

Title: "Observing  $^{31}P$  in the centerband sweep mode."

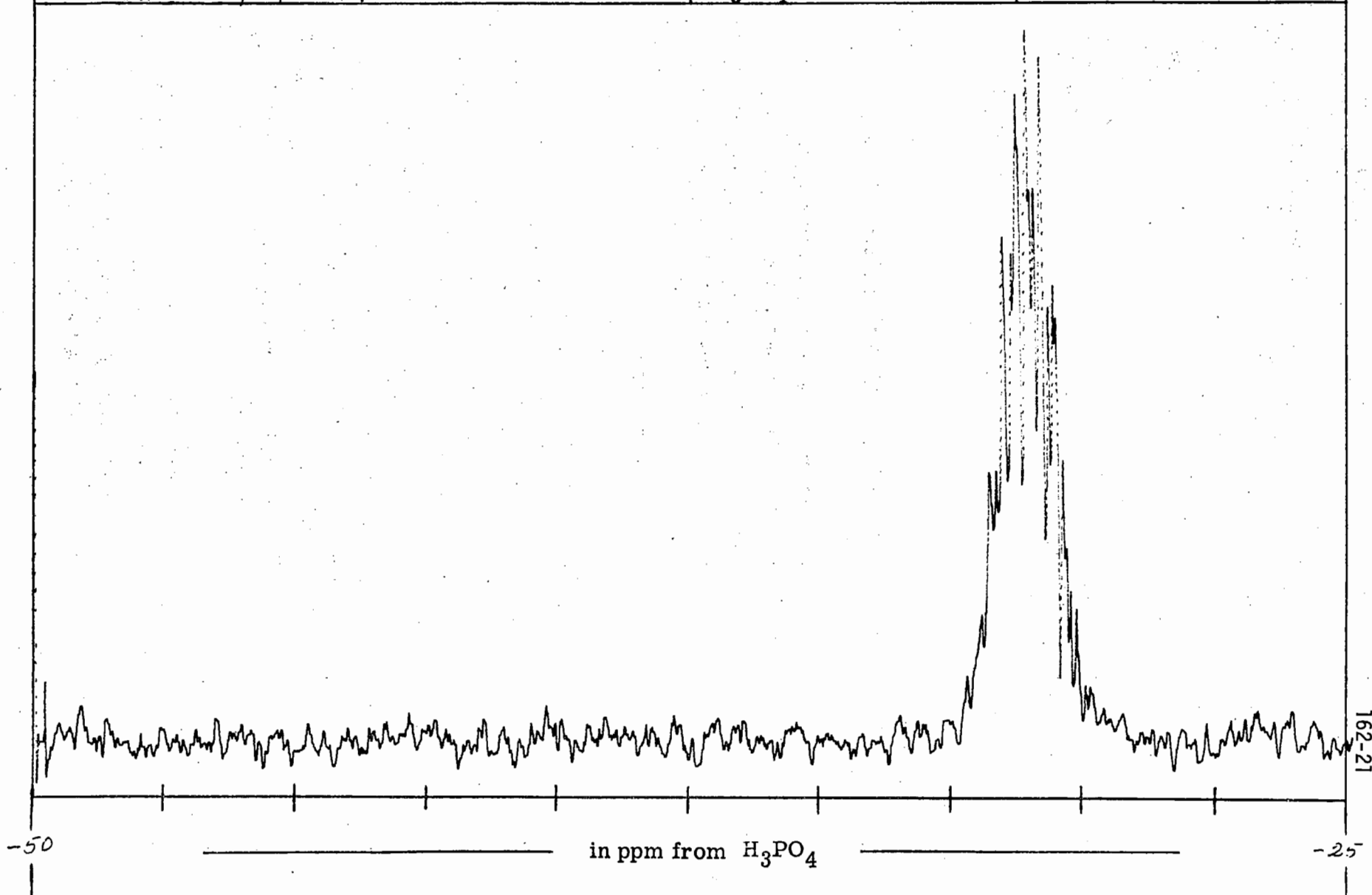
<sup>31</sup>P NMR SPECTRUM  
NO.

OPERATOR GP  
DATE 2/14/72

SAMPLE EAB-HR-151  
*dimethyl methyl phosphonate*  
5 % SOLUTION  
SOLVENT CCl<sub>4</sub>

1 ppm = 40.5 Hz  
( ) H<sup>1</sup> Decoupling  
(x) No Decoupling  
80 Averages  
H<sub>3</sub>PO<sub>4</sub> = 0 ppm

REMARKS  
*CB Sweep Mode*  
*F<sub>4</sub>O<sub>6</sub> Lock*



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162-22

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

Your ref

Our ref

Date 28 Feb 72

USE OF AN FT 100 UNIT IN A TIME-SHARED COMPUTER SYSTEM

Dear Professor Shapiro,

Our spectroscopic laboratories contain a Ferranti Argus 500 computer (16K store, 24-bit word) with a 625K disc backing store. We use the computer in a time-shared mode, incorporating an eight channel multiplexer system to collect data from a variety of experiments simultaneously. Proton Fourier transform NMR facilities have now been incorporated into the system. A Varian FT 100 unit was purchased and attached to our existing HA 100 spectrometer, but the interfacing of this unit to the Argus 500 and the associated software were our own responsibility. The use of a time-shared computer gave us some interesting problems and the notes below may help people who are considering similar systems.

Using the time-shared principle, since it cannot be guaranteed that at any particular instant the computer will be able to accept data, it is necessary for the computer to control the operation of the FT 100 unit. Thus pulse interval control is achieved in our system by having the computer send a continuous train of pulses (at 240  $\mu$  sec intervals) to a small hardware unit, which monitors these and delivers the initiation command itself to the FT 100 unit at desired intervals from 0.25 to 4 sec (or longer with slight modification, if required). The Rf pulse length is left under the normal internal control of the FT 100 unit.

Unfortunately the FT 100 unit does not respond instantaneously to the computer derived initiation command. A varying delay occurs because the FT 100 unit always produces the actual Rf pulse when the lock reference frequency is going negatively through zero. In our system this produces special problems



THE QUEEN'S AWARD  
TO INDUSTRY



- 2 -

since the digital sampling of the free induction decay must always be locked to the actual Rf pulse time, if gating is to be implemented properly.

The varying delay produces a situation where the digital sampling of the FID, although of the same frequency as the computer sampling (it is after all driven by the computer) is out of phase with it by a degree which changes from pulse to pulse. To cope with this, additional circuitry was devised which registers the phase difference for each pulse and utilises a sample and hold amplifier to acquire the samples at the correct time and hold them until the next computer sampling interval.

Collected FID data passes via one of the multiplexer channels and a 14-bit A/D converter onto disc. The multiplexer system requires continuous data acquisition with a channel sampling interval of 240  $\mu$  sec. This in general leads to the acquisition of two sorts of unwanted data:-

(i) Excess data are collected at the end of each FID. Hence a marker bit had to be introduced into the word corresponding to the first digitisation point of each FID, so that the requisite number of points for processing can be selected subsequently by software. Since only 14-bit data are collected, the marker bit is placed in one of the more significant bits of the 24-bit computer word.

(ii) Since the channel sampling interval is fixed, the data acquisition rate can be faster than required, leading to too much data on disc. This calls for a software sort of the data before processing.

Other parts of the system are more straightforward. Communication with the computer is via a teletype in conversational mode and the Cooley-Tukey algorithm is used for transformation. The initial and final phase correction controls of the FT 100 unit are retained and in our system a diplexer samples the variable voltages from these two controls. These voltages are digitised using a 12-bit ADC and placed in core via a digital input. Output from the computer goes via a 10-bit DAC to a storage/variable persistence oscilloscope or to the HA 100 recorder with the stepper motor under computer control.

We would be happy to discuss the system in greater detail with any interested parties, if they would contact us.

Yours sincerely,

*A.E. Fontaine*

A.E. Fontaine

*Don Mathias*

A. Mathias

*A. Margaret Wilde*

A.M. Wilde.

ABBOTT LABORATORIES, SCIENTIFIC DIVISIONS  
NORTH CHICAGO, ILLINOIS 60064

March 1, 1972

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

Dear Professor Shapiro:

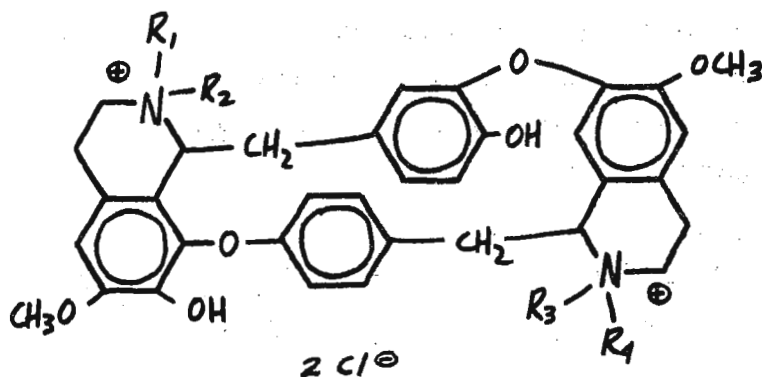
The Solution Conformation  
of (+)-Tubocurarine Chloride

The first postulated and widely accepted structure of (+)-tubocurarine chloride (1), a member of the bisbenzylisoquinoline family of alkaloids (1,2,3), was a tetra-N-methyl diquaternary salt. Recently workers at the Wellcome Research Laboratories have revised this structure (4) and proposed that it is a tri-N-methyl quaternary hydrochloride (2). They further have shown that (+)-chondrocurarine chloride is the tetra-N-methyl diquaternary compound 1 and not a positional isomer of (+)-tubocurarine chloride. These studies profited from the isolation of the di-N-methyl dihydrochloride, (+)-tubocurine chloride (3).

In order to obtain additional nmr evidence for the structure of (+)-tubocurarine chloride, the low field portion of the spectrum in DMSO- $d_6$  was carefully scrutinized. At ambient temperature the resonances are broad and ill defined (Fig. 1a); however, one unusual feature can be observed. A singlet resonance appears at 4.80 ppm which can only be assigned to an aromatic proton of either of the two tetrahydroisoquinoline groups. The doublet to slightly lower field was shown to arise from the proton at one of the asymmetric centers  $\alpha$ -to the ring nitrogen by spin-decoupling experiments.

Interestingly when the solution was heated to 90° and then to 125°, the chemical shift of the doublet resonance remained unaffected while the singlet shifted downfield until it reached 5.08 ppm (Fig. 1b and c).

A number of changes in the position of other aromatic proton resonances are also observed when the temperature is increased. The doublets centered at 6.10 and



- 1  $R_1 = R_2 = R_3 = R_4 = CH_3$   
 2  $R_1 = R_2 = R_3 = CH_3 \quad R_4 = H$   
 3  $R_1 = R_3 = CH_3 \quad R_2 = R_4 = H$

6.52 ppm in the ambient temperature spectrum as well as resonances in the 6.8-7.2 ppm region broaden and coalesce to a single broad resonance at 6.66 ppm at 125°.

The resonances unaffected by heating consist of two additional singlets (6.79 and 6.86 ppm) and an ABX pattern (7.04, 6.89, and 6.54 ppm;  $J_{AX} = 2$  Hz,  $J_{BX} = 0$  Hz, and  $J_{AB} = 8$  Hz). The two singlet resonances arise from the remaining tetrahydroisoquinoline aromatic protons and the ABX pattern from the protons of the trisubstituted aromatic ring. Therefore, by a process of elimination the aromatic resonances which broaden and coalesce can be attributed to the protons of the disubstituted aromatic ring.

These observations can be explained when the solution conformation of (+)-tubocurarine chloride is considered. (Fig. 2). The conformation correctly incorporates the configurations determined by Tomita (5) for the two asymmetric centers.

The bulk of the aromatic rings requires that they be oriented perpendicular to the plane of the tetrahydroisoquinoline rings. This relationship places one aromatic proton of the tetrahydroisoquinoline hydrochloride ring over the center of the disubstituted aromatic ring. Because of the nature of the magnetic anisotropy of the aromatic ring this arrangement results in the anomalously high field chemical shift of the singlet resonance. The proton on the asymmetric carbon of the quaternary tetrahydroisoquinoline ring is oriented at the periphery of three aromatic rings and therefore deshielded relative to the analogous proton of the tetrahydroisoquinoline hydrochloride group which is affected by only two aromatic rings.

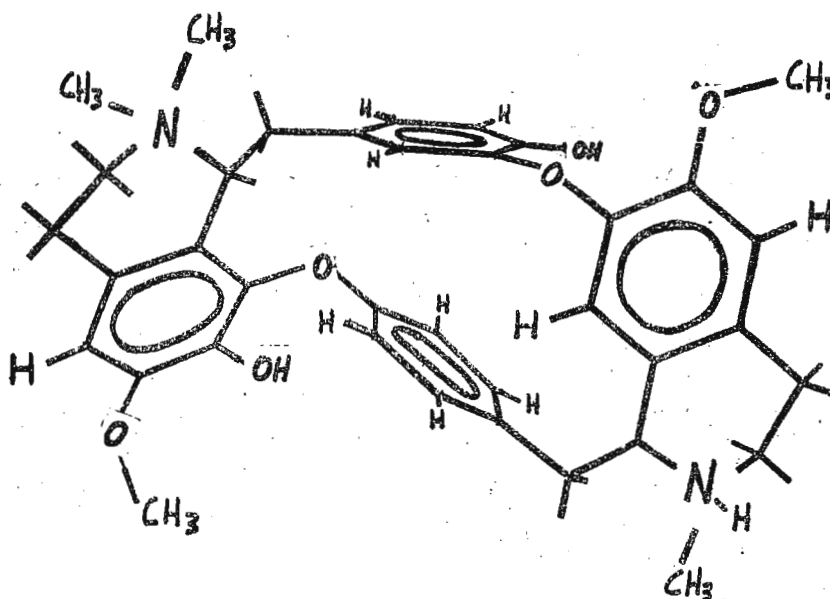


Fig. 2

Dreiding model constructions of this conformation reveal that the disubstituted aromatic ring can rotate along the axis between the p-substituents although nearby substituents are likely to cause this rotation to be hindered. The nmr spectra confirm that at ambient temperature the rotation is hindered and the four protons of this ring are non-equivalent (ABCD system) and give rise to four doublet of doublet resonances. At elevated temperature the rate of rotation increases and the four resonances begin to coalesce to an AA'BB' pattern. Increased rotation of the aromatic ring also affects the chemical shift of the tetrahydroisoquinoline hydrochloride aromatic proton. A shift to lower field is observed since the shielding by the disubstituted aromatic ring decreases as the rotation rate increases due to a change in the time averaged orientation of the two rings.

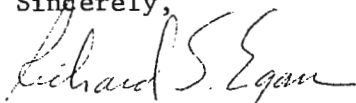
The trisubstituted aromatic ring does not rotate even at elevated temperature because of its meta-attachment to the tetrahydroisoquinoline rings. Therefore the resonances of these ring systems are unaffected by elevated temperature as is the chemical shift of the proton on the asymmetric carbon of the tetrahydroisoquinoline quaternary salt group.

These considerations confirm in part the structure proposed by the Wellcome group. In addition, evidence for the solution conformation including the presence of biphenyl-like hindered rotation has been obtained. Totally analogous results have been obtained with 1 and 3.

#### REFERENCES

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- (2). M. Kulka, *ibid*, Vol. VII, 1960, p. 439-470.
- (3). M. Curcumelli-Rodostamo and M. Kulka, *ibid*, Vol. IX, p. 134-170.
- (4). A. J. Everett, L. A. Lowe, and S. Wilkinson, *Chem. Comm.*, 1020 (1970).
- (5). M. Tomita and J. Kunitomo, *Yakugaku Zasshi*, 82, 741 (1962); *C. A.*, 58, 4613 (1963).

Sincerely,



Richard S. Egan  
nmr lab, D-482

msg

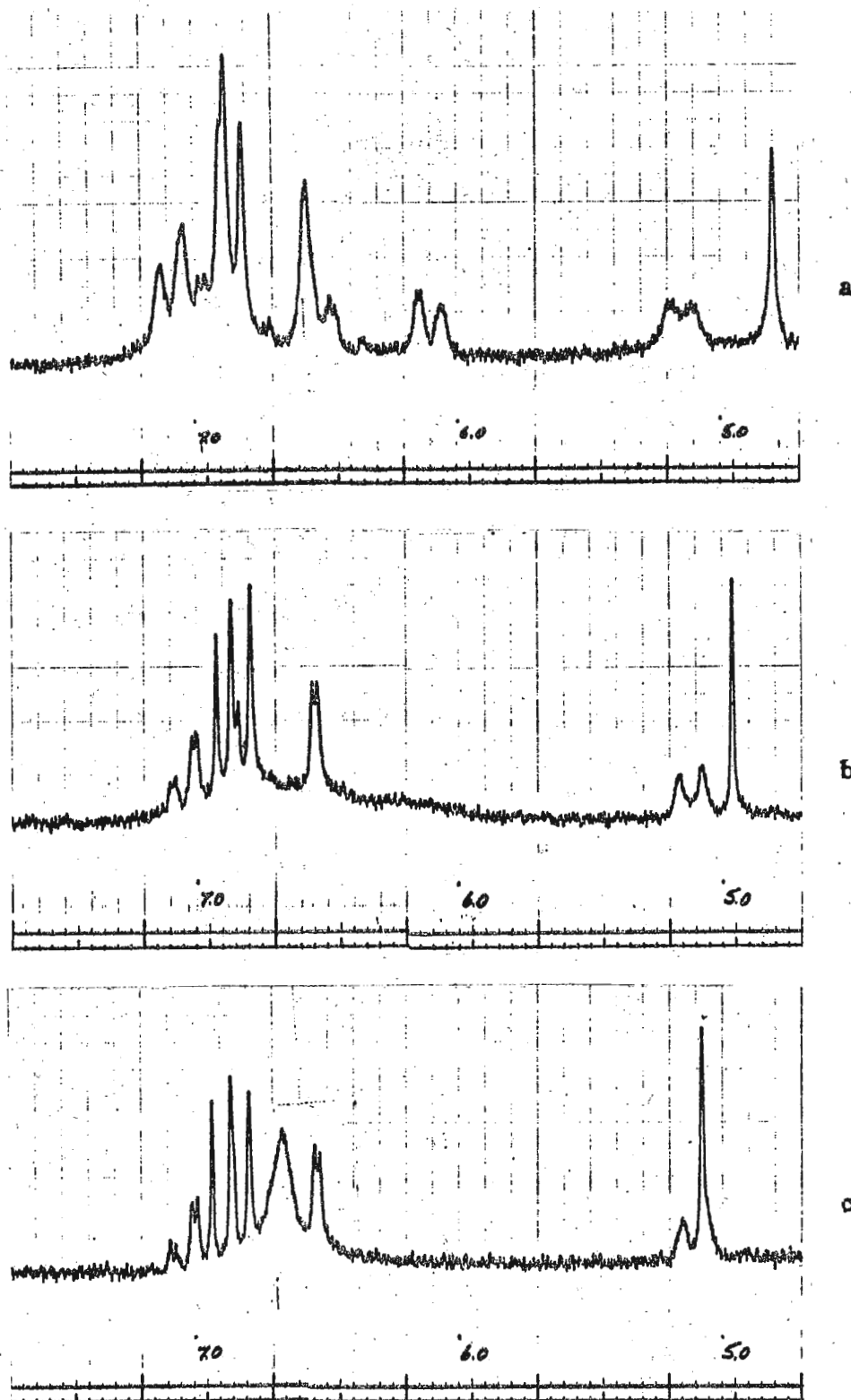


Fig. 1 Downfield region of the nmr spectrum of (+)-tubocurarine chloride in  $\text{DMSO-d}_6$  solution at various temperatures.

a = ambient, b =  $90^\circ$ , c =  $125^\circ$

## UNIVERSITI MALAYA

Department of Chemistry  
Lembah Pantai  
KUALA LUMPUR  
MALAYSIA



ALAMAT KAWAT: UNIVSEL  
TALIPON: 54361 (6 Saraf)

February 26, 1972

Bil. Kami:

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

Dear Professor Shapiro:

HOW TO SHIFT THE MALAYAN PENINSULA  
OR  
THE USE OF  $\text{Pr}(\text{TTA})_3$  AS A SHIFT REAGENT FOR BENZYLIC SYSTEM

Keeping up with the "in-thing" in lanthanide chemistry, we are currently investigating the use of various lanthanide(III) complexes as shift reagents. Last winter when we saw the clouds appearing behind the Pantai Hills (our University is situated in very pleasant surroundings in Pantai Valley), some of our final year students got up the courage to investigate various aspects of lanthanide chemistry. Mr Kong Sian Chin thought that he might succeed in moving the three peaks of the Pantai Hills and started using tris-thenoyl-trifluoroacetate complex of Pr(III) as shift reagent for benzyl alcohol (for historic reason only).

He tumbled on a very "hot-field" and he was pleasantly surprised to see that all peaks (ortho, meta,  $\text{CH}_2$  and OH protons) in benzyl alcohol move up-field as expected, except for the peak of para proton, which exhibited an unexpected down-field shift. This "pulling apart" effect of  $\text{Pr}(\text{TTA})_3$  reagent got us started with our romance with the benzylic system and sure enough the up-field shift of the ortho and meta protons and the down-field shift of the para proton were also observed for benzylamine and dibenzylamine (Figure).

When the "romance" was at its peak, I picked up the bottles of dibenzylether and tribenzylamine just to confirm our observations. The peaks of "Pantai Hill" showed some resistance and remained practically unshifted (Figure). This was quite a surprise for us and we are at present busy checking all the benzylic systems we can get our hands on to reveal the "Benzylic Mystery".

Sincerely yours,

*S. P. Sinha*  
Shyama P. Sinha

P.S.

Kindly credit this letter towards the subscription of Dr. R.D. Green.

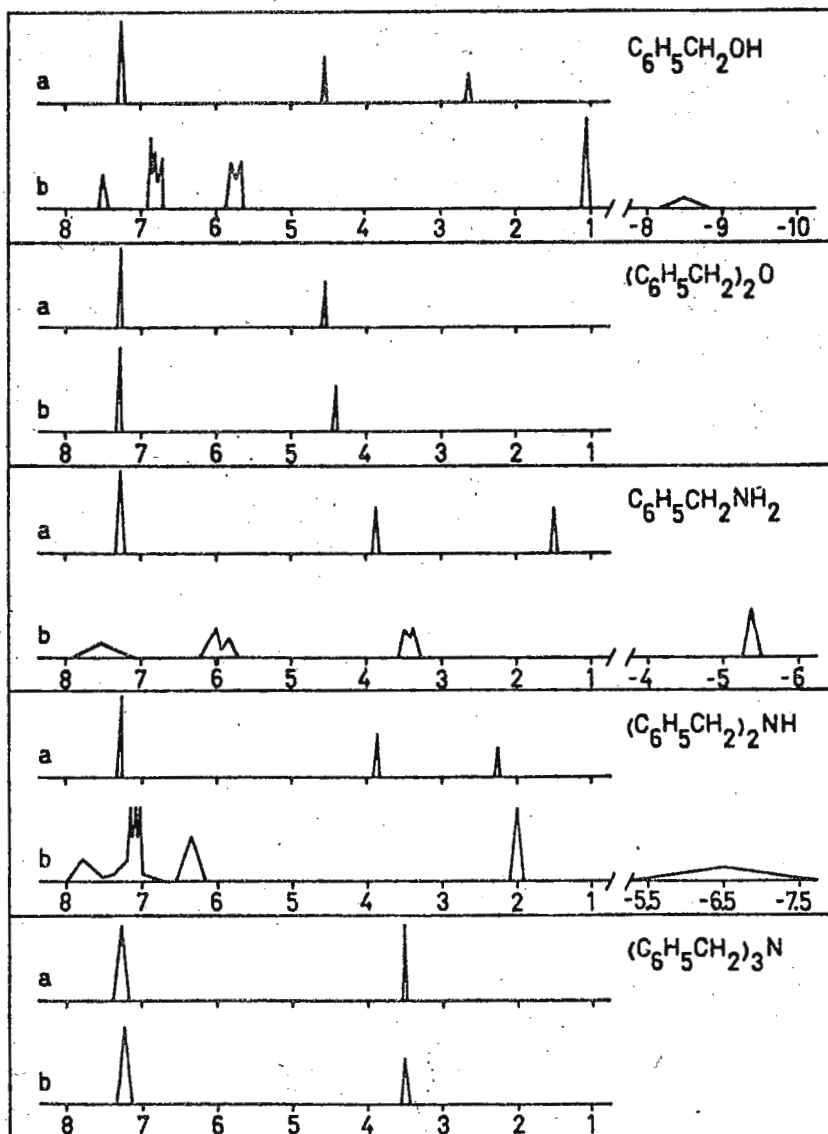


FIGURE : (a) 60 MHz spectra of benzylalcohol, dibenzylether, benzylamine, dibenzylamine and tribenzylamine in  $\text{CDCl}_3$   
 (b) Spectra obtained after the addition of  $\text{Pr}(\text{TTA})_3$  in a mole ratio  $\text{Pr}(\text{TTA})_3$ :substrate = 0.1 - 0.2

JOB WANTED

PAT W. FLANAGAN

Pat W. Flanagan  
 RR 2, Box 227  
 Ponca City, Oklahoma 74601  
 405-762-4627

Married, 2 children  
 U. S. Citizen  
 Good Health  
 Born June 20, 1931

JOB OBJECTIVE: The application of physical and instrumental techniques to problems in organic chemistry. Principal experience is with nuclear magnetic resonance, with some experience in electron spin resonance and mass spectrometry. Want job with industrial, governmental, or institutional organization that considers organic chemistry of prime importance, or with academic institution where emphasis is on teaching. Willing to reorient. Long-term goal is technical management.

WORK EXPERIENCE:

1960-Present                      Analytical Research Section  
    Continental Oil Company  
    Ponca City, Oklahoma

Established, organized, operated, and maintained nuclear magnetic resonance laboratory. Developed methods for structure elucidation and quantitative analysis by NMR. Applied NMR to problems in petrochemical R&D, petrochemical plant operations, and refinery operations. Did majority of maintenance on Varian HR-60 and HA-100 instruments. Some technical supervision of one chemist and one technician. Established ESR laboratory function. Some recent experience in interpretation of mass spectral data. Publications: approximately 25.  
 Reason for leaving: reduction-in-force termination.

1957-1960                      Petrochemical Research Division  
    Continental Oil Company  
    Ponca City, Oklahoma

Synthetic organic chemist and physical-organic chemist. Reactions of organoaluminum compounds. Six U. S. patents. Reason for leaving: intra-company transfer.

EDUCATION:

<u>School</u>	<u>Degree</u>	<u>Major</u>	<u>Minor</u>	<u>Year</u>
Miami U. (Ohio)	B.S.	Chemistry	Math	1953
Ohio State U.	Ph.D.	Organic Chem.	Physical Chem.	1957

I plan to attend the 13th ENC, April 30 - May 4, 1972.

*Pat W. Flanagan*





The University of Western Ontario, London 72, Canada

Faculty of Science  
Department of Chemistry

March 3, 1972.

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

Dear Barry:

POSITION AVAILABLE

I would like to draw to the attention of the readers of TAMU newsletter that the Chemistry Department, University of Western Ontario is beginning a search for a Senior Scientific Officer. Dr. Clark would be pleased to receive inquiries from anyone interested. A brief description follows.

Applications are invited for the post of Senior Scientific Officer from persons with substantial experience in the field of nuclear magnetic resonance spectroscopy. The position involves responsibility for the operation of most major instruments in the Department, with particular emphasis on n.m.r. and mass spectroscopic facilities, as well as involvement in the research activities of the Photochemistry Unit within the Department. The appointee will be a member of the support staff of the Department and will hold a Ph.D or M.Sc. degree in Chemistry. The appointment will be made for 2 years in the first instance. Salary negotiable but not less than \$10,000. Applications should be sent to Dr. H.C. Clark, Head, Department of Chemistry, University of Western, Ontario, London, Canada, as soon as possible.

Best regards,

*Jake*

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TAMU NMR NEWSLETTER

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