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Newsletter

RECEIVED JUN 4, 1976

No. 212

May, 1976

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DEADLINE DATES: No. 213: 31 May 1976  
 No. 214: 5 July 1976

(Due to vacation scheduling, it will  
 be necessary that all contributions for  
 the June issue be in by this date.)

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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SCHOOL OF PHARMACY  
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

March 1, 1976

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

Title: 1. Water Proton  $T_1$ ,  $T_2$ , and  $T_{1\rho}$  Measurements Fit to Log Normal Distribution of Correlation Times for Packed Erythrocytes (Adult and Sickled) at Low Temperature

Dear Barry:

We have been making proton NMR relaxation time measurements on water in packed red blood cells, both normal adult and sickle, in an attempt to understand the interactions of water with cellular components and the motion of the water associated with those components chiefly hemoglobin. In order to simultaneously account for all our  $T_1$  data (at different frequencies),  $T_2$  data, and  $T_{1\rho}$  data (at several different rf power levels), all measured over a wide temperature range, it has been necessary to use a distribution of correlation times with three maxima for studies of erythrocytes above freezing and with two maxima for studies below the freezing point of bulk water.

The  $T_{1\rho}$  measurements have made it possible to sample water molecules with large ( $\sim 10^{-5}$  to  $10^{-6}$  sec) correlation times. With this additional data, not available in previous investigations, we have noted a maximum at about  $10^{-6}$  sec which could not previously have been observed with ordinary  $T_1$  and  $T_2$  measurements. We presently ascribe the three maxima to bulk water, water "loosely bound" to hemoglobin, and water "tightly bound" to hemoglobin. Each type of water has a distribution of correlation times. At temperatures much below  $0^\circ$ , only two maxima are obtained which correspond to the bound water.

The distribution of correlation times for packed adult erythrocytes has been determined by simultaneously fitting all the  $T_1$ ,  $T_2$ , and  $T_{1\rho}$  data. A computer fit to a log normal distribution,

$$\psi(Z) = \frac{1}{BV\pi} \exp[-(Z/B)^2],$$

$$Z = \ln(\tau_c/\tau_c^*),$$

was made.  $\tau_c$  is the correlation time and  $\tau_c^*$  is the median of the distribution. The results of the computer fit for packed erythrocytes at  $-55^\circ$  are shown in the accompanying figure. The parameters for the fit are



Professor B.L. Shapiro  
March 1, 1976

$$\tau_c^*(1) = 1.3 \times 10^{-8} \text{ sec, } B = 3.2, \text{ Fraction} = 0.84, E_a = 9 \text{ kcal/mole}$$

$$\tau_c^*(2) = 1.85 \times 10^{-6} \text{ sec, } B = 0.85, \text{ Fraction} = 0.16, E_a = 7.3 \text{ kcal/mole}$$

We would also like to invite applications for a post-doctoral position. Research into the role played by water in biological tissue will be the primary focus of the post-doc. In addition to the pulsed NMR apparatus, we have a multinuclei XL-100 with Nicolet FT set-up for use in this research. The stipend will be in the range \$11,000-\$12,500 and is renewable after the first year. Interested applicants should send a resume to Thomas L. James and have two letters of recommendation sent.

Sincerely,

*Tom*

Thomas L. James  
Assistant Professor of Chemistry  
and Pharmaceutical Chemistry

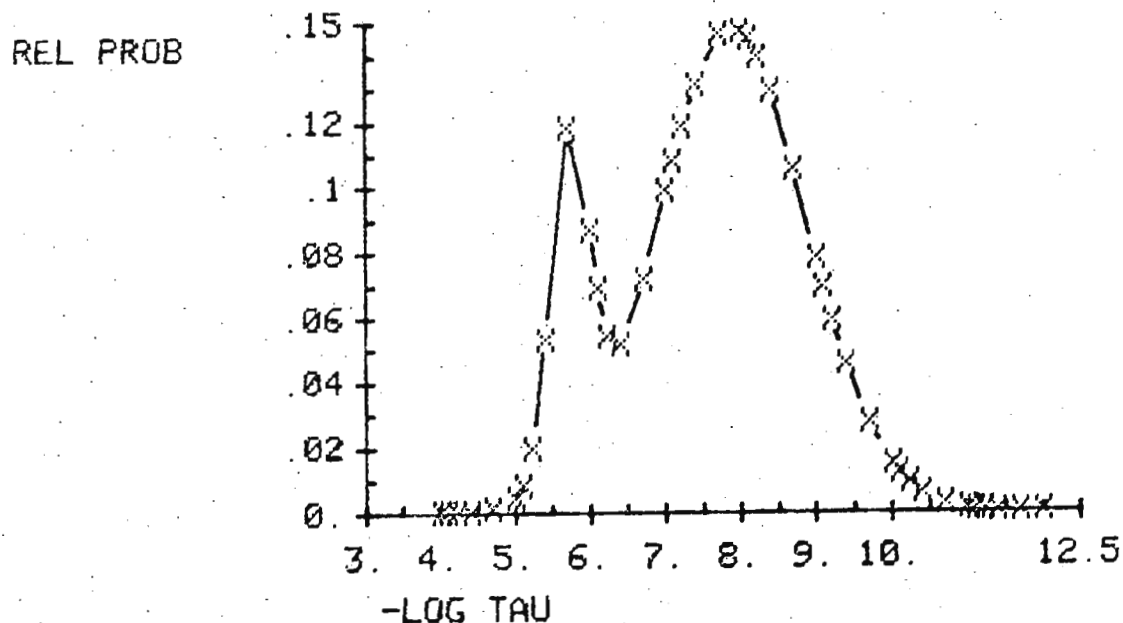
*Tack*

Irwin D. Kuntz  
Associate Professor of Chemistry  
and Pharmaceutical Chemistry

*Adam Zipp*

Adam Zipp  
NIH Post-Doctoral Fellow

TLJ:dc



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DEPARTMENT OF CHEMISTRY

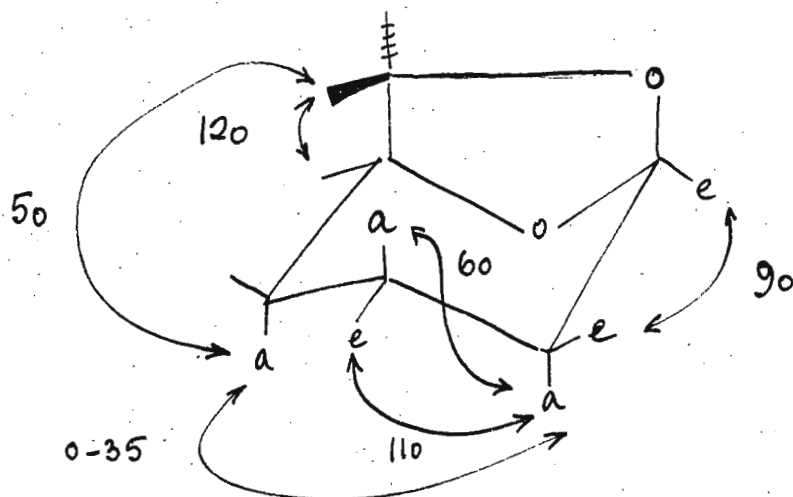
March 19, 1976

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

Dear Barry:

Further Proton  $R_1$ -values

As part of our continuing interest in proton spin-lattice relaxation we have measured the  $R_1$ -values for all the ring protons of the eight, isomeric 1,6-anhydro- $\beta$ -D-hexopyranose triacetates. This gives us 56 separate  $R_1$ -values from which we can obtain by simple regression analysis values for the specific interproton relaxation rates; these are summarized below. Since we know from other experiments that these protons relax



Interproton relaxation  
Contributions - in  
msec<sup>-1</sup>.

exclusively via the dipole-dipole relaxation mechanism, we can use these values to calculate the geometry of these molecules. From the standpoint of n.m.r. spectroscopy it is interesting to find that one can intercompare the proton  $R$ -value of different molecules in much the same way as chemical shifts and coupling constants.

These measurements were made by Klaus Bock whilst he was on sabbatical leave here from the Technical University of Denmark.

With all best wishes,

Yours sincerely,

*L.D. Hall*

L.D. Hall

LDH:lm1



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

U S A

~~MIAMI~~ Sesto, 29/3/1976

da citare nella risposta 20/SEAN/LC

Subject : 2,4-/2,6- Isomer ratio in commercial toluene di-iso-  
cyanates.

Commercial toluene di-isocyanate (TDI) is a mixture of 2,4- and 2,6-isomers. A rapid and accurate method to determine the 2,4-/2,6- isomer ratio is not known even if some IR<sup>(1)</sup> and GC<sup>(2)</sup>, procedure have been reported. Recently a proton NMR<sup>(3)</sup> and <sup>13</sup>C NMR<sup>(4)</sup> method have been also suggested. About the proton NMR method the analysis is done in hexafluorobenzene as solvent observing the CH<sub>3</sub>- resonances.

The CH<sub>3</sub> resolution of the two isomers, however, is not good enough and is such that it interferes with a straightforward and accurate quantitative analysis on the bases of the integrated spectrum.

We currently determine the 2,4-/2,6- isomer ratio in commercial toluene di-isocyanates since several time, using pyridine bases as solvents. In particular, the best separation and resolution of the CH<sub>3</sub>- resonances is observed in quinoline, as shown in the hereby attached Figure. In quinoline the CH<sub>3</sub>- resolution is normally good, ca. 1.5 Hz at half-width vs. ca. 3.5 Hz of the spectrum in hexafluorobenzene as reported<sup>(3)</sup>. The  $\delta$  values are :

$\delta$  = 1.81 for the 2,4-isomer and  $\delta$  = 1.76 for the 2,6 isomer.

The points of inflection of the integrals, being well defined, allows a rapid and accurate analysis.

your sincerely,

*Cancellieri* *Cavalli*  
(G. Cancellieri) (L. Cavalli)

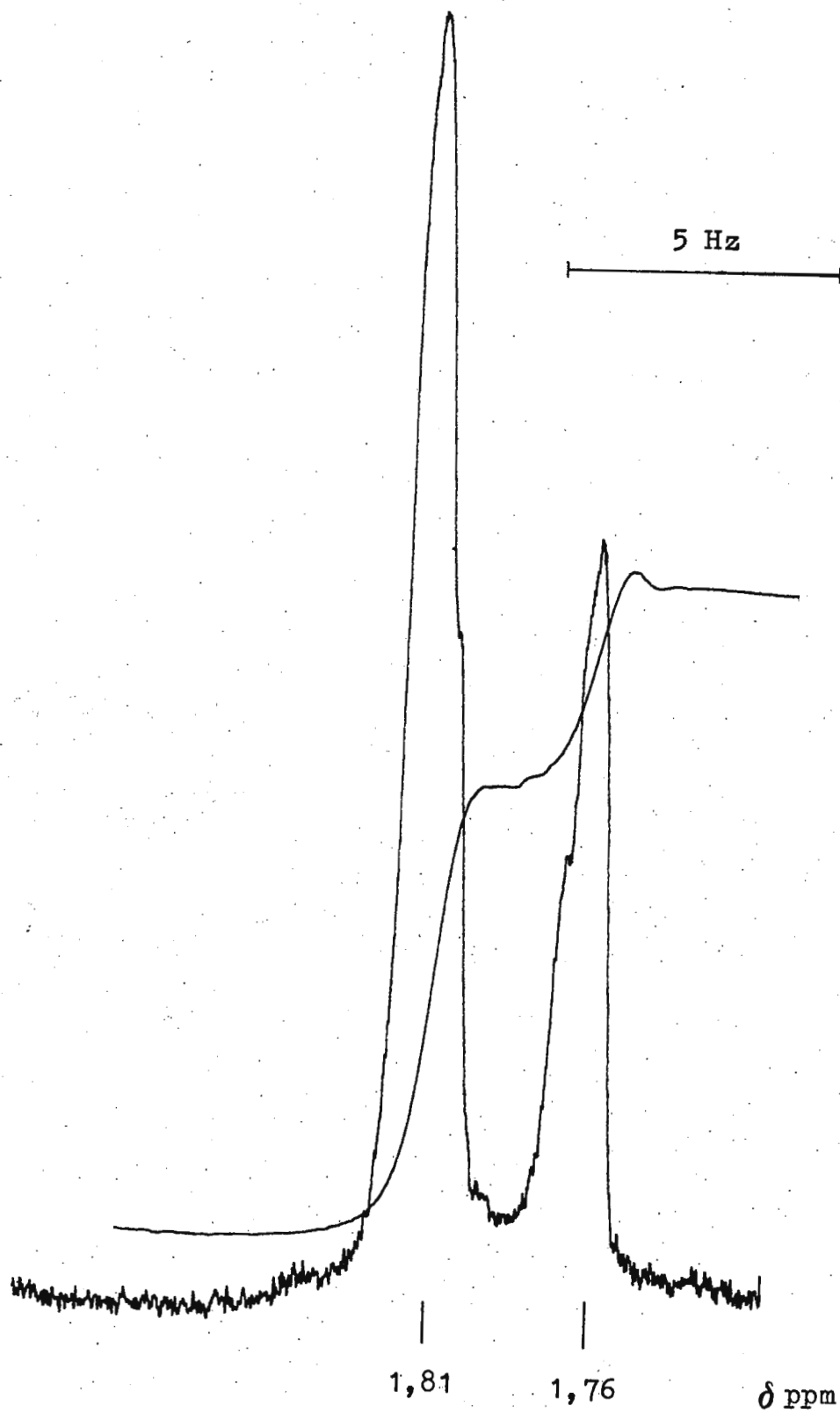
- 1) ASTM 1638-70
- 2) B.G. Belen'Ku, V.A. Orestova and Yu. E. Eizner, Zh. Analit. Khim., 20, 934, 1965.
- 3) M.R. Platten, Org. Magn. Resonance 7, 306, 1975.
- 4) I.K. O'Neill and M.A. Pringer, Org. Magn. resonance 6, 398, 1974.

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60 MHz, Spectrum of Commercial  
Toluene di-isocyanate in Quinoline



DEPARTMENT OF ORGANIC CHEMISTRY  
**The University of Sydney**

March 29, 1976

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

N.S.W. 2006

BOND FIXATION BY ELECTRONIC EFFECTS

Dear Barry,

It has been recognized for some time<sup>1</sup> that the absolute magnitudes of the (negative) long-range coupling constants  $^4J_{\text{cisoid Me-C=C-H}}$  vary monotonically with the bond-order of the double bond, although we believe<sup>2</sup> that the previously proposed relationships should be modified. This effect has been usually considered in connection with a series of hydrocarbons such as (1)-(4) and has been applied<sup>3</sup> to the study of the electronic structure of polynuclear aromatic hydrocarbons, but should also reflect any bond-fixation<sup>4</sup> in benzene derivatives with suitably located electron-donating and electron-withdrawing groups, such as (5).

In fact it can be seen that orthobenzylic coupling constants in a series of simple m-nitrotoluenes (Table 1), vary in the manner expected from simple VB considerations (5b) when strongly electron-donating groups are present at C-4. This series is not really very suitable for such an investigation because of possibilities of variation in the average conformation of the nitro group with respect to the plane of the ring and was chosen only because of the availability of the materials. We are now preparing a series of the corresponding nitriles (5, X = electron-donor, Y = CN) and there are many obvious variations on this theme.

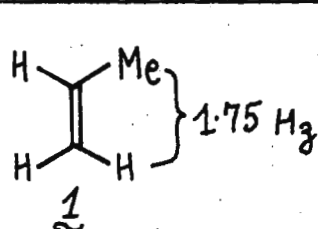
With best regards  
 yours sincerely

*S. Sternhell*

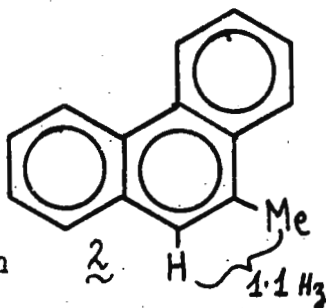
S. Sternhell

<sup>1</sup>Jackman and Sternhell, "Applications of NMR spectroscopy in organic chemistry", Ch. 4-4 (Pergamon, 1969); Barfield and Chakrabarti, Chem. Revs.,

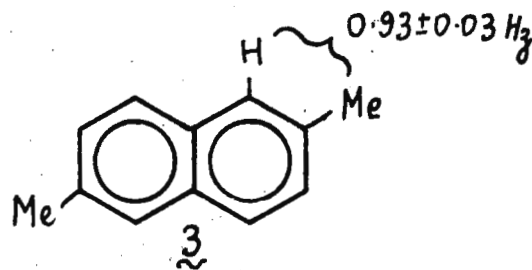
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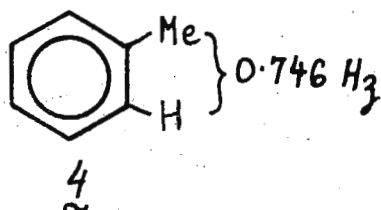
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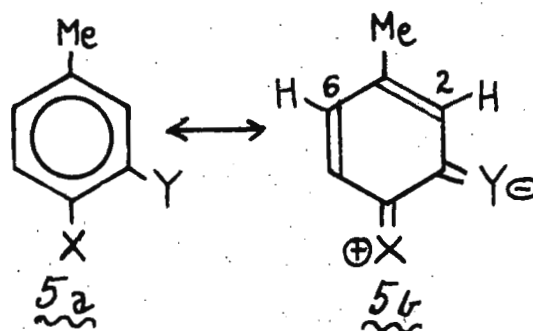


Table 1 <sup>a</sup>

X	Y	$^4J_{\text{Me}, \text{H}-6}$ (Hz)	$^4J_{\text{Me}, \text{H}-2}$ (Hz)
OH	NO <sub>2</sub>	0.62 $\pm$ 0.05	1.00 $\pm$ 0.05
NH <sub>2</sub>	NO <sub>2</sub>	0.51 $\pm$ 0.03	0.90 $\pm$ 0.03
F	NO <sub>2</sub>	0.67 $\pm$ 0.03	0.75 $\pm$ 0.03
OAc	NO <sub>2</sub>	0.69 $\pm$ 0.03	0.73 $\pm$ 0.03
OMe	NO <sub>2</sub>	0.68 $\pm$ 0.04	0.69 $\pm$ 0.06
Cl	NO <sub>2</sub>	0.70 $\pm$ 0.06	0.70 $\pm$ 0.05
I	NO <sub>2</sub>	0.70 $\pm$ 0.06	0.70 $\pm$ 0.06

<sup>a</sup> This work was performed by D. Antonjuk and R. Grant as part of their senior undergraduate laboratory work.

ת.ד. 2053  
 באר שבע 84120  
 הקריה החדשה  
 64111 ס.  
 הקריה הישנה  
 71241 ס.  
 P.O. BOX 2053  
 BEERSHEVA 84 120, ISRAEL  
 NEW CAMPUS  
 PHONE 64111  
 OLD CAMPUS  
 PHONE 71241

הפקולטה למדעי הטבע  
 המחלקה לכימיה  
 FACULTY OF NATURAL  
 SCIENCES  
 DEPARTMENT OF CHEMISTRY

אוניברסיטת  
 בן גוריון  
 בנגב  
 BEN GURION  
 UNIVERSITY  
 OF THE NEGEV



: תאריך / DATE

: מספרנו / OUR REF: SM/IS

30 March 1976

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

Dear Professor Shapiro:

Title: Is There a Cutoff Frequency?

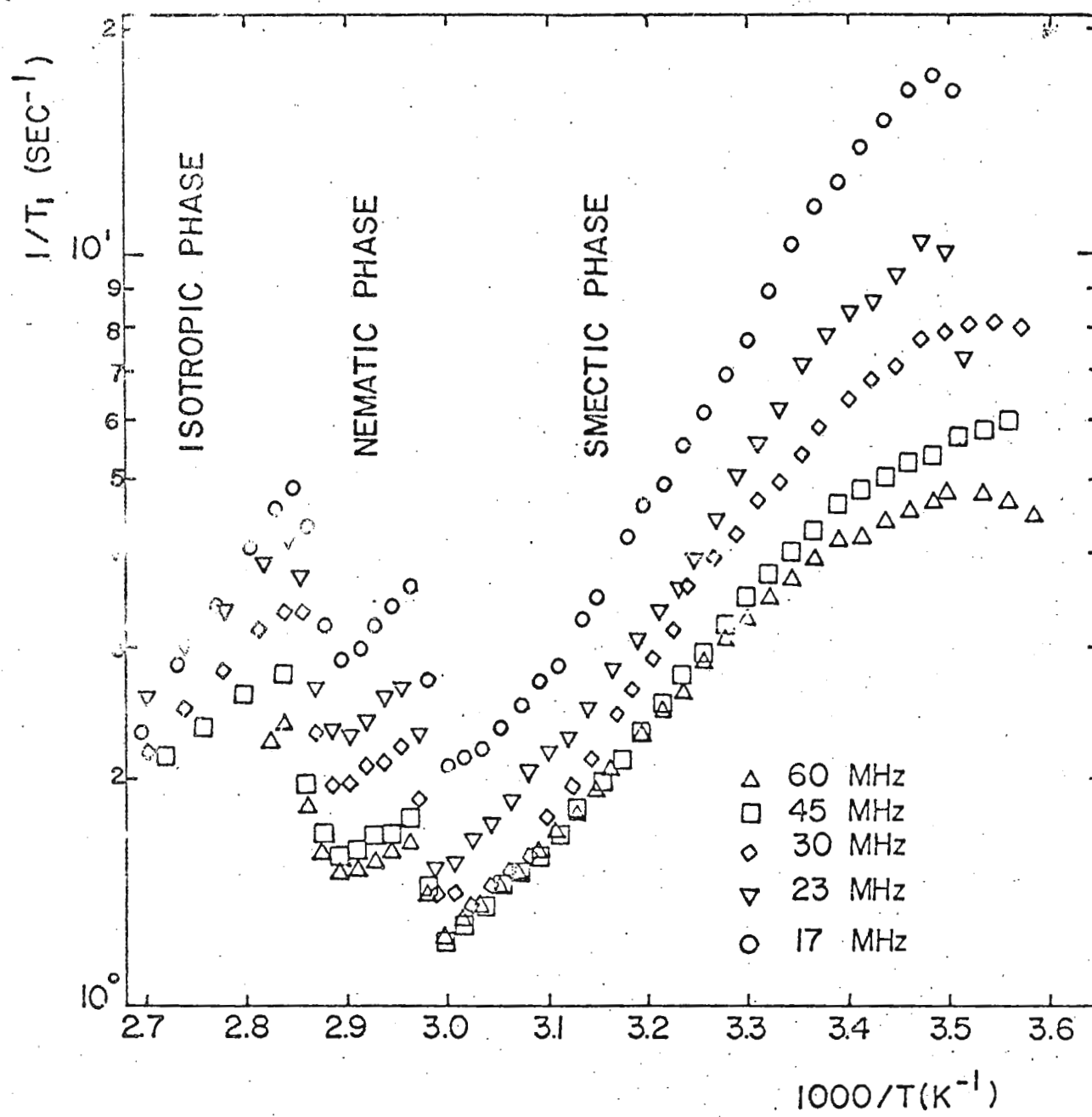
As you know, there have been attempts to explain the  $T_1$  relaxation in liquid crystals in terms of the fluctuation of the order parameter and a critical cutoff frequency. However, the effect has been questioned, at least in the case of the relaxation of some nematogens. Recently, we have prepared some very long liquid crystals (octyloxy-benzylidene proylaniline) in an attempt to characterize the parameters governing relaxation. This particular compound exhibits a smectic and nematic phase and  $T_1$  studies on it as a function of temperature and frequency suggest that the relaxation of the smectic phase can be explained in terms of a critical cutoff frequency (see figure). This is perhaps not too surprising since the critical frequency is an inverse function of the viscosity and the length of the molecule both of which are quite large in this system.

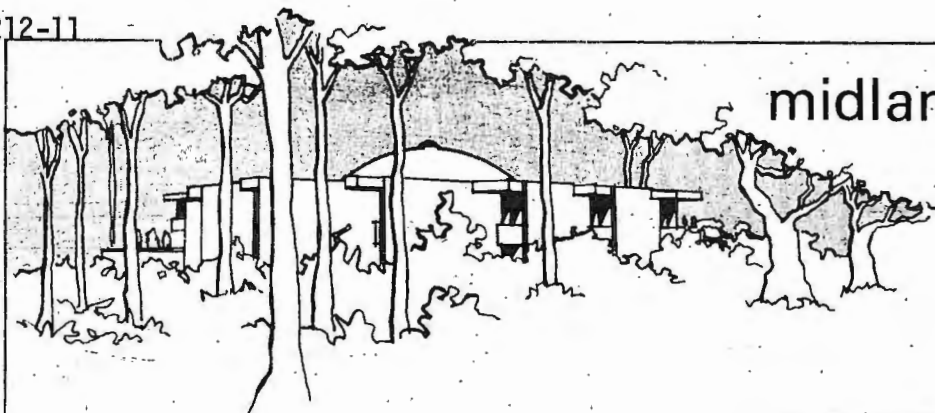
Credit for this work goes to my coworkers Drs. S. Goren and C. Korn.  
 Please credit this to the account of Dr. D. Kost.

Sincerely,

Stephen Marks







## midland macromolecular institute

1910 West St. Andrews Drive  
(517) 631-9450  
Midland, Michigan 48640

April 2, 1976

Dr. Barry L. Shapiro  
Texas A & M University  
Department of Chemistry  
College Station, TX 77840

Dear Barry:

We have a high field fourier transform nmr spectrometer at MMI which is currently being used only about 1/3 of the time by our staff and, thus, can be made available to the general scientific community.

Our system operates at 260 MHz for protons and can be used for variable temperature experiments. We also have the capability of observing many other nuclei and have obtained spectra from C-13, P-31, F-19, Si-29, Cd-113, Li-7, Pt-195, Mg-25 and Na-23.

Although our facility is not supported by governmental agencies, we will offer spectrometer time at a reasonable price. Anyone interested in purchasing spectrometer time should write or call the Midland Macromolecular Institute.

Sincerely,

*Robert J. Kostelnik*

Robert J. Kostelnik

jae



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UNITED STATES  
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION  
PITTSBURGH ENERGY RESEARCH CENTER  
4800 FORBES AVENUE  
PITTSBURGH, PENNSYLVANIA 15213

April 2, 1976

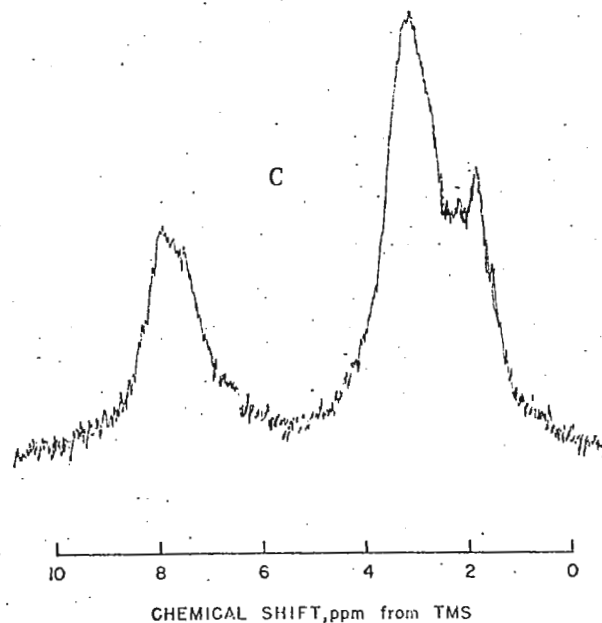
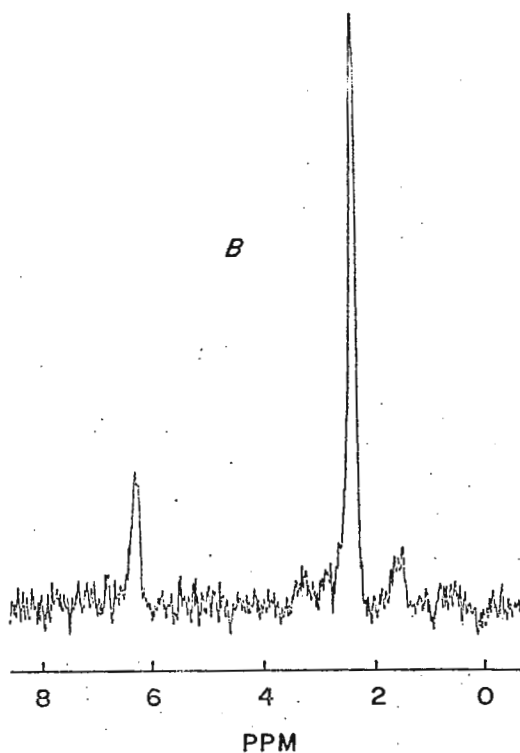
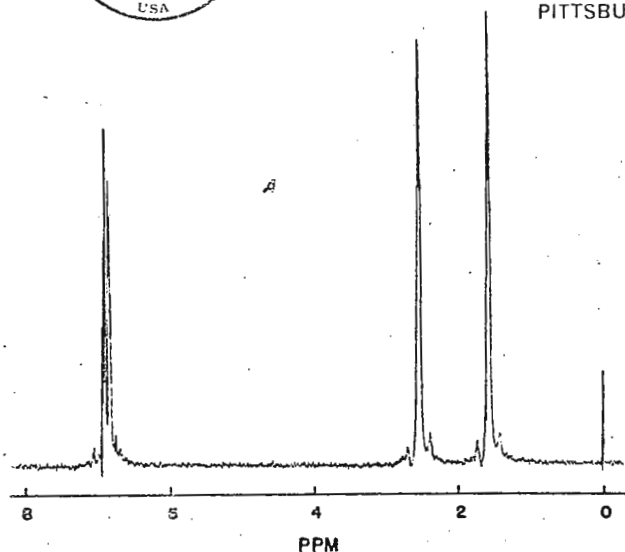
$^2\text{H}$  NMR STUDIES OF  
COAL LIQUEFACTION

Dear Barry:

We are currently using  $^2\text{H}$  nmr to study the incorporation of stable isotopes during coal liquefaction. The proton spectrum (A) of a partially deuterated tetralin gives little information about the distribution of the label. The  $^2\text{H}$  spectrum (B), however, indicates that preferential incorporation had taken place at alpha sites. The  $^2\text{H}$  spectrum (C) of a SYNTHOIL coal liquefaction product obtained simply by heating in an atmosphere of pure  $\text{D}_2$  shows a broad distribution of the label. Again, preferential incorporation of the deuterium at benzylic sites had occurred. These materials will be used as vehicle oils in future experiments to investigate hydrogen transfer in coal liquefaction processes.

Sincerely yours,

H. L. Retcofsky  
Research Physicist





## Organisch chemisch laboratorium

Croesestraat 79  
Utrecht 2503  
Telefoon 030-882311

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

Datum  
Uw kenmerk  
Ons kenmerk  
Onderwerp

April 5, 1976

Peak positions and peak intensities in FT Spectroscopy  
Bug in SIMEQ-II

Dear Professor Shapiro,

In FT-NMR spectroscopy one encounters some problems in the determination of exact peak-positions and peak-intensities in the frequency-domain spectrum. The first parameter is a must for accurate chemical shift determinations and therefore most FT programs contain a routine to determine the exact peak position (which does not coincide with the position of the data point with the maximum amplitude in the transform) by an interpolation method using the amplitudes in the maximum and the two adjacent data points.

The exact peak intensities were deemed of much less interest and hence, these are not calculated in most programs. The reported peak intensities are then the amplitudes for the data points with the highest intensity. Relative peak intensities could, of course, be determined by integration but, for extremely narrow peaks, this procedure is less satisfactory. For the cases in which exact intensities are required i.e. NOE and  $T_1$  measurements, one assumes that the intensity for the maximum data point becomes proportional to the peak intensity by using rather excessive peak broadening.

We found this situation not satisfactory and therefore designed a way to obtain the exact peak position, peak amplitude and peak width directly from the frequency-domain spectrum. The peak intensity is then proportional to the product of peak amplitude and peak width. The basic assumption we made is that three data-points,  $w_{-1}$ ,  $w_0$  and  $w_{+1}$ , with amplitudes  $A_{-1}$ ,  $A_0$  and  $A_{+1}$  resp.

determine a Lorentzian line  $A(w) = \frac{A_{\max}}{1 + B(w - w_{\max})^2}$  with position  $w_{\max}$ ,

amplitude  $A_{\max}$  and half-height width  $\Delta w_{\frac{1}{2}} (= 2B^{-\frac{1}{2}})$ . The data-point  $w_0$  is the data-point with the highest amplitude and  $w_{\pm 1}$  are adjacent points (see figure 1). The frequency-interval between two adjacent points is  $\Delta w$ .

We obtain the following results for  $w_{\max}$ ,  $A_{\max}$  and  $\Delta w_{\frac{1}{2}}$

$$w_{\max} = w_0 + \frac{1}{2} \alpha \Delta w \quad 1$$

$\alpha$ , the skewness of the peak, is defined by

$$\alpha = \frac{A_{+1} - A_{-1}}{A_{+1} + A_{-1} - \frac{2A_{+1}A_{-1}}{A_0}} \quad 2$$

$$A_{\max} = \frac{A_0}{1 - \frac{1}{8\alpha} \frac{A_0 A_{+1} - A_0 A_{-1}}{A_{-1} A_{+1}}} \quad 3$$

$$\Delta w_{\frac{1}{2}} = 2\Delta w \left[ \frac{1}{\frac{A_0 A_{+1} + A_0 A_{-1}}{2A_{-1} A_{+1}} - 1} - \frac{1}{4} \alpha^2 \right]^{\frac{1}{2}} \quad 4$$

This set of formulae is in general quite easy to introduce into the existing software. An alternative solution would be to print the values  $A_{-1}$ ,  $A_0$  and  $A_{+1}$  instead of only  $A_0$  in the intensity print procedures and calculate  $A_{\max}$  and  $\Delta w_{\frac{1}{2}}$  if needed. We use at the moment this latter procedure and are quite satisfied with the improvement in the accuracy of NOE and  $T_1$  measurements achievable with this method provided the signal to noise ratio is good.

#### Bug in SIMEQ-II

In the transformation of SIMEQ into SIMEQ II software multiply and divide routines were replaced by hardware routines. However, as these routines are not completely equivalent, a bug was introduced into the square-root subroutines, which in some special cases, especially when coupling constants that are integer multiples of 2 are used, may lead to an erroneous result. In practically all cases the occurrence of the error is directly obvious from the spectrum.

The error could be corrected by increasing or decreasing the coupling constant

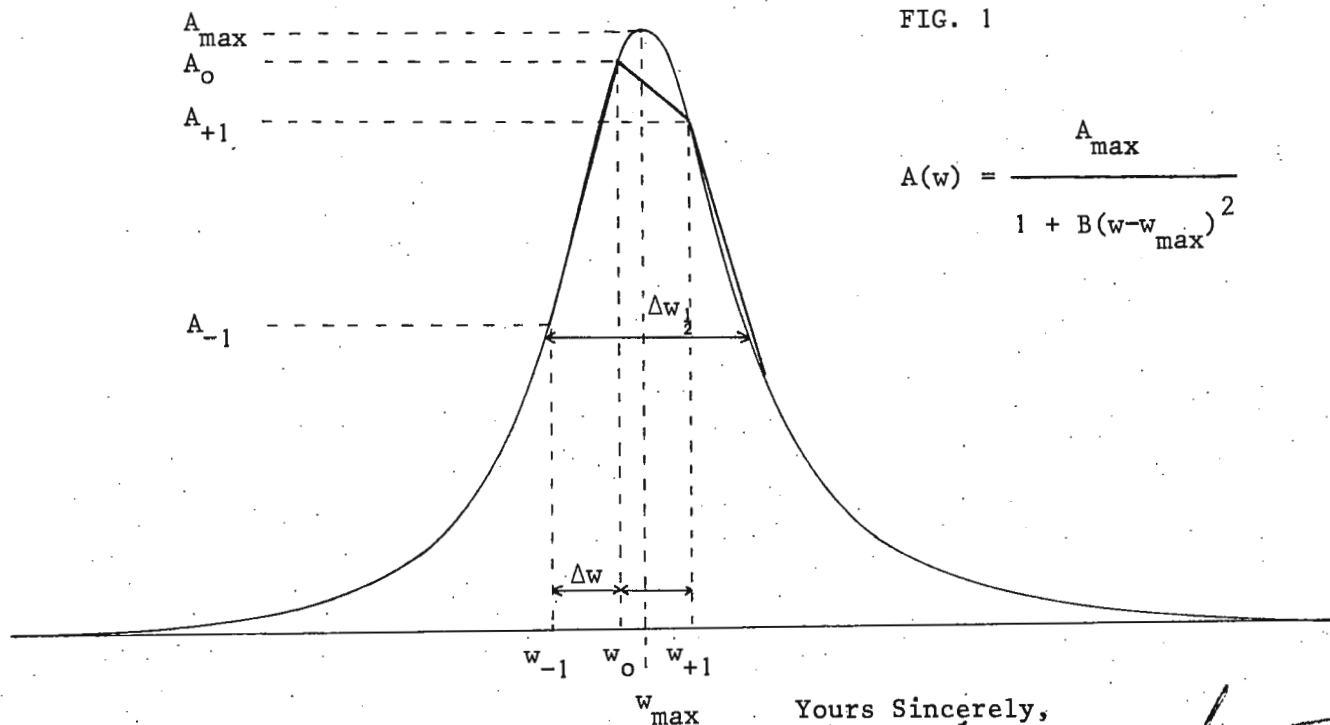
by a small amount, say 0.001 Hz.

We finally located the bug. It is easily removed from the software, after adapting the program to the system configuration, by changing the locations of table I with AID or by hand.

A tape suited to your system is then obtained by dumping the program from 0 - 10246, execution address 0.

Table I

6227	5112	5113
6230	5041	3004
6231	124324	6543
6232	4301	5000
6233	54327	5000
6255	4041	5041
6256	14305	124277
6257	124313	4551
6260	4541	4052
6261	4151	14302
6262	4050	124310
6263	34277	4541
6264	5062	4141



Yours Sincerely,

Dr. M.J.A. de Bie

A. Boelee



Before you order  
a Fourier transform accessory  
for your nmr spectrometer  
you should consult  
Transform Technology Inc.  
The name is new  
but the personnel have  
many years experience  
in the spectroscopy field.  
Write or call collect  
to discuss your requirements.



## Remember this ad?

We ran this ad in mid-1972 when six of us formed Transform Technology Incorporated with the help of Nicolet Instrument Corporation. Now, less than four years later we have over three dozen employees and are now a Nicolet operating division, known as Nicolet Technology Corporation.

What has happened since our first ad? Well, we don't mind tooting our horn by pointing out that NTC has become established as a leader in the development of FT NMR equipment. We have developed, produced and installed scores of FT accessories for use on instruments such as the XL-100, HR-220, T-60, R-12 and R-32. In fact, for over a year we have been the leader in U.S. sales of FT data systems. Now we're working on becoming the leader in overseas sales as well.

Why the success story? We feel it's because we're responsive to customers' needs. Being a relatively small group of dedicated souls we can move quickly in the development of equipment which utilizes the latest techniques.

Consider some of our "firsts" in commercial equipment:

**FIRST** to employ a single sideband crystal filter for improved signal-to-noise ratio,

**FIRST** to provide phase shifted rf pulses for high resolution  $T_2$  studies,

**FIRST** to use Quadrature Phase Detection,

**FIRST** to provide plots of relaxation recovery curves with data points, and

**FIRST** to develop a complete software package which includes provision for five methods of measuring  $T_1$  values and three methods for  $T_2$  values.

You can be sure that we are actively working on new "firsts." For example, we'll be demonstrating a complete Fourier Transform Mass Spectrometer very soon. To repeat the closing statement from our original ad—write or call collect to discuss your requirements. Maybe we can work together to add another "first."



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

POLITECNICO DI MILANO  
ISTITUTO DI CHIMICA

20133 MILANO - Piazza Leonardo da Vinci, 32

Tel. 292.109 - 292.110

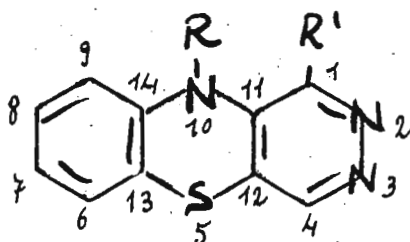
Milano, March 30th, 1976

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

Dear Professor Shapiro,

"Unusually strong lowfield  $\gamma$  effects"

The  $^{13}\text{C}$  investigation of a series of 2,3-diazaphenothiazines(\*) has shown the existence of significant  $\gamma$ ,  $\delta$  and  $\epsilon$  effects all directed to lowfield.



	R	R
I	H	H
II	H	Cl
III	H	$\text{N}(\text{CH}_2)_5$
IV	Me	H
V	Me	Cl
VI	Me	$(\text{CH}_2)_5\text{N}$

In particular the magnitude of the  $\gamma$  effects is quite unusual as far as we know. Moreover it is interesting that the nuclei in question, C-12 and C-13, are quaternary carbons, while, on the basis of the current notions regarding the  $\gamma$  effect in term of steric polarisation, they should not be affected. But recent findings of significant downfield  $\delta$  effects cast some doubt on the interpretation by which steric crowding must be associated with upfield shift. Actually anthracene and 9-methylantracene show the same shift for the bridgehead carbons C-4a and C-10a.

In the present case the molecules are not planar and different conformations can exist in solution. Thus

the lowfield shifts for the N-10 methyl substituted derivatives are due in part to the change of the equilibrium distribution of the conformers, with a consequent decrease of the N-10 lone pair participation into the aromatic system. But such large deshieldings, as well as  $\Delta\delta_{C_{12}}$  upon substitution at C-1 (V-IV, VI-IV) and the observed  $\sigma$  and  $\pi$  effects are difficult to interpret on the basis of delocalization effects only. Steric contribution should also occur, which cannot be explained simply by the steric polarisation mechanism used for C-H bonds.

$\sigma$  effects

	IV-I	V-II	VI-III	V-IV	VI-IV
$\Delta\delta_{C_{12}}$	+5.0	+11.5	+13.1	+8.0	+9.0
$\Delta\delta_{C_{13}}$	+4.7	+ 6.9	+ 7.7		
$\Delta\delta_{C_9}$	0.0	+ 0.9	+ 0.6		

$\delta$  effects

	XI-X	XII-X		XI-X	XII-X
$\Delta\delta_{C_{14}}$	+2.7	+3.7	$\Delta\delta_{Me}$	+7.5	+3.5

$\pi$  effects

	II-I	XI-X	XII-X
$\Delta\delta_{C_9}$	+1.5	+2.9	+2.3
$\Delta\delta_{C_{13}}$		+2.9	+4.1

- (\*) G.Fronza, R.Mondelli, G.Scapini, G.Ronsisvalle, F.Vittorio.  
 "  $^{13}C$  NMR of N-Heterocycles. Conformation of phenothiazines and 2,3-diazaphenothiazines."  
 submitted to J. Magnetic Resonance.

with all best regards



(R. Mondelli)

AMSTERDAM, April 2, 1976

Uw ref.:

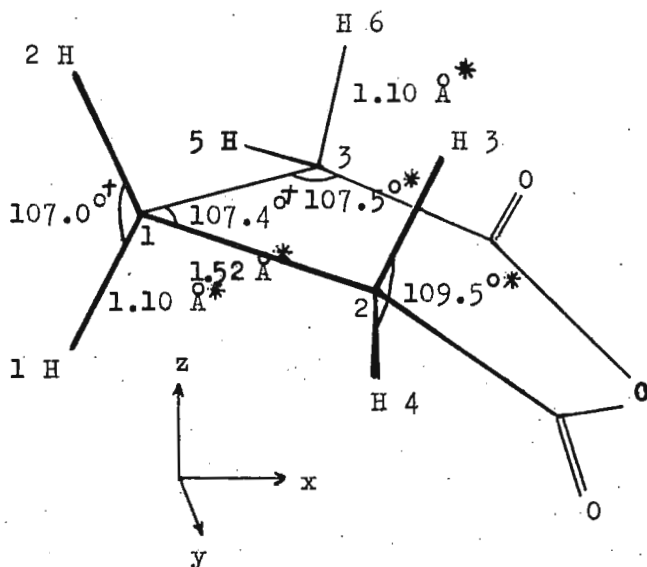
Onze ref.: 76s36/JB/mvg

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

Dear Professor Shapiro,

Liquid crystal NMR of glutaric anhydride and 1,2,4-trifluorobenzene.

Recently, we have interpreted the  $^1\text{H}$ -spectrum of glutaric anhydride dissolved in a nematic liquid crystal, in order to assess the conformation of this molecule. In the literature different suggestions have been given as regards its structure; the "sofa"-conformation seems most favoured (1). Of course, liquid crystal PMR can only provide relative positions of protons, but these can often be related to the structure of the whole molecule. Preliminary calculations for the methylene groups are consistent with the sofa model. The interconversion frequency between the two possible sofa conformations is fast on the NMR timescale but slow compared with the effective reorientation as the orientation of the proton skeleton has to be described by three motional constants.



\* assumed

+ calculated

$$\angle(\text{H}_3\text{C}_2\text{C}_1, \text{H}_2\text{C}_1\text{C}_2) = 51.6^\circ +$$

motional constants:

$$C_{3z}^2 - r^2 = -0.23$$

$$C_{x^2-y^2} = 0.27$$

$$C_{xz} = -0.22$$

Starting from the above model, and assuming reasonable bond angles and bond lengths, the experimental dipolar couplings can be fitted within 0.01 Hz. Work is in progress to determine a reliable value of the torsional angle  $\angle(\text{H}_3\text{C}_2\text{C}_1, \text{H}_2\text{C}_1\text{C}_2)$ .

1,2,4-Trifluorobenzene is interesting from quite another point of view, namely because of the probable presence of anisotropic indirect FF couplings. The molecule is rather unsymmetrical, but if it may be assumed to be planar, three motional constants suffice. An advantage of the asymmetry is that there are fifteen different anisotropic couplings. The analysis of several  $^{19}\text{F}$  and



<sup>1</sup>H spectra has now nearly been completed and calculations of the geometry and anisotropic contributions are in progress and seem to be promising. 212-21

Yours sincerely,

*Bulthuis* *H. van As* *C. van Putten*

J. Bulthuis

H. van As

C. van Putten

(1) F.J. Koer, T.M.W. van Asbeek, C. Altona; Recl. Trav. Chim. Pays-Bas 92, 1003 (1973)

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SANTA BARBARA • SANTA CRUZ

SCHOOL OF PHARMACY  
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

April 5, 1976

Postdoctoral Openings

Dear Barry:

We presently have available two postdoctoral positions. The first position is for someone interested in using intermolecular nuclear Overhauser effect measurements, relaxation time measurements, and chemical shifts on <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C nuclei to investigate the details of the interactions between substrates and enzymes. The second position is designed for someone interested in the role of water in erythrocytes, in particular abnormal erythrocytes such as sickle cells. T<sub>1</sub>, T<sub>2</sub>, T<sub>1ρ</sub> and diffusion coefficient measurements of water protons are the major, but not the only, parameters employed in the erythrocyte study.

Our NMR facilities include a Varian XL-100-15 with Nicolet Fourier transform capabilities (including quadrature phase detection). Within the next few months we will also have a broad band probe so that any external frequency synthesizer can mix frequencies with the spectrometer carrier frequency to generate spectra for any nucleus which resonates between 10 and 40 MHz at 23.5 Kgauss. I am also a "major outside user" with time allotted on the Bruker 360 MHz instrument located in the Stanford Magnetic Resonance Laboratory.

We also have a small pulsed NMR spectrometer which can be used for measuring T<sub>1</sub>, T<sub>2</sub>, T<sub>1ρ</sub> and self-diffusion coefficients (using pulsed gradients and the "stimulated echo" method). The accessible frequencies range from 2 to 44 MHz.

The stipend for each position is \$11,000-12,000 per year. Interested applicants should send a curriculum vitae and arrange for two letters of recommendation to be sent to me.

Sincerely,

*Tom*

Thomas L. James  
Assistant Professor of Chemistry  
and Pharmaceutical Chemistry

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

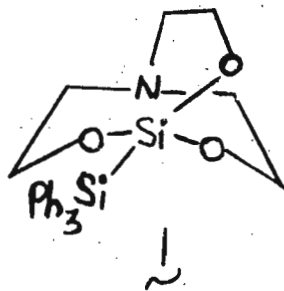
Professor B. L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station  
Texas 77843

Subject: Silicon-29 Chemical Shifts and Coupling Constants  
of Some Disilanes and Silatranes

Dear Barry:

We are presently continuing our studies of directly bonded silicon-silicon coupling constants. Most of this work will appear shortly in a communication<sup>1</sup>, so we won't detail the results here. Briefly, we found a linear correlation between  $^1J_{SiSi}$  and  $^1J_{SiBC}$  for a series of disilanes,  $Me_3Si^ASi^BMe_2X$ , indicating the likelihood that the same factors govern the coupling constants in each case. There is also a strong correlation with substituent electronegativity in the examples we examined.

We have since looked at a few more values of  $^1J_{SiSi}$  and are presently attempting to prepare 1-(triphenylsilyl) silatrane (1) for comparison with  $Ph_3SiSi(OEt)_3$ . In the course of this

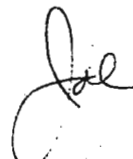


synthetic work we have gathered some  $^{29}Si$  chemical shifts for 1-substituted silatranes, and have found shifts of slightly over 20 ppm to higher field relative to the analogous triethoxysilanes. This new data is collected in the Table. It is noteworthy that the values obtained for  $Me_3SiSiMe_2CN$  fall on the line in the plot of  $^1J_{SiSi}$  vs  $^1J_{SiBC}$ , providing that the tentative value assigned to  $^1J_{SiBC}$  is correct. We are presently checking this.

Regards,



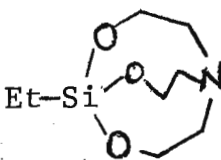
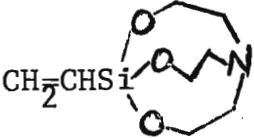
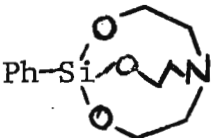
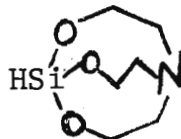
E. A. Williams



J. D. Cargioli

- 1 This work was conducted in conjunction with K. Sharp and P. Sutor of the University of Southern California, as well as T. Farrar and K. Ishibitsu of JEOL (J. Amer. Chem. Soc., in press).

TABLE

<u>Compound</u>	<u><math>\delta_{\text{Si}}</math> (ppm)<sup>a</sup></u>	<u>J (Hz)</u>
	-66.5	
	-82.3	
	-81.4	
	-83.8	$^1J_{\text{SiH}} \approx 275$
$\text{HSi}(\text{OEt})_3$		$^1J_{\text{SiH}} = 286$
$(\text{EtO})_3\text{Si}^{\text{A}}\text{Si}^{\text{B}}\text{Ph}_3$	A = -50.1 B = -29.0	$^1J_{\text{SiSi}} = 164.0$
$\text{Me}_3\text{Si}^{\text{A}}\text{Si}^{\text{B}}\text{Me}_2\text{CN}$	A = -18.1 B = -32.3	$^1J_{\text{SiSi}} = 86.3$
		$(^1J_{\text{Si}^{\text{B}}\text{CH}_3} = 42.2)^{\text{b}}$

<sup>a</sup> Negative values upfield from TMS

<sup>b</sup> This value is tentative

☒ 1455 de Maisonneuve Blvd. West  
Montreal, Quebec H3G 1M8

☐ 7141 Sherbrooke Street West  
Montreal, Quebec H4B 1R6

## DEPARTMENT OF CHEMISTRY

April 20, 1976



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

Dear Barry:

IMPROVEMENTS IN HA-100  $^{13}\text{C}$  FT OPERATION

Since converting our HA-100 to pulse and Fourier transform operation for  $^{13}\text{C}$ , we have continued to up-grade the system, particularly the computer side of the operation. Initially, our main concern was to get the system operating. More recently we have been improving the efficiency and ease of operation.

We have added a Southwest Technical Products Corporation CT-1024 video terminal. This is a very economical unit, available in kit-set form. It has a full keyboard and two pages (16 lines each) of memory. The pages may be used separately, or in sequence. We find it convenient to record our current operating parameters on one page, and to use the other page for on-going instructions. The whole, or portions of a page may be erased as required.

Since we use a homonuclear lock, and must have a suitable lock signal (decoupled solvent or capillary reference) present, we cannot easily avoid dynamic range problems, the FID being dominated by the lock signal. In order to extend the dynamic range, we can write intermediate blocks of data on magnetic tape, using a sufficiently small number of transients per block that dynamic range has not been degraded significantly through excessive divisions of the data (necessary to avoid word overflows). The blocks are averaged in double precision arithmetic at the end of the run, then converted back to single precision. Three passes through the tape are required for 4K points, one third of the block being processed during each pass. The averaged data are written on the tape following each pass. Finally, the three blocks of averaged data are read from the tape as a single (4K) block. When this procedure is used, the final division is not carried out until averaging is complete and maximum signal-to-noise improvement has been achieved. A somewhat similar procedure (using disc storage) has been reported by Canet et al.<sup>2</sup>

We have managed to achieve considerable improvements in running times and in operating convenience through the use of more efficient programming techniques. The HP 2114A computer is rather slow, since it lacks hardware arithmetic, so that inefficient programming is costly in time. The Fourier transform, phase

correction, and digital filtering routines have now been greatly speeded up. Since the computer must be shared with other users, the program package must be re-loaded frequently. We now have the complete package stored in absolute program form as the first file of each data magnetic tape. The package is conveniently loaded by a single command from the terminal.

The system is being used mainly for  $^{13}\text{C}$  spectra of nitrogen heterocyclic compounds, and steroids.

Best regards,

Yours sincerely,

*Laurie*

L.D. Colebrook

<sup>1</sup> L.D. Colebrook, TAMU NMR Newsletter, 198, 31 (1975).

<sup>2</sup> D. Canet, C. Goulon-Genet, and J.P. Marchal, TAMU NMR Newsletter, 199, 17 (1975).

CONT'D. FROM P. 26...

#### Liquid Crystal Parameters for Hexafluorobenzene

	$J_{ij}$	$D_{ij}^{\text{exp}}$	$D_{ij}^{\text{ind}}$	$D_{ij}^{\text{dir}}$
ortho	-22.16±0.02	241.48±.20	-6.64±0.09	248.12±0.09
meta	- 3.15±0.02	45.18±0.02	-2.56±0.03	47.74±0.03
para	+ 3.95±0.03	32.20±0.03	+1.17±0.04	31.03±0.04

$$C_{3z^2-r^2} = 0.10279 \pm 0.00008$$

#### Ratios of Anisotropic Couplings\*

	Determined from Hexagonal Symmetry Model	From Experimental $D_{ij}$	Thermotropic value (Ref.1)	From $D_{ij}^{\text{dir}}$
Dortho	1.0000	1.0000	1.0000	1.0000
Dmeta	0.1925	0.1871	0.1869	0.1924
Dpara	0.1250	0.1333	0.1337	0.1251

\*All values are relative to the ortho value.

DEPARTMENT OF CHEMISTRY

April 5, 1976

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

Dear Barry:

Anisotropic Couplings in Hexafluorobenzene in an  
Ordered Medium

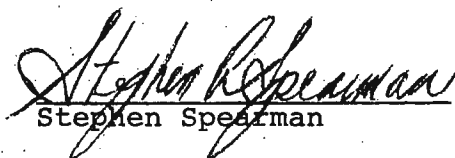
We have recently completed the NMR study of hexafluorobenzene oriented in the lyotropic mesophase derived from potassium laurate. The analysis of the fluorine spectrum provided not only the  $J_{ij}$  coupling values for hexafluorobenzene, but also anisotropic coupling information for the molecule.

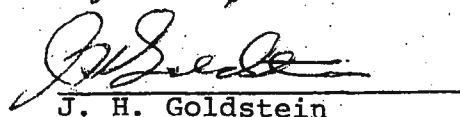
If hexafluorobenzene is assumed to have hexagonal symmetry, then the ratios of the dipolar couplings can be determined from symmetry. However, a previous thermotropic study<sup>1</sup> showed that the distance ratios calculated from experimental anisotropic couplings tend to deviate from the expected values. In that work, the deviations were attributed to pseudo-dipolar couplings which were calculated by assuming that the ortho and para  $D_{ij}^{ind}$  were proportional to corresponding  $J_{ij}$  values.

In this present study we found that the experimentally determined distance ratios also deviated from hexagonal symmetry values. Moreover, the ratios of the experimental anisotropic couplings were very similar to those calculated in the thermotropic work. Following the procedure of the previous study, pseudo-dipolar couplings were calculated and the experimental  $D_{ij}$  values were separated into  $D_{ij}^{dir}$  and  $D_{ij}^{ind}$ , and the molecular orientation was determined.

The accompanying table lists the liquid crystal parameters obtained in this study.

1. L. C. Snyder, J. Chem. Phys., 43 (11), 4041 (1965).

  
Stephen Spearman

  
J. H. Goldstein



# University of Durham

Department of Chemistry

Science Laboratories, South Road, Durham, DH1 3LE

Telephone: Durham 64971 (STD code 0385)

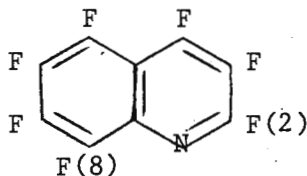
14th April, 1976.

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

## $^3J_{F,F}$ to $^7J_{F,F}$ in heptafluoroquinoline

Dear Professor Shapiro,

We have recently completed analyses of the  $^{19}\text{F}$  spectra of several polyfluoroazanaphthalenes, of which the most important is heptafluoroquinoline, and were surprised at the magnitudes of some of the inter-ring coupling constants. These results are corroborated by analyses of spectra from derivatives and other geometric isomers such as polyfluoroisoquinolines and hexafluoroquinazoline. The  $\pi$ -electron delocalisation dominates the long-range coupling constants and the well-known "zig-zag" and "extended zig-zag" pathways are apparently unimportant. Inter-ring coupling constants, ignoring the through-space  $J_{F,F}^{\text{peri}}$ , are positive over an odd number of bonds, and vice-versa.



J	Hz	J	Hz
4,5	+48.0	2,3	-27.6
4,6	+ 4.55	2,4	+26.5
4,7	- 3.4	2,5	- 3.1
4,8	+ 1.5	2,6	+ 8.3
5,6	-17.9	2,7	- 1.5
5,7	+ 1.9	2,8	+ 6.1
5,8	+14.95	3,4	-14.5
6,7	-19.15	3,5	+ 7.0
6,8	+ 2.45	3,6	- 2.5
7,8	-17.1	3,7	+ 8.15
		3,8	- 4.05

Yours sincerely,

*R.S. Matthews* → *Royston*

R.S. Matthews & A. Royston



April 8, 1976

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

Dear Barry,

$^{13}\text{CH}_4$  gas-to-liquid shifts

We have just completed measurements and interpretation of the gas-to-liquid shifts of  $^{13}\text{CH}_4$  (both the  $^{13}\text{C}$  and the  $^1\text{H}$ ). The general conclusions are broadly as follows:

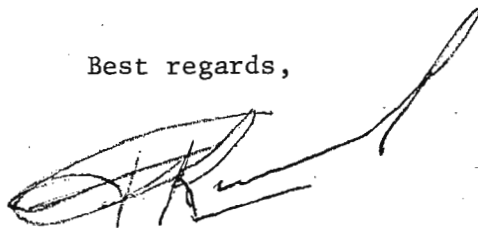
1. The  $^1\text{H}$  shifts in isotropic solvents follow very well the predictions of the  $\sigma_w$  (Van der Waals) ~~our~~ reaction field model which was recently published (1). They follow also reasonably well the binary collision model (2) predictions, though with somewhat larger scatter. Anisotropic solvents give deviations, from which reasonable values for  $\sigma_a$  are deduced.
2. The  $^{13}\text{C}$  shifts are large, ranging roughly from 5 to 12 ppm. These medium shifts, even when corrected for  $\sigma_a$  (from the  $^1\text{H}$  measurements) correlate very poorly with either  $\sigma_w$  model. In fact any plot of experimental vs calculated shows that a best-straight-line misses the origin by some 3-4 ppm.
3. Obviously the  $^{13}\text{C}$  shifts carry an extra, as yet unidentified term. No model error can be responsible as is demonstrated in the figure, where experimental  $^1\text{H}$  and  $^{13}\text{C}$  shifts are compared. Since the maximum imaginable error in  $\sigma_w = \sigma_{\text{exp}} - \sigma_b - \sigma_a$  for either  $^1\text{H}$  or  $^{13}\text{C}$  is 0.05 ppm this unknown factor must be in the  $^{13}\text{C}$  shifts and must be many ppm large with a variation between solvents of at least several ppm.
4. If one defines  $\sigma_w = -BE^2$  (or  $= -BF^2$ ), the B parameter can be determined from gas-phase measurements by varying the density. Using the binary collision model (2) we found  $B(\text{CH}_4) = 0.57 \times 10^{-18}$  and  $B(\text{CH}_4) = 22.4 \times 10^{-18}$  esu. In gas-to-liquid shifts one expects a similar behaviour, except that an extra, apparently universal, constant is required;  $\sigma_w = -KBE^2$ . For our  $^1\text{H}$   $\text{CH}_4$  data we find  $KB = 1.16$  or  $K = 1.97$  close to the  $K = 1.76$  reported earlier. However, if we force the  $^{13}\text{C}$  gas-to-liquid data to fit the statistical model we find  $KB = 11.58$  or  $K = 0.53$ . This makes no sense whatsoever, since K measures the difference between the effective potential in a liquid and an ideal bimolecular potential; therefore K should be constant for a given solute, independent of nuclear species. This once more shows the existence of another effect. Electric field effects are either zero or too small to be effective. The only possible effect one can think of is a repulsion effect. In  $^1\text{H}$  shifts, this repulsion effect, if it exists, is proportional to the dispersive  $\sigma_w$  effect and therefore escapes detection, but in  $^{13}\text{C}$  this need not be the case at all.

5. All this shows that internal referencing in  $^{13}\text{C}$  will lead to big errors, if data with different reference compounds or different solvents are compared.



F.M. Mourits

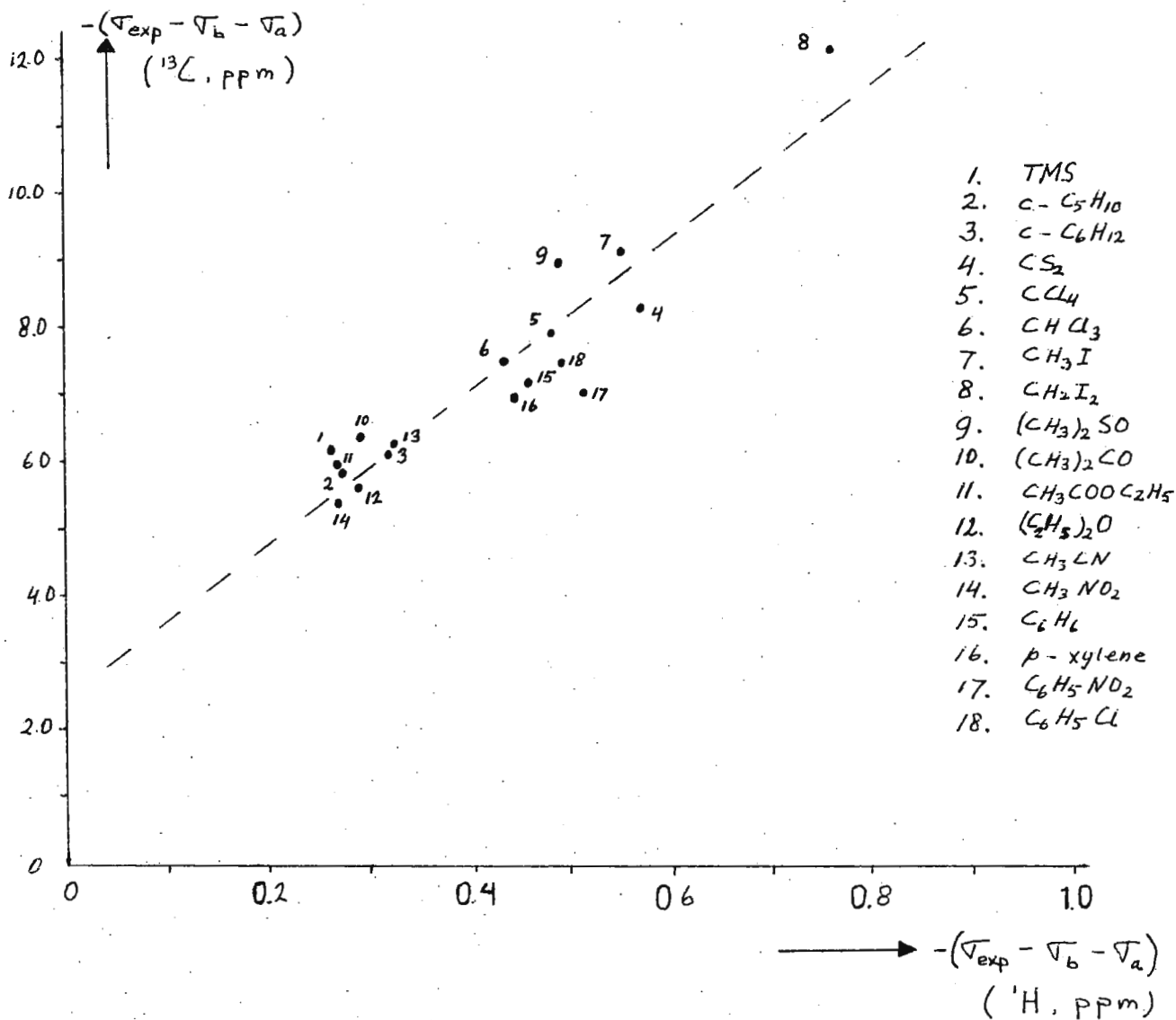
Best regards,



F.H.A. Rummens, D.Sc.  
Professor

FHAR/11

References; (1) F.H.A. Rummens, Can. J. Chem. 54, 254-69, 1976  
(2) W.T. Raynes, A.D. Buckingham, H.J. Bernstein J. Chem. Phys. 36, 3481 (1962)





## THE PROCTER &amp; GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175  
CINCINNATI, OHIO 45247

April 8, 1976

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

Multinuclei Detection on a Bruker HX-90 Spectrometer

Dear Barry:

Thanks to the consultation and services of Dan Traficante, we have converted our Bruker HX-90 spectrometer to multinuclei capability (D. D. Traficante, et al, J. Magn. Resonance, 15, 484 (1974)). A block diagram of our multinuclei spectrometer is shown in the figure. Since most of the components were either available or made in our laboratory, the total cost of the modification was under \$15,000. The only significant difference between our system and the one in the above cited paper is that the Bruker variable capacitor (C7) was left in place and a mini-phononjack was added so that fixed capacitors could be placed in parallel with C7. We found this change necessary because of arcing problems at high voltages in the tuning capacitor recommended by Traficante. Changeover from one nucleus to another in the frequency range of 6.5 to 40 MHz requires: (1) placing the correct fixed capacitor in the phononjack; (2) tuning the rf coil and tuned rf power amplifier to the frequency of the desired nucleus; and (3) selecting the proper mixing frequency on the frequency synthesizer. Total time for a complete changeover is about five minutes. Based upon  $^{13}\text{C}$  S/N measurements, the sensitivity of the system after the modification is equivalent to the original Bruker system.

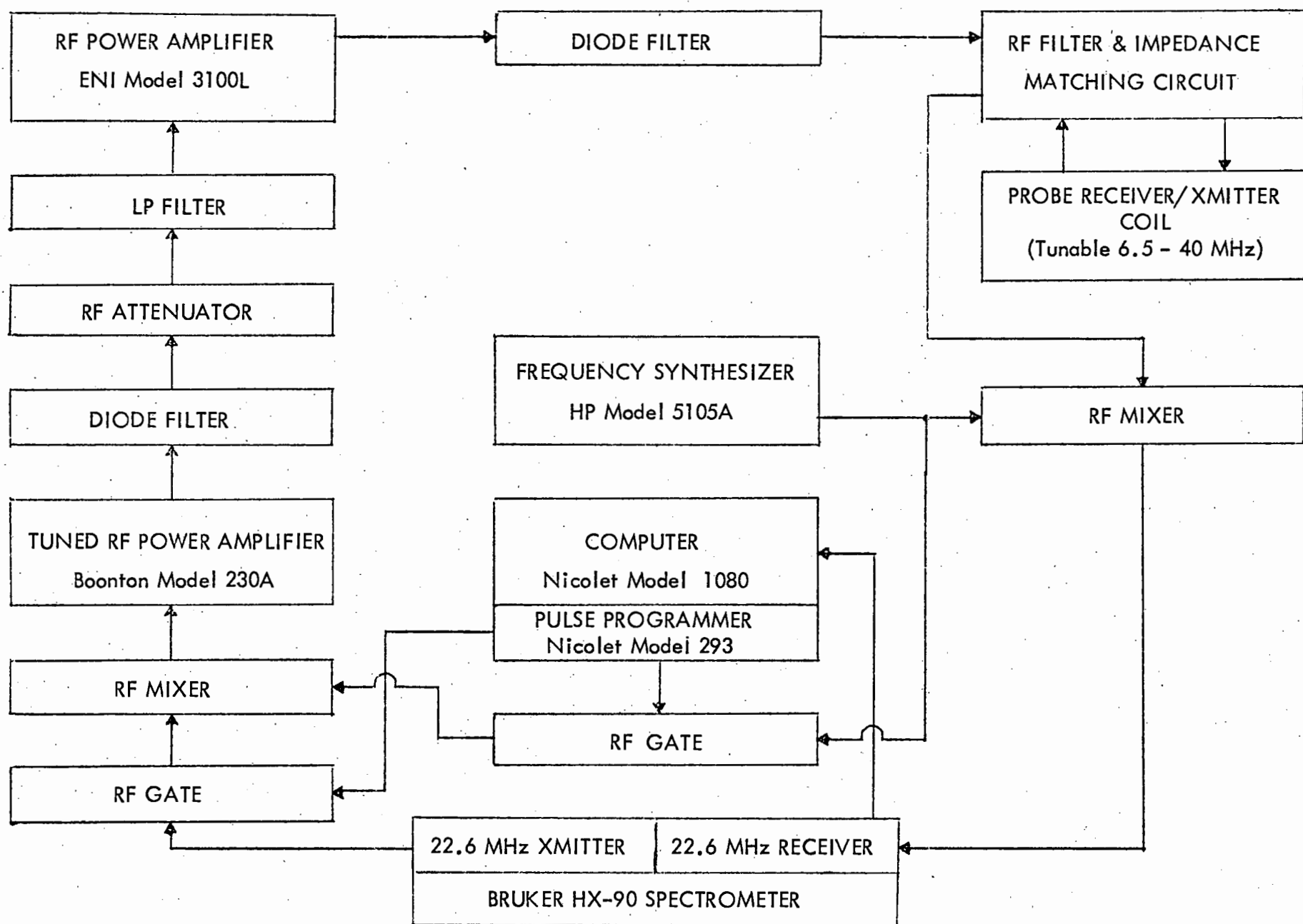
We have been operating in this configuration for the past four months with no major difficulties. So far we have successfully recorded  $^2\text{H}$ ,  $^{13}\text{C}$ ,  $^{23}\text{Na}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$  and  $^{195}\text{Pt}$  spectra from numerous different samples. Needless to say, we are more than pleased with this multinuclei modification.

Sincerely yours,

THE PROCTER & GAMBLE COMPANY  
Research and Development DepartmentL. R. Isbrandt  
Miami Valley Laboratories

blk

Attachment



MULTINUCLEI FOURIER TRANSFORM NMR SPECTROMETER



Eidg. Technische Hochschule  
Zürich-Hönggerberg

Institut für Molekularbiologie und Biophysik

CH-8049 Zürich

Prof. Dr. K. Wüthrich

Tel. (01) 57 57 70

8049 Zürich, April 13, 1976

KW/as

Prof. B.L. Shapiro  
Department of Chemistry  
Texas A and M University  
College Station/Texas 77843  
USA

# $^{15}\text{N}$ NMR Spectra of Isotope Enriched Peptides

Dear Barry:

The old trick of growing bugs on an isotope-enriched medium to obtain isotope-labelled metabolites is tremendously helpful in  $^{15}\text{N}$  NMR of biomolecules<sup>1</sup>. We have thus obtained  $^{15}\text{N}$ -ferrichrome from  $^{15}\text{N}$ -enriched Ustilago sphaerogena cultures<sup>2</sup>. The  $\text{Al}^{3+}$ -complex of the cyclohexapeptides (Gly<sup>3</sup>-Gly<sup>2</sup>-Gly<sup>1</sup>-Orn<sup>1</sup>-Orn<sup>2</sup>-Orn<sup>1</sup>, where Orn is  $\delta$ -N-acetyl- $\delta$ -N-hydroxy-L-ornithine) has a rigid conformation and the six residues exhibit distinct  $^{15}\text{N}$  amide resonances. Of the hydroxamate resonances, which are  $\sim 85$  ppm to lower field than the amide resonances, two have essentially identical chemical shifts, while the third line is shifted by  $\sim 0.77$  ppm to higher fields, probably reflecting the imperfect symmetry of the octahedral complex (rhombically distorted according to X-ray and ESR crystallographic data for the ferric complex). Fig. 1 shows a partially relaxed proton noise-decoupled  $^{15}\text{N}$  spectrum of 99.5%  $^{15}\text{N}$ -enriched alumichrome in  $\text{d}_6$ -DMSO. It is seen that the six amides are near the equilibrium magnetization, whereas the hydroxamate spins are still mostly inverted. The different line widths and spin-lattice relaxation rates arise mainly from the different  $^1\text{H}$ - $^{15}\text{N}$  dipolar interactions of the peptidyl and hydroxamate nitrogens. Fig. 1 also shows that the chemical shifts of the amide nitrogens span over  $\sim 15$  ppm, which confirms the earlier observations through indirect detection ( $^{15}\text{N}$ - $^1\text{H}$  double resonance experiments<sup>3</sup>). The  $T_1$ 's of the hydroxamate nitrogens are  $\sim 10$  sec, i.e. they relax roughly 20 times slower than the amide nitrogens. Fig. 2 depicts an inversion recovery plot following the usual  $180^\circ$ - $\tau$ - $90^\circ$  sequence. Interestingly, the  $T_1$ 's of the amide nitrogens differ measurably, probably reflecting conformational features of the molecule. Preliminary gated  $^1\text{H}$ -irradiation experiments showed full NOE's for the peptidyl nitrogen resonances. Further experiments and analysis of the data in conjunction with  $^1\text{H}$  and  $^{13}\text{C}$  spin-lattice relaxation measurements are in progress.

Sincerely yours,

M. Llinás

Miguel Llinás

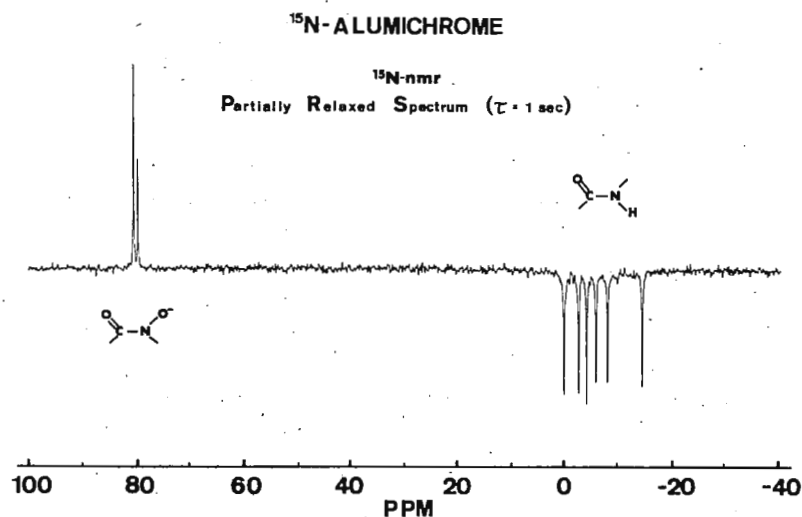
K. Wüthrich

Kurt Wüthrich

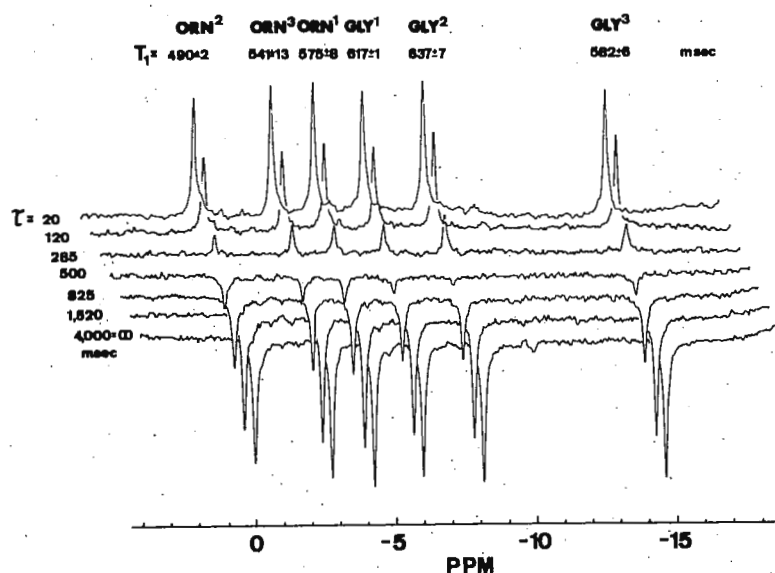
## References:

- 1) M. Llinás, D.M. Wilson & M.P. Klein, TAMUNN 191, 51 (1974).
- 2) M. Llinás, K. Wüthrich, W. Schwotzer and W. v. Philipsborn, Nature 257, 817 (1975).
- 3) M. Llinás, W. Horsley & M.P. Klein, to be published. (Presented in part in K. Wüthrich, NMR in Biological Research: Peptides and Proteins. North Holland, Amsterdam 1976).





**Fig. 1:** Partially relaxed proton noise-decoupled <sup>15</sup>N-NMR spectrum of 99.5% <sup>15</sup>N-enriched alumichrome. 1.4 ml of a 0.07-M solution of the peptide in d<sub>6</sub>-DMSO was used. The spectrum was recorded at 10.13 MHz on a Varian XL-100 spectrometer, sample size 12 mm, T = 45°. The chemical shifts are referred to the temperature invariant Orn<sup>2</sup> resonance.



**Fig. 2:** Spin-lattice relaxation ( $180^\circ$ - $\tau$ - $90^\circ$  sequence) of the alumichrome <sup>15</sup>N amides resonances. In all, eleven data points were used for the inversion recovery plot. The  $T_1$ 's are indicated together with uncertainties which are the standard errors resulting from the least squares fit. The experimental conditions are the same as for Fig. 1.



E. I. DU PONT DE NEMOURS & COMPANY  
INCORPORATED

WILMINGTON, DELAWARE 19898

CENTRAL RESEARCH & DEVELOPMENT DEPARTMENT  
EXPERIMENTAL STATION

April 7, 1976

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

Dear Barry,

$^{13}\text{C}$  NMR of Fluorinated Compounds Using Wide-Band  $^{19}\text{F}$  Decoupling

In the absence of  $^{19}\text{F}$  decoupling,  $^{13}\text{C}$  spectra of heavily fluorinated molecules are both weak and complex. Recently, we modified our Bruker HFX-90/Digilab NMR-3 system to obtain  $^{13}\text{C}\{^{19}\text{F}\}$  spectra. Since  $^{19}\text{F}$  resonances cover a wide chemical shift range, simultaneous decoupling of several kinds of fluorine can be difficult, e.g., the  $\text{CF}_3$  and  $\text{CF}_2$  resonances in perfluorinated alkanes are separated by about 4 KHz at 84.67 MHz. Since the Bruker BSV2 decoupler would not cover such ranges, we assembled a decoupler consisting of a Schomandl ND100M synthesizer driving an ENI Model 350L 50 watt wide-band amplifier. Noise modulation is provided by a WAVETEK Model 132 noise generator and a Hewlett-Packard mixer.

Since the decoupler coil of the WH-90 probe head that we were using would not sustain the application of more than 20 watts of RF, we constructed a more robust insert. The decoupling coil was mounted with ceramic cement on a glass tube fitted with a side arm for nitrogen gas cooling. The crossing point of the gold foil was insulated with ceramic paper. A hole was drilled in the probe head to admit a stream of nitrogen gas for additional cooling. The insert will operate with up to 50 watts of continuous decoupling power without excessive sample heating. Sensitivity is comparable to that of a normal insert.

Decoupling efficiency was measured by observing the  $^{13}\text{C}$  resonance of  $\text{C}_6\text{F}_6$  while offsetting the decoupler frequency from the

<sup>19</sup>F resonance. Using 32 watts of RF power, noise modulated at 10 KHz, the <sup>13</sup>C peak height was down to one half at ± 4 KHz giving a useful <sup>19</sup>F decoupling range (95 ppm). We originally planned to decouple widely separated <sup>19</sup>F resonances by combining two or more decoupling frequencies from separate synthesizers or by audio side-band generation. However, at these power levels, the off-resonance decoupling signals cause Bloch-Siegert shifts of several kilohertz! In favorable cases, these can be dealt with empirically. A more complete discussion of this effect will be given elsewhere.

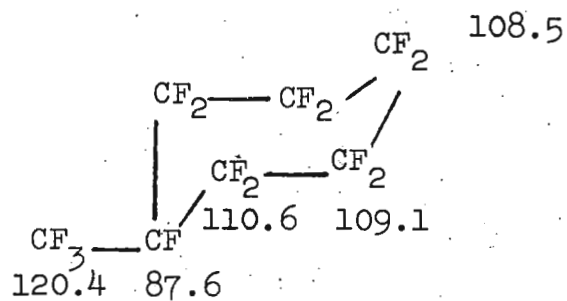
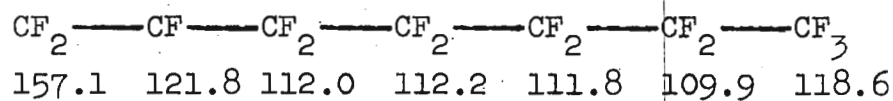
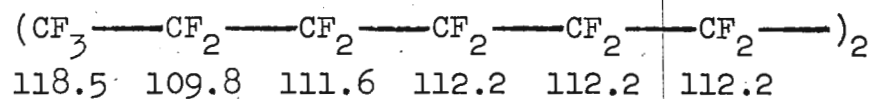
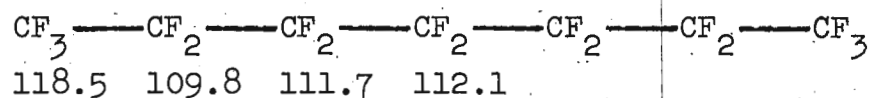
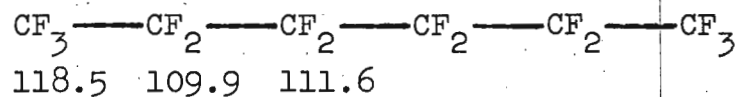
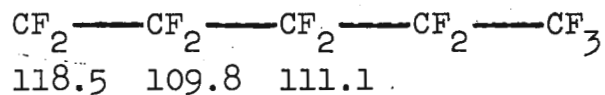
We have determined <sup>13</sup>C chemical shifts for a number of perfluorinated compounds, some of which are listed on the following page. Samples were run as mixtures with hexafluorobenzene and referenced by taking  $\delta(\text{C}_6\text{F}_6) = 139.4$  (referenced against dioxane = 67.4). Chemical shift differences are generally less than is seen for the corresponding hydrocarbons but are large enough to be structurally useful. The chemical shifts of the four n-perfluoroalkanes are adequately reproduced by a Grant and Paul expression with  $B = 124.8$ ,  $\alpha = -8.6$ ,  $\beta = +1.8$  and  $\gamma = +0.5$ .

Derick W. Ovenall  
James J. Chang

**Derick W. Ovenall**  
*James J. Chang*

DWO:JJC/dew  
4/7/76

<sup>13</sup>C Chemical Shifts of Some Perfluorinated Compounds



Perfluorocyclohexane

108.8



THE UNIVERSITY OF NEW ENGLAND

ARMIDALE, N.S.W.

DEPARTMENT OF ORGANIC CHEMISTRY

212-37

April 22, 1976

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

Dear Professor Shapiro,

Title: A Simple Method of Pulsing Electron-tube Circuits from TTL Signals

When I subtitled my previous contribution (Newsletter No. 204, p. 15), "Resuscitation for Machines (or Persons) in extremis", I did not realize just how significant the last two words were. In November, 1975, however, our V4336 probe gave up the ghost, and a month or so later I was diagnosed for urgent cardiac surgery which was carried out in January, 1976. You will understand why I ask that you accept now a relatively trivial item which may nevertheless be of interest to others who possess an ageing n.m.r. spectrometer they would like to adapt to newer methods.

Ours is a 10-year-old Varian HA60-IL instrument on which we wish to introduce a pulse-modulated lock system. The V4311 r.f. transmitter/receiver employs only electron-tube circuits, and papers we have consulted imply that everyone knows how such circuits are gated and give no details. Electronics text-books suggest that application of a sufficiently large negative voltage to the grid is the way to cut off an electron tube, and indeed we employ this method in the power-amplifier stages of our C-13 PFT system. Switching of negative voltages by TTL devices (HI output typically ca +3V, LO typically ca +300mV) requires subsidiary circuits and of course a means of producing the appropriate negative voltage itself. Mr. F.B. Hanson of this Department suggested and has obtained the desired gating simply by interposing a 2N3643 transistor (other NPN fast switching transistors would no doubt work equally well) between the cathode and bias resistor of the tube to be switched. The transistor is turned fully on when +3V is applied to the base, and the tube functions normally, but there is no output from the tube when less than ca 1V is applied. This method with use of a TTL-pulse generator works well in the cathode circuits of the V4311 receiver-mixer stage and transmitter final-output stage; an unswitched parallel duplicate of the latter stage must however be installed to provide the appropriate reference r.f. for the i.f. phase detector in the receiver which is required to be ON when the transmitter output to the probe is OFF.

The convenience of this system is maintained if the switching pulses are produced from the "lock-box" internal manual oscillator (or other sine-wave source) by use of a comparator that detects zero crossings even though operated from a single +5V supply as required for TTL devices. The LM339 appears to be especially convenient because one or two others of this quad of independent comparators may be used with an appropriate timing capacitor and a few resistors to construct a one-shot to generate a transmitter-ON pulse of desired width, but we have not yet completed construction of this section.

Yours sincerely,

*N. V. Riggs*  
N.V. RIGGS

## The University of Manitoba

Department of Chemistry  
Winnipeg, Manitoba  
Canada R3T 2N2



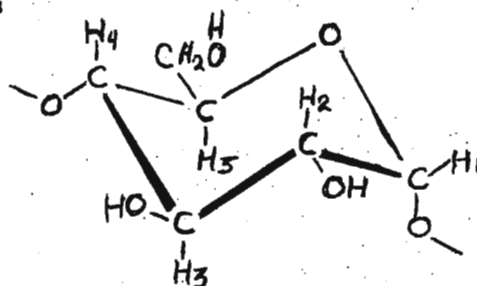
April 13, 1976.

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

Dear Dr. Shapiro:

#### $\alpha$ -CD INCLUSION COMPLEXES

$\alpha$ -Cyclodextrin is the smallest member of the series of Schardinger dextrins, consisting of six D-glucose units linked by  $\alpha$ 1,4 glycosidic bonds. X-ray crystallographic studies (1 and references therein) have established that  $\alpha$ -CD has a toroidal topography with a central void with a diameter of  $5\text{\AA}$ . The molecule is capable of forming adducts by including into the cavity a variety of molecular species such as  $\text{H}_2\text{O}$ , benzene derivatives, iodine, etc. Demarco and Thakar (2) have demonstrated that addition of certain aromatics to an aqueous solution of  $\beta$ -CD (which has seven glucose units) resulted in pronounced changes in the magnetic shielding of hydrogens located on the inner surface of the toroid while hydrogens located on the outer surface were unaffected by the addition, an observation consistent with the formation of an inclusion complex. Don Wood and I, in collaboration with Wolfram Saenger, have been using PMR to study the binding of p-iodoaniline (pIA) to  $\alpha$ -CD in aqueous ( $\text{D}_2\text{O}$ ) solution; their inclusion complex in the solid state has recently been described (1,3). In Figure 1 we show a 220 MHz proton spectrum of  $\alpha$ -CD (0.042 M;  $30^\circ\text{C}$ ;  $\text{pD} = 2.7$ ; 250 Hz sweep) in the absence of pIA and in the presence of pIA (0.028M). The  $\text{H}_1$  resonance has been used for internal referencing.) The aromatic clearly has little effect on the relative shifts of the  $\text{H}_1$ ,  $\text{H}_2$  and  $\text{H}_4$  hydrogens on the external surface of the toroid. However,  $\text{H}_3$  and  $\text{H}_5$  experience a large shielding and deshielding respectively in the presence of pIA. These effects are most easily interpreted if an inclusion complex similar to that found in the crystal state is assumed, i.e. one with the iodine atom juxtaposed with the  $\text{H}_5$  hydrogens of the glucose units and the  $\text{H}_3$  hydrogens located above the aromatic ring. The results of a concentration study are shown in Figure 2 as a  $\Delta\delta$  versus R plot where  $\Delta\delta_2$  is the shift of  $\text{H}_2$ , etc., relative to the  $\text{H}_1$  resonance of the sugar and R is the pIA: $\alpha$ -CD concentration ratio. From the plot, estimates of the equilibrium constant for association ( $1000 \text{ mole}^{-1}$ ) and the  $\Delta G^\circ$  for association ( $-4.0 \text{ kcal/mole}$ ) were obtained.



This study was extended to other substituted anilines with a bromo, nitro, hydroxyl or cyano para to the  $\text{NH}_2$  group. In each case the  $\text{H}_3$  is shielded in the presence of the aromatic whereas the  $\text{H}_5$  is not greatly influenced. That the iodine atom is so far unique in its pronounced deshielding effect on  $\text{H}_5$  is somewhat disturbing.



Please credit this to Ted Schaefer.

Sincerely,

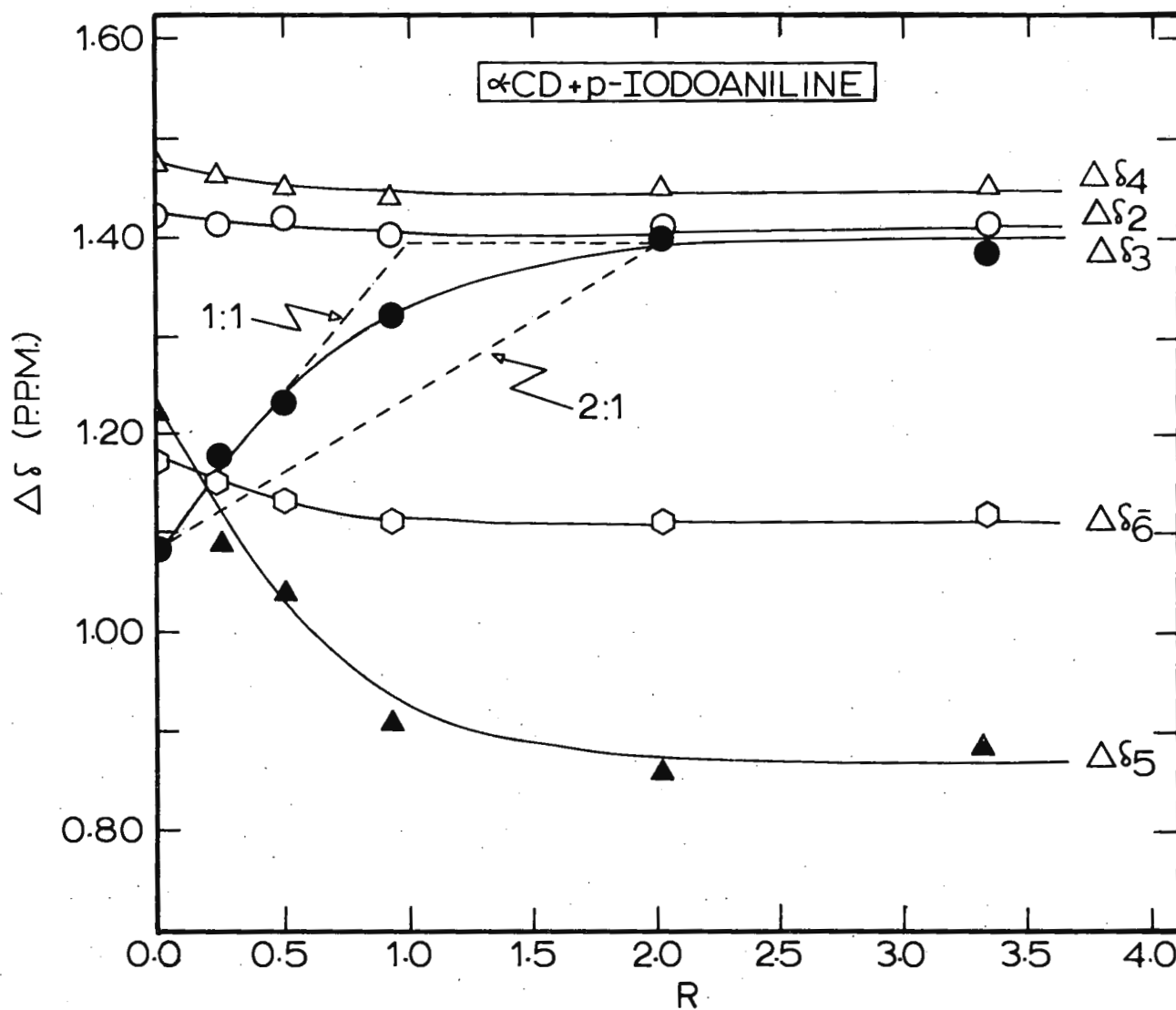
Frank  
Hruska

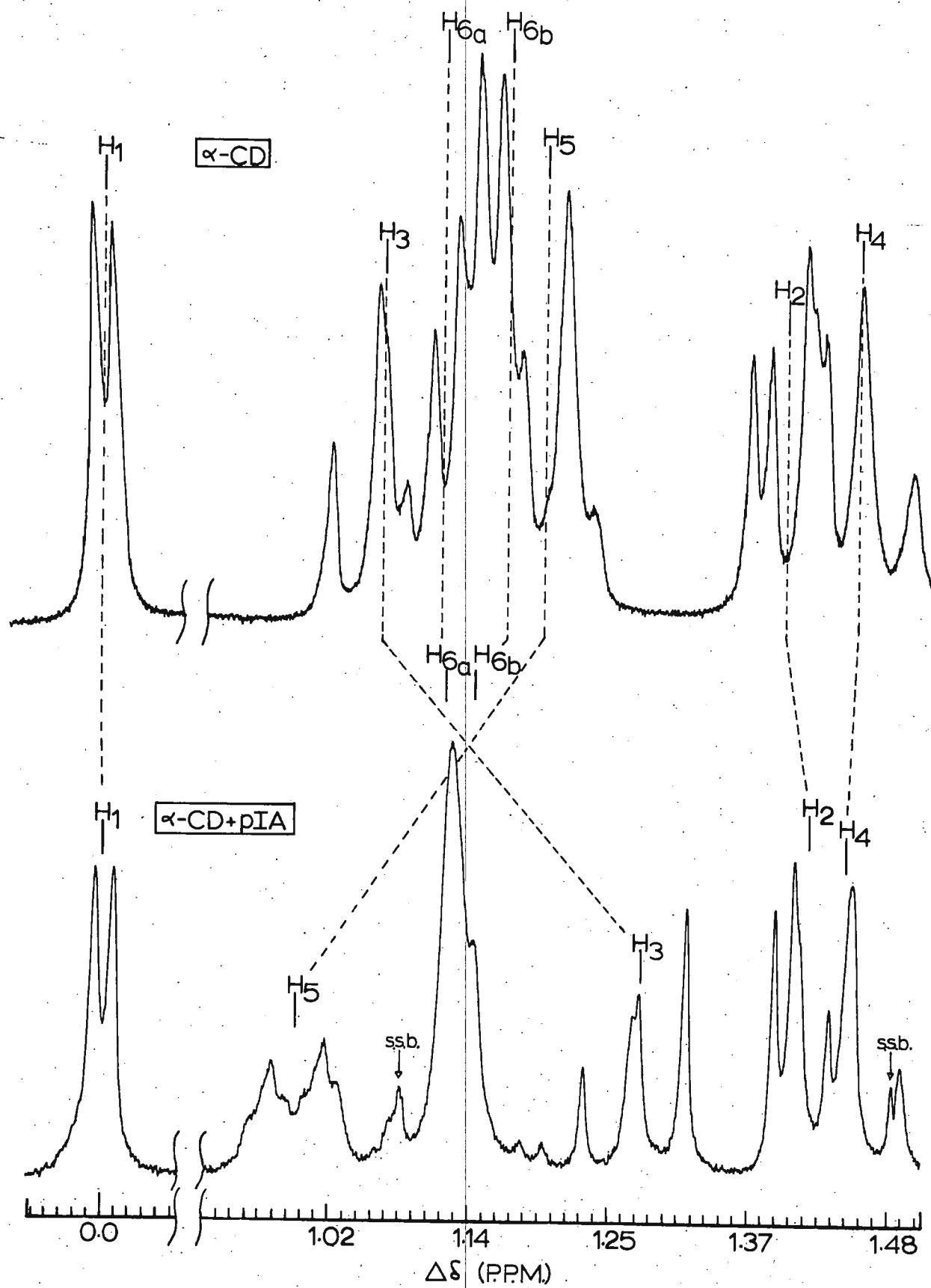
F. E. Hruska,  
Associate Professor

FEH/lm

#### REFERENCES

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2. P. V. Demarco and A. L. Thakar, Chem. Commun. 2 (1970).
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## THE OHIO STATE UNIVERSITY

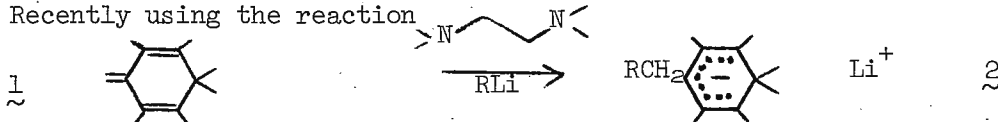
April 14, 1976

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

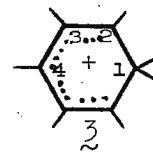
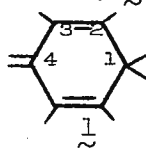
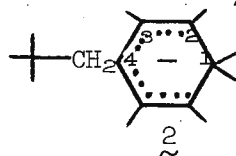
<sup>13</sup>C Shifts in R<sup>+</sup>, R<sup>-</sup>/deuterated Solvents

Dear Barry:

The different treatments which relate <sup>13</sup>C shift to electron density in π-conjugated species lead one to predict the shifts in ions of the same structure but opposite charge should reflect through the hypothetical shift of the unchanged species. Normally such comparisons cannot be made due to the effects of ion pairing or deformations which cause the structures of the ions to become different. Recently using the reaction



we have prepared several 4-alkyl-1,1,2,3,5,6-hexamethylcyclohexadienyl lithiums, 2, and compared the ring <sup>13</sup>C shifts (ref. to TMS) with a well known carbonium ion of similar structure 3 and parent triene, 1.



Position	<u>1</u>	<u>3</u>	<u>2</u>
1*	41.3	57.8	37.7
2	137.3	192.4	83.9
3	124.8	140.4	127.6
4	142.1	192.4	92.6

\*Shifts, <sup>13</sup>C/TMS

Notice how almost everything reflects through the values for triene 1 with the exception of position 3. Suggestions are welcome.

Other matters---we have become increasingly concerned about the exorbitant cost of deuterated solvents, especially ethers and hydrocarbons. Now might be a good time to publish a few of the more useful recipes. Some are buried in the literature but many have never been published at all. I am interested in reader's comments.

Best wishes

Sincerely yours,

Gideon Fraenkel  
 Professor of Chemistry

Department of Chemistry 140 West 18th Avenue Columbus, Ohio 43210 Phone (614) 422-2251

GF:es



Medical Research Council

reference

National Institute for Medical Research  
The Ridgeway, Mill Hill  
London NW7 1AA

telegrams Natinmed London NW7  
telex 922666 (Natinmed London)  
telephone 01-959 3666

14th April, 1976.

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

Dear Barry,

Improved method of suppressing solvent signals in FT  
 $^1\text{H}$  NMR experiments using a gated noise-modulated  
irradiation field

In most of our  $^1\text{H}$  FT experiments we are faced with the well-known problem of having to suppress the large solvent signal to avoid the dynamic range problems. Many experimental procedures have been proposed to decrease the intensity of the solvent signal (1-8), the most commonly used technique being to irradiate the intense solvent signal with a continuous (5) or gated (1,6,7) double resonance frequency. Successful use of this method requires a knowledge of the precise irradiation frequency and consequently in experiments where the sample conditions are changed (as in pH titration or a variable temperature experiment) the optimum irradiation frequency must be redetermined for each experiment. Furthermore, for a spectrometer with a homogeneous decoupling field (such as the Varian XL 100) the residual solvent peak after suppression is coherent in phase and amplitude for each pulse. Thus in a spectrum accumulation experiment such signals will add directly and cause problems if the word length of the memory is limited. We propose here a simple method of overcoming both these difficulties by using a noise modulated (bandwidth  $\sim 10$  Hz) decoupling field to irradiate the intense signal for time  $\tau$  ( $\tau = 0.1$  to 1 sec) prior to detecting the free induction decay from the analytical pulse. Thus the sequence we use is the same as that proposed by Campbell and coworkers (1) except that noise modulated irradiation rather than single frequency irradiation is used, the noise modulated field being gated off during the analytical pulse and the acquisition of the FID. Because of the bandwidth of the noise decoupler the condition set on finding the exact irradiation frequency is considerably relaxed and this greatly facilitates successful operation. More importantly, the residual solvent signals after each noise modulated

irradiation are random in phase and amplitude and in an accumulation experiment the signals average in a similar manner to the spectral noise giving an extremely small residual signal.

A ten-fold improvement in signal suppression relative to that observed with gated single frequency irradiation is obtained using a noise-modulated (10 Hz bandwidth) irradiation. Even when the irradiation frequency is set 10 Hz away from that of the solvent signal, a noise-modulated irradiation is still three times more efficient than irradiation with a single frequency exactly on the solvent peak.

We use this procedure routinely to suppress the residual solvent signals in aqueous solutions of proteins.

Yours sincerely,

*Jim Feeney G.C.K. Roberts*

B.J. Kimber, J. Feeney G.C.K. Roberts.

1. I.D. Campbell, C.M. Dobson, G. Jeminet and R.J.P. Williams, FEBS Letters 49, 115 (1974)
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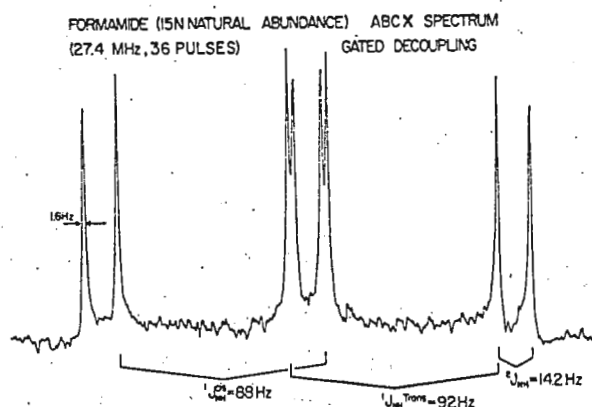
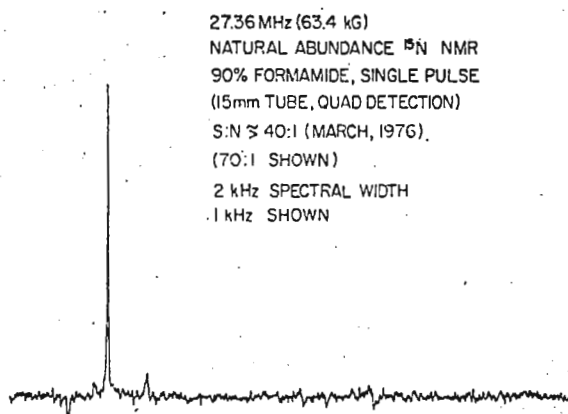


From George C. Levy

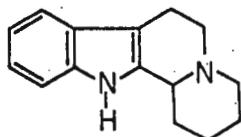
Dear Barry,

High Sensitivity  $^{15}\text{N}$  NMR at 63kG

We have recently initiated natural abundance  $^{15}\text{N}$  studies with our QUAD FT modified Bruker HX-270. Using 15mm diameter nmr tubes, we have sensitivity for  $^{15}\text{N}$  as shown below (fig.1). Needless to say we are pleased at this factor of 8-10 over that obtained on a Varian XL-100 (12mm tubes). Figure 2 shows the undecoupled  $^{15}\text{N}$  spectrum of 90% formamide (natural abundance, 36 pulses!).



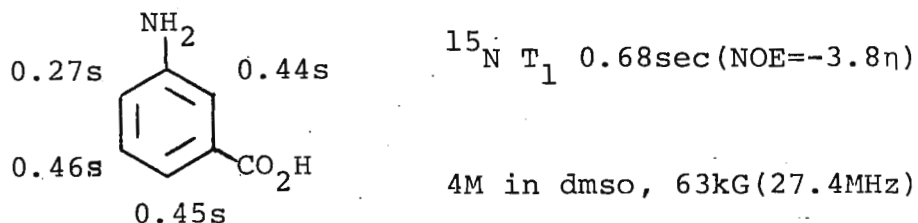
Our first study has been evaluation of  $^{15}\text{N}$  spin-relaxation parameters in representative organic molecules. Early results indicate that  $^{15}\text{N}$  spectroscopy may not be as difficult as anticipated for larger organic molecules.

I (1M in  $\text{CDCl}_3$ ,  $30^\circ$ ) $T_1$  NH 3.5sec (NOE = -5%) $T_1$  NR<sub>3</sub> 25sec (NOE = -5%)(data at 18.2 MHz - collaboration  
with C.H. Bradley and G.W. Gribble)

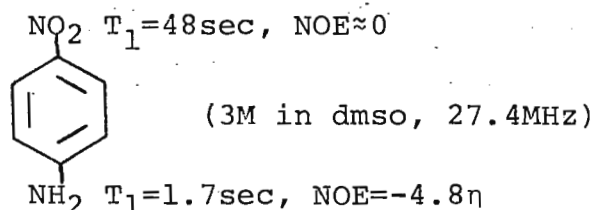
In the sixteen carbon alkaloid, I, both nitrogens are totally relaxed by  $^{15}\text{N}(^1\text{H})$  dipolar interactions. Also,  $T_1$  for the tertiary nitrogen was only 2-3 times longer than previously observed  $T_1$ 's for the non-protonated carbons in I (these measurements were done at 42kG).



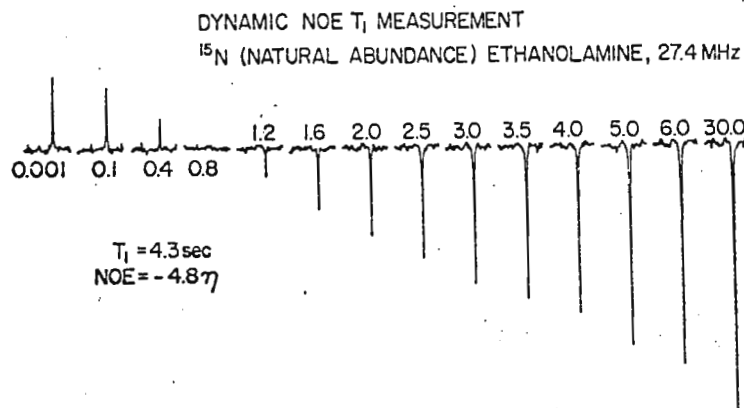
In m-aminobenzoic acid we observed  $^{13}\text{C}$  and  $^{15}\text{N}$   $T_1$ 's as follows:



To avoid mis-informing you:  $^{15}\text{N}$   $T_1$ 's are not necessarily short and dipolar, as shown in the following example:



One final example: 2-aminoethanol.



Shown above in Fig. 3 the  $^{15}\text{N}$   $T_1$  and NOE determined in a single Dynamic NOE FT experiment. Note that the DNOE  $T_1$  method is especially pleasing for  $^{15}\text{N}$  with a large, negative, NOE.

Looks like an inversion-recovery spectrum doesn't it?

Warmest Regards,

George C. Levy  
 Associate Professor

Clive E. Holloway  
 Professor-on-Sabbatical  
 (York University,  
 Toronto)

Richard C. Rosanske  
 Director, NMR Facility

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

April 21st 76

Dear Barry,

"WHITEWASH"

No longer content with the information which can be extracted from a single NMR spectrum, chemists are moving more and more to techniques which examine intensity as a function of not one but two parameters. This raises the age-old problem of representing<sup>1</sup> three-dimensional data in a strictly two-dimensional medium such as the Newsletter and similar learned literature.

Sequential stacks of NMR spectra create a three-dimensional effect. Following Sawyer<sup>2</sup> we offer to any interested party a computer program for "whitewashing" such a display, point by point. The equivalent operation on computed (i.e. theoretical) data has been available for some time<sup>3,4</sup> and many computer centers offer standard packages for this. White ink is a tedious alternative. Our program remembers every interpolation step of our CFT-20 chart recorder trace by trace, suppressing any section of any trace considered to be "behind" another previous trace. The applications include the clarification of relaxation plots, two-dimensional spectroscopy<sup>5,6</sup> and certain forms of zeugmatographic display. The figure illustrates the performance.<sup>7</sup>

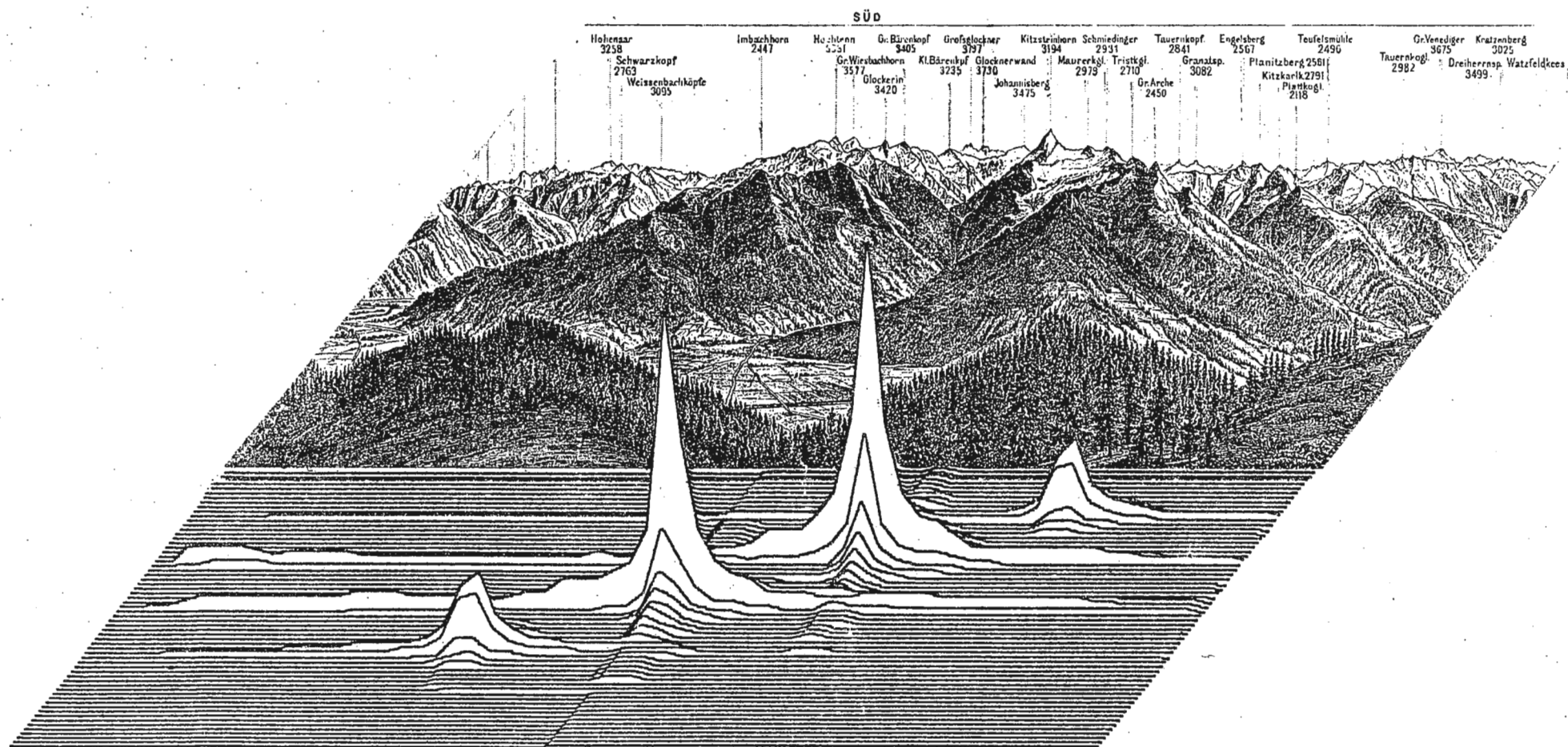
There are two practical disadvantages: our datastorage is disc-based (Diablo) and our working program is a modification of the early CFT-16 Revision A, so it seems unlikely that anyone would find the patch directly applicable, but it might serve as a useful model. Xerox copies of the listing will be sent on request.

In the earnest hope of reinstatement,

We remain, Yours sincerely,

*David Turner Ray*  
David Turner, Ray Freeman

1. L. Da Vinci, Notebooks
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3. R. Freeman, R. R. Ernst, and W. A. Anderson, J. C. P. 46, 1125 (1967).
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7. K. Baedeker, Handbuch (1883).





14 April 1976

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

*Roche Products Limited · PO Box 8 · Welwyn Garden City · Hertfordshire AL7 3AY  
Telephone Welwyn Garden 28128 · Telex 262098*

Title: Pitfalls with TMS salts

Dear Barry

Following your blue and pink missiles, which as usual caught us at the wrong time, I would like to report some unusual spectral observations with the internal references TSP ( $\text{Me}_3\text{Si CD}_2\text{CD}_2\text{CO}_2\text{Na}$ ) and DSS ( $\text{Me}_3\text{Si CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ ).

In the aqueous solutions of several well-known aryl ethanolamine hydrochlorides with  $\beta$ -blocking activity, (ca 0.2 M) and ca 2 mg of TSP or DSS, the trimethyl silyl  $^1\text{H}$  peak moves upfield by up to 40 Hz (0.4 ppm). The shift was calibrated using two secondary internal references (t-butanol, acetone or dioxan). As shown in the Table, the shifts are very large in propranolol and buforalol, but considerably less in oxpranolol, practolol and pindolol. The shifts are clearly due to the ring current effects of the aryl groups, which in some cases must lie close to the  $\text{Me}_3\text{Si}$ -group.

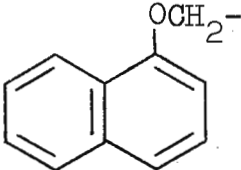
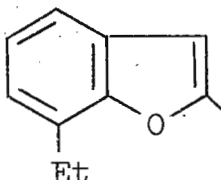
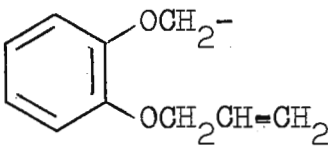
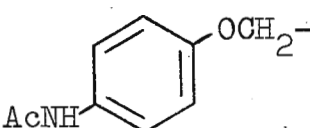
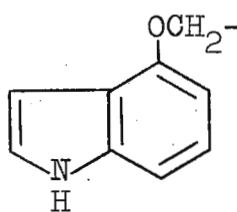
Large shifts of this type have been previously reported for purine and purine nucleosides.<sup>1</sup> Although we do not yet understand the differences observed in the Table, it is clear that TSP and DSS are unreliable reference compounds for aryethanolamines and possibly for other water soluble aromatic compounds of this type.

Yours sincerely

Dr W A Thomas

1. D.H.Live and S.I. Chan, Org.Mag.Res., 1973, 5, 275.

TABLE

Compound *	R <sub>1</sub>	R <sub>2</sub>	$\Delta TSP_{(ave.)}^{\dagger}$	$\Delta DSS_{(ave.)}$
Propranolol		-CHMe <sub>2</sub>	28	39
Buforalol		-CMe <sub>3</sub>	22	26
Oxprenolol		-CHMe <sub>2</sub>	3	5
Practolol		-CHMe <sub>2</sub>	2	2
Pindolol		-CHMe <sub>2</sub>	4	6

\* general structure  $R_1 \cdot CH(OH) \cdot CH_2 \cdot NH_2^+ \cdot R_2 \quad Cl^-$

$\dagger$  high field shift in Hz at 100 MHz; relative to internal t-BuOH, acetone or dioxan.

27th April 1976



University of Salford

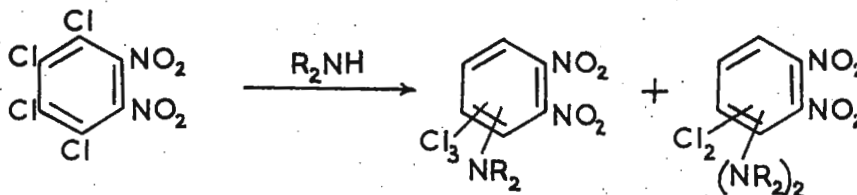
Salford M5 4WT

Department of Chemistry  
and Applied ChemistryDr. B.L. Shapiro,  
Tamunmr Newsletter,  
College of Science,  
Texas A & M University,  
College Station,  
Texas 77843,  
U.S.A.

Dear Barry,

A major drawback in assigning c.m.r. signals of benzenoid carbons results from the non-additivity of substituent effects when the substituents are ortho to each other. We have recently tackled this problem, with remarkably good results, by using hexachlorobenzene as our standard of comparison rather than benzene. The steric congestion factor is already present in the standard.

As a typical problem, we have examined the products from substitution of chlorines by secondary amines in 1,2-dinitro-tetrachlorobenzenes (Scheme)<sup>1</sup>.

Scheme

By taking hexachlorobenzene (132.5 ppm) and the shifts of pentachloronitrobenzene and pentachlorodimethylaniline as standards of comparison (see Table) correct structures (in each case the amine substitutes ortho to the nitro-group) were easily obtained - even when four contiguous substituents were involved! The other possible structures were all far from comparable with the calculated shifts (see Table).

Assignments corroborated by comparison of the proton decoupled, gated and undecoupled (proton-decoupler off) spectra. Clearly, even better results would be obtained by use of other appropriate pentachloroanilines as standards rather than the dimethyl analogue.

We are currently investigating other substituents - including hydrogen to check the generality of this method to any contiguously substituted benzene derivative.

*O. Meth-Cohn*  
O. METH-COHN,

1. Compounds supplied by Dr. A. Heaton, Liverpool Polytechnic.

Table

Shifts (found and calculated) of aromatic carbons

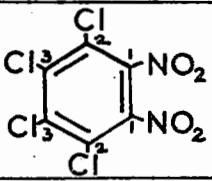
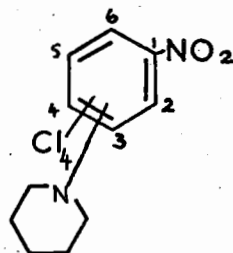
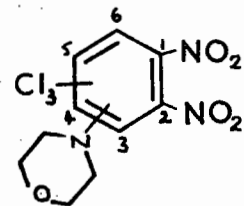
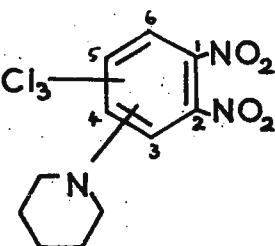
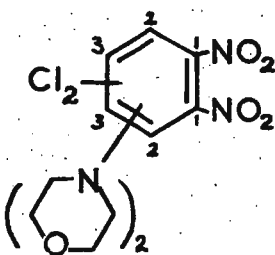
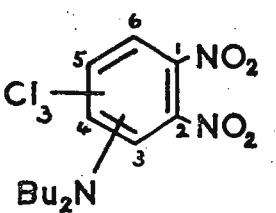
Compound		Shift, ppm (shift relative to C <sub>6</sub> Cl <sub>6</sub> )					
		C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
C <sub>6</sub> Cl <sub>6</sub>		132.5	132.5	132.5	132.5	132.5	132.5
C <sub>6</sub> Cl <sub>5</sub> ·NO <sub>2</sub>		148.3 (+15.8)	124.6 (-7.9)	133.3 (+0.8)	136.1 (+3.6)	133.3 (+0.8)	124.6 (-7.9)
C <sub>6</sub> Cl <sub>5</sub> NMe <sub>2</sub>		147.1 (+14.6)	133.9 (+1.4)	131.7 (-0.9)	129.7 (-2.8)	131.7 (-0.9)	133.9 (+1.4)
	Found	142.9 (+10.4)	128.7 (-3.8)	141.6 (+9.1)			
	Calc	140.4	125.4	136.9			
	Δ	2.5	3.3	4.7			
	Found	148.6	142.2	134.3	135.6	129.9	123.8
	Calc (2-)	149.7	139.2	134.7	135.3	130.5	123.8
	Δ	1.1	3.0	0.3	0.3	0.6	0.0
	Calc (3-)	147.4	126.0	147.9	137.5	132.4	121.8
	Calc (4-)	145.5	126.0	134.7	150.7	134.7	126.0
	Found	140.3	141.5	141.5	138.1	137.8	122.3
	Calc (3-)	139.6	141.8	140.0	138.3	136.0	122.6
	Δ	0.7	0.3	1.5	0.2	1.8	0.3
	Calc (4-)	137.6	139.5	126.8	151.5	138.3	124.5

Table continued;

Compound	Shift, ppm (shift relative to C <sub>6</sub> Cl <sub>6</sub> )					
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
	Found	139.2	142.1	143.4	137.4	120.3
	Calc (3-)	139.6	141.8	140.0	138.3	122.6
	Δ	0.4	0.3	3.4	0.9	2.3
	Calc (4-)	137.6	139.5	126.8	151.5	124.5
	Found	141.3	138.8	138.3		
	Calc (2,2')	141.0	137.5	136.6		
	Δ	0.3	1.3	1.7		
	Calc (3,3')	136.8	152.9	126.0		
	Found	142.0	142.5	142.5	139.0	121.9
	Calc (3-)	139.6	141.8	140.0	138.3	122.6
	Δ	2.4	0.7	2.5	0.7	0.7
	Calc (4-)	137.6	139.6	126.8	151.5	124.6



## New 18-mm Probe for the XL-100

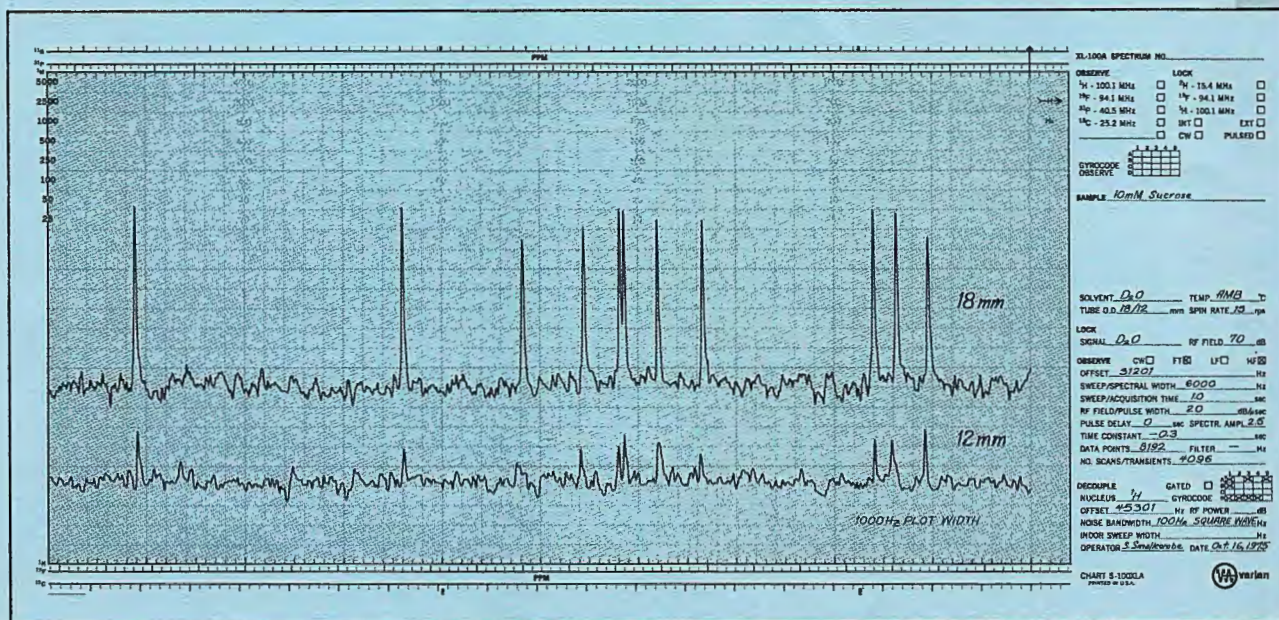
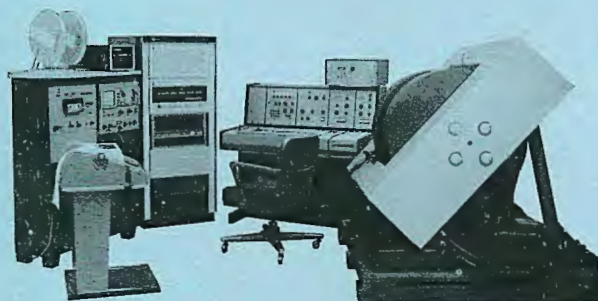
# $^{13}\text{C}$ Spectra 10 Times Faster

Now Varian XL-100 users can run natural abundance  $^{13}\text{C}$  spectra at millimolar concentrations. Varian's new V-4418 Variable-Temperature Probe accommodates 18-millimeter sample tubes and boosts sensitivity to over three times that of the standard 12-mm probe. Compare the two spectra of 10 mM sucrose—clearly this new probe could extend the application of  $^{13}\text{C}$  NMR to entirely new areas of chemical research.

The V-4418 is Varian's latest offering to the scientist who needs  $^{13}\text{C}$  spectra of samples of limited solubility or limited molarity; or who studies certain equilibria and requires low concentration; or who works with relaxation properties that are best studied at low concentration. The V-4418 lets him use samples less concentrated by a factor of 3, or reduces the time required for an experiment by a factor of 10—with results second to none.

Not only is the absolute sensitivity of the V-4418 Probe outstanding, it also offers excellent sensitivity per milliliter of solution, an important asset if you study scarce or expensive (most often both) macromolecules. The Probe develops its full sensitivity potential with 6 milliliters, a volume only three times that required with the standard 12-mm probe!

And that's not all. When the V-4418 Probe is used together with the recently introduced single-sideband filter, overall sensitivity of the XL-100 increases by a factor of 5. Or, in terms of time savings, these combined capabilities reduce a formerly 24-hour experiment to a routine 1-hour run.



Compare these two broadband proton-decoupled carbon spectra of 10 mM sucrose in  $\text{D}_2\text{O}$ , one using an 18-mm sample, the other the standard 12-mm sample! Data were accumulated for 4096 transients, with a one-second acquisition time and a 90° pulse.

For further information contact your local Varian representative or write to:  
Varian Instruments, 611 Hansen Way,  
Box D-070, Palo Alto, CA 94303.



Sample tube  
shown actual size.



# QUADRATURE DETECTION

Is Standard On JEOL's FX100 FT NMR  
and Built-In Digital\* Phase Shifters  
Permit Precise Alignment

**Digital Quadrature Detection (DQD)** is the simultaneous detection of an FT NMR signal with phase sensitive detectors whose reference signals are in separate quadrants, digitally shifted 90° in their r.f. phases. This results in an increase in sensitivity by  $\sqrt{2}$  (~40%), which means sample running times are cut in half on a routine basis over conventional techniques.

Because digital phase control is a basic part of the FX100, Digital Quadrature Detection (resulting in this higher FT NMR performance) is now possible.

**Digital Phase Shifters (DPS)** make use of the very rapid rise times of an r.f. digital logic device, thus phase "jitter" is minimized, and phase accuracy and phase stability are optimized. The r.f. output frequency phase can be precisely set at 0°, 90°, 180° or 270° relative to the master oscillator. The result is a system that is virtually free of imperfect phase angles or phase drift.

The exclusive JEOL digital phase shifting technique, in contrast to the more commonly used analog method, essentially eliminates "ghosting" or false images in the final spectrum — a problem which occurs all too frequently in analog systems.

In addition, we have located the DPS in the IF stage to allow all nuclei to be observed without supplementary phase shifters for each frequency.

Similar capabilities  
are available on the  
FX60 Spectrometer  
as optional accessories.

## Performance Characteristics:

### Micro <sup>13</sup>C/<sup>1</sup>H Dual Frequency Probe

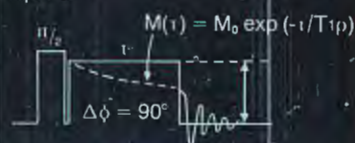
Sample: 10 μg/20 μl solution

Time: 5 minutes

Nucleus: Proton (<sup>1</sup>H)

Sample shown is phenacetin.

$T_{1\rho}$  is the transverse relaxation time in the rotating frame and is useful for studies of chemical dynamics in liquids.

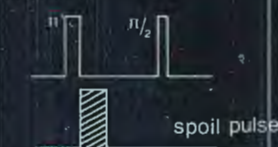


Sample shown is chlorobutane.

**Spin tickling** is a double resonance technique used in both homo and hetero nuclear experiments for the selective identification of spin-spin interactions.

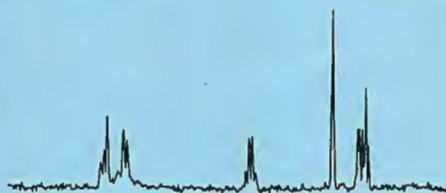
Sample shown is dibromopropionic acid.

**Homospoil** is a technique for eliminating phase and intensity errors which can occur during  $T_1$  measurements.

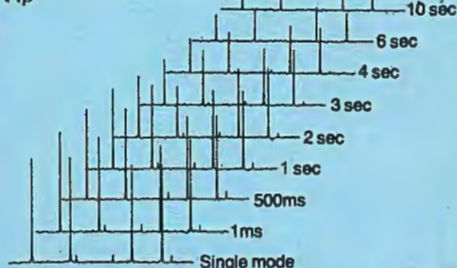


Sample shown is ethylbenzene (distortions are magnified to illustrate the technique).

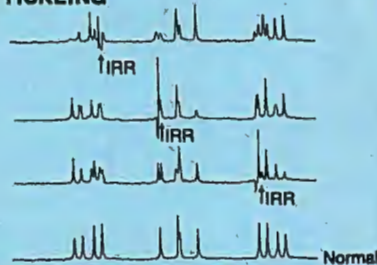
## C/H DUAL FREQUENCY MICRO PROBE



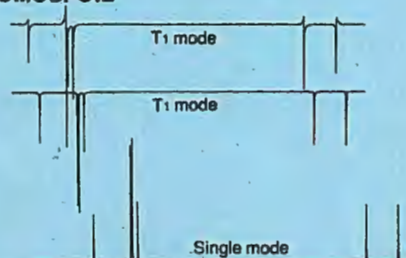
## $T_{1\rho}$



## SPIN TICKLING



## HOMOSPOIL



For further information, call or write . . .

\* Patent Pending

**JEOL**  
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