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No. 208

January, 1976

J.A. van Koeveringe, C. Erkelens and J. Lugtenburg Deuterium Protium Exchange on Carbon in Carbenium Ions. . . . .	1	R. J. Highet ROH to ROD Exchange as an Aid in the Inter- pretation of $^{13}\text{C}$ Spectra . . . . .	30
F. De Pessemmer, D. Tavernier and M. Anteunis Vinyllic $^1\text{H}$ -NMR Downfield Shift and OH $\cdots \pi$ -Electron Bonding . . . . .	3	F. Lefèvre and A. Mannschreck Use of Chiral Auxiliary Compounds in the Study of Intramolecular Processes. . . . .	31
D. M. Doddrell and D. T. Pegg Determination of Relaxation Times in Paramagnetic Complexes. . . . .	5	S. Brownstein Methylene Non-Equivalence in Complexed Ethers. . .	34
G.E. Maciel, J.L. Dallas and J.J. Ackerman Poor Man's $^1\text{H}$ FT in A Nonproton Configuration . .	8	O. Lutz and A. Nolle- $^{33}\text{S}$ - NMR with Our New Multipurpose Spectrometer	36
R. W. Dunlap and G. J. Ray $90^\circ$ Pulses and a Computer Problem on a CFT-20 . .	11	B. Forrest and R. J. Cushley Phytanic Acid and Membrane Permeability. A $^{31}\text{P}$ LIS Study. . . . .	38
T. E. Evans Position Available. . . . .	13	F. W. Wehrli Spin-Rotation Relaxation of a Quadrupolar Nucleus. . . . .	41
J. W. Cooper Noise in the Fourier Transform. . . . .	14	D. P. Kelly Angular Dependence of $^1\text{J}_{\text{C}\alpha\text{H}}$ in Carbocations. A New Criterion for Interpreting NMR Spectra of Carbocations. . . . .	44
J. Delmau, J.C. Duplan and A. Briguet Relaxation de $^{29}\text{Si}$ . . . . .	15	M. Schrey and R. Kosfeld Analysis of High Resolution NMR - Spectra Using Real-Time-Computer . . . . .	46
S. Patt, O. Jardetzky and W. Conover Saturation-Recovery $T_1$ 's (Reinvention of the Wheel) . . . . .	17	H. S. Gutowsky Proton Tunneling, Photosynthesis, and Post- doctoral Position Available. . . . .	50
R. D. Knapp $^{31}\text{P}$ NMR of Synthetic Phosphatidylcholine. . . .	20	B. Knüttel and S. Kaplan Position Available . . . . .	54
W. Stempfle, J. Klein and E. G. Hoffmann Faster DNMR-Programs with Greater Numerical Stability . . . . .	22		
W. S. Brey and L. W. Jaques Fluorocarbon $^{13}\text{C}$ Spectrum . . . . .	26		
G. A. Gray Nitrogen Chemical Shift Assignments Using NOE and $T_1$ Measurements . . . . .	29		

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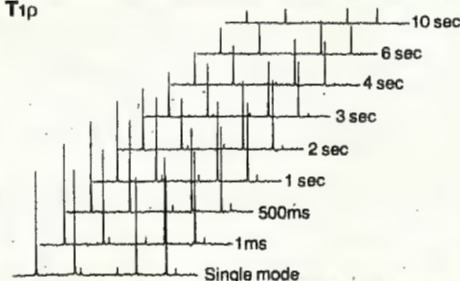
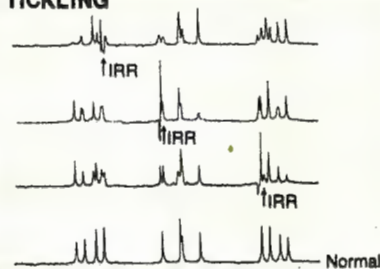
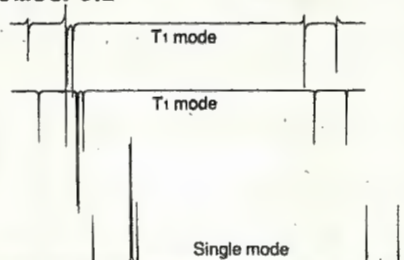
AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 208

Ackerman, J. J. . . . .	8	Kaplan, S. . . . .	54
Anteunis, M. . . . .	3	Kelly, D. P. . . . .	44
Brey, W. S. . . . .	26	Klein, J. . . . .	22
Briguet, A. . . . .	16	Knapp, R. D. . . . .	20
Brownstein, S. . . . .	34	Knüttel, B. . . . .	54
Conover, W. . . . .	17	van Koeveringe, J. S. . . . .	1
Cooper, J. W. . . . .	14	Kosfeld, R. . . . .	46
Cushley, R. J. . . . .	38	Kowalewski, V. J. . . . .	55
Dallas, J. L. . . . .	8	Lefevre, F. . . . .	31
Delmau, J. . . . .	16	Lugtenburg, J. . . . .	1
Doddrell, D. M. . . . .	5	Lutz, O. . . . .	36
Dunlap, R. W. . . . .	11	Maciel, G. E. . . . .	8
Duplan, J. C. . . . .	16	Mannschreck, A. . . . .	31
Erkelens, C. . . . .	1	Nolle, A. . . . .	36
Evans, T. E. . . . .	13	Patt, S. . . . .	17
Forrest, B. . . . .	38	Pegg, D. T. . . . .	5
Gray, G. A. . . . .	29	de Pessemier, F. . . . .	3
Gutowsky, H. S. . . . .	50	Ray, G. J. . . . .	11
Highet, R. J. . . . .	30	Schrey, M. . . . .	46
Hoffmann, E. G. . . . .	22	Stempfle, W. . . . .	22
Jacques, L. W. . . . .	26	Tavernier, D. . . . .	3
Jardetzky, O. . . . .	17	Wehrli, F. W. . . . .	41

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LEIDEN, November 5, 1975

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

Dear Professor Shapiro:

Deuterium Protium Exchange on Carbon in Carbenium ions

For the sake of comparison with bile pigments we are interested in the chemistry of protonated pyrromethenes and the related - 2 furyl - 2'pyrryl-methyl-carbenium ions.

We could prepare: I =  + in good yield.

In the  $^1\text{H}$ -N.M.R. spectrum of I dissolved in  $\text{CD}_3\text{OD}$  the signal of  $4'\text{H}$  or  $6\text{H}$  is missing.

The spectrum of I in  $\text{CD}_3\text{CN}$  shows the signals of all the carbon-bonded hydrogens, however the signal-noise ratio is low because of low solubility.

For comparison: II =  + was synthesized.

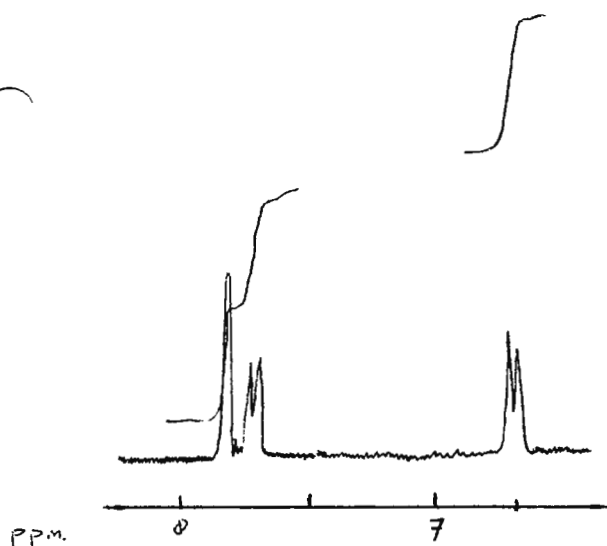
The low field part of the  $^1\text{H}$ -N.M.R. spectrum of II in  $\text{CD}_3\text{OD}$  virtually superimposable on that of I in  $\text{CD}_3\text{OD}$ . Bearing in mind charge delocalisation, the signals in the low field region can be assigned unambiguously.

100 M C/S NMR (JEOL PS 100)

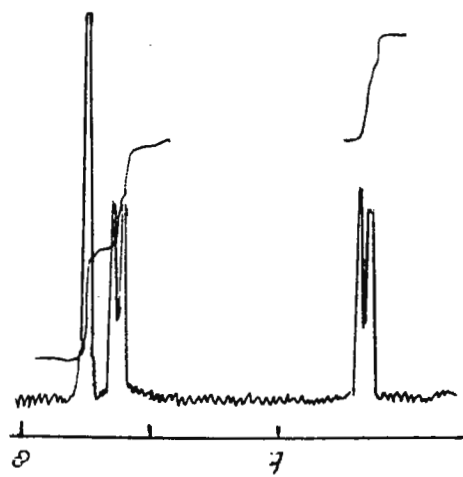
<u>I</u> in $\text{CD}_3\text{OD}$		<u>II</u> in $\text{CD}_3\text{OD}$	
in ppm	Signal	in ppm	
2,52 s	5 $\text{CH}_3$	2,45 s	
6,69 d*	4 H	6,65 d	
7,71 d*	3 H	7,62 d	
7,82 s	6 H	7,74 s	
2,75 s	3' $\text{CH}_3$ or 5' $\text{CH}_3$	2,73 s	
—	4' $\text{H}^{**}$	—	
2,79 s	5' $\text{CH}_3$ or 3' $\text{CH}_3$	2,80 s	

\*  $J_{4,3} = 3,75 \text{ hz}$

\*\* In II the 4' H is replaced by an ethylgroup.



I in  $\text{CD}_3\text{OD}$



II in  $\text{CD}_3\text{OD}$

We hope very soon to be able to check these results with  $^{13}\text{C}$  NMR spectroscopy.

Sincerely,


John A. van Koevinge

Cees Erkelens

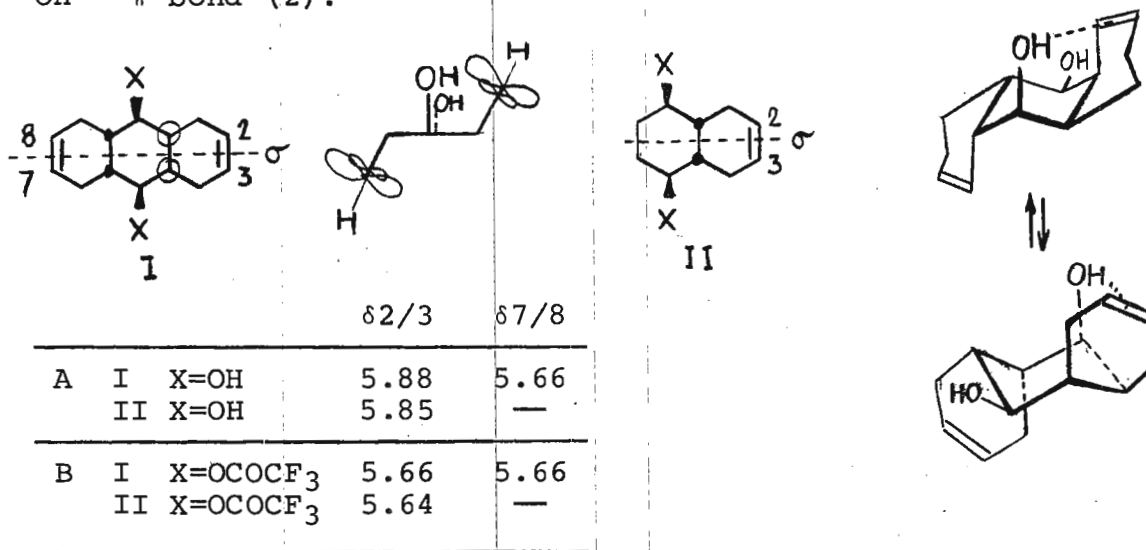
Johan Lugtenburg

# Vinylic $^1\text{H}$ -nmr downfield shift and OH $\cdots \pi$ -electron bonding.

Dear Barry,

The hydrogen bond between OH and a  $\pi$  electron cloud is a documented phenomenon, especially for aromatic systems (1). There are however to our knowledge no experimental data available for the influence of the O-H  $\cdots$   bonding on the chemical shift of the olefinic protons. We now present evidence that a downfield shift results.

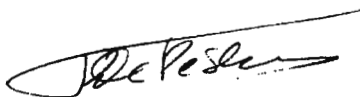
The diol A is known from the I.R. spectrum to form an OH  $\cdots \pi$  bond (2).



In A and B, the vinylic 2 and 3 atoms, and also 7 and 8, are exchanged by the horizontal  $\sigma$  plane\* (above coalescence tem-

\* It is convenient (3) to deduce these equivalences from the "mean" conformation represented in the conventional way in the left upper corner, and whose less common "side-on" view is also shown.

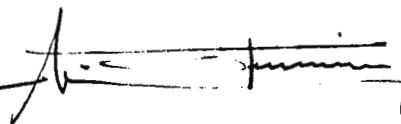
perature of ring reversal) and have therefore the same chemical shift. The pairs (2,3) and (7,8) are however not exchanged by an element of symmetry, and hence their chemical shifts differ in principle. However, the groups (OH in A,  $\text{OCOCF}_3$  in B) that make the (2,3) and (7,8) vinylic protons non-equivalent are rather far away. Therefore the pairs (2,3) and (7,8) in compound B, where a hydrogen bond is excluded, have the same chemical shift (within experimental error) at 300 MHz, although ester groupings in general have large anisotropic contributions. We accept therefore that the anisochronism between (2,3) and (7,8) in A with  $\text{X}=\text{OH}$  ( $\Delta\delta = 0.22$  ppm in  $\text{CDCl}_3$ ) is the result of  $\text{CH} \cdots \pi$  bond formation, where the shift of the high field olefinic pair coincides precisely with that observed in B, and the donor  $\pi$ -bond results in a deshielding of the vinylic protons (2,3). This is corroborated by the data reported for the cis-decalane derivatives II.



F. De Pessemier



D. Tavernier



M. Anteunis

- (1) P. v.R.Schleyer, D.S. Trifan and R. Bacsikai, J.Am.Chem.Soc., 80 6691 (1958).
- (2) R.K. Hill, J.G. Martin and W.H. Stouch, J.Am.Chem.Soc., 83, 4006 (1961).
- (3) J.E. Leonard, G.S. Hammond and H.E. Simmons, J.Am.Chem.Soc., 97, 5052 (1975).





# GRIFFITH UNIVERSITY

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28th November, 1975.

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

Dear Professor Shapiro,

## Determination of Relaxation Times in Paramagnetic Complexes

In connection with our study of  $T_1$  and  $T_2$  values in paramagnetic transition-metal complexes, we have found that when  $T_1 \approx T_2$  (and  $< 50$  msec) our HX-90, under normal conditions, does not produce a reasonable set of PRFT spectra for  $T_1$  determination. The problem arises from transverse magnetization remaining after the  $180^\circ$  pulse being shifted into the detection plane by the following  $90^\circ$  pulse. The problem can be eliminated by using the Bruker Phase Alternation Pulse Sequence (PAPS) where the phase of the observation pulse is shifted  $180^\circ$  on successive pulses and the polarity of the ADC is reversed. Figure 1 displays how bad the problem can be without the PAPS sequence.

To understand how residual transverse magnetization is removed by the PAPS sequence consider the following. Normally the  $180^\circ$  pulse of the  $180^\circ$ - $\tau$ - $90^\circ$  sequence creates a diagonal density matrix in the rotating reference frame. In practice, however, because of many reasons (finite pulse power, offset from the carrier frequency, coil design, etc.) the  $180^\circ$  pulse is not perfect, and the density matrix following the pulse is likely to have non-zero off-diagonal elements,  $\rho_{12}$  and  $\rho_{21}$ , for a spin-half system. The diagonal matrix elements will alter as a function of  $T_1$  and  $\rho_{12}$  and  $\rho_{21}$  will be a function of  $T_2$ . A further non-perfect  $90^\circ$  pulse after time  $\tau$  will alter the density matrix to give off-diagonal elements which are functions of both  $T_1$  and  $T_2$ .

More precisely, if we let the second pulse be represented by a field  $H_1$  along the y-axis of the rotating frame, the transformed density operator is

$$\begin{aligned} \rho'(\tau) &= e^{-i \int_0^t J_y \gamma H_1 dt} \rho(\tau) e^{+i \int_0^t J_y \gamma H_1 dt} \quad (\hbar = 1) \\ &= R \rho(\tau) R^* \quad (\text{say}) \end{aligned}$$

We have assumed here that the pulse time  $t$  is short enough to replace  $\rho'(\tau + t)$  by  $\rho'(\tau)$ . Writing

$$\int_0^t \gamma H_1 dt = \theta,$$

and taking matrix elements gives



$$\begin{aligned} \langle 1 | \rho'(\tau) | 2 \rangle &= R_{11} R_{12}^* \rho_{11}(\tau) + R_{11} R_{22}^* \rho_{12}(\tau) + R_{12} R_{12}^* \rho_{21}(\tau) \\ &\quad + R_{12} R_{22}^* \rho_{22}(\tau) \end{aligned}$$

with a similar expression for  $\rho_{21}'(\tau)$ , where  $R_{ij}^* = \langle i | R^* | j \rangle$ . Because  $J_y$  has zero diagonal elements in the representation we are using, upon expanding the exponential and taking the diagonal elements, the terms involve  $\theta^n$  where  $n$  is odd will be zero. Consequently  $R_{11}$  and  $R_{22}$  are invariant under the transformation  $\theta \rightarrow -\theta$  that is, are even functions with respect to  $\theta$ . Similarly  $R_{12}$  and  $R_{21}$  will involve only terms for which  $n$  is odd, and will consequently be odd functions with respect to  $\theta$ . It follows that  $R_{11} R_{12}^*$  and  $R_{12} R_{22}^*$  will be odd and  $R_{12} R_{12}^*$  and  $R_{11} R_{22}^*$  will be even functions. Thus the signal, which depends on  $\langle 1 | \rho'(\tau) | 2 \rangle$ , will be related to  $\rho_{11}(\tau)$  and  $\rho_{22}(\tau)$ , which are functions of  $T_1$ , by an odd function of  $\theta$ , and to  $\rho_{12}(\tau)$  and  $\rho_{21}(\tau)$  which are functions  $T_2$ , by an even function of  $\theta$ . The signal  $S_1$  from the first PAPS pulse sequence will be

$$S_1 = F(\theta, T_1) + f(\theta, T_2)$$

where  $F$  is odd and  $f$  is even. On phase inversion the sign of  $H_1$  is changed and thus  $\theta$ , and we get the second signal in the PAPS sequence as

$$\begin{aligned} S_2 &= F(-\theta, T_1) + f(-\theta, T_2) \\ &= -F(\theta, T_1) + f(\theta, T_2) \end{aligned}$$

giving, by appropriate data accumulation

$$\frac{1}{2}(S_1 + S_2) = f(\theta, T_2)$$

and 
$$\frac{1}{2}(S_1 - S_2) = F(\theta, T_1)$$

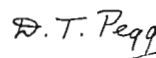
We conclude that while the general signal involves two decay processes,  $T_1$  and  $T_2$ , PAPS gives a signal which is a function of  $T_1$  only, consequently a true PRFT sequence results. We note that a True Inversion Time Sequence (TITS) gives a signal which only depends on  $T_2$  and in principle the PAPS sequence without the ADC polarity inversion would measure  $T_2$  (actually  $T_2^*$ ). The above analysis does not need to make any assumptions about the form of the functions  $f(\theta, T_2)$  and  $F(\theta, T_1)$ .

We have also been able to measure  $T_1$  via a  $90^\circ$ - $\tau$ - $90^\circ$  pulse sequence using PAPS. here, it is well known that transverse magnetization cause severe problems when measuring  $T_1$ . PAPS eliminates these difficulties.

Yours sincerely,

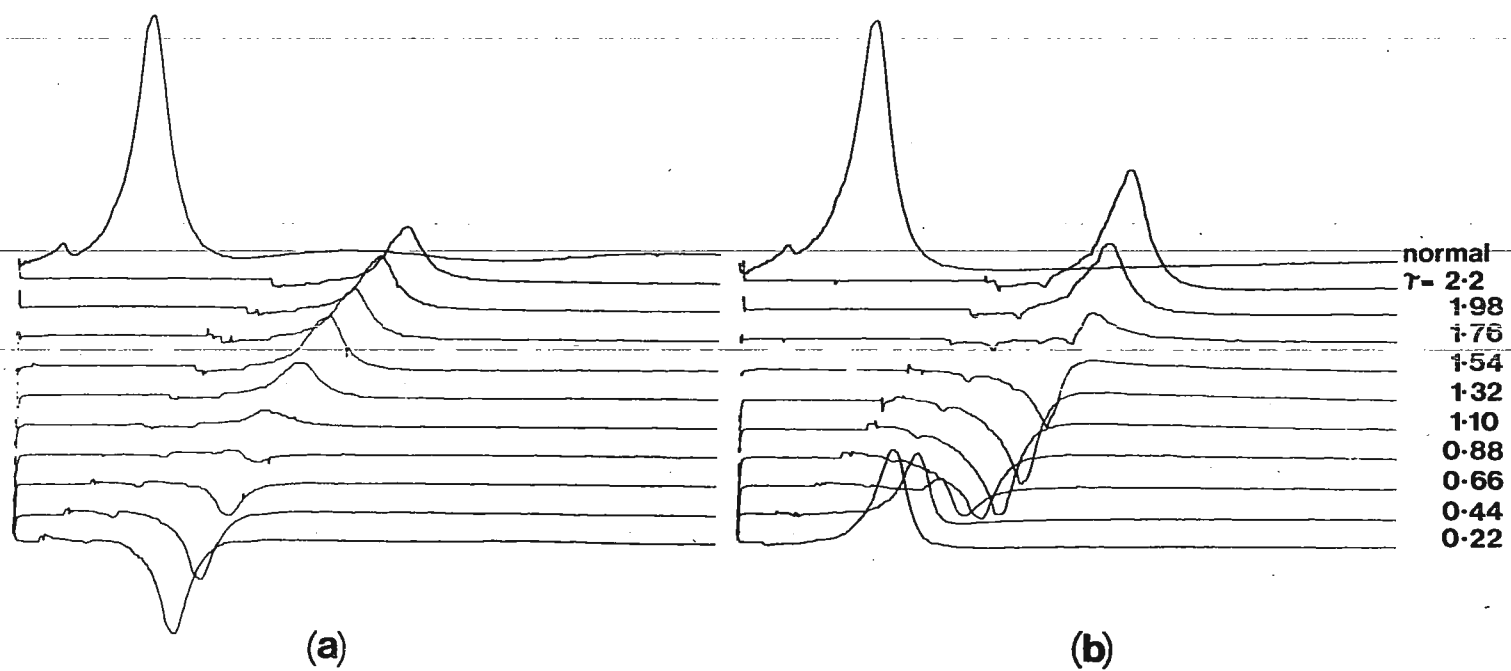


D.M. Doddrell



D.T. Pegg

Figure Caption: (a) PRFT sequence on the  $\text{CH}_3$  proton resonance of copper acetylacetonate using PAPS,  $\tau$  is in msec.  $T_1 = 3.6$  msec.  
(b) PRFT sequence without PAPS.



Department of Chemistry

Colorado State University  
Fort Collins, Colorado  
80523

December 1, 1975

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

Dear Dr. Shapiro:

Upon reading the letter from C. Brevard in the October Newsletter, we thought a similar experiment done routinely in our lab might be of interest to readers interested in multi-nuclear nmr. Presently this lab is investigating the solution chemistry of a variety of metal salts in aqueous and non-aqueous media. Since we usually operate in the external lock mode (reported in the June 1975 Newsletter) while observing nuclei of low sensitivity, choosing a reference scheme has been a considerable problem.

We typically operate in the broad band configuration<sup>1</sup> using a modified Bruker HFX-90 and a United Development Corp. broad band preamplifier. The range of frequencies which may be derived by our broad band transmitter network is from 4 to 55 MHz.<sup>2</sup> However, by simply changing a few cable connections we are also able to easily observe the <sup>1</sup>H nmr signals (90 MHz) for the system under observation - without perturbing the probe. This enables us to reference our primary resonance to a <sup>1</sup>H resonance in the sample (typically a solvent resonance but it could be some other internal <sup>1</sup>H signal).

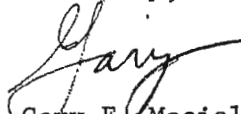
Briefly this procedure is as follows. The broad-band network is, in normal operation, adjusted for the primary nucleus of interest and the standard, narrow band receiver coil of the Bruker insert is tuned to the primary frequency (e.g., 4.19 MHz for Ag-109). The decoupler coil of the Bruker insert is generally tuned to the <sup>1</sup>H NMR frequency (90 MHz) and this coil serves as a transmitter for either CW proton decoupling or for <sup>1</sup>H FT experiments. It is found that the receiver coil of the Bruker insert can serve the dual purpose of receiving the primary NMR signal or the <sup>1</sup>H NMR signal. To examine the primary nucleus, the broad-band configuration is arranged according to the scheme of Figure 1A. To examine the <sup>1</sup>H nucleus, the cable connections are changed according to Figure 1B. The complete changeover requires less than one minute.



This approach has the limitation of observing  $^1\text{H}$  signals at 90 MHz with a receiver coil tuned to an alternate frequency. This results in low  $^1\text{H}$  (S/N) when compared to standard  $^1\text{H}$  NMR spectra. However, most solvent  $^1\text{H}$  resonances are readily observable in a single pulse with (S/N) of 200/1 or greater.

Because the  $^1\text{H}$  (S/N) is unusually large, the  $^1\text{H}$  FID can be used to trim up the homogeneity of the magnetic field of each sample by adjusting the shim currents while observing repetitive solvent FID's on an oscilloscope.

Sincerely,

  
Gary E. Maciel  
Professor

  
J.L. Dallas

  
J.J. Ackerman

#### References

1. H.C. Dorn, L. Simeral, J.J. Natterstad and G.E. Maciel, J. Magn. Resonance, 18, 1(1975).
2. A narrow band matching network (match box) is required to impedance match the amplifier and the transmitter coils. To change this match box for a new frequency requires pulling the probe out of the magnet.

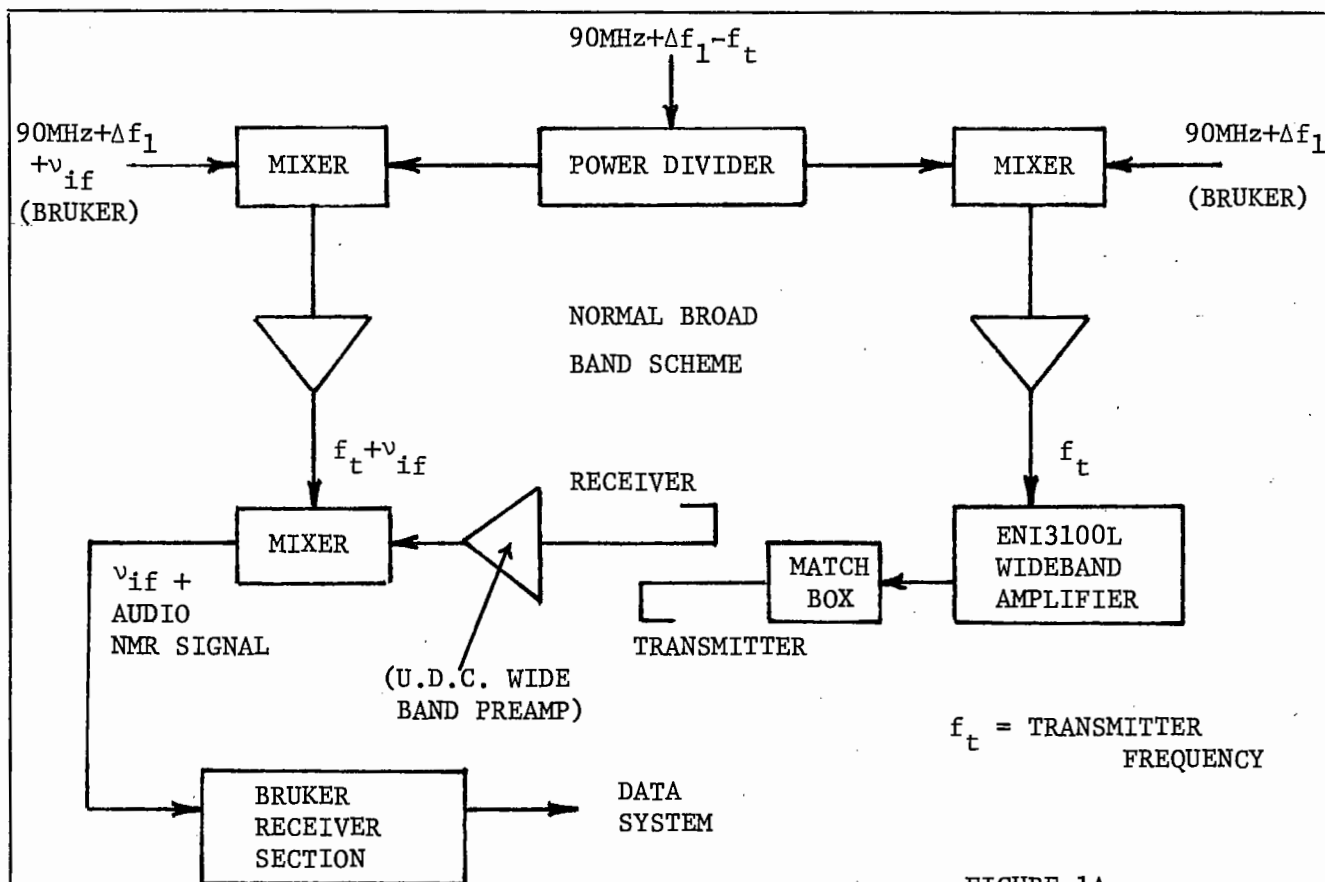
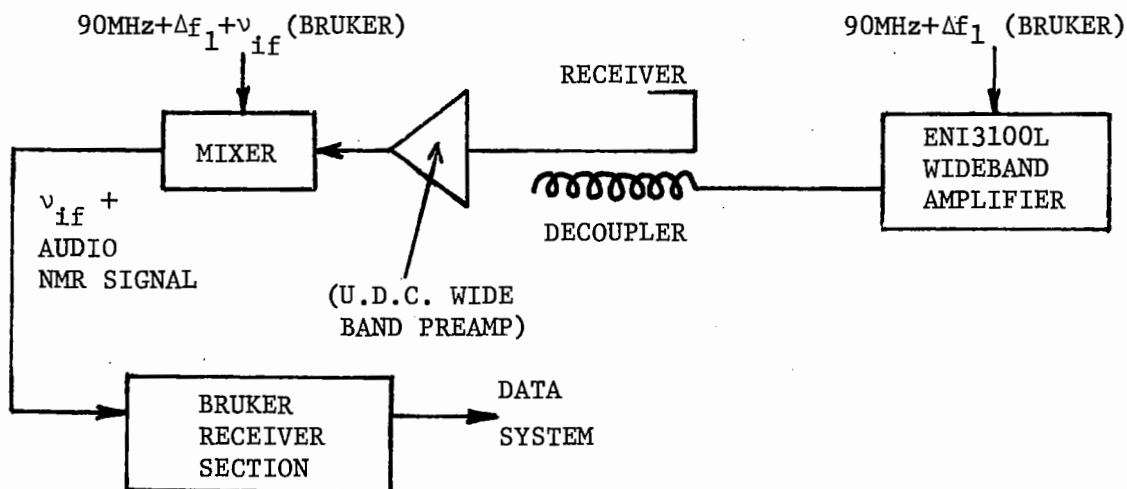


FIGURE 1A



MODIFIED PROTON SCHEME (90 MHz)

FIGURE 1B

## Standard Oil Company (Indiana)

Amoco Research Center  
P.O. Box 400  
Naperville, Illinois 60540  
312-420-5111

December 3, 1975

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

Subject: 90° Pulses and a Computer Problem on a CFT-20

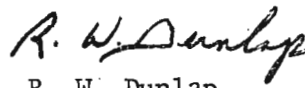
Dear Barry:

Our CFT-20 is entering its second year of operation in our laboratory and a few observations have been made which might be useful to others. We have developed a technique to determine the pulse width of a 90° pulse. This technique is considerably shorter and less tedious than the one described in the Varian manual. The sample we use is a 60% (w/v) solution of Carbowax-1000 dissolved in acetone-d<sub>6</sub>. The transmitter offset (TO), filter bandwidth (FB) and end of plot (EP) parameters are set at 66 (i.e. near resonance) 500 and 500 respectively with the remaining parameters set as usual for the ethylbenzene sample. The pulse width (PW) is then varied in the vicinity of a 180° or 360° pulse. Under these conditions the FID has the usual sinusoidal decay expected of a near resonance response. Since the phase of the FID and the phase of the peak in the transformed spectrum are related, a 180° pulse width is determined as that width which causes the FID to just change phase. On a CFT-20 this is easily determined from observing the pulse width at which the first few data points of the FID pass thru a line (created by having EP = 500) corresponding to zero. This is illustrated in Figure 1 where the 180° pulse was determined to be 48 μs giving a 90° pulse of 24 μs. Since there is no need to transform the FID and plot the spectrum, the time necessary to determine the pulse width corresponding to a 90° pulse is reduced to a few minutes.

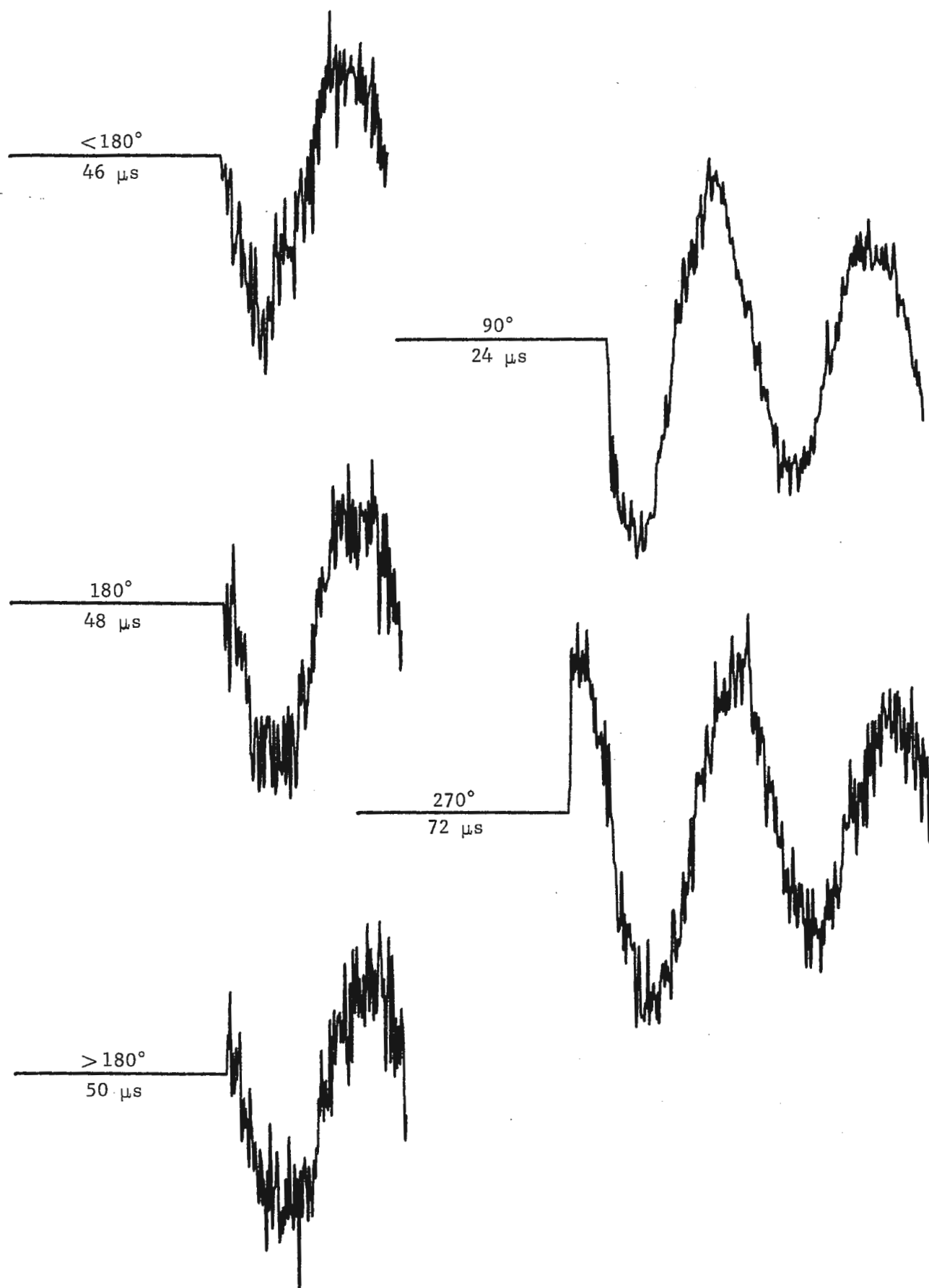
We have encountered a computer problem with our CFT-20. In obtaining <sup>13</sup>C spectra of ethylene-propylene copolymers, ODCB is used as a solvent. The ODCB peaks are 30 times as intense as the strongest peak in the polymer spectrum. Consequently, no signal to noise enhancement is obtained after about 5000 scans. We have avoided this problem by switching to tetrachlorothiophene (TCT) as a solvent. The TCT peaks are of the same intensity as the polymer peaks and the dynamic range problem is avoided. Fortunately, no solvent shift effects have been detected.

  
G. J. Ray

GJR:RWD:sls

  
R. W. Dunlap



FID Phase Changes As A Function Of Pulse Width



DOW CHEMICAL U.S.A.

December 4, 1975

MICHIGAN DIVISION  
MIDLAND, MICHIGAN 48640

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

Dear Barry:

We are looking for a recent graduate at the Ph.D. level to fill an immediate opening in our laboratory. The job consists primarily of the application of high resolution NMR to the solution of industrial analytical problems. The person we are seeking will have to be highly motivated, self starting, and have to interact with production, development, and research people. Our problems involve quantitative determinations as well as qualitative structure work. A broad interest in chemistry would be most helpful.

Our NMR equipment consists of a Varian XL-100-15 with Digilab Data System, an HA-100, and several 60 MHz spectrometers. We also anticipate the purchase of a dedicated C-13 spectrometer in the very near future.

Applicants should write to me at the address below for an application form. The Dow Chemical Company is an equal opportunity employer and all qualified applicants are encouraged to reply.

Sincerely,

*Thomas E. Evans*

Thomas E. Evans  
Analytical Laboratories  
574 Building  
Phone: (517)-636-5325

nhc





DEPARTMENT OF CHEMISTRY

TUFTS UNIVERSITY

MEDFORD, MASSACHUSETTS 02155

December 4, 1975

Dr. B.L. Shapiro  
 TAMUNMR Newsletter  
 College of Science  
 Texas A & M University  
 College Station, Texas 77843

"Noise in the Fourier Transform"

Dear Barry:

We have been continuing experiments and calculations on the effects of round-off error in the Fourier transform and have come to the conclusion that dynamic range after the transform is markedly affected by both word length and transform length. The effects are not quite as severe as those predicted by Welch<sup>1</sup> who based his calculations and experiments on the assumption that all data points are full at the beginning of the transform but the limitations are such that a maximum dynamic range of 30000 to 40000 to one is the best that can be expected even in a twenty-bit word. The values for a 16-bit word are substantially less as shown below.

<u>size</u>	<u>w=20</u>	<u>w=16</u>
4096	43691	3942
8192	43691	5350
16384	34953	4855
32768	43691	4855

These data were obtained by synthesizing free-induction decays having an LB=0.4 and having peaks with gradually increasing dynamic range. The effects of double precision calculations and of a single precision sine look-up table are still being investigated. Further we have found that the noise generated in the transform process is indeed coherent noise and can not be removed by block averaging. A paper summarizing all of the experimental data has been submitted to J. Mag. Res.

Sincerely,

James W. Cooper  
 Assistant Professor

1. P.D. Welch, IEEE Trans. Audio Electroacoust., AU17, 151 (1969), also reprinted in "Digital Signal Processing," L.R. Rabiner and C.M. Rader editors., IEEE Press (1972).



UNIVERSITÉ CLAUDE BERNARD, LYON I

## LABORATOIRE DE SPECTROSCOPIE ET DE LUMINESCENCE

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69621 VILLEURBANNE - FRANCE  
TÉL. (78) 52.07.04

VILLEURBANNE, le 22 décembre 1975

Professor B.L. SHAPIRO  
TEXAS A and M. UNIVERSITY  
Department of Chemistry  
COLLEGE OF SCIENCE

COLLEGE STATION, Texas 77843  
U.S.A.

Relaxation de  $^{29}\text{Si}$ 

Cher Docteur SHAPIRO,

Equipés depuis peu d'un XL 100, nous avons différé notre contribution aux TAMU NMR Newsletters espérant être en mesure de communiquer des résultats intéressants sur la relaxation de  $^{29}\text{Si}$ . Malheureusement, l'appareillage pour la mesure de  $T_1$  n'est pas encore en place et nous nous bornerons à vous faire part de nos premiers résultats d'effet Overhauser :

Poursuivant une étude de  $^{29}\text{SiHCl}_3$  entreprise sur le proton, nous avons effectué des mesures sur  $^{29}\text{Si}$  qui, à 5 % près, présente un effet Overhauser nul.

L'expression 
$$= \frac{I_{\text{DR}} - I_{\text{SR}}}{I_{\text{SR}}} = \frac{\gamma_{\text{H}}}{\gamma_{\text{Si}}} \frac{0,5 R_{\text{dd}}}{R_{\text{dd}} + R_{\text{other}}} \text{ avec } \frac{\gamma_{\text{H}}}{\gamma_{\text{Si}}} \neq -5$$
 montre que  $R_{\text{dd}} \ll R_{\text{other}}$ .

A vrai dire ce résultat ne saurait surprendre car nous savons bien que dans  $\text{SiHCl}_3$ , molécule de petite dimension, le mécanisme de relaxation prépondérant est la spin rotation \* et ceci d'autant plus que nous avons travaillé sur un échantillon scellé à une température (30°C) supérieure à la température d'ébullition. Nous espérons confirmer, grâce à des mesures de relaxation à température variable, nos résultats concernant le mouvement des molécules de  $\text{SiHCl}_3$ .

Recevez, Cher Docteur SHAPIRO, nos sentiments les meilleurs.

  
J. DELMAU

  
J.C. DUPLAN

  
A. BRIGUET

\* G.C. LEVY, J.D. GARGIOLI, P.C. JULIANO et J.D. MITCHELL, J. magn. Res., 8, 399 (1972), J. Am. Chem. Soc., 95, 3445 (1973).

A. BRIGUET, J.C. DUPLAN et J. DELMAU, Mol. Phys., 29, 837 (1975), J. de Physique, 36, 897 (1975).



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STANFORD UNIVERSITY  
STANFORD, CALIFORNIA 94305

STANFORD MAGNETIC RESONANCE LABORATORY

(415) 497-4062  
(415) 497-6153

December 5, 1975

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

Dear Barry,

SATURATION-RECOVERY  $T_1$ 'S  
REINVENTION OF THE WHEEL

The accurate measurement of spin-lattice relaxation times is a problem which is on everyone's mind. As recently summarized by Levy<sup>1</sup>, various techniques show different dependences on factors such as miscalibration of pulses, distance off-resonance,  $H_1$  inhomogeneity, etc. The use of equations which include these factors is in many cases indispensable for obtaining accurate results. Nothing, however, can replace the selection of an experimental technique which minimizes the various difficulties. In this regard, the most critical factor in measuring accurate relaxation times is the preparation of the magnetization to a precisely known state at some time in the experiment. Any imprecision, caused by pulse miscalibration, distance off-resonance,  $H_1$  inhomogeneity, or whatever, will introduce "distortion" into the observed behavior of the magnetization with time and will certainly reduce the expected accuracy.

Some time ago, Markley *et al.*<sup>2</sup> observed in a footnote that one could measure  $T_1$ 's by a saturation-recovery technique, using white noise to saturate an entire spectrum. That paper focussed on the reduction in time made possible by such a technique in connection with the measurement of long relaxation times. We would like to focus on another aspect of that experiment, i.e., the fact that one can prepare a spin system to a known ( $M_0=0$ ) state of magnetization at a known time ( $t=0$ ). Furthermore, one can directly monitor that state to verify this. In the standard inversion-recovery  $T_1$  sequence<sup>3</sup>, for example, components of the magnetization left in the x-y plane by the  $180^\circ$  pulse complicate the immediate monitoring of the z-magnetization without the intervention of a homogeneity spoiling pulse, and the observation of spectra with  $M(t)=-M_0$  is rarely possible. In a saturation experiment, however, there is no net x-y magnetization at time zero, so that an (almost) immediate monitoring of the z-magnetization is possible. At the same time one has dispensed with the need to calibrate pulse lengths and worries about  $H_1$  inhomogeneity and distance off-resonance. The only requirement is a decoupler capable of saturating the spins of interest.

This experiment is demonstrated in the accompanying figure, which is a  $T_1$  measurement of ribonuclease. We present the downfield (A) and the upfield (B)



Dr. B. L. Shapiro  
December 5, 1975

regions of the spectrum at 360 MHz, with  $\tau$  values from bottom to top of .01, .04, .08, .1, .2, .4, .7, 1.0, and 1.5 seconds. Note that one can look at these spectra and be confident that at time zero the magnetizations did indeed start at 0. Decoupling power used in these experiments was approximately 20 times normal single frequency decoupling experiments. 0.5 second was allowed to re-saturate the spectrum after each pulse. The approach of spin systems to complete saturation is a non-trivial theoretical problem, given either single frequency<sup>4</sup> or white noise<sup>5</sup> decoupling (which is not used on our Bruker spectrometer in any case). The experimental approach of lengthening the time for saturation until no magnetization is seen at short values of  $\tau$  is probably the best solution to the problem in general.

One additional feature should be noted. Like the progressive-saturation experiment<sup>6</sup>, no estimate of  $T_1$  is needed to begin the experiment, and thus no wastage of time is incurred. Unlike the progressive-saturation experiment, however, the acquisition time and/or the decay of magnetization in the x-y plane following the sampling pulse do not place a limitation of the selection of  $\tau$  values, and hence there is no limitation on the  $T_1$ 's which can be measured. The only limitation which must be mentioned is that, for white noise decoupling at least, the net z-magnetization in the presence of the decoupling is<sup>5</sup>

$$\overline{M_z} = M_0 / (1 + \sigma^2 T_1 / 2)$$

where  $\sigma^2$  is the constant power spectral density. In other words, and as everyone knows intuitively, it is harder to saturate resonances with short  $T_1$ 's. We repeat, however, that although this may interfere with the experiment, the state of magnetization at small values of  $\tau$  is subject to direct experimental measurement.

Sincerely,



Steve Patt



Oleg Jardetzky



Woody Conover

Enclosure

SP/OJ/WC/skh

<sup>1</sup>G. C. Levy and I. R. Peat, J. Mag. Res., 18:500 (1975)

<sup>2</sup>J. L. Markley, W. S. Horsley, and M. P. Klein, J. Chem. Phys., 55:3604 (1971)

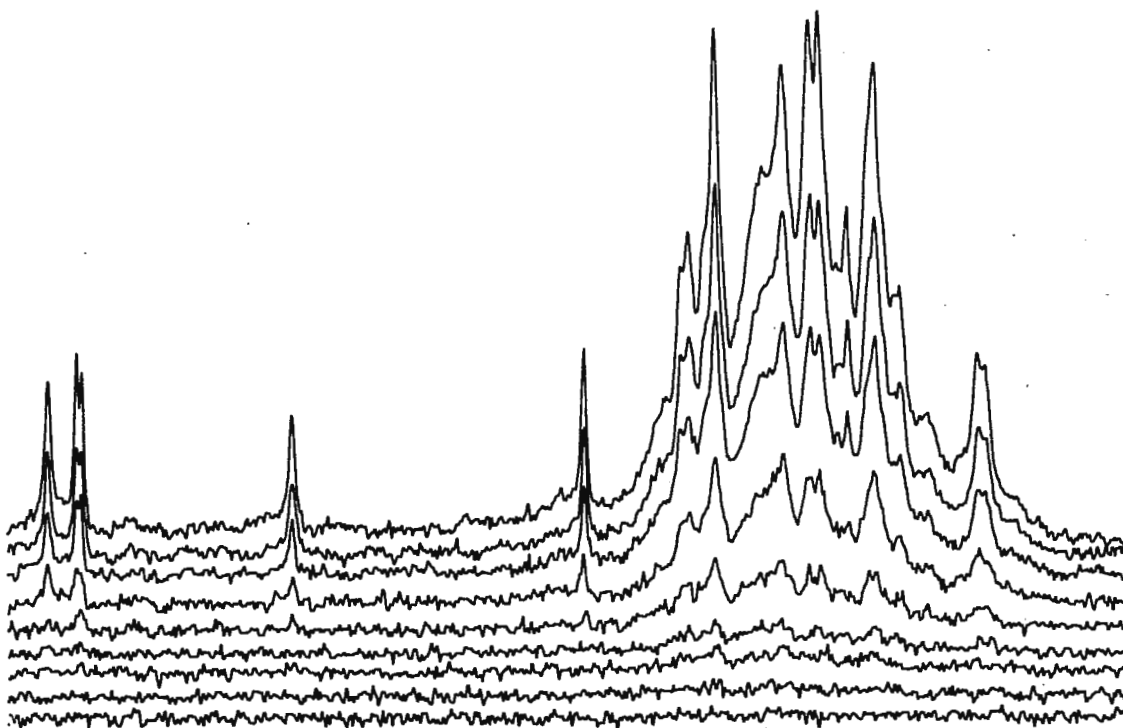
<sup>3</sup>R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, J. Chem. Phys., 48:3831 (1968)

<sup>4</sup>H. C. Torrey, Phys. Rev., 76:1059 (1949)

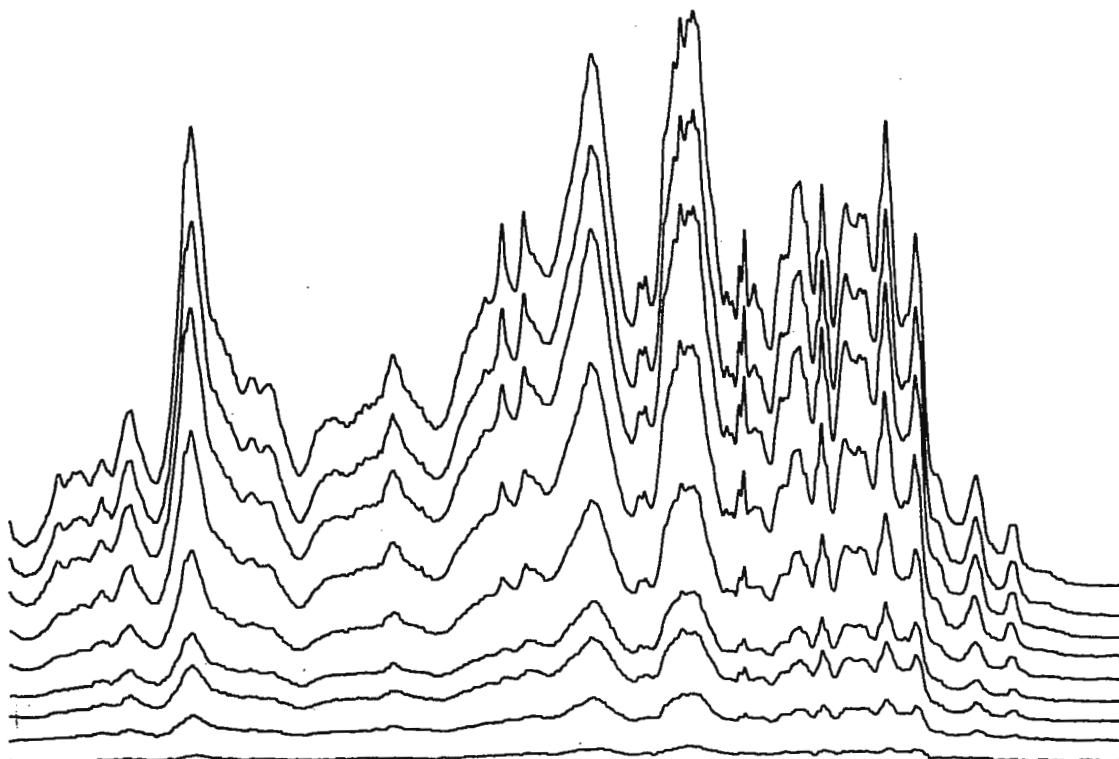
<sup>5</sup>R. R. Ernst, J. Mag. Res., 3:10 (1970)

<sup>6</sup>R. Freeman and H. D. W. Hill, J. Chem. Phys., 54:3307 (1971)

A)



B)



RNAse A, 36 mg/ml, pH 2.07, 26°C, 200 75° pulses each,  
taken on an HXS-360 spectrometer

BAYLOR COLLEGE OF MEDICINE  
TEXAS MEDICAL CENTER  
HOUSTON, TEXAS 77025

December 11, 1975

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

Dear Dr. Shapiro:

TITLE:  $^{31}\text{P}$  NMR of Synthetic Phosphatidylcholine

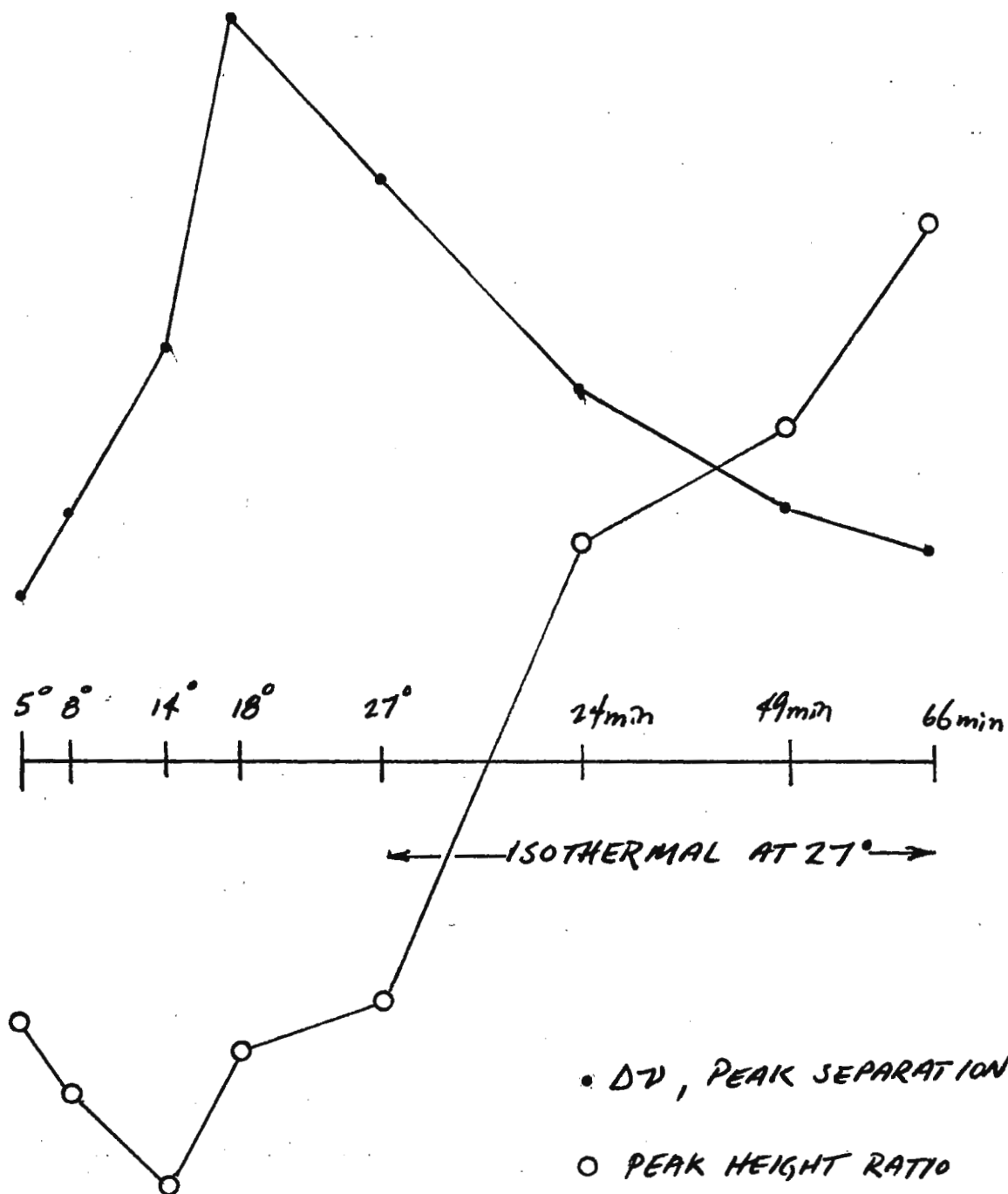
We have been examining the structural stability of aqueous sonicated dispersions of dimyristoyl phosphatidylcholine. By using paramagnetic ions to resolve the inner from the outer  $^{31}\text{P}$  (nuclei) nuclear resonances, we have monitored the effect of certain apolipoproteins on permeability and fluidity of bilamellar vesicles as a function of time and temperature. In some cases, the paramagnetic nucleus is trapped inside the vesicle so as to minimize perturbation of the exposed lipid layer. The effect of free paramagnetic ions in solution is cancelled by addition of EDTA. All spectra were taken in  $\text{H}_2\text{O}$  without spinning the sample using  $^{19}\text{F}$  external lock, each spectrum requiring about ten minutes analysis time. The result of one experiment is shown graphically below. Here  $\text{Pr}(\text{NO}_3)_3$  is trapped inside the vesicles and  $^{31}\text{P}$  spectra are recorded as a function of temperature and time. Although the gel  $\rightarrow$  liquid crystalline transition temperature for this lipid is around  $24^\circ\text{C}$ , the lines begin to sharpen at about  $8^\circ$  and are clear at  $14^\circ$ . Above  $24^\circ$ , there is leakage of the  $\text{Pr}^{+3}$  through the bilayer with an equilibrium half-life of hours.

Yours sincerely,



Roger D. Knapp

RDK/dm



$^{31}\text{P}$  NMR OF DIMYRISTOYL LECITHIN +  $\text{Pr}(\text{NO}_3)_3$



December 3, 1975

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

Title: Faster DNMR-Programs with  
 greater numerical stability.

Dear Professor Shapiro,

We have now succeeded in correcting certain problems\* in the programs DNMR 2 and 3 (QCPE 140 and 165, respectively) developed by Prof. Binsch, et al., for the treatment of exchange problems in spin-coupled systems.

I. When, for a given set of parameters, equal eigenvalues arise within a factorized submatrix (e.g., in the disappearance of coupling), the routine ALLMAT fails since it can then produce equal eigenvectors. Subsequent inversion with the routine NVRT then becomes impossible.

II. We have found the very rationally written "EISPACK" routines (Lecture Notes in Computer Science, Vol. 6: B.T. Smith, J.M. Boyle, B.S. Garbow, Y. Ikebe, V.C. Klema and C.B. Moler, Matrix Eigensystem Routines-EISPACK Guide, Springer Verlag 1974) to be extremely useful for diagonalization. The problem mentioned in I. does not then occur, since this routines take into account from the beginning the possibility that eigenvalues can be equal. Furthermore, this algorithm is up to 3 times faster for a system of 4 nuclei.

III. To be able to use the EISPACK routines, it was necessary to convert the main programs DNMR 2 and 3, and the routines TRAMAT and NVRT from complex into the real notation. The routine NVRT was rewritten to stabilize the inversion algorithm.

At the same time, a considerable further reduction of the core requirement was achieved by more rational programming (2 of the 4 largest-dimensioned arrays were removed).

IV. In addition, the Fortran I/O system was not used, which for a PDP-10 results in a saving of 7K. Also the plotting or display, together with calculation of the Lorentzian lineshapes, is carried out by a separate program. It is now possible to handle problems of up to 5 different nuclei with DNMR 2 and 3. In the example given, the effective core requirement for 5 nuclei (dimension of the submatrices 100x100) is now 55K instead of 102K on a PDP-10; the CPU time was 130 minutes for 12 spectra (or rate constants).

V. Lastly, we had to correct a programming error in the version of DNMR 3 submitted from QCPE. In the routine MAGEQ after statement 29 it should read:  $NX=2.*IME(1,I)$  and before statement 6:  $NBIN=NBIN*(NX-LL)$  since N appears in COMMON.

Example: Zirconium- $\eta^3$ -tetraallyl mutual  $\sigma, \pi$ -exchange.

4 spectra selected from 12 calculations.

W. Stempfle

W. Stempfle

J. Klein

J. Klein

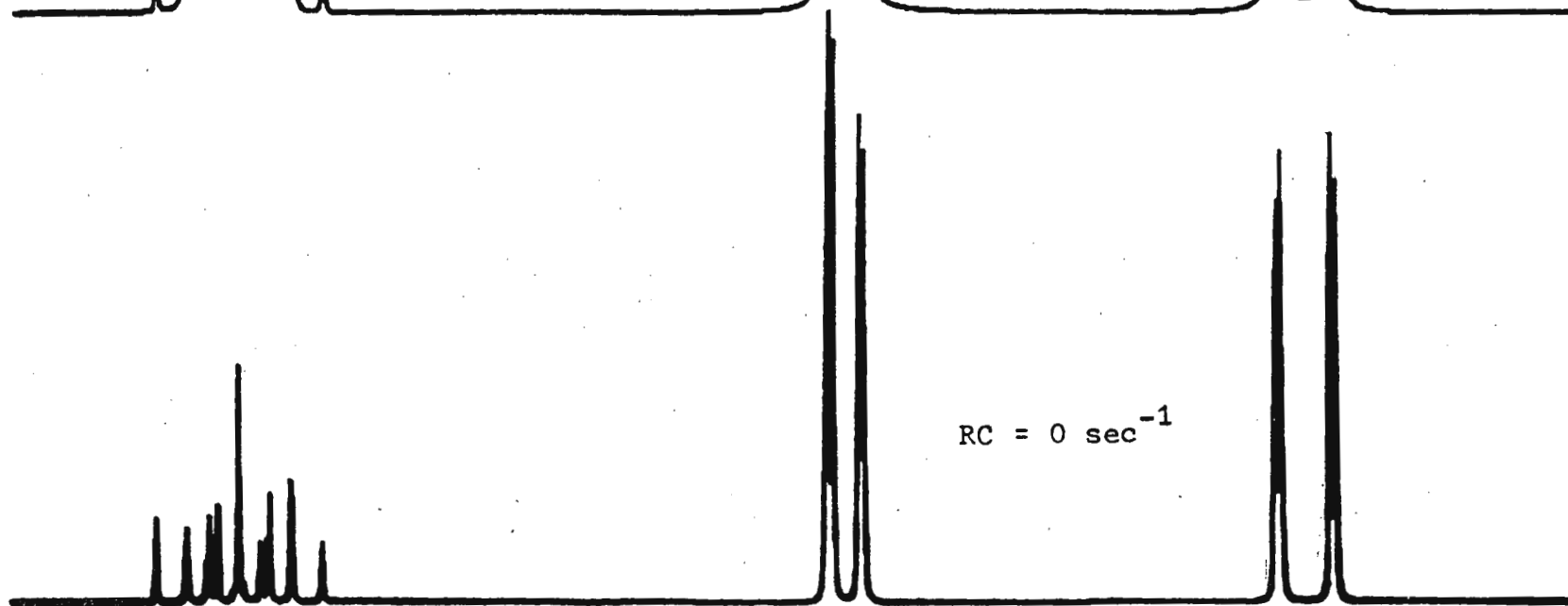
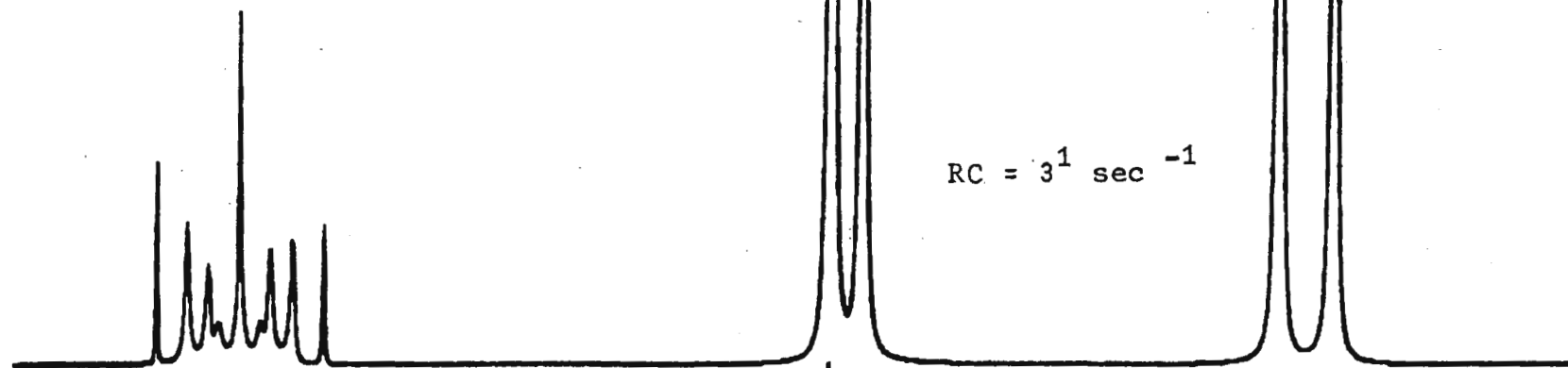
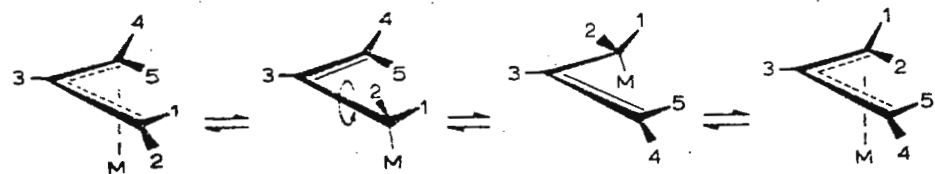
best wishes

E. G. Hoffmann

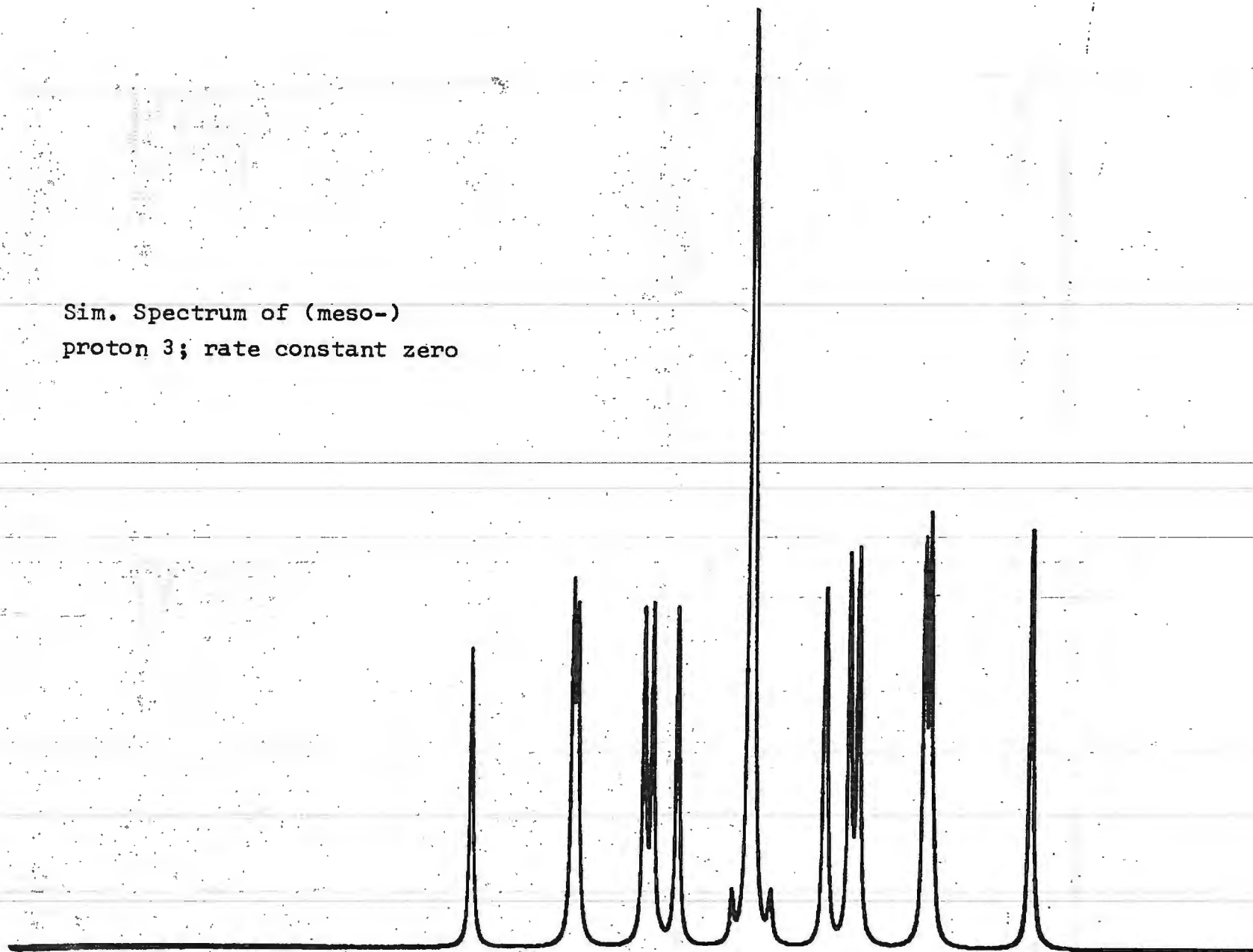
E. G. Hoffmann

\* See: Program description of QCPE 140 p.13; also S. Brownstein, TAMU Newsletters 184, 33, 1973; and several private communications.

ERRATUM (TAMU NMR Letters, 197-47): Chemical shifts for  $C_1$  in the table should read Z 17.1 ppm - E 12.1 ppm.



Sim. Spectrum of (meso-)  
proton 3; rate constant zero



RU DNMRIN

NUMBER OF NUCLEI, CONFIGURATIONS, MUTUAL EXCHANGE,

SETS OF RATE CONST.S

5,3,1,4

NUMBER OF EQUIVALENT SETS 5

NUMBER OF "SYMETRY PAIRS" 0

CHEMICAL SHIFTS 822,690,516,690,822

COUPLING WITH 1 1.5,15.5,0.0

COUPLING WITH 2 9.0,5.0

COUPLING WITH 3 9,15.5

COUPLING WITH 4 1.5

EXCHANGE VECTOR 2 2,1,3,4,5

EXCHANGE VECTOR 3 1,2,3,5,4

RELAXATION TIME 1

RC(1,2) 0

RC(1,2) 3

RC(1,2) 6561

RC(1,2) 19683

RC =  $3^8$  sec<sup>-1</sup>RC =  $3^9$  sec<sup>-1</sup>



UNIVERSITY OF FLORIDA  
GAINESVILLE, 32611

DEPARTMENT OF CHEMISTRY

December 17, 1975

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

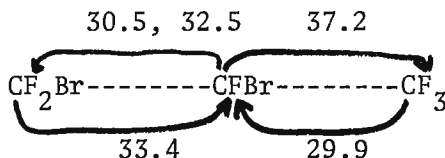
Fluorocarbon  $^{13}\text{C}$  Spectrum

Dear Barry:

We are continuing our investigations of a variety of fluorinated organic molecules, particularly with respect to the carbon-13 spectra, with emphasis on carbon-fluorine coupling constants. Our results are obtained on an XL-100-15 spectrometer and NTC Fourier transform unit with a 36K memory and disk. Recently we have been finding the NTCFT program most convenient and reliable in operation. In addition, pulsed irradiation of fluorine has turned out to be extremely useful for producing well-resolved, coupled spectra of fluorocarbon derivatives. Although the wide range of fluorine chemical shifts makes it difficult to decouple all the nuclei in a molecule, and attempts to do this usually result in broadening or loss of most of the carbon resonances, the available Gyrocode power seems quite adequate to yield a substantial Overhauser effect. Most of our spectra are taken in 5 mm sample tubes because we are generally limited by the amount of material available.

Your readers may be interested in the accompanying spectrum which we obtained recently on  $\text{CF}_2\text{BrCFBrCF}_3$ , a system which illustrates several aspects of the results we have been obtaining. The top section is the portion to lower field and the bottom section is the portion to higher field. The doublets marked A, together with a smaller one at lower field which is not shown, form a quartet for the  $\text{CF}_3$  carbon, and the doublets marked B correspond to the  $\text{CF}_2\text{Br}$  carbon. The patterns marked C form a large doublet for the  $\text{CFBr}$  carbon, with a  $^1J$  of 273 Hz. For the  $\text{CF}_3$  group,  $^1J$  is 287 Hz, and it is particularly interesting that the  $\text{CF}_2\text{Br}$  group has two different  $^1J$  values, of about 312 and 313 Hz, reflecting the influence of molecular asymmetry. The smaller value for the mid-chain carbon is typical, and the  $\text{CF}_3$  value is just what is expected for such a unit with a neighboring carbon having either two halogens or a carbonyl oxygen--it would fall below 275 for a methylene group neighboring and increase above 310 for a sulfur attached.

Each part of the  $\text{CFBr}$  doublet (labeled C) consists of sixteen peaks: the pattern is a quartet from coupling to the  $\text{CF}_3$ , doubled and then doubled again by slightly different coupling constants to the two non-equivalent  $\text{CF}_2\text{Br}$  fluorines. The magnitudes of the two-bond couplings are represented in the following diagram:



Inspection of these numbers shows that replacement in the methyl group of a fluorine by a bromine increases the two-bond coupling of the carbon on which the replacement occurs, but reduces the two-bond coupling of the remaining fluorines to the adjacent carbon.

With respect to chemical shift effects of fluorine and bromine substitution, reference to data in the compilations of Levy and Stothers indicates that the substitution of one of these atoms in a hydrocarbon gives a quite reproducible carbon shift to high frequency by 60 to 20 ppm, respectively. If multi-halogen substitution were additive, the  $\text{CF}_3$  carbon should be about 40 ppm to higher frequency than the  $\text{CF}_2\text{Br}$  carbon, compared to an observed difference of 3 ppm. Further, the  $\text{CF}_2\text{Br}$  is only about 20 ppm to higher frequency than the  $\text{CFBr}$  carbon. This result is consistent with many others we have observed, in that there seems to be a sort of saturation effect--once a shift of 110 to 120 ppm from TMS is reached, further halogenation has little influence. There is perhaps some relation to the results observed on successive substitution of bromines in methane.

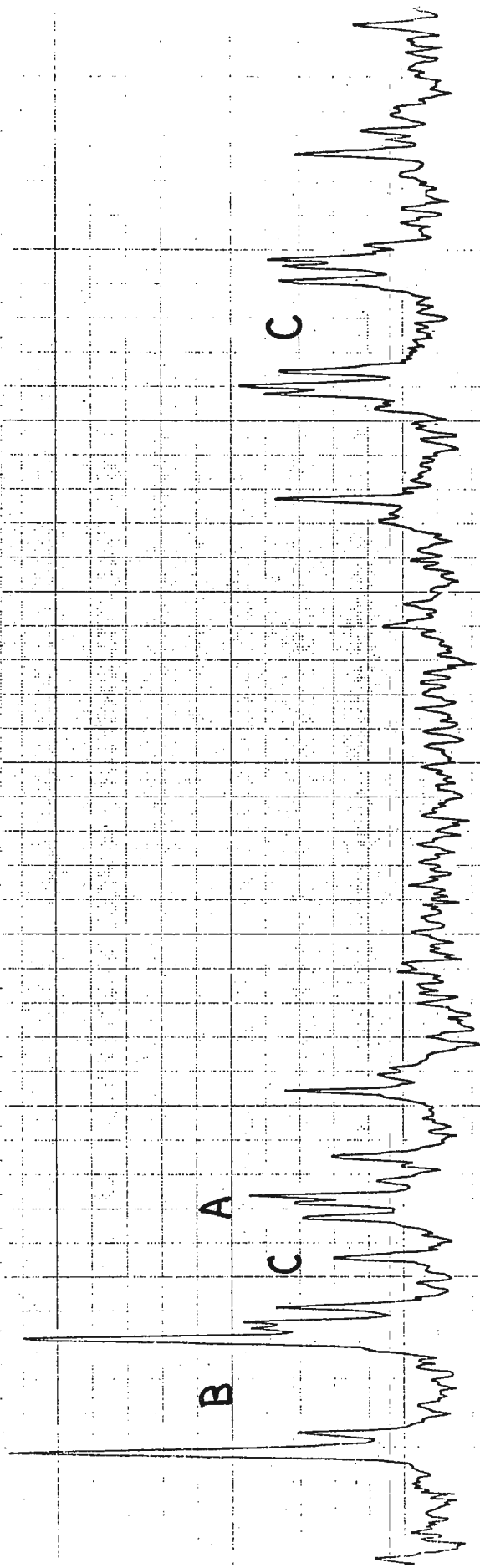
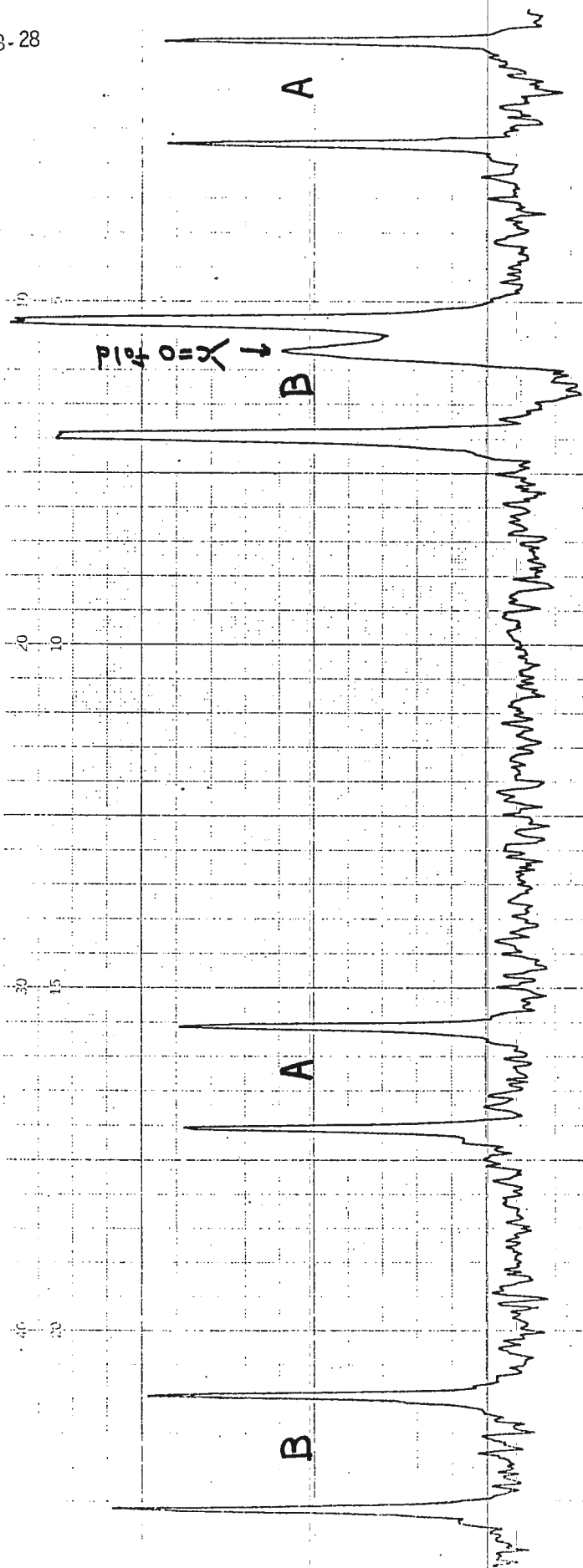
With best wishes for the New Year,

*Wallace*

Wallace S. Brey

*Larry W. Jaques*

Larry W. Jaques



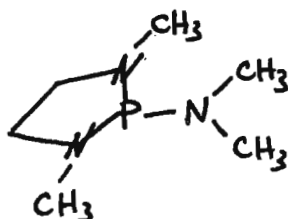
varian /instrument division  
25 route 22/springfield/new jersey 07081  
tel. (201) 379-7610



December 18, 1975

Dear Barry,

We've been continuing our natural abundance  $^{15}\text{N}$  nmr investigations of organophosphorus compounds and have come up with some interesting results. As I reported in my last letter (TAMNMRN 197-46)  $[(\text{CH}_3)_2\text{N}]_3\text{P}$  has a  $^{31}\text{P}$ - $^{15}\text{N}$  coupling of +59.1 Hz. We have since done  $T_1$  and NOE measurements and find  $\sim 80\%$   $\text{NOE}_{\text{max}}$  and a  $^{15}\text{N}$   $T_1$  of  $\sim 100$  sec. Since these are non-protonated nitrogens we should expect a long  $T_1$  but the very large NOE indicates that here the  $T_1$  is dominated by dipolar interactions with the nearby protons. These results aid in the assignment of the heterocycle (courtesy Dorothy Denney, Rutgers):



Without knowledge of the expected NOE and  $T_1$ 's, no reliable assignment can be made, even though one doublet in the  $^{15}\text{N}$  spectrum is about twice as intense as the other. The inverted nature of the signals along with the results for  $[(\text{CH}_3)_2\text{N}]_3\text{P}$  make interpretation within the dipolar mechanism fairly safe since 1) the molecule is larger, 2) the methylene bridge protons should relax the  $^{15}\text{N}$  more efficiently than the freely rotating  $\text{N}-\text{CH}_3$  protons, and 3) the natural linewidths of the ring nitrogens should be larger due to the more efficient dipolar relaxation. Since all these factors are also consistent with the two-fold intensity for the ring nitrogens the assignment can be made in a straight-forward manner: Ring nitrogen -341 ppm ( $\text{CH}_3\text{NO}_2$  ext, negative sign indicates shielded with respect to  $\text{CH}_3\text{NO}_2$ )  $J_{\text{PN}} = (+)51.8$  Hz; exo nitrogen -334 ppm,  $J_{\text{PN}} = (+)24.0$  Hz.

Empirically, one would be tempted to assign the 51.8 Hz coupling to the exo-nitrogen in view of the similarity to the coupling for  $[(\text{CH}_3)_2\text{N}]_3\text{P}$ . This large difference in coupling is intriguing and suggestive that  $^{31}\text{P}$ - $^{15}\text{N}$  couplings may be useful in studying subtle effects in nitrogen-containing organophosphorus compounds.

Sincerely yours,

  
George A. Gray

Senior Applications Chemist



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

NATIONAL HEART AND LUNG INSTITUTE

December 19, 1975

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

Dear Barry,

ROH to ROD Exchange as an Aid in the Interpretation of  $^{13}\text{C}$  Spectra

In the investigation of natural products by  $^{13}\text{C}$  nmr spectra, it is often useful to be able to identify those resonances produced by carbons bearing free alcohols, and thus distinguish them from similar signals associated with ethers, esters or epoxides. It is apparently sufficient to shake the  $\text{CDCl}_3$  solution with  $\text{D}_2\text{O}$  and repeat the spectrum. In eighteen alcohols we have examined, the carbonyl carbons are shifted upfield about 0.1 ppm. The actual ranges of the change in chemical shift:

Primary (6)	-0.13 to -0.15 ppm.
Secondary (8)	-0.09 to -0.17
Tertiary (4)	-0.06 to -0.10.

The changes are small, but as the sample has been otherwise unaltered, the other chemical shifts are reproduced within the digital uncertainty of the computer, routinely about 0.05 ppm. Unless our current examination of more complex examples confuses things, the method will allow a count of free hydroxyl groups in an unknown material without derivatization.

It would be even nicer to identify carbons adjacent to free hydroxyl groups, as an aid in establishing a sequence of atoms within an unknown structure. We have found six methyl groups so situated to be shifted -0.06 to -0.10 ppm, and 10 of 12 methylenes -0.05 to -0.10, but more highly substituted carbons are less affected.

These results were obtained on 1 M solutions, using an XL-100 equipped with a Digilab FT system, which allowed the use of 32K FT's, and determination of the chemical shifts to an accuracy to 0.015 ppm.

Yours very truly,

*Bob*

R. J. Highet



Universität Regensburg

FACHBEREICH CHEMIE

F. Lefèvre and A. Mannschreck

 8400 REGENSBURG, 19.12.75  
 Universitätsstraße 31 — Postfach  
 Telefon (0941) 9431

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

Use of Chiral Auxiliary Compounds  
in the Study of Intramolecular Processes

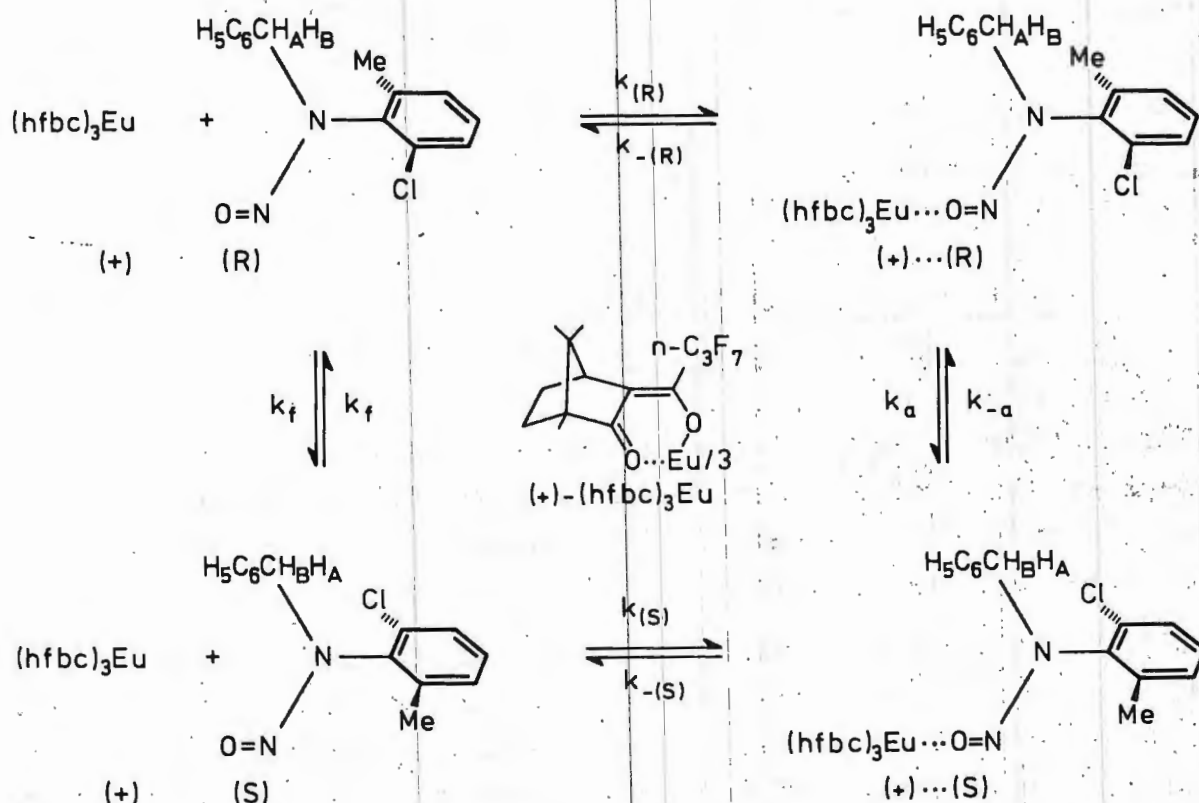
Dear Professor Shapiro,

Optically active auxiliary compounds can be useful for the measurement of rates of intramolecular motions in chiral and prochiral molecules<sup>1)</sup>: the auxiliary compound enables us to distinguish between enantiomers (or between enantiotopic groups).

Concerning the particular case of the nitrosamine given in the figure, the enantiomers (R) and (S) (which have identical  $\delta$ -values) can be interconverted by half-rotation about the N-aryl bond. In the presence of (+)-tris[(heptafluorobutyryl)-camphorato]-europium(III), (+)-Eu(hfbc)<sub>3</sub>, the  $\delta$ -values of (R) and (S) become unequal. Subsequently, the study of temperature-dependent line shapes of suitable <sup>1</sup>H-NMR signals results in the activation parameters of half-rotation. This motion, however, can occur in the free nitrosamine ( $k_f$  in the figure) or in the complexed molecule ( $k_a$  and  $k_{-a}$ ). The problem is: Which of the two processes is rate determining<sup>2)</sup>? The answer to this question should come from the comparison of the activation parameters for the enantiomerization

- A. without an auxiliary compound,
- B. in the presence of the racemic compound (+)-Eu(hfbc)<sub>3</sub>, and
- C. in the presence of the optically active compound (+)-Eu(hfbc)<sub>3</sub>.

Two <sup>1</sup>H-NMR absorptions of our nitrosamine are suitable for line shape kinetics: One AB system for CH<sub>A</sub>H<sub>B</sub> in the absence of an optically active auxiliary compound and one methyl signal split into two singlets by the presence of (+)-Eu(hfbc)<sub>3</sub>. These singlets coalesce when the enantiomerization becomes faster (experiment C); the same is true for the above AB system in the absence of an auxiliary compound or in the presence of (+)-Eu(hfbc)<sub>3</sub> (experiments A and B).



The activation parameters (table) in all three cases agree within our rigorously determined experimental errors<sup>3)</sup>. If one expects the rate of half-rotation for the complexed nitrosamine to differ sufficiently from that for the free one, our results mean that half-rotation in the free nitrosamine ( $k_f$ ) is rate-determining in the presence of  $\text{Eu}(\text{hfbcb})_3$ . The conclusion would be, at least for the system studied, that the use of an auxiliary compound represents a sound kinetic method. It is useful if the molecule of interest does not own a suitable NMR probe in the free state, but does so in a chiral association complex.

Sincerely yours,

*A. Mannschreck*  
A. Mannschreck

F. Lefèvre<sup>4)</sup>

- 1) A.Mannschreck, V. Jonas, and B.Kolb, Angew.Chem. 85, 590, 994 (1973); Angew.Chem.Int.Ed. 12, 583, 909 (1973).
- 2) A similar problem for a completely different system has been dealt with by H.Kessler and M.Molter, Angew.Chem. 85, 1059 (1973), Angew.Chem.Int.Ed. 12, 1011 (1973), and personal communication.
- 3) Slightly negative  $\Delta S^\ddagger$ -values seem to be the rule for N-aryl rotations: W.E.Stewart and T.H.Siddall, III, Chem.Reviews 70, 517 (1970); L.D.Colebrook, S.Icli, and F.H.Hund, Can.J. Chem. 53, 1556 (1975).
- 4) F.Lefèvre, Laboratoire de Chimie Organique Physique, Université de Nantes, F-44037 Nantes, France.

	Experiment*		
	A	B**	C**
$\Delta G^\ddagger_{27}$ [kcal/mol]	16,46 $\pm$ 0.17	16.43 $\pm$ 0.17	16.4 $\pm$ 0.2
$\Delta H^\ddagger_{27}$ [kcal/mol]	14.2 $\pm$ 1.0	13.4 $\pm$ 1.4	13.5 $\pm$ 2.5
$\Delta S^\ddagger_{27}$ [e.u.]	-7.4 $\pm$ 3.5	-10.4 $\pm$ 5.0	-9.5 $\pm$ 9.0

\* All samples contained the same amount of nitrosamine in a mixture of  $C_2Cl_4$ ,  $C_4Cl_6$ , and cyclosilane- $d_{18}$  ( $C_9H_6D_{18}Si_3$ ).

\*\*The molar ratio of  $Eu(hfbc)_3$  and nitrosamine was 0.24.



National Research Council  
Canada

Conseil national de recherches  
Canada

Division of Chemistry

Division de chimie

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

File Référence

December 19, 1975

Methylene non-equivalence in complexed ethers.

Dear Barry:

Now that our mail strike is over I have received your blue letter and hasten to reply. Please be kind enough to send the newsletter copies from October forward which were probably stopped by a mail embargo to this embattled nation.

Yet another example of methylene proton non-equivalence will be presented since this is often a useful tool, or the only tool, for determining what is happening in another part of the molecule. Non-equivalent methylene protons on a carbon bonded to an atom bonded to three different groups are commonplace. There are fewer examples where the atom is bonded to two different groups, and only two examples, thus far, where the atom is bonded to only one group. The latter case is exemplified by the adduct borane-diethyl sulfide where a tetrahedral environment about sulfur is maintained by two ethyl groups, a lone pair of electrons and the ligand  $\text{BH}_3(1)$ .

In the complex of benzyl ethyl ether with  $\text{BF}_3$  the methylene protons are non-equivalent at low temperature but become equivalent as the temperature is raised. From this one can calculate the barrier to inversion about oxygen. To my knowledge this is the first time such a number has been experimentally accessible. For the complex mentioned we find the barrier to be  $4.1 \pm 0.3$  kcal/mole. Some results are shown on the enclosed figure.

Best wishes.

Yours sincerely,

SB/cf

Syd Brownstein

208-36 UNIVERSITÄT TüBINGEN  
PHYSIKALISCHES INSTITUT  
Prof. Dr. O. Lutz  
Dr. A. Nolle

D-7400 TüBINGEN 1, den 23.12. 1975  
Morgenstelle  
Telefon (0 70 71) 29 67 14

Physikalisches Institut, D-7400 Tübingen 1, Morgenstelle

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

U.S.A.

Ihr Zeichen

Unser Zeichen

Ihre Nachricht vom

$^{33}\text{S}$  - NMR with our new multipurpose spectrometer

In the last months we have tested our new spectrometer and have done some systematic investigations on  $^{53}\text{Cr}$  ( $^{53}\text{Cr}$  Fourier Transform Nuclear Magnetic Resonance Studies, B.W. Epperlein, H. Krüger, O. Lutz and A. Nolle and A. Mayr, Z.Naturforsch. 30a, 1237 (1975)).

This spectrometer was built together by Bruker-Physik from their commercial parts available in their high resolution and pulse spectrometers. It was planned as a multipurpose multinuclei FT-spectrometer. It consists of a high resolution 15" magnet, with external ( $^1\text{H}$ ,  $^{19}\text{F}$ ) and internal ( $^2\text{H}$ ) stabilization, a 4 - 100 MHz SXP-pulse-spectrometer, a Bruker BNC 12 data unit with 20 k and a further separate ADC unit with a conversion rate up to 5 MHz.

High-resolution and/or high power experiments can be done in liquids and solids and also fast FID can be observed. Special care was taken for detecting the very often weak signals of the so called "other nuclei".

As an example, the  $^{33}\text{S}$  spectrum of a mixture of a 2.0 molal  $\text{Cs}_2\text{SO}_4$  and a 2.0 molal  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  solution is given on page 2.

Typical experimental parameters are given.

Further work in this field is running.

Sincerely

O. Lutz

O. Lutz

A. Nolle

A. Nolle

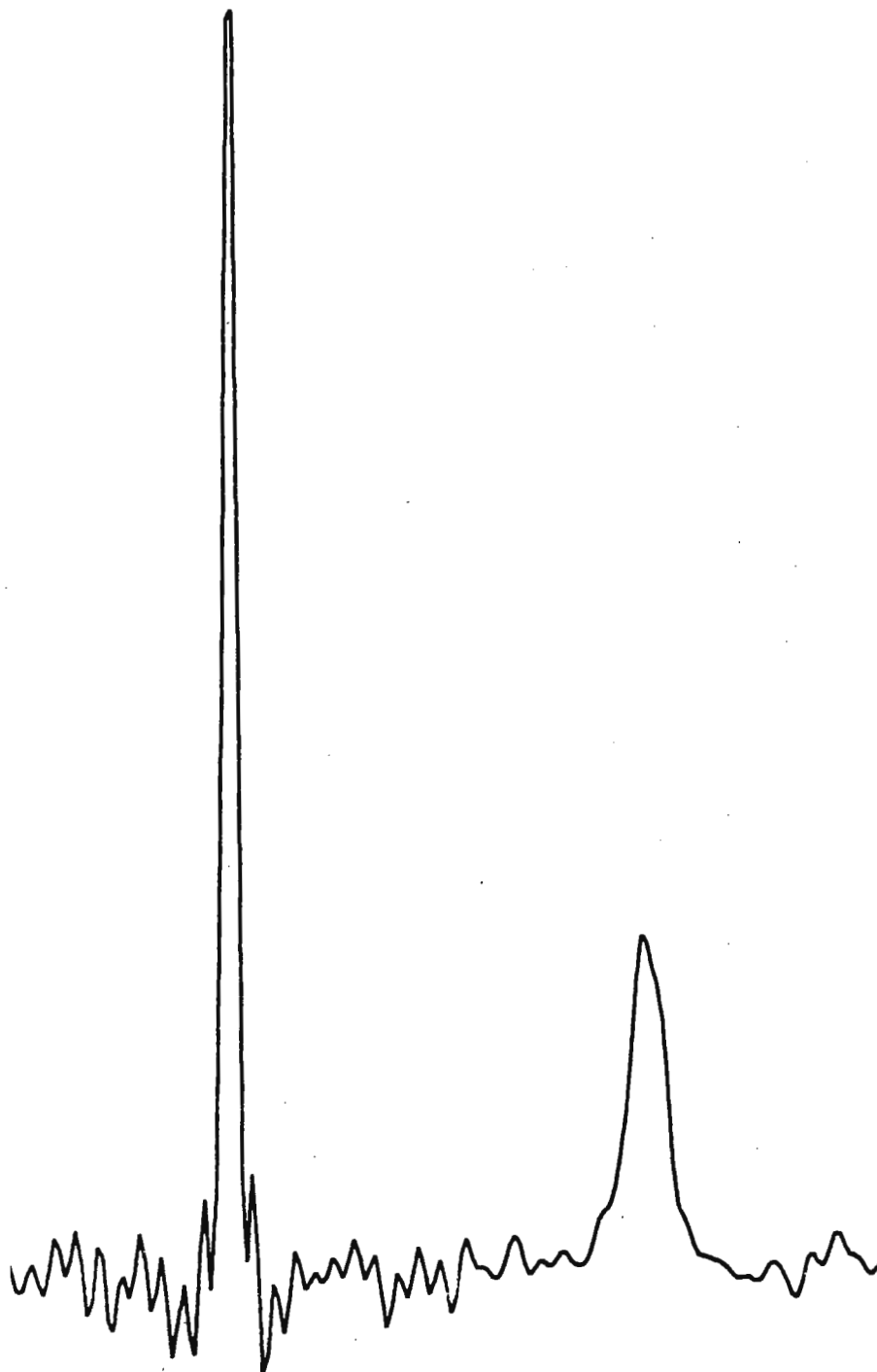
SIMULATION

-65°C

25°C

8.0 6.0 4.0 2.0 1.0





$^{33}\text{S}$ -spectrum of a mixture of a 2.0 molal  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  and a 2.0 molal  $\text{Cs}_2\text{SO}_4$ -solution measured in a 10 mm rotating cylindrical sample (about 1,5 ml). The frequency increases to the right. The narrow line is the  $^{33}\text{S}$  in the sulfate ion, the broader line seems to be the central  $^{33}\text{S}$  in the thiosulfate ion. The shift is about 33.3 ppm.

Experimental parameters: Excitation frequency: 6.905 300 MHz, magnetic field: 2,114 T, pulse repetition rate: 10 Hz, number of pulses: 24 000, total acquisition time: 40 min, experimental spectrum width: 6 kHz, plotted spectrum width: 480 Hz.



SIMON FRASER UNIVERSITY, BURNABY, B.C., CANADA, V5A 1S6  
DEPARTMENT OF CHEMISTRY, 291-3345

22nd December 1975

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

TITLE: Phytanic Acid and Membrane Permeability. A  $^{31}\text{P}$  LIS Study.

Dear Barry,

A number of contributions to TAMU have been concerned with the lanthanide induced shifts (LIS) of  $^1\text{H}$  and  $^{31}\text{P}$  NMR resonance signals of phospholipid vesicles.<sup>1</sup> The addition of  $\text{Pr}^{3+}$  results in a downfield shift for the outside phosphorus nuclei, while the phosphorus nuclei on the inside of the closed vesicles remain unaffected. Thus, the permeability of the model membrane system to  $\text{Pr}^{3+}$  can be studied by observing the rate of disappearance of the "inside" phosphorus resonance.

We have observed the effect of intercalated phytanic acid (3,7,11,15-tetramethylhexadecanoic acid) on the permeability of egg lecithin bilayers using LIS  $^{31}\text{P}$  NMR. It was found that the incorporation of phytanic acid increases the permeability of phospholipid bilayers by approximately 3000 times. This is due to the disruption of normal lipid packing by the branched phytyl chain.

In the accompanying figure, the upper trace, A, represents the spectrum of lecithin vesicles without incorporated phytanic acid, immediately after the addition of 5 mM  $\text{Pr}^{3+}$ . Trace B is the same sample after 937 minutes. In contrast, trace C represents the spectrum of lecithin vesicles with the incorporation of 25 mole % phytanic acid, only 15 minutes after treatment with 5 mM shift reagent. Subsequent addition of sufficient EDTA to complex with the outside  $\text{Pr}^{3+}$  again resulted



in two peaks, the upfield resonance now due to the outside phosphorus nuclei.

A complete discussion of the permeability effects of intercalated phytol compounds will be reported shortly.<sup>2</sup>

It should be noted that the accumulation of branched chain fatty acids has been associated with a number of disorders including methylmalonic aciduria<sup>3</sup> and Refsum's disease.<sup>4</sup>

Sincerely,



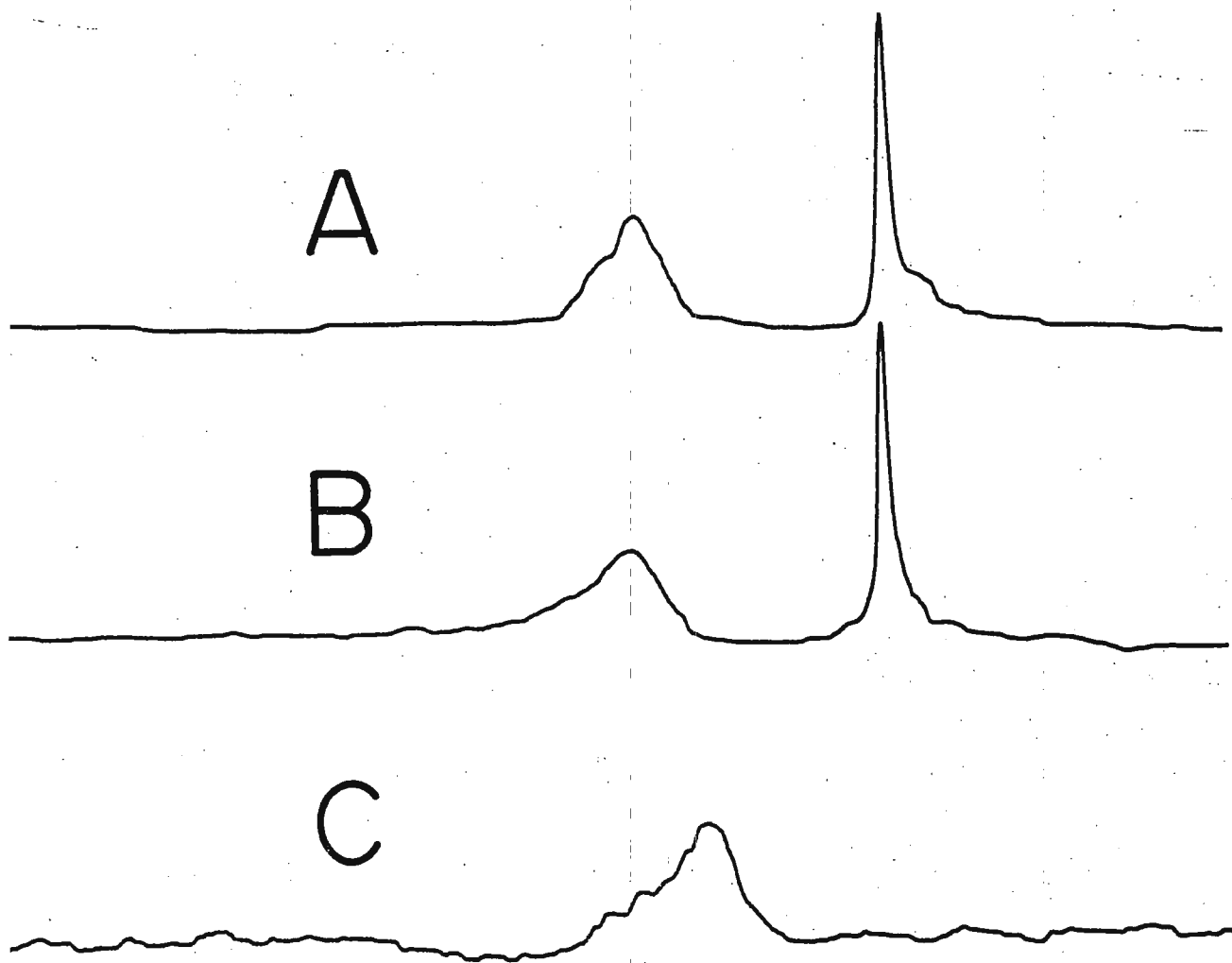
Bruce Forrest



R.J. Cushley  
Associate Professor

RJC:SB

1. TAMU NMR newsletter, 156, 1 (1971); 166, 24 (1972); 192, 43 (1974).
2. R.J. Cushley and B.J. Forrest, Biochem. Biophys. Res. Commun., submitted.
3. G.J. Cardinale, T.J. Carty, and R.H. Abeles, J. Biol. Chem., 245, 3771 (1970).
4. M.C. MacBrinn, and J.S. O'Brien, J. Lipid Res., 9, 552 (1968).





Zug, December 23, 1975

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

### Spin-Rotation Relaxation of a Quadrupolar Nucleus

Dear Barry,

When "scanning" through the periodic table using our Gyrocode-modified XL-100 we detected an unusually narrow line for the quadrupolar beryllium-9 in aqueous  $\text{Be}(\text{NO}_3)_2$  which prompted us to look into the relaxation behaviour of this interesting nucleus.  $^9\text{Be}$  has a spin of  $3/2$ , 100% abundance and resonates at 14.06 MHz. Although, in principle, systems of spherical or cubic symmetry should have zero electric field gradient and hence zero quadrupole coupling constant, it is well known that the symmetry is always perturbed<sup>1</sup>. Thus practically all of the group I, II and III quadrupolar nuclei in the respective solvated ions studied so far were found to relax exclusively by quadrupolar interaction (except for  $^7\text{Li}$ , where a dipolar contribution could be established<sup>2</sup>). In the  $\text{Be}(\text{H}_2\text{O})_4^{2+}$  ion the quadrupole coupling constant appears to be sufficiently small to render quadrupole relaxation relatively inefficient, therefore increasing the probability for a substantial participation of other mechanisms.

At  $28^\circ\text{C}$  a  $T_1$  of 7.7sec was measured in a 1-M solution of  $\text{Be}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ . The results of temperature-dependent  $T_1$  measurements are displayed in Fig.1 where  $\ln T_1$  is plotted against inverse absolute temperature. The temperature dependence is characteristic of at least two competing mechanisms governed by a rotational and an angular momentum correlation time, resp. It is evident that above  $50^\circ\text{C}$  the mechanism is almost exclusively spin-rotation. Proton irradiation afforded an NOE  $\eta = -0.50$  at  $28^\circ\text{C}$  showing that about 15% of the relaxation rate is dipolar-induced. Naturally as motion increases this fraction falls off. At  $80^\circ\text{C}$  e.g.  $\eta = -0.08$  is measured.

The upper curve in Fig.1 represents the relaxation time  $T_1^{Q+SR}$  due to quadrupolar and spin-rotation contributions obtained from temperature-dependent NOE measurements. From the  $T_1$  maximum observed at  $35^\circ\text{C}$   $T_1^Q = 18.8$  sec is derived. This large value of  $T_1^Q$  lets one suspect a quadrupole coupling constant which is sufficiently small to be measurable on a high-resolution spectrometer. Fig.2 shows the  $^9\text{Be}$  spectrum recorded from solid  $\text{Be}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  exhibiting the characteristic first-order quadrupole perturbation pattern expected for an  $I=3/2$  nucleus in an imperfect cubic crystal. The

spectrum yields for the quadrupole coupling constant  $e^2qQ/h=9.8\text{kHz}$ , which is considerably below the value found in beryllium oxide ( $43.2\text{kHz}$ ). Inserting this value into the general equation for quadrupolar relaxation and assuming the motional narrowing conditions to apply one finds for the reorientational correlation time  $\tau_c=1.40\times 10^{-10}\text{sec}$ . This is a rather large value if compared with that of  $\text{H}_2\text{O}$  ( $2.7\times 10^{-12}\text{sec}$  at  $25^\circ\text{C}$  in pure water) suggesting that the ion is rather efficiently locked into the solvent matrix. The value determined for  $\tau_c$  should be treated with care, however, since it is somewhat doubtful whether (a) the quadrupole coupling constant in the solid and in the liquid phase is the same; (b) the relaxation can be described by a rotational correlation time alone and, (c) the water molecules in the first hydration sphere are kinetically stable.

The linearity of  $\ln T_1$  with  $1/T$  in the spin-rotation dominated temperature region indicates the small-step diffusion limit to be applicable. Hence we should be able to derive the spin-rotation constant provided a reasonable estimate can be made for the momentum of inertia.

Further relaxation work on this system as well as on other nuclei with weak quadrupole moments ( $^6\text{Li}$ ,  $^7\text{Li}$ ,  $^{133}\text{Cs}$  etc.) is in progress.

V A R I A N A G  
NMR Applications Laboratory

*Felix W. Wehrli*

F.W. Wehrli

- (1) S. e.g. theories developed by Hertz:  
H.G. Hertz, Berichte der Bunsengesellschaft 77, 531(1973) and subsequent papers.
- (2) D.E. Woessner, B.S. Snowden, Jr. A.G. Ostroff, J.Chem.Phys. 49, 371(1968)
- (3) G.J. Troup, Phys. Let. 2,9(1962)



Fig. 1

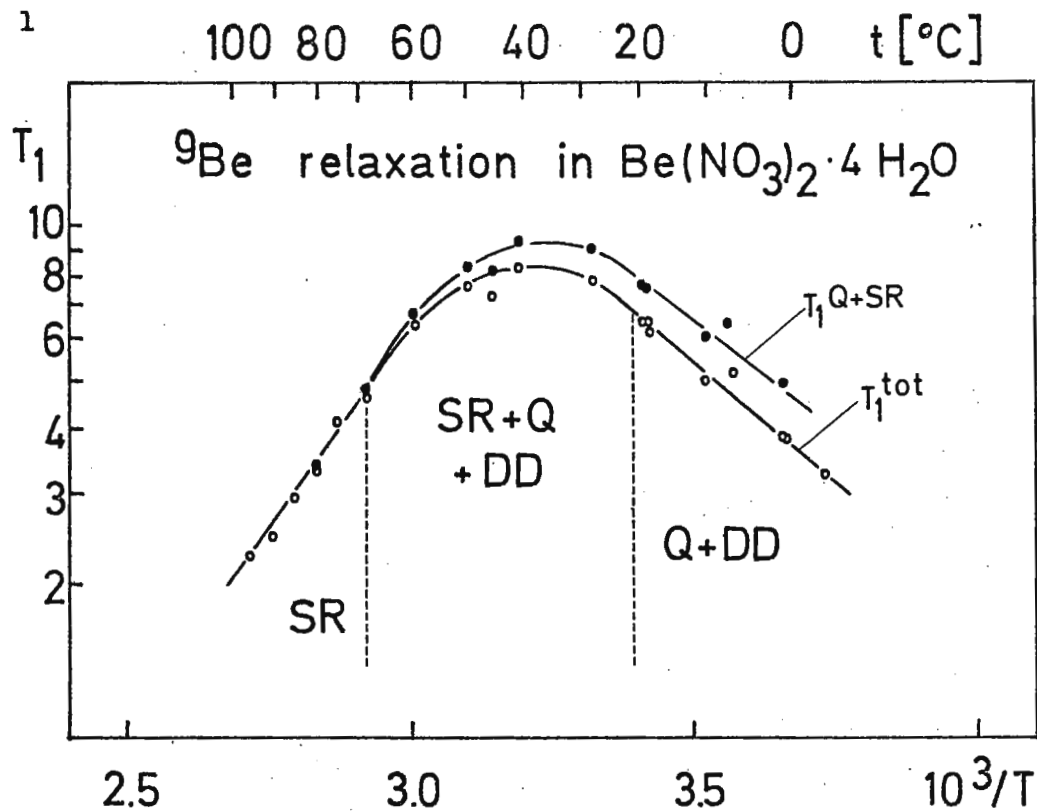
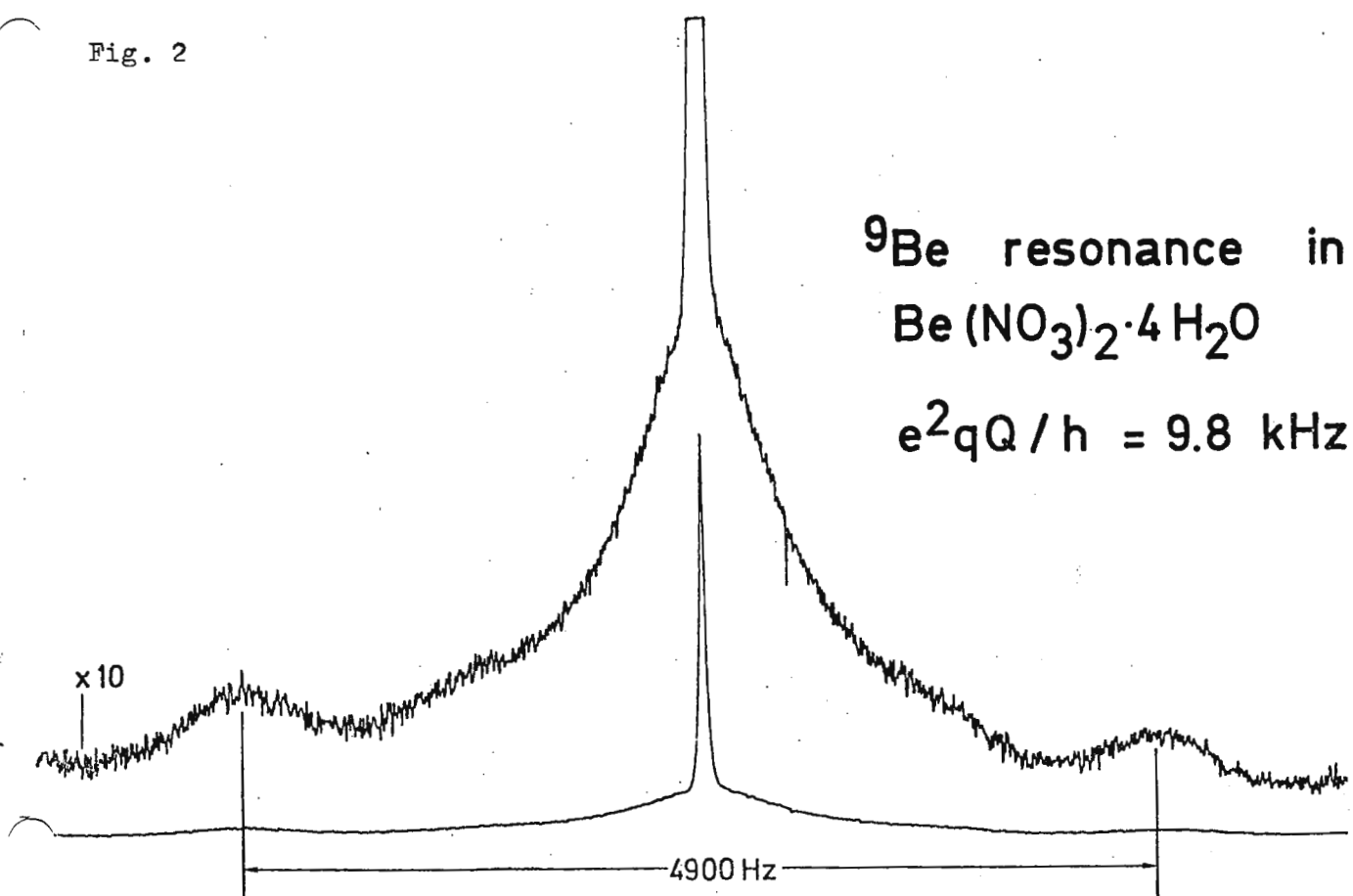


Fig. 2



TELEPHONE  
345 1844

TELEGRAMS  
UNIMELB PARKVILLE



## University of Melbourne

Department of Organic Chemistry

Parkville, Victoria 3052

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

Christmas Eve 1975

Angular Dependence of  $^1J_{C\alpha H}$  in Carbocations.  
A New Criterion for Interpreting NMR Spectra  
of Carbocations.

Dear Dr. Shapiro,

We have been studying the effects of positive charge on the one bond CH coupling constants of adjacent groups ( $J_{C\alpha H}$ ) in a range of alkyl carbocations. These cations were generated quantitatively in super acids at relatively high concentrations (~M) using syringe techniques, and their proton coupled carbon spectra obtained using the normal gated decoupling procedure<sup>1,2</sup>.

It is usually accepted that  $J_{CH}$  increases with the electronegativity of a substituent. When this substituent is a cationic carbon,  $J$  is expected to increase significantly. Measurement of the differences between  $J_{C\alpha H}$  in the carbocations and those in the corresponding ketones  $J_{C\alpha H}$  ( $\Delta J$ ) for static, tertiary cyclopropylcarbinyl, 2-norbornyl and 3-nortricyclyl cations, reveals an increase of ~22Hz for the adjacent methine  $CH^1$ .

However,  $\Delta J$  for methyl groups is only 6Hz and for methylene groups, e.g. in 2-methylnorbornyl and methylcyclopentyl cations, it is zero. (The assignments of the  $\alpha$ -methylene carbons were checked by deuterium labelling in both cases.) The reason for this is that the normal inductive enhancement of  $J$  is opposed by a hyperconjugative interaction between the CH bond and the vacant p-orbital which decreases  $J_{C\alpha H}$  by decreasing the CH bond order, according to equation (1).

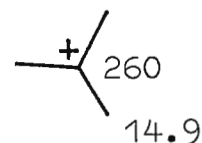
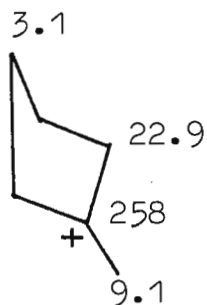
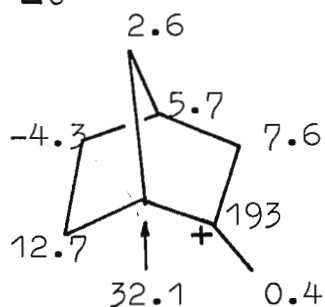
$$\Delta J = 22.5 - 33.1 \cos^2 \theta \quad - - - - - (1)$$

In the case of the above methylene carbons,  $\theta$  is  $30^\circ$  and the hyperconjugative term completely nullifies the inductive enhancement (22.5Hz). In the case of the methine CH in the equilibrating 1,2-dimethylcyclopentyl and bicyclo [3.3.0] octyl cations,  $\Delta J$  is both large and negative as expected for  $\theta = 0$  (although larger and more negative than predicted by (1) which was derived for static ions).

The  $\Delta J$  equation provides an additional method for the assignment of carbon shifts. For example,  $J_{CH_3}$  for the 2-methylnorbornyl cation has been reported as 151 Hz<sup>3</sup>. A re-examination of this ion showed that the original assignments for  $CH_3$  and  $C_4$  should be reversed and that  $J_{CH_3}$  was completely normal at 132 Hz.<sup>4</sup>

A consequence of the corrected assignment for this methyl carbon is that when its shift (827.9) is compared with those in the precursor alcohols (average of exo and endo) this carbon is shown to experience no deshielding upon ion formation, whereas in *t*-butyl and methylcyclopentyl, the methyl carbons are deshielded by 14.9 and 9.1 ppm respectively.

$\Delta\delta$



One cannot therefore assume that carbons adjacent to a cationic carbon will be substantially deshielded and to a greater extent than those further removed. Assignments should therefore be confirmed by other means, for example, by use of equation (1).

We have also used this equation to determine the conformation in acyclic cations, for example, the *t*-amyl cation<sup>4</sup>.

With best wishes for the New Year,

Yours sincerely,

*D.P. Kelly*

D.P. Kelly

1. D.P. Kelly and H.C. Brown, J. Am. Chem. Soc., 97, 3897 (1975).
2. D.P. Kelly and H.C. Brown, unpublished data.
3. G.A. Olah and G. Liang, J. Am. Chem. Soc., 96, 195 (1974).
4. D.P. Kelly, G.R. Underwood and P.F. Barron, in press.

PROFESSOR DR. R. KOSFELD

Abt. f. Phys. Chemie  
der Kunststoffe - RWTH Aachen.

D-51 Aachen, den 10. Dez. 1975  
Templergraben 59

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

Dear Professor Shapiro,

the well-known programs for analyzing high-resolution NMR-spectra need so much storage that they can only run at a computer center. The computer center of the RWTH Aachen is so much engaged that these programs are computed after a turn around time of 2 - 3 days. And normally it is not done with one run.

Therefore we developed a new program, the program ASREY, which runs on the processing computer of the "Abteilung für Phys. Chemie der Kunststoffe". This processing computer possesses a memory size of 8,400 words à 32 bits and a disc with 2,4 Mbyte.

The program is written in BASIC to make the program compatible for other processing computers and also of course for computer centers. It is built in OVERLAY structure. The first two segments calculate constant values, which are needed in the further calculations, and the dimensions of the following segments. By this the memory requirement of the program can be fitted to the problem.

Within the memory size of 8,400 words it is possible to calculate 7 magnetically not equivalent spins. The program considers also magnetically equivalent spins. The first two segments get the quantity of the spins which can be combined to magnetically equivalent groups. If there is no magnetic equivalence each proton is a group of quantity 1. Then these segments calculate all off-diagonal elements of the Hamiltonian in a shortened form:

$$H_{ij}^* = 1/2 \left( I_i (I_i + 1) - m_i (m_i - 1) \right)^{1/2} \left( I_j (I_j + 1) - m_j (m_j - 1) \right)^{1/2} (1)$$

In the iteration run the next segment gets the constants of the spectrum  $\nu_i$  and  $J_{ij}$  and calculates the true off-diagonal elements by

$$H_{ij} = J_{ij} \cdot H_{ij}^*$$

During the iteration  $\nu_i$  and  $J_{ij}$  are changed. The previous programs calculate the values of (1) in each step completely new. The diagonalization of the Hamiltonian is done by a modified "J a c o b i"-procedure. The search for the biggest off-diagonal element of the Hamiltonian was made so fast, that within the boundaries of the accuracy of the processing computer, which is  $10^{-6}$ , the time of calculation of the "Jacobi"-procedure was shorter than the time of the "Housholder-AR"-procedure.

Then we introduced a "refreshing" procedure which improves the rounding off which happens by the shorter length of the words of our processing computer.

At last in the "least square" improvement of the spectral parameters the previous calculation of  $H_{ij}^*$  shows again a big advantage.

When derivating the "Eigenwert" according to the spin-spin-coupling constants  $J_{ij}$

$$\frac{\partial \lambda_m}{\partial J_{ij}} = \left( \frac{\partial A}{\partial J_{ij}} \right)_{mm} = \left( T' \frac{\partial H}{\partial J_{ij}} T \right)_{mm} \quad (3)$$

it is very useful that

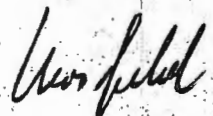
$$\frac{\partial H_{ij}}{\partial J_{ij}} = H_{ij}^* \quad (4)$$

has already been computed.

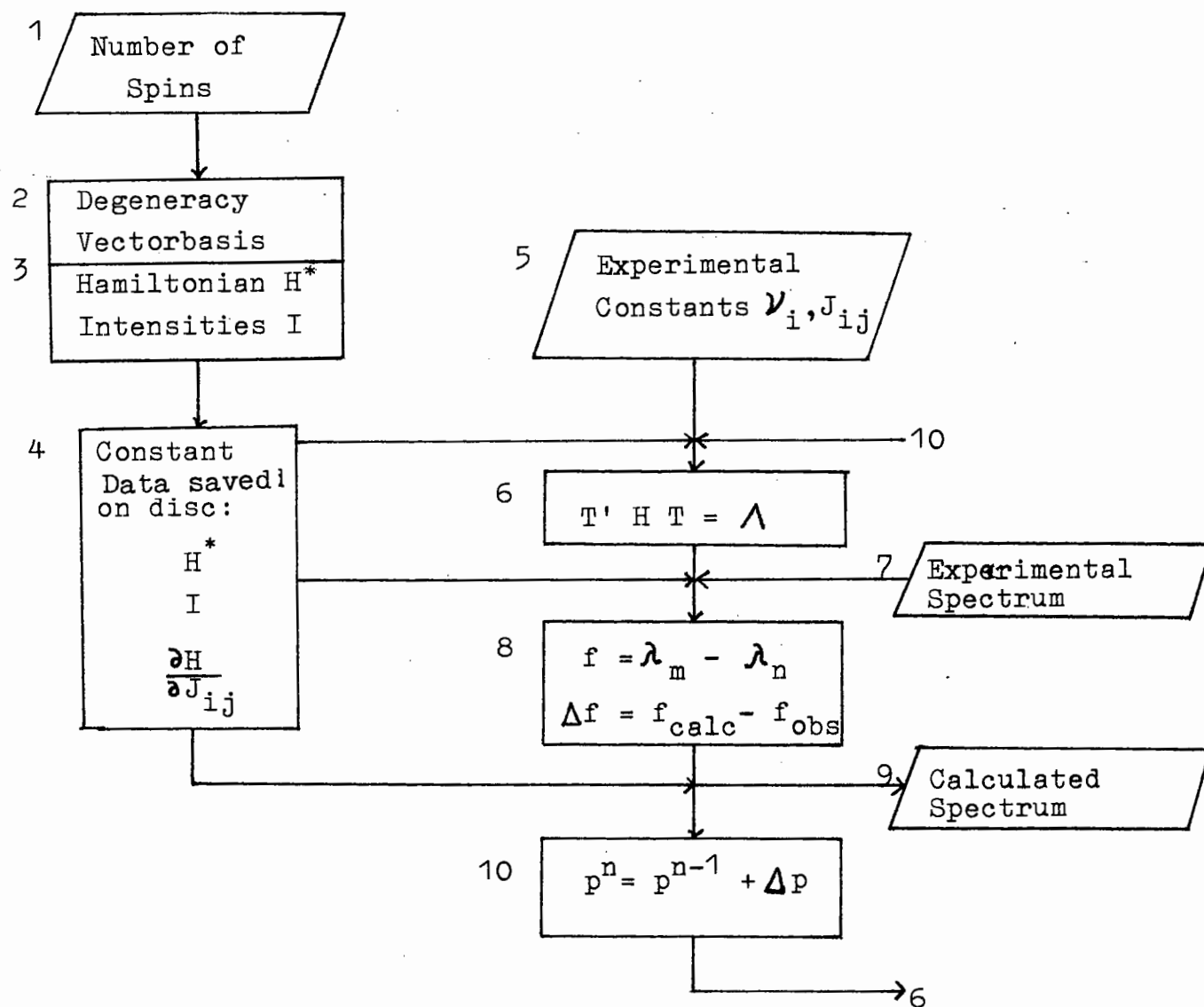
This and some more ideas made the program so small and so fast that the total spectrum is computed within minutes. As the processing computer is available all the time you have no troubles with a computer center any longer.

Yours sincerely

  
(Manfred Schrey)

  
(Robert Kosfeld)





Flow diagram of the program ASREY

# University of Illinois at Urbana-Champaign

School of Chemical Sciences  
Department of Chemistry  
Urbana, Illinois 61801

December 30, 1975

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

TITLE: Proton Tunneling, Photosynthesis, and Postdoctoral Position Available

Dear Barry,

It's been so long since I've contributed to the Newsletter that I feel compelled to make up for lost time. Perhaps I should sign my letter "Mark Twain"! Be that as it may, there are two lines of research here at Illinois where the results may be of particular interest to your readers.

The first of these<sup>1</sup> started out as a study of the proton spin-lattice relaxation in solid, polycrystalline trimethylacetic (pivalic) acid (TMAA), which has a high-temperature plastic phase (fcc) that makes a phase transition at 6.9°C to a brittle phase. In order to identify any complications by the acid proton, the deuterated molecule  $(\text{CH}_3)_3\text{CCO}_2\text{D}$  (d-TMAA) was prepared and the  $T_1$  and  $T_{1\rho}$  for it were compared with those for the ordinary TMAA. The results obtained for  $T_{1\rho}$  in the vicinity of the phase transition are given in Fig. 1.

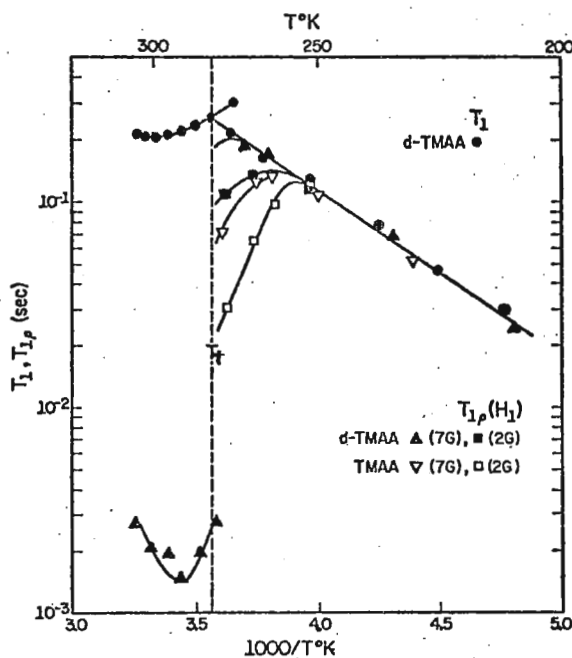


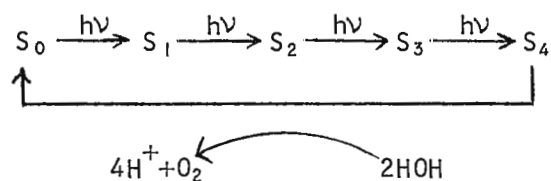
Fig. 1. The temperature dependence of the proton  $T_{1\rho}$  (at 25.3 MHz) for  $(\text{CH}_3)_3\text{CCOOD}$  (d-TMAA) and  $(\text{CH}_3)_3\text{CCOOD}$  (TMAA) measured in the vicinity of the phase transition with two different rf fields.

At lower temperatures (not shown) there are  $T_1$  and  $T_{1\rho}$  minima produced by methyl group and *t*-butyl group rotation. Therefore, the minimum in  $T_1$  (upper left of Fig. 1) is assigned to overall molecular tumbling ( $\omega_0\tau_t \sim 1$ ) while that below it in the figure is assigned to self-diffusion ( $\omega_1\tau_d \sim 1$ ).

It is not uncommon for a new type of molecular motion to change the temperature dependence of the relaxation rate as a transition is approached from lower temperatures. Therefore, it is not surprising to find as shown in Fig. 1 that  $T_{1\rho}$  begins to drop visibly below  $T_1$  as the transition temperature is approached, starting nearly  $30^\circ$  below  $T_t$ . The extent of the decrease is greatest for the smallest  $H_1$ , as predicted, being more than an order of magnitude for an  $H_1$  of 2 G near  $T_t$ .

But what is unexpected is the large "isotopic anomaly"; the decrease is threefold larger for the compound with acid protons (TMAA) than for the deuterated form (d-TMAA). Insofar as we have so far determined, this isotopic difference is real and not an artifact. If it is indeed real, a possible explanation is that the differences in  $T_{1\rho}$  stem from the greater ability of the proton to tunnel quantum mechanically from one hydrogen bond to another during the molecular tumbling process, which could enable the tumbling to proceed more rapidly in TMAA than in d-TMAA.

The second line of research<sup>2,3</sup> deals with the use of proton relaxation rates in aqueous suspensions of chloroplasts to study the nature of the charge accumulating states that lead to oxygen evolution. When the suspensions are exposed to a series of microsecond light flashes, the yield of oxygen after the *n*th flash shows a damped oscillatory pattern, with maxima after 3rd, 7th, 11th, etc., flashes. Such results have been interpreted<sup>4</sup> in terms of a five-step model in which some chemical intermediate accumulates up to four oxidizing equivalents upon successive photoactivation of the oxygen evolving centers:



Here,  $S$  indicates the oxidation state of the intermediate;  $S_4$  represents the most oxidized state.

It has been postulated that in the dark adapted system, only the  $S_0$  and  $S_1$  states are populated, in the ratio of 1:3. Each light flash causes a synchronous progression to the next state, until the  $S_4$  state is formed, which reacts immediately with two water molecules to produce oxygen and regenerate the original  $S_0$  state. This model is consistent with the oxygen evolution, the damping of its oscillation being attributed to "double hits" and "misses" that tend to equalize the populations of the five states. The identity of the charge accumulating center and the mechanism involved are not known in any detail, although they are thought to involve manganese.

In an effort to learn more about the nature of the charge accumulating states, we have performed similar experiments,<sup>3</sup> using a Carr-Purcell train of echoes to measure the proton  $T_2$  of the aqueous medium after the  $n$ th flash. A typical set of results is given in Fig. 2. The oscillatory pattern in  $1/T_2$  shows some striking similarities to the oxygen evolution, but there are some significant differences. Although maxima occur in  $1/T_2$  after the same light flashes as the maxima in oxygen evolution (3rd, 7th, etc.), the minima in  $1/T_2$  are after the 4th, 8th, ... flashes rather than the 6th, 10th, ... for oxygen. Furthermore, the first "cycle" of four relaxation rates in Fig. 2 ( $n = 0, 1, 2, 3$ ) differs greatly from the next three "sawtooths".

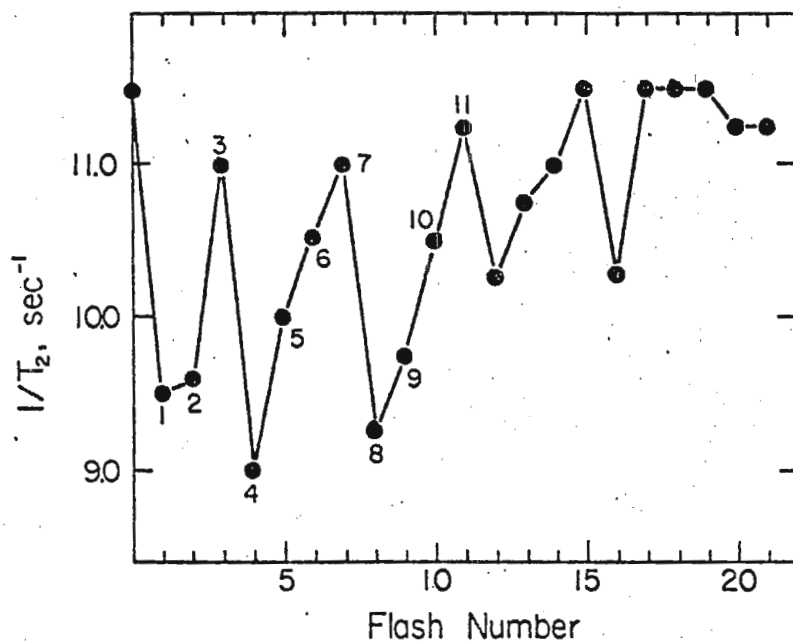


Fig. 2. The proton transverse relaxation rate ( $1/T_2$ ) measured at 25.3 MHz as a function of the flash number in an aqueous suspension of chloroplasts from spinach. Measurements were made on the same sample at room temperature, with 7 minutes dark time between each measurement.

The effects of Mn on water proton relaxation in solution are known to be substantial and very sensitive to oxidation state, so the results tend to confirm its involvement in the charge accumulation process. Also, it's apparent that the model based upon oxygen evolution is oversimplified;  $1/T_2$  for the dark-adapted system ( $n = 0$ ,  $S_0$  and  $S_1$  populated) differs greatly from that after 4 or 8 light flashes which should restore the system to its initial state (except for "misses" and "double hits").


\* \* \* \*

Further work is in progress on these problems. In fact, the third and final point is that I'm interested in appointing a postdoctoral or two who would like to tackle either of these problems or, for that matter, almost any other aspect of the magnetic resonance domain for which we have facilities.

The University of Illinois is an Affirmative Action-Equal Opportunity Employer and encourages applications from members of minority groups and women.

In view of the threefold length of the above I hope you'll count this as a paid-up subscription for at least two periods, if not three. With best personal regards,

Sincerely yours,

  
H. S. Gutowsky  
Professor of Chemistry

HSG:nw

- <sup>1</sup> S. Albert, H. S. Gutowsky, J. A. Ripmeester, submitted to J. Chem. Phys.
- <sup>2</sup> T. Wydrzynski, N. Zumbulyadis, P. G. Schmidt, and Govindjee, Biochim. Biophys. Acta, 408, 349 (1975).
- <sup>3</sup> T. Wydrzynski, N. Zumbulyadis, P. G. Schmidt, H. S. Gutowsky, and Govindjee, Proc. Natl. Acad. Sci., in press.
- <sup>4</sup> P. Joliot and B. Kok, Bioenergetics of Photosynthesis (Academic Press, New York, 1975), pp. 387-412.

# BRUKER-PHYSIK AG KARLSRUHE

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Prof. Barry L. Shapiro  
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Datum

10.12.1975

Dear Professor Shapiro,

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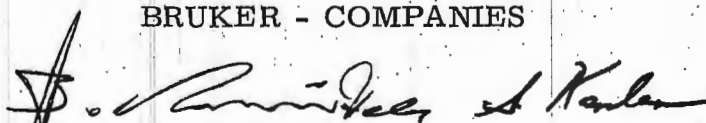
Dr. Donald Ware  
Bruker Instruments, Inc.  
Manning Park  
Billerica, Mass. 01821

or

Dr. Sam Kaplan, presently at  
Bruker Physik AG in West Germany

Best regards,

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(Dipl.-Phvs. B. Knüttel. Dr. Sam Kaplan)



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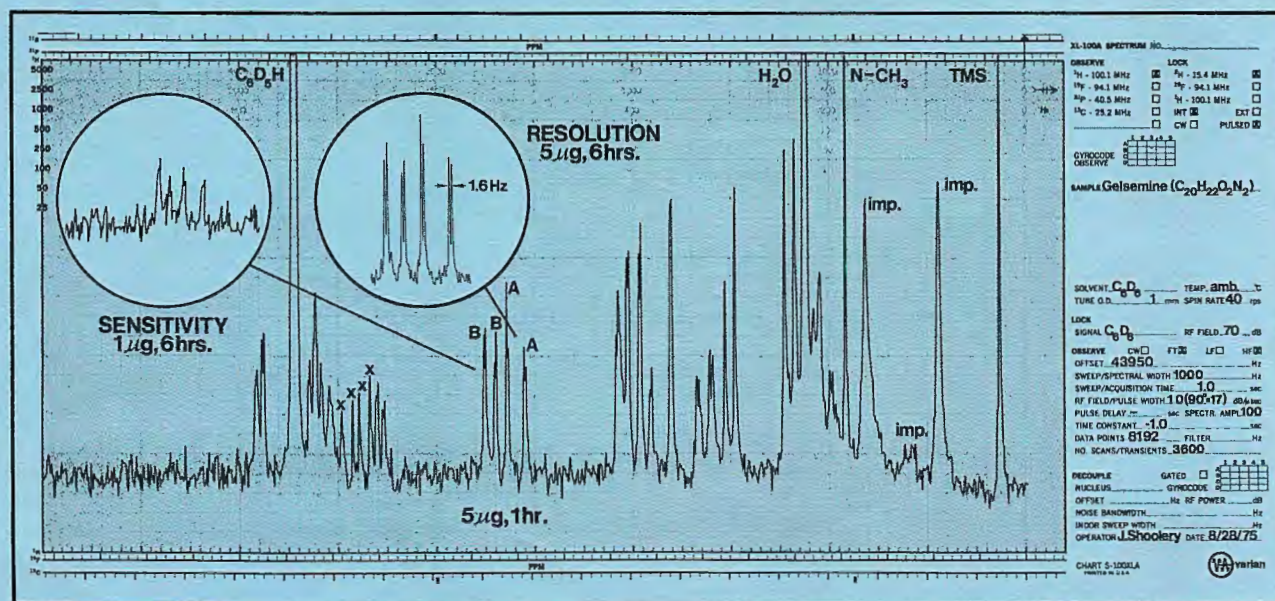
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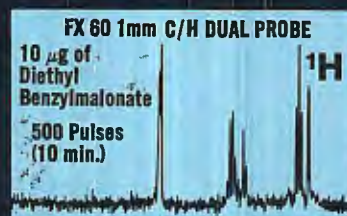


We dissolved 5  $\mu$ g of gelsemine in 5  $\mu$ l of  $C_6D_6$  and pulsed it at one-second intervals for one hour, using a tip angle of 53° (10  $\mu$ sec pulse) and a 2,500-Hz spectral width. Note the clear ABX pattern from the three vinyl protons and the

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