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Newsletter

No. 192

September, 1974

- B J. B. Lambert and S. A. Kahn  
Anisotropy of Carbon-Sulfur Bonds . . . . . 1
- E. Lippert and W. Schroer  
A Simple Device for Analyzing ABC-Spectra . . . . 3
- W. M. Egan  
The Nuclear Overhauser Effect and Disappearing  
(and Appearing) Signals . . . . . 6
- F. F. Ricci, E. Masimov, P. Gentile, P. E. Giua  
and F. Podo  
Hydration and Structure of Surfactant Aggregates  
in TWEEN 80-m-Xylene-water Ternary Systems . . .10
- G. W. Buchanan  
Stereochemical Effects of the S=O Group on  $^{13}\text{C}$   
Shieldings. . . . . 12
- S. Sternhell  
Steric Dependence of Benzylic Coupling . . . . 16
- R. K. Gupta  
A New Approach to Multiple Frequency FT-NMR  
of Various Nuclei on Commercial Spectrometers . .19
- R. K. Harris and K. M. Worvill  
NMR Computer Program Library: Position  
Available . . . . . 22
- B M. L. Maddox  
 $^{13}\text{C}$  NMR Spectroscopy of Some Uridine Deri-  
vatives. . . . . 24
- J. B. Stothers  
 $^2\text{H}$  NMR for Tracer Studies. . . . . 25
- B J. W. Cooper  
Report From Tufts; Request for PDP-11 Users. . .28
- E. D. Becker  
Effect of Hydrogen Bonding on  $^{13}\text{C}$   $T_1$ 's;  
Descendant of NMR Newsletter. . . . . 30
- K. D. Berlin  
NMR Analysis of 1-Benzyl-2-phenyl-3-hydroxy-4,5-  
dimethylphosphol-2-ene-1-Oxide . . . . . 32
- W. M. M. J. Bovée  
Relaxation in AB Systems . . . . . 33
- P. Sehr, G. Wagner and K. Wüthrich  
 $^1\text{H}$  NMR of the Basic Pancreatic Trypsin Inhibitor  
(BPTI) . . . . . 35
- P. Diehl, S. Sykora and J. Vogt  
Automatic Analysis of High Resolution NMR Spectra. .37
- N. Cyr  
Diamagnetic Contribution to  $^{13}\text{C}$  Chemical Shifts . .39 B
- G. Zimmermann  
Problems Involved in The Sample-Temperature Deter-  
mination in Proton Decoupled  $^{13}\text{C}$ -DNMR Measurements .41
- V. Bystrov  
Detection of Protein Stimulated Intermembrane  
Phospholipid Exchange by NMR. . . . . 43
- D. Kost  
Coalescence Measurements, Again: A Simple  
Method for the Evaluation of Coalescence  
Rate Constants of Exchanging AB Systems . . . . 45
- L. F. Johnson  
Trimethylphosphite, 75% Pure. . . . . 47
- D. W. Ovenall  
Chemical Shift Assignments in the  $^1\text{H}$  Spectra  
of Symmetrical Ortho-Disubstituted Benzenes. . . .48
- R. G. Bryant  
Position Available . . . . . 49

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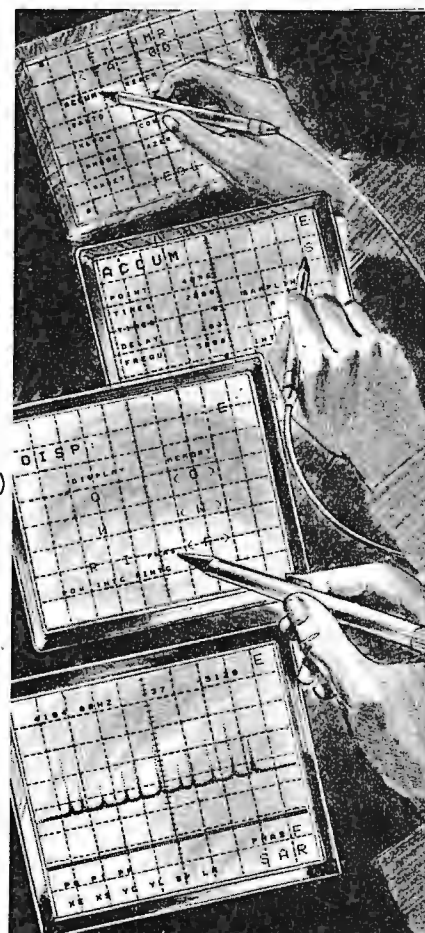
Deadline Dates: No. 193: 7 October 1974  
 No. 194: 4 November 1974

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.

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 192

Becker, E. D. . . . .	30	Lambert, J. B. . . . .	1
Berlin, K. D. . . . .	32	Lippert, E. . . . .	3
Bovee, W. M. M. J. . . . .	33	Maddox, M. L. . . . .	24
Bryant, R. G. . . . .	49	Masimov, E. . . . .	10
Buchanan, G. W. . . . .	12	Ovenall, D. W. . . . .	48
Bystrov, V. . . . .	43	Podo, F. . . . .	10
Cooper, J. W. . . . .	28	Ricci, F. F. . . . .	10
Cyr, N. . . . .	39	Schroer, W. . . . .	3
Diehl, P. . . . .	37	Sehr, P. . . . .	35
Egan, W. M. . . . .	6	Sternhell, S. . . . .	16
Gentile, P. . . . .	10	Stothers, J. B. . . . .	25
Giua, P. E. . . . .	10	Sykora, S. . . . .	37
Gupta, R. K. . . . .	19	Vogt, J. . . . .	37
Harris, R. K. . . . .	22	Wagner, G. . . . .	35
Johnson, L. F. . . . .	47	Worvill, K. M. . . . .	22
Kahn, S. A. . . . .	1	Wuthrich, K. . . . .	35
Kost, D. . . . .	45	Zimmermann, G. . . . .	41



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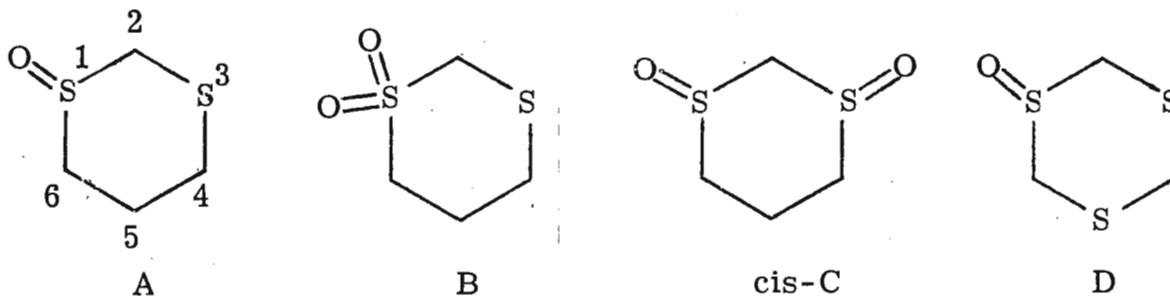
DEPARTMENT OF CHEMISTRY

July 24, 1974

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

Dear Barry:

In conjunction with Frank Carey and Oscar Hernandez of the University of Virginia, we have recently carried out the analysis of the 270-MHz spectra of the following compounds:



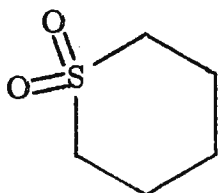
At the slow-exchange limit, the 2-proton resonance of B-D consists of a single AB quartet, and that of A consists of two overlapping AB quartets. The 2-equatorial proton may be identified in each case as the broader or more widely split half of each quartet, because of the W-pathway coupling with the equatorial protons at the 4 and 6 positions. In A, C, and D, the 2-equatorial proton is at lower field than the 2-axial proton, as is the case in cyclohexane. The 2-equatorial proton in B and the 4-equatorial proton in D, however, are at higher field than the respective axial protons.

The 2-axial/2-equatorial chemical-shift difference is determined primarily by the anisotropy of the 3-4 and 6-1 bonds. Examination of these and other sulfur, oxygen, and selenium heterocycles has led us to the conclusion that the diamagnetic anisotropy ( $\chi_L - \chi_T$ ) of the C-C, C-O, C-(SO), and C-(SeO) bonds has the opposite sign to that of the C-S, C-Se, C-(SO<sub>2</sub>), and C-(SeO<sub>2</sub>) bonds. This conclusion has been noted before, at least for the C-S bond. The axial/equatorial order for all the above resonances can be explained by these assignments.

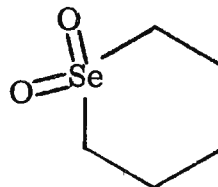
Professor Bernard L. Shapiro

July 24, 1974

After coming to this realization, we were able to clarify a number of long-standing local mysteries. Thus the near-zero chemical-shift difference between the 2 protons in thiane 1,1-dioxide (E) or selenane 1,1-dioxide (F) must be due to contributions from the C-C and from the C-(SO<sub>2</sub>) or C-(SeO<sub>2</sub>)



E



F

bonds that are nearly equal in magnitude but of opposite sign.

Sincerely,



Joseph B. Lambert

Shakil A. Kahn

Title: Anisotropy of Carbon-Sulfur Bonds

<sup>1</sup>E. Campaigne, N. F. Chamberlain, and B. E. Edwards, J. Org. Chem., 27, 135 (1962).

## IWAN N. STRANSKI-INSTITUT

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### A SIMPLE DEVICE FOR ANALYSING ABC - SPECTRA

Dear Barry,

In our study concerning selective solvation of organic substances we investigated the proton spectrum of acrylonitrile in mixtures of  $\text{CCl}_4$  with a strong base HMPT ( $\text{O}=\text{P}(\text{N}(\text{CH}_3)_2)_3$ ). The concentration dependence of the chemical shift is well described in terms of a recently developed statistic model of nearest neighbour structure /1/.

For the analysis of the ABC spectra of the acrylonitrile protons we used the computer programs LAOKOON III and NMRIT. The spectra in pure liquid and  $\text{CCl}_4$  are principally analysed by the parameter set given from Castellano and Waugh /2/. Looking at the level diagram and the spectra we found a simple rule which may be generally helpful to understand ABC spectra.

In the program LAOKOON III the sequence of the spin functions in the set of basis product functions is given by the order of the input data concerning the nuclei (in our case :  $\alpha$ ,  $\beta$ -trans,  $\beta$ -cis ). So the transitions e.g. 1 are labeled in the order shown in fig. 1. In the diagram the levels e.g. (1) are as well characterised by the first order basis spin functions which are used to diagonalise the Spin Hamiltonian.

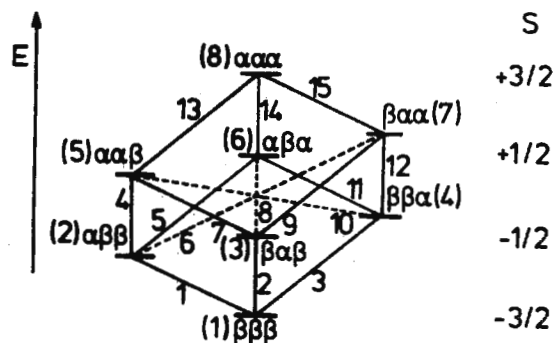


FIG. 1

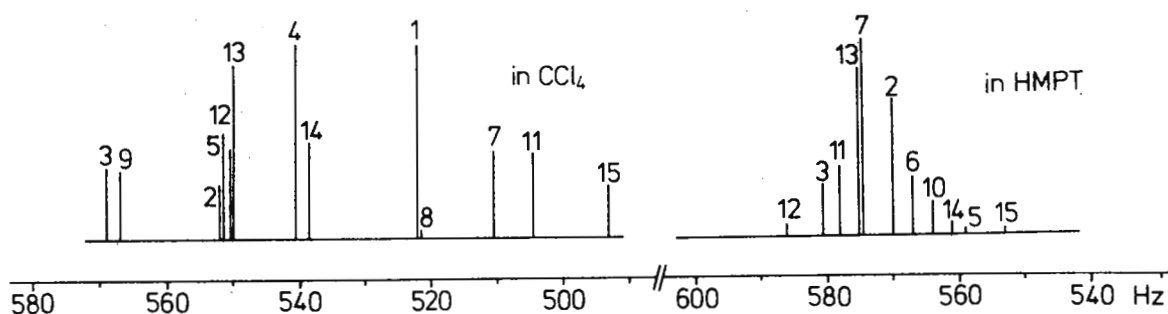


FIG. 2


It is possible to split the ABC level diagram into a set of six pseudo AB systems [3]. In an AB spectrum the strongest lines are transitions which are connected to the lowest energy level belonging to spin quantum number 0. In the ABC system the three strongest lines are those which are the strongest lines in two pseudo AB systems. These transitions are connected to the lowest spin  $(-\frac{1}{2})$  level and/or the lowest spin  $(+\frac{1}{2})$  level. In pure acrylonitrile where the chemical shift increases in the order  $\alpha$ ,  $\beta$ -trans,  $\beta$ -cis, the strong transitions are consequently the lines 1, 4 and 13. In a very crude approximation the transitions can be interpreted as transitions of one nucleus only. 1 belongs to the  $\alpha$ -proton, 4 to the  $\beta$ -trans-proton and 13 to the  $\beta$ -cis-proton.

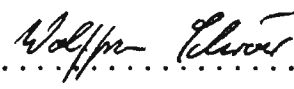
If the concentrations of the base is increased the  $\alpha$ -proton is more shifted to lower field than the  $\beta$ -protons. In the pure base the order of the chemical shift is  $\beta$ -trans,  $\beta$ -cis,  $\alpha$ .

The lowest spin  $(-\frac{1}{2})$  level is the level (2), the lowest  $(+\frac{1}{2})$  level remains the level (5). Consequently the three strongest lines which are the strongest lines in two pseudo AB systems now belong to the transitions 2, 7 and 13.

It might be quite helpful to the analysis of AB spectra that the strongest lines can be characterised in the shown way.

Yours sincerely,

  
 .....  
 (Ernst Lippert)

  
 .....  
 (W. Schröer)

#### Literature

- / 1 / W. Schröer, Ber. Bunsenges. Phys. Chem. in press,  
 W. Schröer, E. Lippert, Ber. Bunsenges. Phys. Chem. in press.
- / 2 / S. Castellano, J.S. Waugh, J. Chem. Phys. 37, 1941 ( 1962 ).
- / 3 / P. Diehl, R.K. Harris, R.G. Jones, Progr. NMR-Spectr. Vol. 3  
 ( Ed. J.W. Emsley, J. Feeney, L.H. Sutcliffe ) Oxford 1967.



**CHEMICAL CENTER****PHYSICAL CHEMISTRY 2**

19 July 1974

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

Dear Barry:

THE NUCLEAR OVERHAUSER EFFECT AND DISAPPEARING  
 (AND APPEARING) SIGNALS

Assuming exclusive dipole-dipole relaxation, the  $\text{noe}^1$  between two spin 1/2 nuclei, I and S, is given by,

$$f_I(S) = \frac{\gamma_S}{\gamma_I} \cdot \frac{\sigma_{IS}}{\rho_I} \quad (1)$$

where,

$$\sigma_{IS} = \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} \left[ \frac{6\tau_c}{1 + (\omega_I + \omega_S)^2 \tau_c^2} - \frac{\tau_c}{1 + (\omega_I - \omega_S)^2 \tau_c^2} \right]$$

$$\rho_I = \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6} \left[ \frac{3\tau_c}{1 + \omega_I^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_I - \omega_S)^2 \tau_c^2} + \frac{6\tau_c}{1 + (\omega_I + \omega_S)^2 \tau_c^2} \right]$$

(It is assumed that the molecular reorientation may be described by a single correlation time,  $\tau_c$ ).

Under extreme narrowing conditions ( $\omega^2 \tau_c^2 \ll 1$ ), equation 1 reduces to,

$$f_I(S) = \frac{\gamma_S}{2\gamma_I} \quad (2)$$

the normally encountered noe. However, when the extreme narrowing

19 July 1974

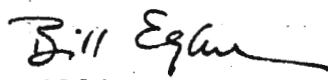
Professor B. L. Shapiro

condition is not fulfilled, as may occur with biomacromolecules where  $\tau_c$  is on the order of  $10^{-8}$ , drastic changes in the noe (relative to that given by the eq. 2 limit) may take place. Indeed, such effects have been observed<sup>2</sup> and discussed.<sup>2-4</sup>

We thought that some NEWSLETTER readers might be interested in seeing these changes in the noe graphically. The accompanying Figure depicts the dependence of the noe on  $\tau_c$  for  $I = {}^1\text{H}$ ,  ${}^{19}\text{F}$ ,  ${}^{13}\text{C}$ , and  ${}^{29}\text{Si}$  with  $S$ , the irradiated nucleus being  ${}^1\text{H}$  in all instances. Field strengths corresponding to nominal  ${}^1\text{H}$  resonance frequencies of 60, 100, 220 and 300 MHz (curves A, B, C, and D of the figure, respectively) were employed for each case.

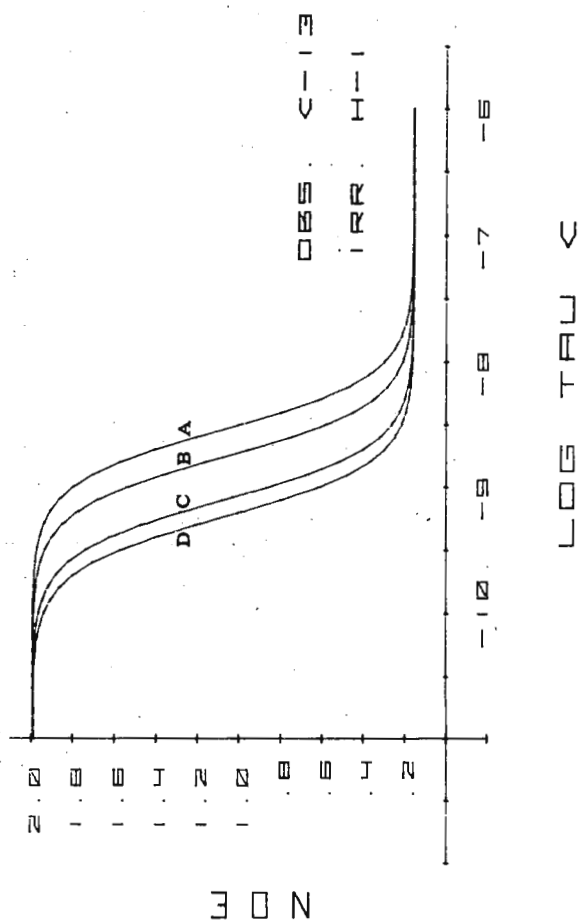
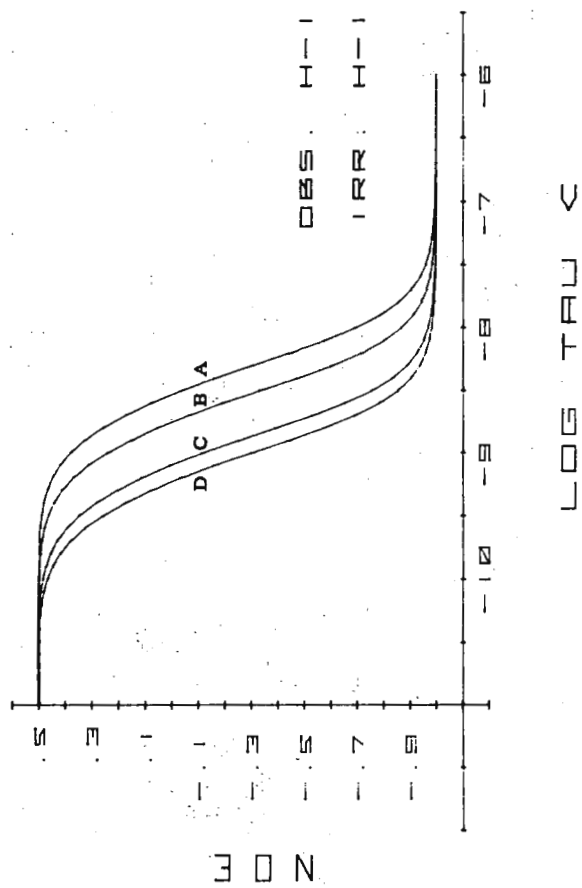
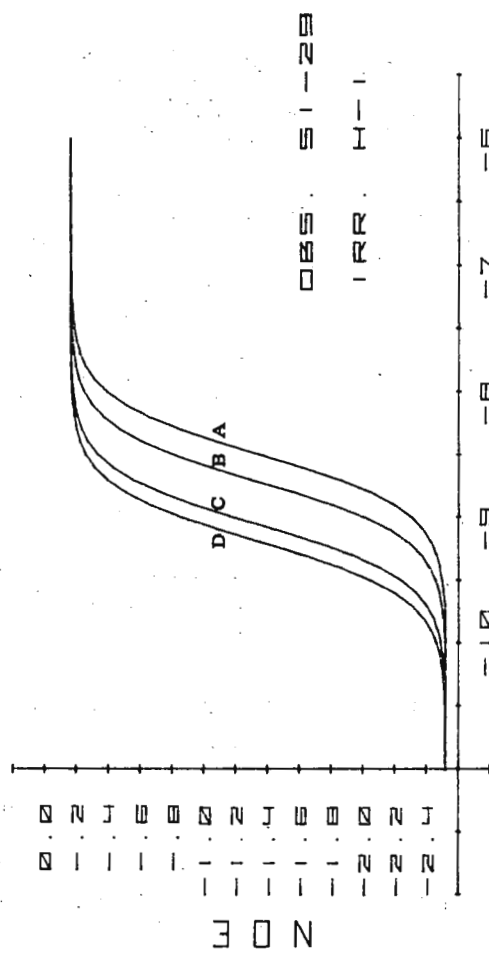
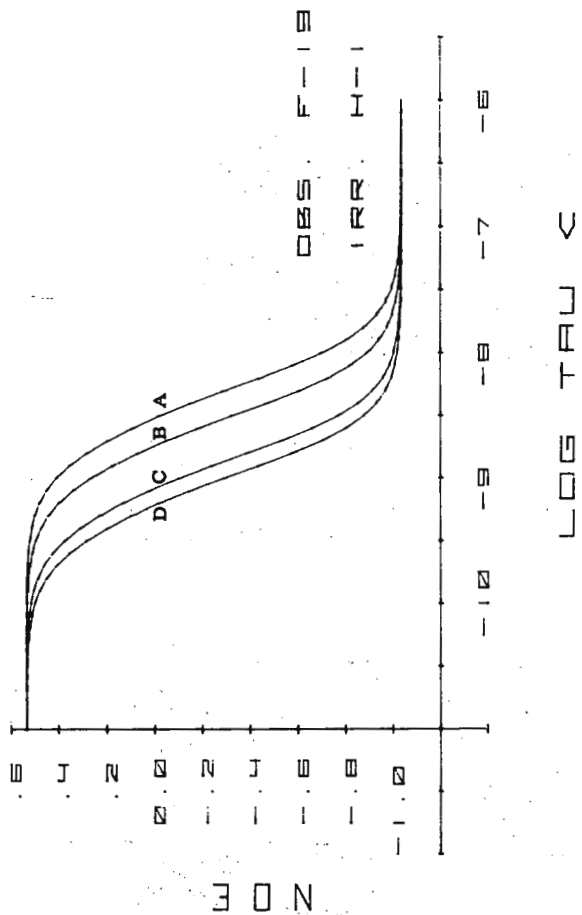
It is interesting to note that for the cases of two protons or a proton-fluorine pair that as  $\tau_c$  becomes long, the noe approaches -1.0, i.e., the signal disappears. For  ${}^{13}\text{C}$ , in contrast,  ${}^1\text{H}$  irradiation always produces an enhancement, although this enhancement is slight for long correlation times. The noe at  ${}^{29}\text{Si}$  is initially (i.e., when  $\tau_c$  is short) negative since the sign of  $\gamma_{\text{Si}}$  is opposite to that of  $\gamma_{\text{H}}$ ; as  $\tau_c$  increases, the silicon signal thus progresses from strongly negative, to zero, to positive and of nearly normal intensity. The limiting, non-extreme narrowing noes are -1.0, -1.04, 0.15, and -0.16 for  ${}^1\text{H}$ ,  ${}^{19}\text{F}$ ,  ${}^{13}\text{C}$ , and  ${}^{29}\text{Si}$ , respectively.

With best wishes,

  
William M. Egan

#### References

1. For terminology and a discussion of the noe, see J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect: Chemical Applications," Academic Press, New York, N. Y., 1971.
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4. D. Doddrell, V. Glushko, and A. Allerhand, J. Chem. Phys., 56, 3683 (1972).



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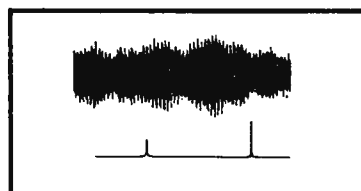
**STOCHASTIC RESONANCE** — This technique involves random noise modulation of the rf excitation frequency, leading to a broadband excitation whose response is measured and Fourier transformed much as in conventional pulsed-FT nmr. Its principal advantage lies in the fact that much less rf power is needed to excite the chemical shift range of interest and that it has the same Fellgett's advantage of FT nmr.

**RAPID SCAN NMR** — In this technique, a spectral region is swept at a rate much greater than allowed for by slow passage conditions and the resulting ringing spectrum correlated with a spectrum of a single ringing line or of a theoretical line. Its principal advantage lies in the ability to acquire data rapidly even in the presence of strong solvent lines, without requiring that these lines be part of the signal averaged data.

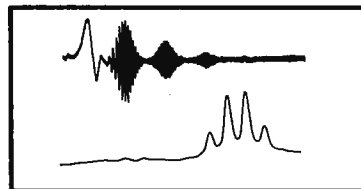
**HOMOSPOIL  $T_1$  SEQUENCE** — This sequence allows the rapid measurement of long  $T_1$ 's without the long  $5xT_1$  waiting period needed by the inversion-recovery sequence. It is accomplished by a  $-(90\text{-spoill-tau-}90\text{-sample-spoil})$ - sequence.

**QUADRATURE DETECTION NMR** — This technique allows  $\sqrt{2}$  enhancement over conventional pulsed nmr since the rf carrier can be placed in the center of the spectral region and dual phase detectors used to receive the response. The two resulting free induction decays are Fourier transformed using a complex transform which results in a single frequency domain spectrum.

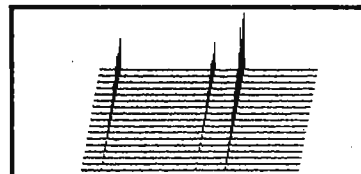
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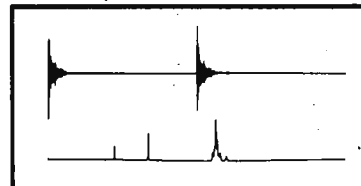
R. R. Ernst, *J. Mag. Res.* 3 10-27 (1970); R. Kaiser, *J. Mag. Res.* 3 28-40, (1970); J. Cooper and R. Addleman, 13th Experimental Nmr Conference (1972); E. Lippmaa, private communication.



J. Dadok and R. F. Sprecher, 13th and 14th Experimental Nmr Conferences (1972, 1973); E. Becker, paper in press.



J. L. Markley, W. J. Horsley and M. P. Klein *J. Phys. Chem.* 55 3804 (1971); R. Freeman and H. D. W. Hill, *ibid.* 54 April (1971); G. G. McDonald and J. S. Leigh, Jr., *J. Mag. Res.* 9 358 (1973).



J. Schaeffer and E. O. Stejskal, 15th Experimental Nmr Conference (1974), and *J. Mag. Res.* March (1974) (in press); J. D. Elliott, et al., *Adv. Mag. Res.* 5 117 (1971)

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Prof. B. L. Shapiro  
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Texas A&M University  
College Station, Texas 77843

Hydration and Structure of Surfactant Aggregates  
in TWEEN 80-m-Xylene-water ternary systems.

Dear Prof. Shapiro,

recent studies (1) have shown that CW and FT PMR techniques may provide a useful tool for assessing the nature of nonionic detergent micelles in aqueous solutions, in terms of a) arrangement and relative mobility of the various parts of the detergent molecules; b) the extent to which these parts come into contact with the solvent. It is also known that "inverted" micelles of surfactants can be formed in nonaqueous solvents (2). It appears therefore interesting to assess potentials and limits of the PMR methods for studying molecular structures, hydration and local mobilities in ternary systems formed by a nonionic surfactant, a nonpolar solvent and water.

We report in this letter preliminary results obtained at 90 MHz on homogeneous isotropic solutions of TWEEN 80 (polyethoxyethylene (20) sorbitan monooleate - Atlas Chemical Industries, Inc.) - m-xylene - water. The spectra reported in the Figure have been obtained analysing with a spectrometer Bruker HF - 90 (operating in the CW mode) four samples respectively formed by adding to a 20% w/w TWEEN 80 in xylene binary system the following amounts of water: a) 0%; b) 2.2%; c) 4.5%; d) 5.6% (w/w). The average ratio of the TWEEN ethoxy units to the water molecules varies from 2.5 to 1 on going from samples b) to d). The amplified dotted inserts in the high-field region of the spectra show the detailed shapes of the oleic chain terminal methyl group. Chemical shifts are measured vs. the aromatic xylene protons (lock signal).

In the TWEEN-xylene spectrum the ethoxy units give rise to one unresolved asymmetric band; its average position, downfield shifted of about 20 Hz with respect to the resonance of polyethoxyethylene chains diluted in xylene (3.3% w/w) indicate that the polar chains of TWEEN are only partially exposed to the aromatic solvent. Both the positions and intensities of the new  $-CH_2CH_2O-$  peaks appearing at lower fields, upon addition of increasing amounts of water, are taken as an indication that hydrated ethoxy units of the surfactant are progressively removed from the exposure to the aromatic solvent. The water signal appears narrower and down-field shifted with increasing the water content in the system. Progressive saturation measurements have finally indicated higher local mobilities for the ethoxy chains segments more exposed to xylene. The mobility of the exposed units decrease on going from sample a) to sample d).

These preliminary results suggest that aggregates with properties of reversed micelles are formed in the TWEEN 80'-xylene binary system, with the ethoxy segments partially distributing between the (polar) internal core and the peripheral (mainly non polar) region. Upon water solubilization a larger number of  $-CH_2CH_2O-$  units are allowed to participate in the formation of the internal core; in this region the ethoxy groups mobility is partially restricted through H-bonding to water molecules. Graphic

analysis of the  $-\text{CH}_2\text{CH}_2\text{O}-$  signals can provide information on the equilibrium distribution of the ethoxy chain segments between the internal and external regions of the surfactant aggregates.

$T_1$  measurements will be carried out in a near future, when a Varian XL-100 Pulsed-Fourier Transform NMR spectrometer will be installed in our Institute.

Independent physico-chemical studies are also in progress (Dr. Giua) for studying the micellar properties in the mentioned systems. (Dr. G. Némethy is thanked for interesting discussions and suggestions).

Yours sincerely,

*Franca Podo*

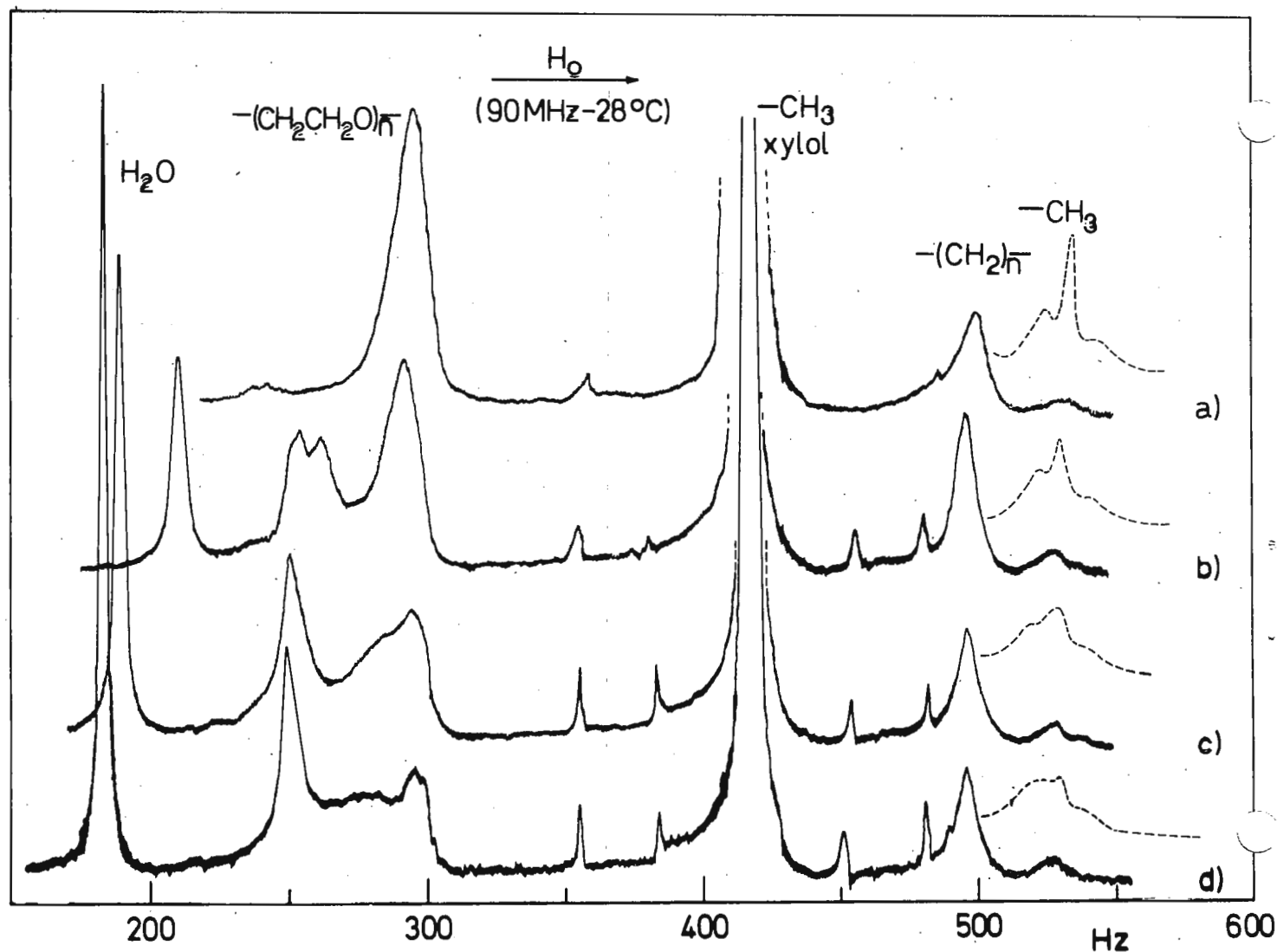
(F. F. Ricci, E. Masimov<sup>(a)</sup>, P. Gentile,  
P. E. Giua<sup>(b)</sup> and F. Podo)

a) on leave of absence from Baku University, USSR.

b) Istituto di Acustica O. M. Corbino, Roma.

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- 2 - P. Becker, "Nonionic Surfactants". M. J. Schick, Ed. -Marcel Dekker, New York, N. Y. (1967), Vol. 1, p. 511.



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DEPARTMENT OF CHEMISTRY

July 23, 1974

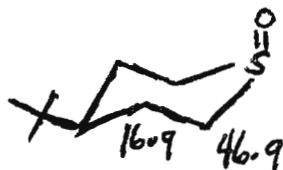
Professor B.L. Shapiro  
Dept. of Chemistry  
Texas A & M University  
College Station Texas  
U.S.A. 77843

"Stereochemical Effects of the S=O  
Group on  $^{13}\text{C}$  Shieldings"

Dear Barry,

Some of our earlier work<sup>(1)</sup> showed the remarkably large influence of S=O geometry on  $^{13}\text{C}$  shieldings of trimethylene sulfites at the carbon  $\beta$  to the S atom. Recently we have examined some sulfoxides to ascertain the magnitude of the  $\alpha$  steric effect and to aid in the assignment of spectra of some sultines provided by Tony Durst.

Shifts for cis and trans -4-t-butylthiane-1-oxide ( $\delta$  from TMS) are shown below. Major differences occur at both the  $\alpha$  and  $\beta$  carbons and in each case the isomer with the axial S=O shows the greatest shielding.



I



II

In the cis isomer the shielding at the  $\beta$  position is unlikely to have an anisotropic origin and may be interpreted as a "gauche -  $\gamma$ " steric shift since the  $\beta$  carbon is gauche to the S=O in I, but anti in II. Any bright suggestions from your readers as to the possible origin of the  $\alpha$ -effect would be welcome at this stage!

Lambert<sup>(2)</sup> has shown that thiane-oxide itself shows a slight preference for the conformation III a.

Professor B.L. Shapiro

July 23, 1974



The  $^{13}\text{C}$  spectra at low temperatures verify this and also show the large shielding differences for  $\alpha$  and  $\beta$  carbons with stereochemistry. At  $+30^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ , thiane oxide exhibits 3 sharp resonances in ratio of 2:2:1 at  $\delta = 47.5, 18.9$  and  $24.7$  respectively for carbons  $\alpha, \beta$  and  $\gamma$  to the S atom. On cooling, the  $\alpha$  and  $\beta$  carbon resonances broaden as illustrated ( $T_c = -40^\circ\text{C}$ ) and the  $\gamma$  carbon remains sharp. F.T. spectra were recorded with a Pulse Interval = 0.2 seconds so that the  $\text{CD}_2\text{Cl}_2$  resonance is wiped out. The spectrum at  $-93^\circ$  clearly shows the slight preference for III a. Interestingly without the *t*-butyl group the  $\alpha$ -effect has increased to 7 ppm, from 5.5.

Please credit this to John ApSimon's subscription.

Best regards,

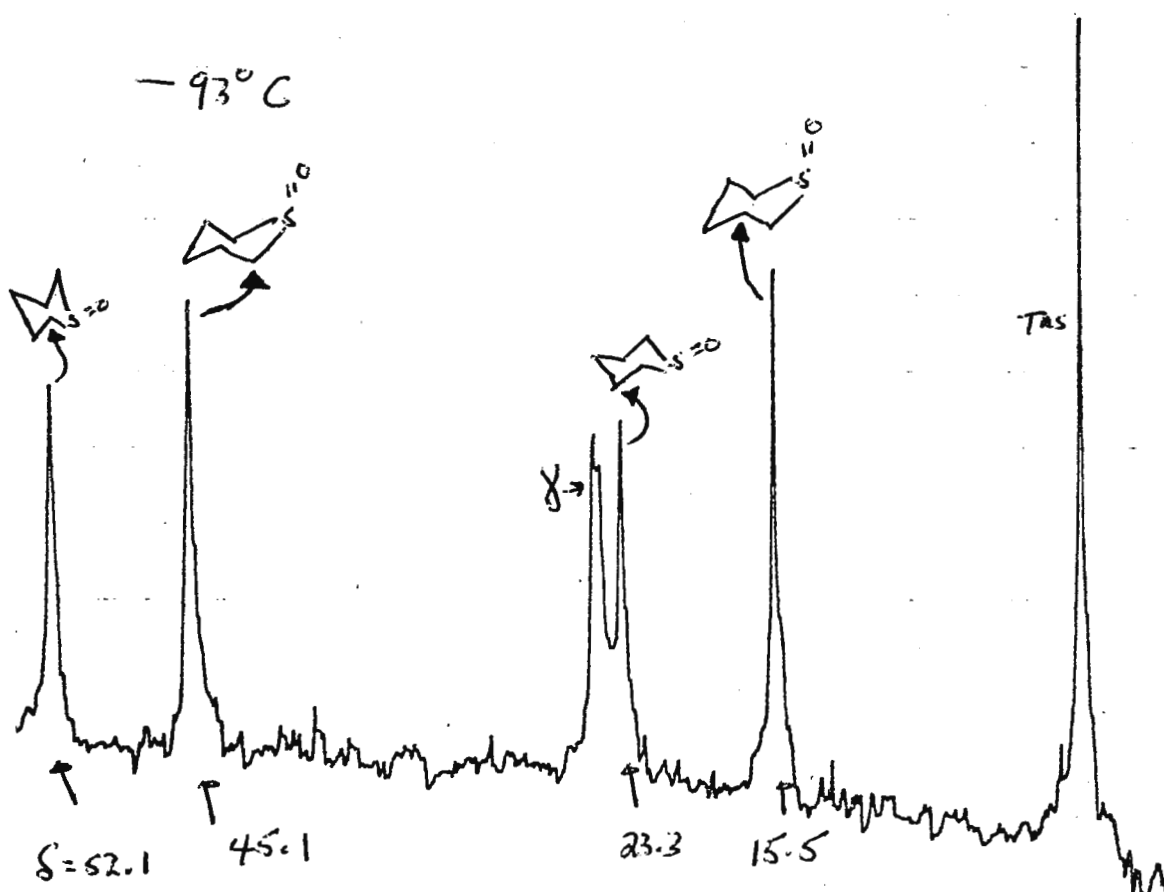
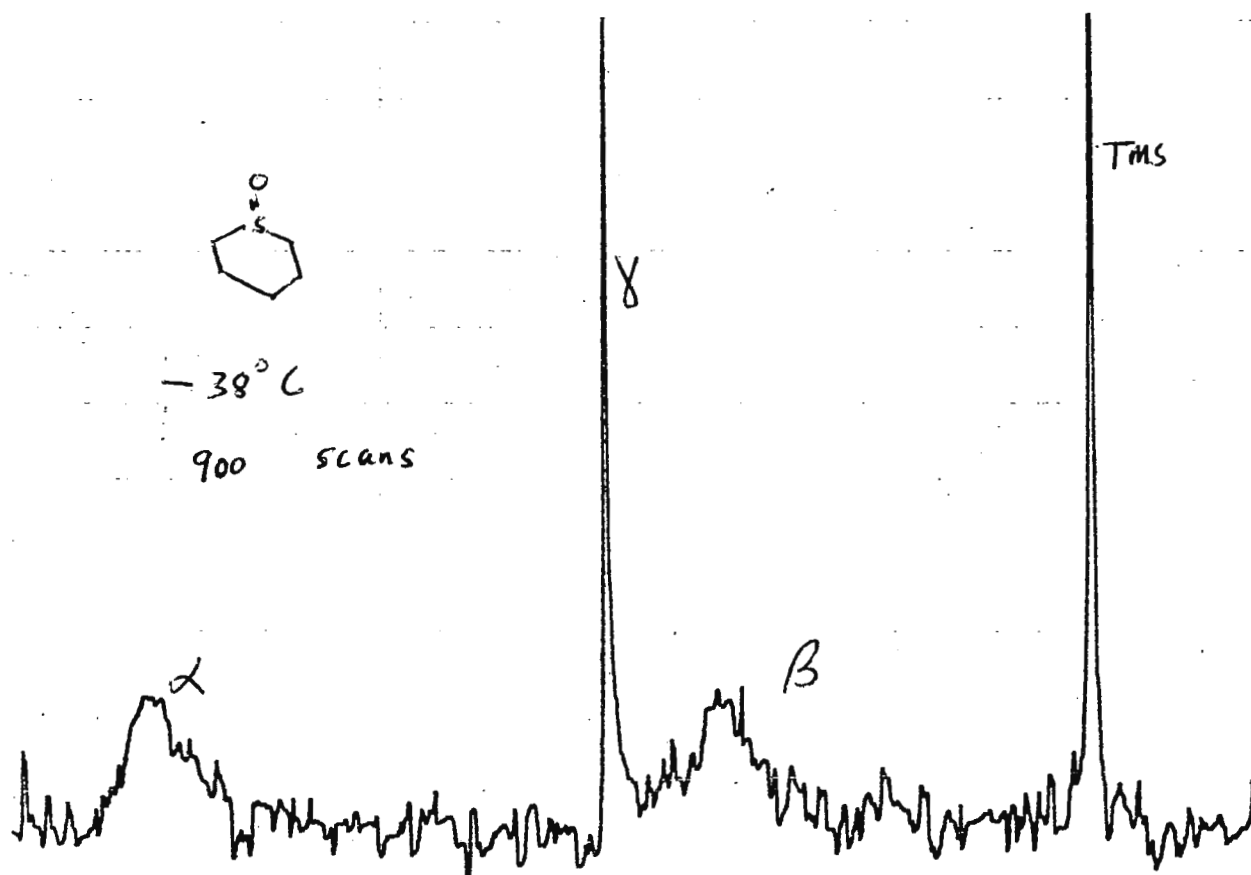
G.W. Buchanan  
Assistant Professor

/mak

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Department of Organic Chemistry  
**The University of Sydney**

SYDNEY, N.S.W. 2006

July 30, 1974

## IN REPLY PLEASE QUOTE:

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

STERIC DEPENDENCE OF BENZYLIC COUPLING

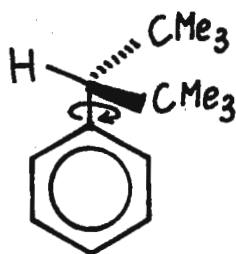
Dear Barry,

We have a long-standing<sup>1</sup> interest in benzylic coupling, i.e. coupling between protons on  $sp^3$  hybridized benzylic carbon atoms and ring protons. Earlier theoretical and empirical results have been reviewed<sup>2</sup> and many interesting data and calculations have appeared since, especially from Schaefer's group<sup>3</sup>. However few of the experimental results available in the literature are useful for the purpose of determining the steric dependence of benzylic coupling and we have been gathering data which we consider suitable by virtue of: (i) minimal substitution by electronegative groups; (ii) standard hybridization; (iii) well-defined stereochemistry; and (iv) analysable spin-systems.

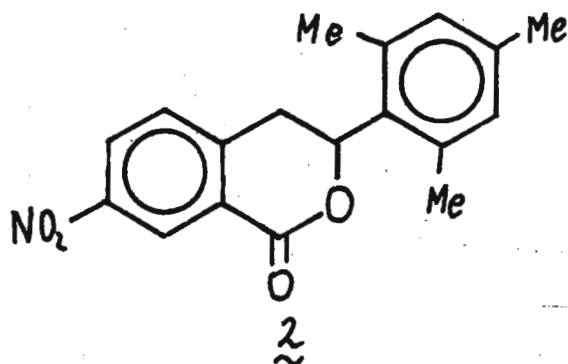
Cedric Fallick has now assembled preliminary data from compounds (1)-(4) and several others as part of his PhD work here and these results can be compared with Schaefer's INDO calculations<sup>3</sup>. It can be seen that the trends are reasonable but an interesting reversal can be seen for the values of  $^4J_{ortho}$  for  $\phi = 0$  and  $180^\circ$ . [Fig.1].

Compound (1) is of some additional interest: the data used here are derived from a massively deuterated sample whose proton NMR spectrum (with decoupling of  $^2H$ ) at room temperature consists of five signals of equal intensity broadened or split by benzylic coupling.

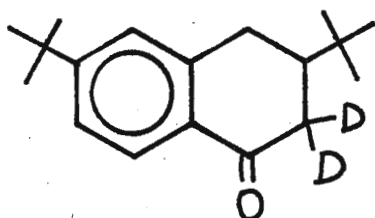
We have a series of such derivatives, all of which have rotational barriers of ca 22 k.cal/mole about the  $sp^2-sp^3$  carbon-carbon bond and ground states with the conformation depicted here



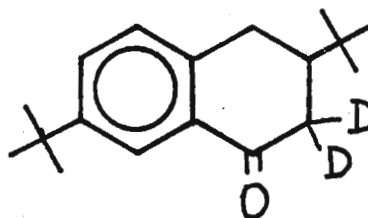
1



2



3



4

as determined on the basis of arguments detailed elsewhere<sup>4</sup> for a series of closely related carbinols.

With best regards

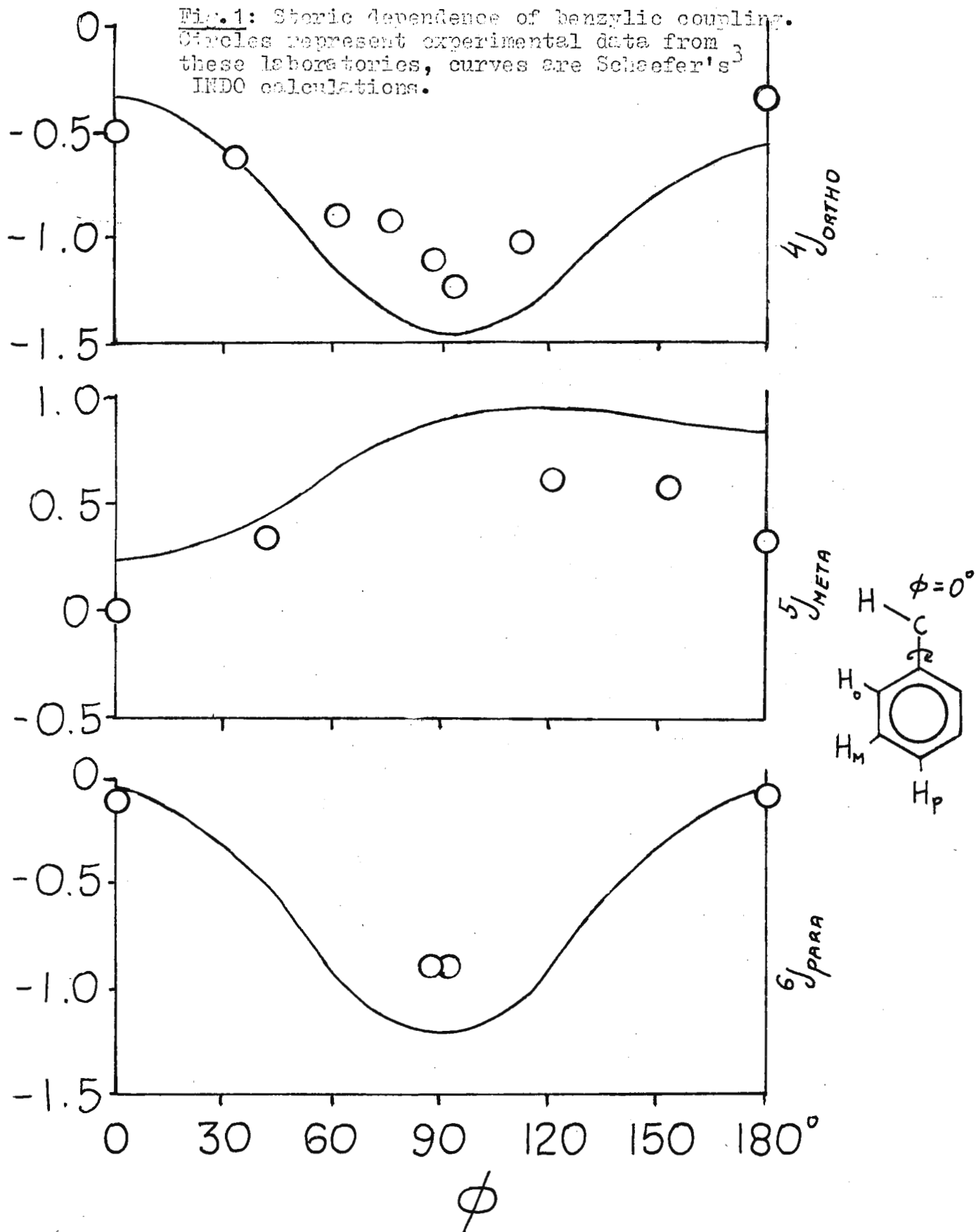
yours sincerely

*S. Sternhell*  
S. Sternhell

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Fig. 1: Steric dependence of benzylic coupling.  
 Circles represent experimental data from  
 these laboratories, curves are Schaefer's<sup>3</sup>  
 INDO calculations.



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August 5, 1974

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

Re: A New Approach to Multiple Frequency FT-NMR of Various  
Nuclei on Commerical Spectrometers

Dear Professor Shapiro:

Interest in NMR studies of uncommon nuclei and in frequency dependence studies with such widely studied nuclei as  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{17}\text{O}$  has increased considerably in recent years. In magnetic resonance studies in our laboratory aimed at understanding the role of metal-enzyme-substrate and inhibitor interactions, at least two or more frequencies are often desirable to arrive at unambiguous values of correlation times which in turn are used for structural determinations. Thus, we are currently interested in frequency dependent relaxation studies with a variety of nuclei, particularly,  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $^{23}\text{Na}$ ,  $^7\text{Li}$  and  $^{13}\text{C}$ . In addition, we have also been interested in similar studies with the  $\text{Tl}^+$  nucleus (1) which is known to replace  $\text{K}^+$  in many enzymatic systems without loss of activity (2). It may be noted that none of the previously proposed general methods of observing various nuclei (3-5) are directly applicable here.

In this communication we wish to describe a new approach to carry out such studies without the need for additional electronic instrumentation specifically tuned to each desired frequency and nucleus. Although we have successfully used this approach with our system only (Varian XL-100-15 FT), the underlying principles are equally applicable to other systems. The Varian spectrometer employs a heteronuclear field/frequency lock on deuterium and the lock channel operates at a fixed frequency of 15.351 MHz. Transmitter-receiver networks operating at 100, 94.077, 40.481, 32.084, 25.144, 19.865, 13.56, 10.133, 7.6696 and 7.2238 MHz are available as standard options on this system, for observing  $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{17}\text{O}$ ,  $^{15}\text{N}$ ,  $^{33}\text{S}$  and  $^{14}\text{N}$ , respectively at 23.5 K gauss.

Our new approach consists of lowering the D.C. magnetic field below 23.4 K gauss so as to resonate the desired nucleus at the appropriate frequency (one of the several mentioned above: 100, 94.077, 40.481, 32.084, 25.144, 19.865, 13.56, 10.133, 7.6696 or 7.2238) and choosing another appropriate lock nucleus with a resonance frequency within a range of about  $\pm 2$  MHz around 15.4 MHz. (Our lock channel is tunable only over this narrow range).

Professor Bernard L. Shapiro  
August 5, 1974

With a simple modification of the lock channel then, a field/frequency lock at the new field strength can be obtained. The simple modification is basically that described by Ellis *et al.* (3), the important difference being that the choice of the new lock frequency within the specified range is dictated by the new nucleus chosen and not by deuterium. The new lock frequency is provided by the Gyrocode Spin Decoupler (3, 6). The choice of lock nuclei is based on their sensitivity, linewidth and solubility considerations. We have successfully used proton, deuterium, boron, phosphorous, lithium, thallium, fluorine and sodium locks. The sample tube assembly consists of two parts, a 12mm O.D. outer tube (Wilma Glass Co., Buena, N.J., Cat. No. 516-0) and a 5mm O.D. inner tube (Wilma Glass Co., Cat. No. 520). A 12mm probe insert (receiver coil) is used. The lock solution resides in the outer tube and the sample under observation inside the inner tube. A Teflon plug is used as a vortex suppressor. The sensitivity of this arrangement may be somewhat lower owing to filling factor considerations and to the lower magnetic field. The former may not be a disadvantage for much biochemical work, however, since the filling factor is usually suboptimal, often being determined by the limited quantity of the sample available. We routinely operate on 0.2-0.3 ml sample volumes. The lower magnetic field may actually be an advantage because of larger relaxation effects (6, 7). Two examples of the use of this approach are presented in Fig. 1.

Sincerely yours,



R. K. Gupta

RKG/sm

P.S. This work was done in Dr. A.S. Mildvan's laboratory at ICR. Please credit it to his account.

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Professor Bernard L. Shapiro  
August 5, 1974

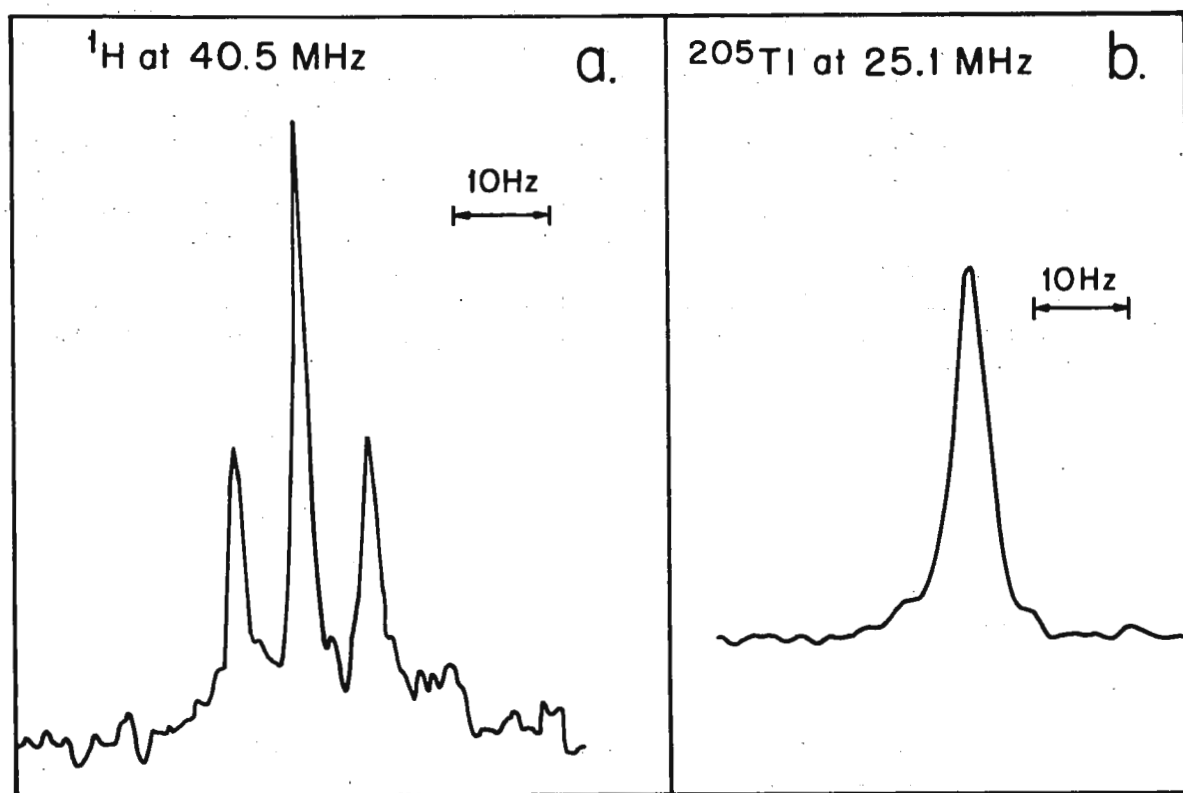


Fig. 1- (a) Single pulse  $^1\text{H}$  FT spectrum of the methyl triplet of 0.5 M ethanol solution in  $\text{D}_2\text{O}$  at 40.5 MHz. The field was locked on Li resonance in a saturated solution of lithium chloride in  $\text{D}_2\text{O}$  doped with  $\sim 10$  mM copper chloride. The lock resonance frequency  $\sim 15.7$  MHz was obtained using the Gyrocode matrix A3,4,5; B1,3,4,5; C1; D2. (b) Single pulse FT spectrum of  $^{205}\text{Tl}$  in 0.3 M thallium nitrate solution in  $\text{H}_2\text{O}$  at 25.1 MHz. The field was locked on  $^{11}\text{B}$  resonance in a saturated solution of boron trifluoride in ether. The lock resonance frequency of  $\sim 14$  MHz was obtained using the Gyrocode matrix A1,2,4,5; B3,5; C1; D2.



## University of East Anglia

Dr. R.K. Harris

School of Chemical Sciences  
University Plain, Norwich NOR 88C  
Telephone Norwich (0603) 56161  
Telegrams UEANOR NORWICH  
England

2 August 1974

## NMR COMPUTER PROGRAM LIBRARY : POSITION AVAILABLE

Dear Barry,

Readers of T.A.M.U.N.M.R. may wish to know of the progress of the NMR Program Library we described earlier (T.A.M.U.N.M.R. 158 - 20, November 1971). We now have about 24 working programs documented, including routines for spectral analysis, liquid crystal spectra, chemical exchange, quadrupolar nuclei, double resonance, and relaxation effects. These are all written in FORTRAN, and are described in a recently-issued revised Manual plus Bulletin No. 8. These documents are at present issued free of charge, and anyone who wishes to be on our mailing list should write to one of us, preferably R.K.H.

In fact Kevin is leaving shortly for another job, and there is therefore a vacancy (from 1 October 1974) for a Senior Research Associate. His brief is to co-ordinate and develop the Library, and he would have a pretty free hand to do so in the direction he wished. The post would be attractive to a chemist or physicist who wishes to gain full-time experience in computing. A background in either NMR or computing is desirable. The salary will be in the range £2118 - £2580 per annum, depending on qualifications. Applications, or requests for further information, should be sent to R.K.H. as soon as possible.

Yours sincerely,

*Robin**Kevin*

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

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August 9, 1974

192-24

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


SUBJECT:  $^{13}\text{C}$  NMR Spectroscopy of some Uridine Derivatives

Dear Barry:

The installation of our Bruker WH-90 last November was received with great rejoicing and was promptly followed by an inundation of samples for  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  studies. This aptly named spectrometer has indeed proven to be a reliable Work Horse in continuous operation 24 hours a day, 7 days a week.

A large portion of our  $^{13}\text{C}$  studies are on carbohydrates and I have a couple of examples of an upfield  $\beta$  shift as well as a downfield  $\gamma$  shift. The spectra were measured in 10 mm tubes using 95% acetone/ $\text{D}_2\text{O}$  with internal TMS. A flip angle of  $33^\circ$  and a repetition rate of 0.9 seconds were used to collect 8K points and zero filled to 16K. Both off resonance and coherent decoupling were used to identify the resonances.

Sincerely yours,



Michael L. Maddox, Ph.D.  
 Staff Researcher  
 Institute of Organic Chemistry

	5' IU	5' IU 4' Ome	$\Delta\delta$	5' IU 2'3' IS	5' OI 2'3' IS 4' OMe	$\Delta\delta$
4	164.53	163.72	-.81	163.85	163.78	-.07
2	151.72	151.40	-.32	151.36	151.30	-.06
6	142.36	142.42	+.06	144.21	143.79	+.58
5	103.15	103.41	+.26	103.05	103.22	+.17
1'	90.80	92.13	+1.53	95.45	92.39	+3.06
4'	83.74	104.42	+20.68	88.13	106.27	+18.14
3'	74.28	73.53	-0.75	85.40	84.85	-0.55
3'	74.09	74.19	+0.10	85.08	85.24	+0.16
5'	6.92	4.68	-2.24	6.11	5.95	-0.16
OC(=O)				114.79	116.32	+1.53
Me } Is				27.37	26.40	-0.97
Me }				25.45	26.44	+0.69
OMe		49.28			49.51	



The University of Western Ontario, London, Canada

Faculty of Science  
Department of Chemistry

August 12, 1974

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

Dear Barry

$^2\text{H}$  nmr for tracer studies

In response to your pink letter I would like to describe some of our recent work utilizing  $^2\text{H}$  spectra for mechanism studies. As DePuy has recently pointed out (TAMU Newsletter, 186, 38), the power of  $^2\text{H}$  nmr for tracer studies does not seem to be generally recognized but there are hosts of systems which could be profitably studied using the method. A few years ago, when we began using  $^{13}\text{C}$  spectra to follow deuterium incorporation, a fair degree of success was realized but there are two disadvantages which  $^2\text{H}$  spectra eliminate. The well-known problem of  $^{13}\text{C}$  integrations is one, which, although not insurmountable, requires caution, somewhat large samples (~100 mg) and a fair amount of instrument time. The second limitation concerns the lower limit of detection for lightly labelled centres; experience here places this limit around 3-5%. With  $^2\text{H}$  spectra, however, 1%  $^2\text{H}$  at a given position is nearly 2 orders of magnitude above natural abundance and is readily detected since natural abundance spectra can be obtained with current instruments. As DePuy showed, the use of shift reagents overcomes the problem of a relatively narrow chemical shift range but with samples containing a variety of nonequivalent deuterium nuclei overlapping signals can be difficult to integrate precisely since some line broadening accompanies the greater shift dispersion. Our remedy for the latter problem utilizes line shape fitting assuming Lorentzian curves for each absorption. For this purpose the BMDX85 program, Biomedical Computer Program X-series Supplement, edited by W.J. Dixon, Univ. of Calif. Press, Berkeley, 1969, was modified for me by Dr. L. L. Coatsworth.

To illustrate some typical results two spectra are shown in the Fig. Both are fenchone samples which were subjected to  $t\text{-BuO}^-/t\text{-BuOD}$  for several hours to follow the course of deuterium exchange via homoenolization. A preliminary account of this work using  $^{13}\text{C}$  spectra was included in JACS 94, 8582 (1972) but the system has now been reexamined by  $^2\text{H}$  nmr particularly to locate the lightly deuterated sites. In the upper spectrum, a sample from 40 hr. treatment exhibits three signals, exo-6-, endo-6-, and 8-D (exo-Me) in order of increasing shielding. The full line is the computer fitted spectrum while the small triangles are the experimental points. The individual bands are also drawn. The spectrum was obtained in  $\text{CHCl}_3/\text{C}_6\text{F}_6$  (4:1) containing 0.03 equiv. of

Dr. B. L. Shapiro

August 12, 1974

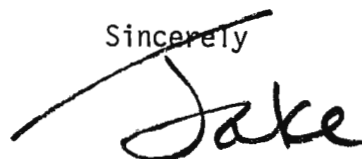
Pr(fod)<sub>3</sub>. The lower spectrum is that of a 300 hr. sample in CHCl<sub>3</sub>/C<sub>6</sub>F<sub>6</sub> (1:4) containing 0.26 equiv. of Pr(fod)<sub>3</sub>. In this case the signals are in order of increased shielding: endo-6,-8,-9-, exo-6 and 10-D. The fitting was done with 472 data points but only every second point is plotted. The three methyl signals were assigned by selective decoupling in the <sup>13</sup>C spectrum for which the three methyl carbons are readily assigned. This particular sample contained 1.94 atoms D by mass spectrometry which from the <sup>2</sup>H spectrum is distributed as C-6, 0.64 (endo) 0.65 (exo); C-8, 0.42; C-9, 0.16; C-10, 0.06. (For the 40 hr. sample: total D = 1.18; C-6, 0.38 (endo), 0.70 (exo), C-8, 0.10.)

The spectra were obtained on a XL-100-15 system operating at 15.4 MHz with an internal <sup>19</sup>F lock and proton noise decoupling. The normal Varian FT program was modified by Charlie Peters to permit one to get a listing of the signal intensity in each channel of the memory (or at any other desired interval). The paper tape produced is converted to a card deck by the PDP-10 and a Cyber 73 computer does the curve fitting iteratively. If one gets convergence, a mag tape is generated for the plotter to get the final display as illustrated in the Fig. It appears that this approach provides intensity data with precisions of the order of 1%. The method has been employed for a number of systems so far with good success; one example of which will appear shortly in JCS Chem. Comm., the homoenolization of adamantanone, which also illustrates the neat and unequivocal assignments provided by <sup>2</sup>H nmr.

I trust this will restore my "subscription" to the newsletter for another few months.

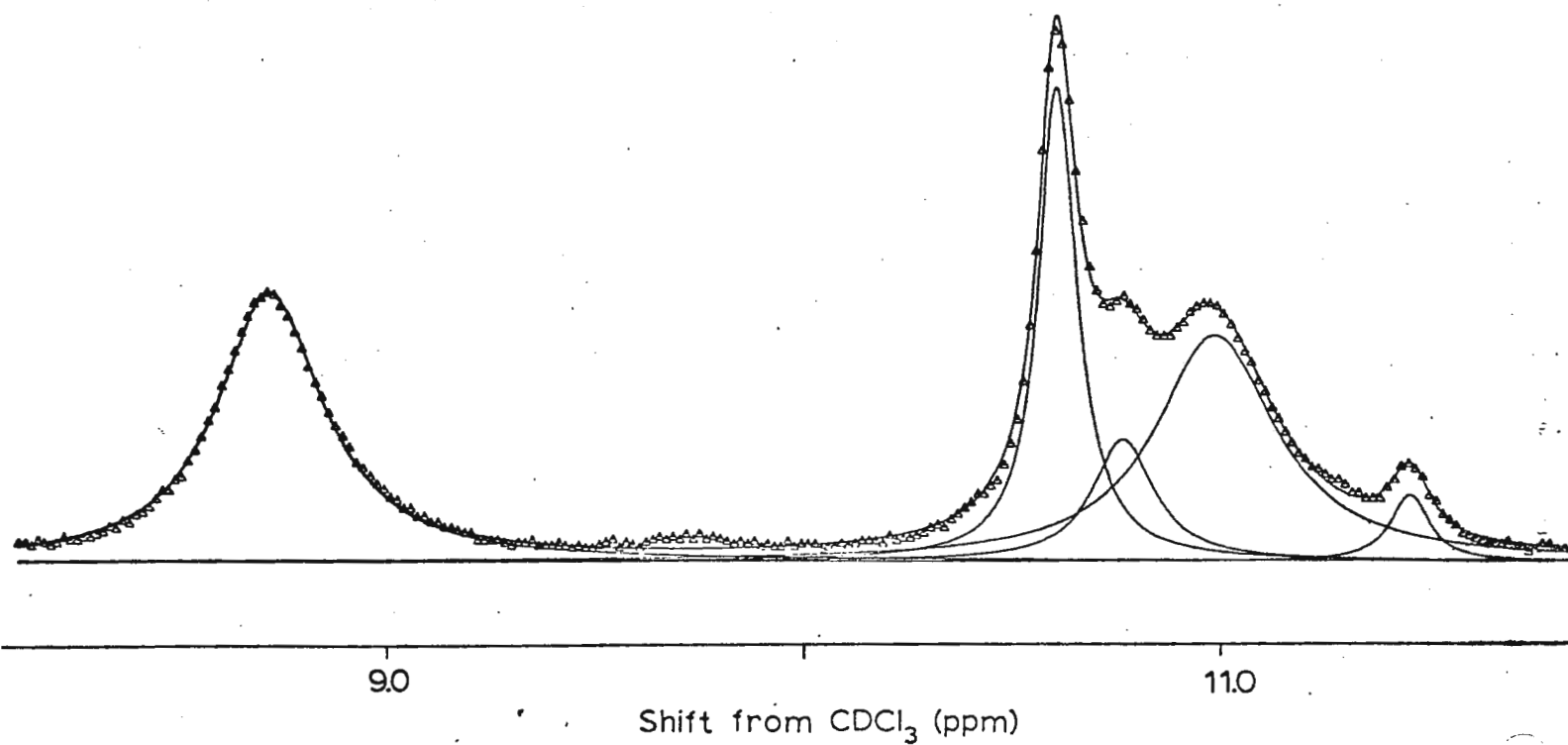
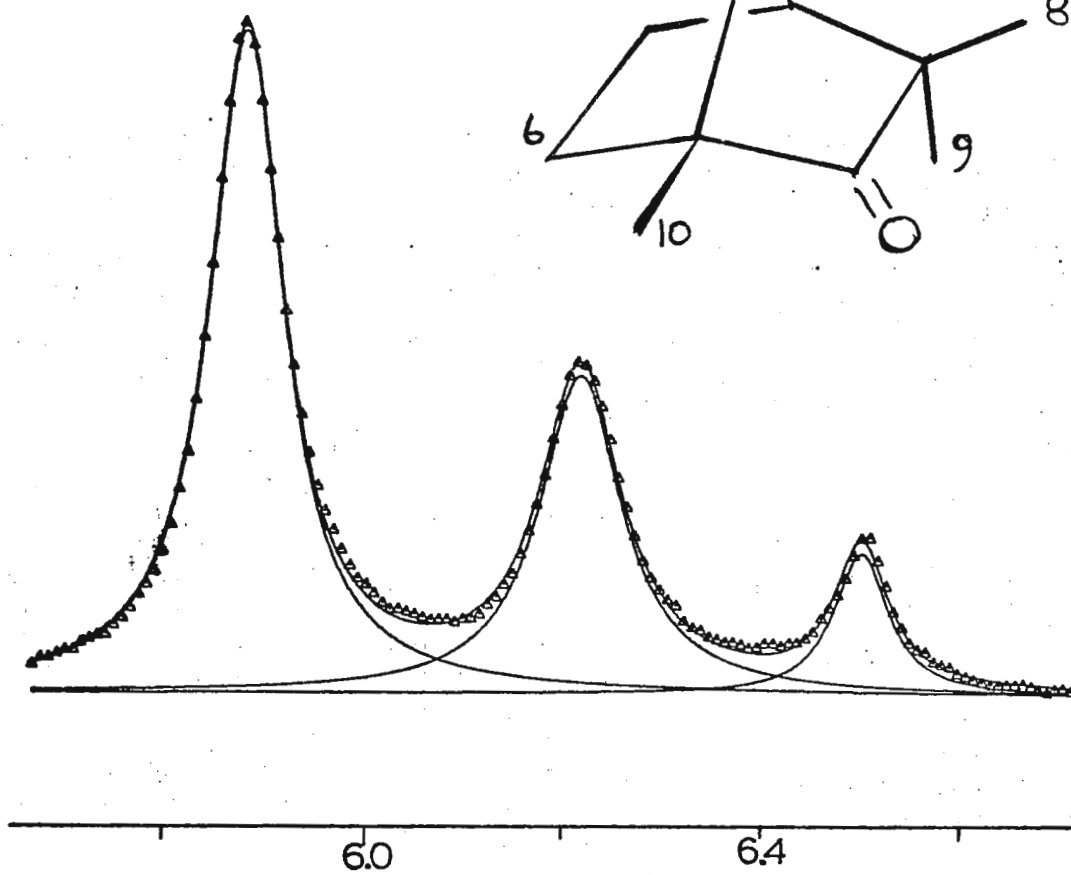
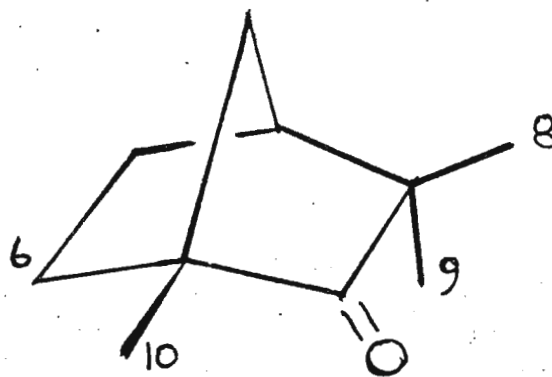
Best regards.

Sincerely



J. B. Stothers  
Professor of Chemistry

JBS/et





DEPARTMENT OF CHEMISTRY

TUFTS UNIVERSITY

MEDFORD, MASSACHUSETTS 02155

August 14, 1974

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

Title- "Report from Tufts; Request for PDP-11 Users"

Dear Barry:

As you can see from the letterhead, I have moved to Tufts as of this fall where I will be teaching and researching both Computers in Chemistry and Nmr problems. Our nmr equipment is currently an HA-100 and the inevitable, ubiquitous A-60. However, we do hope to add FT equipment as soon as we can find funds.

Our computer equipment is a PDP-11/40 with the lab front end (LDP) and 8K of core. I would be most happy to hear from people who are using a PDP-11 in nmr and would be willing to share their programs or from people who have a PDP-11 and would like to discuss its uses.

Sincerely,

James W. Cooper  
Assistant Professor



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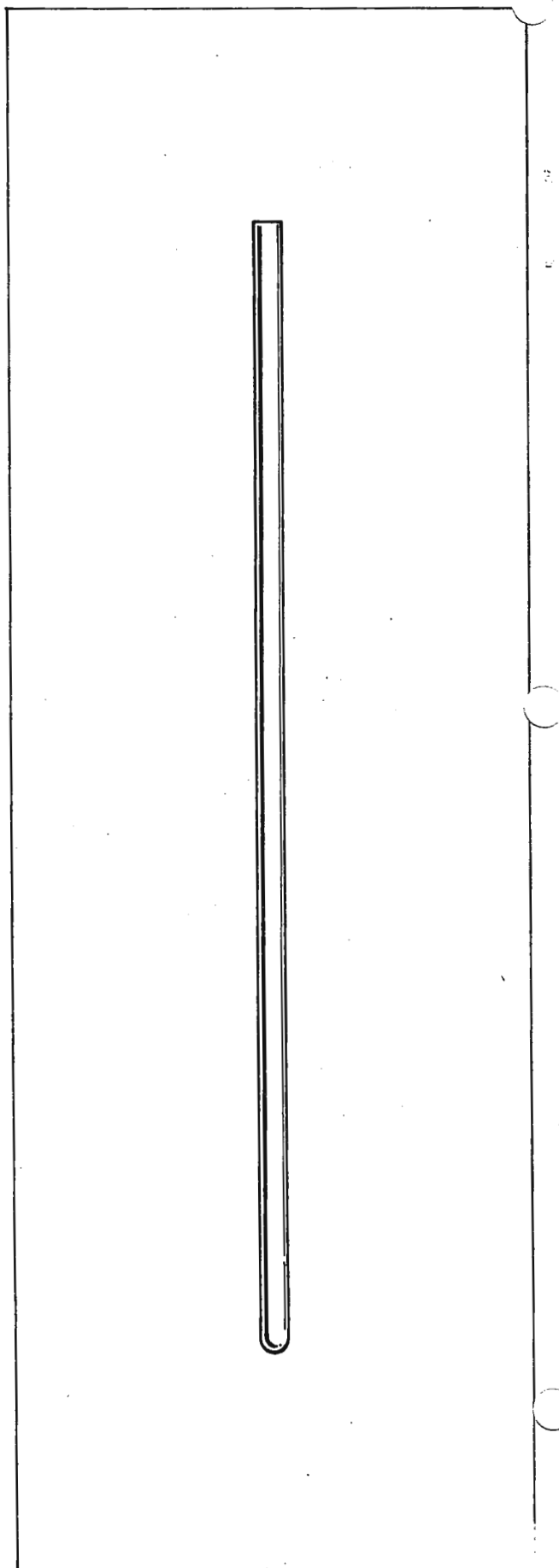
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## DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE  
NATIONAL INSTITUTES OF HEALTH  
BETHESDA, MARYLAND 20014

Building 2, Room 120

August 7, 1974

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

Dear Barry:

Effect of hydrogen bonding on  $^{13}\text{C}$   $T_1$ 's; Descendant of  
NMR Newsletter

It has been shown that intermolecular hydrogen bonding causes a shortening of the spin-lattice relaxation time of  $^{13}\text{C}$  in carboxylic acids<sup>1</sup> and in phenol<sup>2</sup>. Such a result would be expected for dipolar relaxation, since intermolecular H-bonding leads to the formation of larger molecular species with, presumably, longer rotational correlation times. In an attempt to investigate this process more quantitatively than has been done heretofore, Ed Tucker and I studied the relaxation of the carbinol carbon of tert-butanol. NOE results indicate that this carbon is relaxed primarily by dipolar interactions. We found that  $T_1$  (at 28°C) varies from 14 sec for the neat liquid to 50 sec in a 0.06 M solution in hexadecane- $\text{d}_{34}$  and increases to 90 sec in a 0.05 M solution in  $\text{CCl}_4$ . (The larger variation in  $\text{CCl}_4$  solutions results both from a greater viscosity difference between  $\text{CCl}_4$  and t-butanol and from a difference in the H-bonding equilibria.) For the  $\text{C}_{16}\text{D}_{34}$  solutions we had previously made extensive studies of the H-bonding equilibria of t-butanol.<sup>3</sup> This earlier work, using vapor pressure measurements, infrared spectroscopy and proton NMR chemical shift determinations, demonstrated that monomer, trimer and higher polymers are present, with negligibly small amounts of dimer. In fact, all these data can be very well represented by a monomer-trimer-hexamer model. Although this model is not necessarily the most reasonable physically, it is instructive to apply it to the  $^{13}\text{C}$   $T_1$  results. With the previously determined equilibrium constants and with the simplifying assumption that a single rotational correlation time  $\tau_c$  exists for each H-bonded species and is proportional to the molecular weight of the species, we can calculate the percentage of each species present at each measured total alcohol concentration and also the percentage contribution of each species to  $\tau_c$ , hence to the relaxation rate,  $R_1$  ( $\equiv 1/T_1$ ). The results are as follows:

Conc. M	Percentage Contribution						R <sub>1</sub> (calc.) sec <sup>-1</sup>	R <sub>1</sub> (obs.) sec <sup>-1</sup>
	1-mer		3-mer		6-mer			
	C	R <sub>1</sub>	C <sup>a</sup>	R <sub>1</sub>	C <sup>a</sup>	R <sub>1</sub>		
0.060	80	56	19	39	1	5	0.016	0.020
0.126	59	29	33	49	8	22	.023	.021
0.209	44	17	39	44	17	39	.029	.033
0.403	28	8	39	34	33	58	.037	.040
1.017	15	3	31	22	54	75	.047	.042
10.5 <sup>b</sup>	2	< 1	12	7	86	93	.071	.071

<sup>a</sup>Percentage of monomer units.<sup>b</sup>Neat liquid.

Prof. B. L. Shapiro  
August 7, 1974

Even at the lowest concentration studied, where monomer accounts for 80 per cent of the alcohol, the monomer contributes only a little over half of the relaxation. At higher concentrations the monomer contribution to  $R_1$  drops rapidly. The weighting of the various species is quite different for relaxation and for chemical shift: the former is analogous to the "weight-average molecular weight" often determined for polymeric systems, while the latter is analogous to the "number average molecular weight." The values headed " $R_1(\text{calc.})$ " give a one parameter least squares fit to the observed  $R_1$ 's. Our measured  $R_1$ 's show the predicted concentration dependence, but further data are needed for a more quantitative check. It does appear that relaxation times for  $^{13}\text{C}$  (and probably  $^2\text{H}$ , as well) should provide valuable information on H-bonding equilibria.

Turning to another subject, many readers of the NMR Newsletter may be aware that about six years ago we organized a Raman Newsletter, patterned in format and policies very closely after TAMUNMRN. The RNL has been well received and continues monthly publication. That Newsletter, in turn, has now served as the prototype for The Transform, a quarterly publication centered around Fourier transform infrared (edited by R. O. Kagel, Dow Chemical, and R. J. Jakobsen, Battelle). Perhaps it should be subtitled "Grandson of NMR Newsletter." In any event, Barry, you and Aksel certainly had a good idea many years ago when you started the NMR Newsletter, not only for NMR but for many other fields as well. Best wishes for continued success with TAMUNMRN and in indirectly siring progeny.

Sincerely,

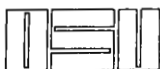


Edwin D. Becker, Chief  
Laboratory of Chemical Physics  
National Institute of Arthritis,  
Metabolism and Digestive Diseases

<sup>1</sup>T. D. Alger, D. M. Grant and J. R. Lyster, Jr., J. Phys. Chem. 75, 2539 (1971).

<sup>2</sup>(a) G. C. Levy, J. Mag. Res. 8, 122 (1972); (b) G. C. Levy, J. D. Cargioli and F. A. L. Anet, J. Amer. Chem. Soc. 95, 1527 (1973).

<sup>3</sup>E. E. Tucker and E. D. Becker, J. Phys. Chem. 77, 1783 (1973).



# Oklahoma State University

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

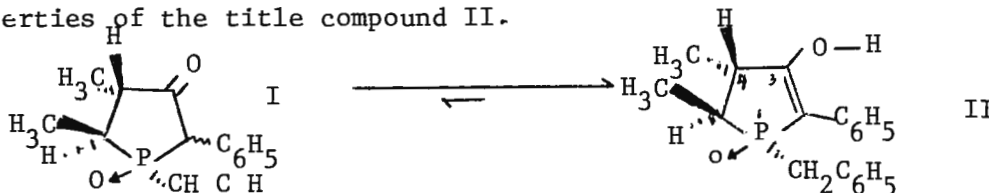
August 19, 1974

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

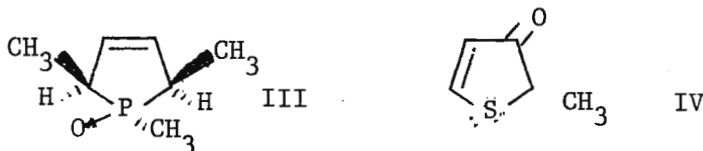
Title: NMR analysis of 1-Benzyl-2-phenyl-3-hydroxy-4,5-dimethylphosphol-2-ene-1-Oxide

Dear Dr. Shapiro:

We have just completed a rather thorough PMR and  $^{31}\text{P}$ PMR study of the properties of the title compound II.



In  $\text{DCCl}_3$  (with 4-5 drops of  $\text{F}_3\text{CCO}_3\text{H}$  added to achieve solution),  $^{31}\text{P}$ PMR analysis indicated a 22:78 ratio of I:II with  $\delta$  values at -57.7 and -51.6 (for cis and trans isomers) in I and -70.4 and -68.4 (for cis and trans isomers) in II (all relative to 85%  $\text{H}_3\text{PO}_4$ ). PMR analysis of the same type of solution showed  $J_{\text{HCCH}} = 7 \text{ Hz}$ ,  $J_{\text{PCH}} = 7 \text{ Hz}$  and  $J_{\text{PCH}_2} = 18.0 \text{ Hz}$ .<sup>1</sup> Thus, a trans arrangement of the  $\text{P} \rightarrow \text{O}$  group and the  $\text{C}-\text{H}$  bond at  $\text{C}_5$  is suspect in view of the  $J_{\text{PCH}} = 6.50 \text{ Hz}$  for III.<sup>2</sup> A recent X-ray analysis of solid II confirmed our initial diagnosis from NMR data.



Unfortunately, no example could be found of a related 3-ketotetrahydrothiophene analog. Interestingly, IV is reported<sup>3</sup> to exist in solution as a 1:4 ratio of the keto:enol forms.

We trust this will serve as our contribution.

Sincerely yours,

*K. D. Berlin*

K. D. Berlin, Regents Professor

1. Some enol in the solid state has been predicted for a series of phospholan-3-ones; see R. Bodalski and K. Pietrusiewicz, *Tetra. Letters*, 4209 (1972).
2. J. C. Breen, I. Featherman, L. D. Quin, and R. C. Stock, *Chem. Commun.*, 657 (1972).
3. A. B. Hörnfeldt, *Acta Chem. Scand.*, 19, 1249 (1965).



# Technische Hogeschool Delft

## Laboratorium voor Technische Natuurkunde

Magnetic Resonance Group

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

Uw kenmerk

Uw brief van

Ons kenmerk

Delft, Nederland, Lorentzweg 1, tel. 01730-33222

13th August 1974

toestel: 6041

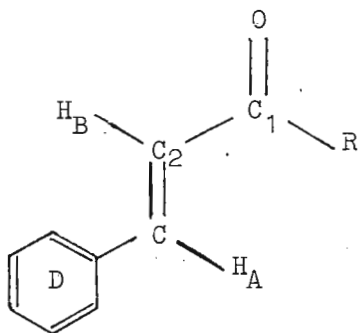
Onderwerp

Dear Professor Shapiro,

### Relaxation in AB systems

By means of the initial rate approximation technique<sup>(1)</sup>, the following relaxational parameters of the AB system I ( $J_{AB} = 16.3 \text{ Hz}$ ,  $\delta_{AB} = 60 \text{ Hz}$  at  $75 \text{ MHz}$ ) have been determined from the longitudinal relaxation rates,  $T_D$ ,  $T_{xA}$ ,  $T_{xB}$  and  $C$ .  $T_D^{-1}$  is the dipolar relaxation rate, resulting from the dipolar interaction between proton A and B.

The external relaxation (by external is meant: outside the AB system) is described by the random field model (1, 2).  $T_{xA}^{-1}$  and  $T_{xB}^{-1}$  are the relaxation rates of proton A, resp. B, caused by the external random field at the sides of A, resp. B, (H, resp. H'). The correlation factor  $C$  equals 1 if H and H' are completely correlated and  $C = 0$  if they are completely uncorrelated. The results are given in the table.



I R = CH<sub>3</sub>

II R = DCH<sub>3</sub>

III R = DCD<sub>3</sub>

	T (s)	$T_{xA}$ (s)	$T_{xB}$ (s)	C
25 mol%	43.5	11.5	21.3	0.33
15 mol%	58.3	15.1	26.8	0.28
7.5 mol%	65.8	17.0	32.8	0.22
infinite dilution in DCCl <sub>3</sub>	71.1	27.7	36.4	0.22

Because of the conjugated double bonds, the molecule will tend to have a planar configuration. If it is assumed that the molecular motion is isotropic, and if the correlation time for methylrotation,

resp. rotation about the  $C_1-C_2$  bond is much smaller, resp. larger than the overall molecular correlation time,  $\tau_c$ , one can calculate  $\tau_c$  from the  $T_1$  value of the  $CH_3$  group at infinite dilution;  $\tau_c = 1.44 \times 10^{-11}$  s. Substituting  $\tau_c$  in the expression <sup>(1)</sup> for  $T_D$  gives  $T_D = 71.2$  sec. At infinite dilution the external random fields  $H$  and  $H'$  consist only of the dipolar field produced by the methyl group. From the possible configurations of the molecule can be calculated that proton A is about 2.3 times more efficiently relaxed by the  $CH_3$  group than B. This is reasonably reflected in the values of  $T_{xA}$  and  $T_{xB}$ . The low value of  $C$  at infinite dilution is not in disagreement with calculations of Noggle <sup>(2)</sup>, if the internal motions of the molecule are taken into account. As the concentration increases intermolecular interactions will become more important and the value of  $C$  approaches to what is usually found for this interactions,  $C \sim 2/3$  <sup>(1,2)</sup>. From these results one might conclude that the random field model gives a reasonable description of the external relaxation of the AB systems. Preliminary measurements on compound II solved in acetone, unrealistic results are found.  $T_D$  differs an order of magnitude from the expected value, and  $C$  is about 1. In the moment two possible causes for this discrepancy are investigated. Firstly it is known that the random field model only can give an approximate description of the external relaxation <sup>(3)</sup>. Secondly, in strongly coupled spin systems with asymmetrical external relaxation, the initial rate approximation may give wrong time constants <sup>(4)</sup>. The results of the table may therefore be incorrect. To exclude the possible errors introduced by the initial rate approximation, the relaxational parameters are determined again by means of a kind of selective transient Overhauser effect, in which experiment the longitudinal relaxation of the line under investigation is single exponential. Next time I hope to report you about the results.

Still one remark about the longitudinal relaxation measurements. In the Freeman and Wittekoek way <sup>(1)</sup> selectivity is achieved by choosing the RF level so low, that only the line under investigation is perturbed. If the relaxation times become too short a higher RF level is desired. It is then often possible to raise it in such a way, that when a  $90^\circ$  or  $180^\circ$  pulse is applied to a certain time, the nearest line is turned  $n \times 360^\circ$  about its effective field in the rotating frame ( $n = 1, 2, 3, \dots$ ), while the other lines are practically undisturbed. In this way selectivity is maintained, if the height of the decay after a  $90^\circ$  sampling pulse is taken as a measure for  $M_z(t)$ .

#### References:

1. R. Freeman, S. Wittebroek, R.R. Ernst, J. Chem. Phys. 52, 1529 (1970)
2. J.H. Noggle, J. Chem. Phys. 43, 3304 (1965)
3. V. Sinivee, J. Magn. Res. 11, 143 (1973)
4. I.B. Campbell, R. Freeman, J. Magn. Res. 11, 143 (1973)

Please credit this contribution to Prof. J. Smidt, who received your blue reminder.

Sincerely yours,

W.M.M.J. Bovée



Eidg. Technische Hochschule  
Zürich-Hönggerberg

Institut für Molekularbiologie und Biophysik

CH-8049 Zürich

Prof. Dr. K. Wüthrich

Tel. (01) 57 57 70

8049 Zürich, July 29, 1974

KW/as

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

<sup>1</sup>H NMR OF THE BASIC PANCREATIC TRYPSIN INHIBITOR (BPTI)

Dear Barry:

Thank you for the blue reminder which I would like to answer with the following remarks to the above theme:

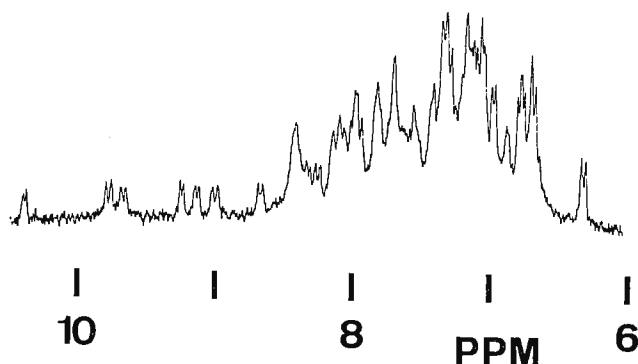
Recent investigations have shown that BPTI represents in many respects a model case for <sup>1</sup>H NMR studies of proteins. Here we would like to illustrate this point with an outline of the investigation of the exchange kinetics of the labile protons in BPTI.

Because of the small molecular weight (6'500), the <sup>1</sup>H NMR spectrum of BPTI contains a sizeable number of well separated lines, some of which also show resolved spin-spin coupling. Yet, in spite of the small size, the globular conformation of BPTI shows an unusual stability with respect to denaturation by heat or by chemical agents, and as a consequence it can be studied over a wide range of temperature and pH.

Measurements of the exchange rates of the labile protons in proteins have attracted considerable interest for studies of the solution conformations<sup>1)</sup>. The conventional methods used for these studies are infrared spectroscopy and tracer techniques with <sup>3</sup>H. Both these methods provide only information on the overall exchange of the labile protons. In BPTI <sup>1</sup>H NMR makes possible to investigate the exchange kinetics of a considerable number of individual protons which can under favorable circumstances be assigned to specific regions of the molecule. This promises to provide a quite detailed insight into the dynamics of the solution conformation of BPTI.



As is seen in the figure, BPTI contains 7 labile protons between 8,5 and 11 ppm which exchange sufficiently slowly at 87° to be observable as well resolved doublet resonances, and additional labile



Spectral region from 6 - 11 ppm of the 270 MHz  $^1\text{H}$  NMR spectrum of a BPTI solution in neutral  $\text{H}_2\text{O}$  at 87°C.

protons appear between 7,5 and 8,5 ppm. From their fine structure and their low field positions, most of these lines have been assigned to internally hydrogen bonded amide protons of the polypeptide backbone. At ambient temperature, a total of 25 slowly exchanging protons are observed in this spectral region<sup>2),3)</sup>, which corresponds approximately to the number of internal hydrogen bridges in the X-ray structure of BPTI. These spectral features have now been used to measure the rates of exchange of these protons with  $^2\text{D}$  of  $\text{D}_2\text{O}$  at 22° and 45° in a series of solutions covering the pH range from 0.1 to 7.4. As for random coil peptides, the plots of exchange rate vs. pH pass through a minimum<sup>1)</sup>, the position of which varies for the individual protons between pH 2.7 and 4.6. The protein conformation is, however, markedly manifested in the absolute rates of exchange, and in the overall profile of their pH dependence. Four groups of protons with markedly different exchange kinetics could be distinguished. This, the observed spin-spin coupling constants, and comparison with the X-ray structure have led to tentative assignments of most of the amide proton resonances to specific positions in the polypeptide chain, so that the different accessibility for contact with the solvent of individual segments of the polypeptide chain in the globular conformation of BPTI can be clearly demonstrated.

Sincerely yours,

*Peter Sehr*

*G. Wagner*

*K. Wüthrich*

#### References

Peter Sehr

Gerhard Wagner

K. Wüthrich

- 1) A. Hvidt and S.O. Nielsen, Adv. Protein Chem. 21, 287 (1966)
- 2) A. Masson and K. Wüthrich, FEBS Letters 31, 114 (1973)
- 3) S. Karplus, G.H. Snyder and B.D. Sykes, Biochemistry 12, 1323 (1973)

Prof. Dr. P. Diehl

Dr. S. Šykora

J. Vogt

Prof. B.L. Shapiro

Texas A &amp; M University

College of Science

Department of Chemistry

COLLEGE STATION, Texas 77843

U.S.A.

"Automatic Analysis of high resolution NMR spectra?"

Dear Barry,

The analysis of high resolution NMR-spectra by computer is known to be a tedious and time consuming problem. This is particularly true for oriented molecules of low symmetry for which there may be up to five unknown and unpredictable order parameters. Obviously for such cases a trial and error method will fail.

This obstacle prompted us to again study the problem of spectral analysis and to try to ascertain whether there exists a possibility to analyse spectra with little or no preknowledge of parameters, such that a complete automation of the process could become possible.

We started with the idea that the computer should be able to analyse spectra similarly to the spectroscopist i.e. it should compare a trial spectrum as a whole with the experimental spectrum, trying to reproduce progressively its rough as well as its fine features until the two spectra coincide.

Such an approach would mean that the spectrum must be transformed into a set of figures each of which carries information on the whole spectrum. We proceeded as follows:

The spectral intensity  $I(\omega)$  as a function of the frequency  $\omega$  is transformed as below

$$\mathbb{I} \{f(\omega)\} = \int_{-\infty}^{+\infty} I(\omega) f(\omega) d\omega$$

where  $f(\omega)$  is a family of functions  $f_1(\omega), f_2(\omega), \dots, f_n(\omega)$ , called the basis. The resulting  $n$  numbers  $\mathbb{I} \{f_i(\omega)\}; (i=1, 2, \dots, n.)$  are functions of the spectral parameters. Vice versa when a suitable basis is chosen, the transforms generated from the experimental spectrum can be used to determine the unknown parameters. For this determination a least square fit is adopted. Obviously for such a fit no interpretation of the spectrums is required. In principle the starting parameters may be random.

This brief outline, however, conceals many problems as e.g. choice of the basis, occurrence of spurious local minima, rate of convergence, sensitivity to experimental errors etc. We are still fighting with these problems but as we have some success we hope to be able to publish soon a more detailed preliminary paper on this subject.

Yours sincerely,

*Peter* *Stan Sykora*  
P. Diehl S. Sykora J. Vogt



## DEPARTMENT OF CHEMISTRY

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McGILL UNIVERSITY

P.O. BOX 6070, STATION 'A', MONTREAL, QUE., CANADA H3C 3G1

August 21, 1974.

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

Diamagnetic Contribution to  $^{13}\text{C}$  Chemical Shifts

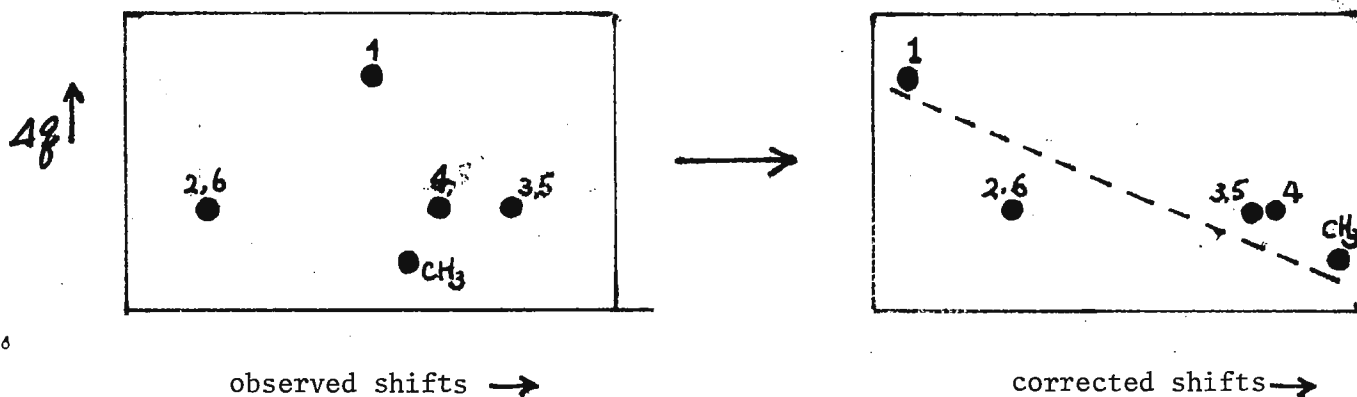
Dear Dr. Shapiro:

The contribution of the diamagnetic shielding term for  $^{13}\text{C}$  nucleus which arises from the rest of the atoms in a molecule has been evaluated for a variety of mono- and di- substituted cyclohexanes and cyclopentanes. Substraction of this portion of the diamagnetic term from the observed  $^{13}\text{C}$  chemical shift yields a corrected shift<sup>1</sup>, which shows a better linear correlation with the charge density on the carbon atom than does the observed shift.

The average diamagnetic shieldings were calculated by the formula proposed by Flygare and Goodisman<sup>2</sup>:

and the charge densities were calculated by various methods including those of Del Re<sup>3</sup>, Extended Huckel<sup>4</sup> and CNDO/2<sup>5</sup>.

Typical examples are illustrated below for 1,1 dimethyl cyclohexane.



Professor B.L. ShapiroAugust 21, 1974


It has been shown in a number of instances that charge density is the dominant factor determining the observed  $^{13}\text{C}$  shifts<sup>6</sup>, but this does not seem to hold true for compounds without electronegative groups. It is reasonable to obtain the improvement in the linear relation between the charge density and the corrected  $^{13}\text{C}$  chemical shift when charge independent diamagnetic terms were subtracted from the observed shifts. For various other methylcyclohexanes, linear correlations were found to be improved by a factor of two in terms of the average vertical deviation from their best fit lines.

With methylcyclohexanols and methylpentanols, which have hydroxyl groups, a good linear relation already exists without a diamagnetic correction being made but, nevertheless, a significant improvement in the order of chemical shifts with respect to that of the charge density was found for almost all of the compounds when the correction was applied.

It appears, therefore, that the diamagnetic term accounts in large measure for  $^{13}\text{C}$  chemical shift differences between diastereomers. Calculations show, similarly, that it may account importantly for the more strongly shielded  $^{13}\text{C}$  nuclei of six-, than of the related five-membered ring alicyclic compounds.

1. J. Mason, J. Chem. Soc., 1038(1971).
2. W.H. Flygare and J. Goodisman, J. Chem. Phys., 49, 3122(1968).
3. G. Del Re, J. Chem. Soc., 1031(1958).
4. R. Hoffman, J. Chem. Phys., 39, 1397(1963).
5. J.A. Pople and M. Gordon, J. Amer. Chem. Soc., 89, 4253(1967).
6. e.g. H. Spiesecke and W.G. Schneider, Tetrahedron Lett. 468(1961).

Sincerely,

  
N. Cyr

NC/ce

Institut für Organische Chemie  
Laboratorium Niederrad  
Universität Frankfurt am Main

6 Frankfurt/M., 23.8.1974  
Sandhofstr.  
Telefon: (0611) 6301 - 6033

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

Dear Professor Shapiro,

Title: Problems Involved in the Sample-Temperature Determination  
in Proton Decoupled  $^{13}\text{C}$ -DNMR Measurements.

The reliability of NMR line-shape results essentially depends  
on the accuracy of the temperature measurements <sup>1,2)</sup>.

During  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR measurements at our Bruker-HX 90 and  
temperature control unit B-ST 100/700, we realized that the  
displayed temperature corresponds to the actual temperature  
in the probe only in cases of low decoupling power.

At one instant the following temperature values were determined:

$^1\text{H}$ -decoupling power (dB)	temperature (K) measured		
	in the gas flow with copper- constantan thermocouple a)	in the NMR tube with Hg- thermometer b)	alcohol- thermometer b)
16	362	313	308
18	337	309	306
20	320	305	304
22	311	<b>303</b>	<b>303</b>

a) thermocouple not optimized (see text).

b) bulb adjusted to the middle of the coil.

Our usual power for off-resonance proton decoupling is  $\approx 22$  dB, for wide-band  $\approx 18$  dB.

The values were measured at constant gas flow (Nitrogen at room temperature without any temperature adjustment). At high gas flow rates even an independence of the temperature of the medium in the NMR tube was observed (air;  $\text{CDCl}_3$ ;  $\text{H}_2\text{O}-\text{D}_2\text{O}$  1:1)

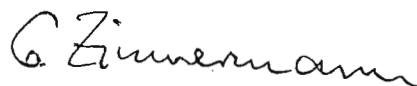
The values in the second column also depend on the length of the unshielded tip of the thermocouple and are also strongly affected by the geometrical location of the end loop of the thermocouple to surrounding coils. Rotation about an angle of  $180^\circ$  results in a maximum and a minimum of the temperature display.

Obviously the unshielded tip of the thermocouple which is located in the gas flow under the tube, can act as an antenna for the magnetic fields of the decoupler coil and / or its connections. We adjusted the thermocouple exactly on a minimum temperature and found that only in this position the temperature display is independent of the  $^1\text{H}$ -decoupling power.

In this case the temperatures measured by the thermocouple are in good agreement with the values of column four (alcohol thermometer), while decreasing the temperature below room temperature results reproducible increasing deviations between an alcohol thermometer (in the sample) and the temperature display unit.

Please, credit this contribution to H. KESSLER.

Yours sincerely



G. ZIMMERMANN

1) H.S. GUTOWSKY, TAMU Newsletter 186, 25 (1974).

2) G.J. MARTIN and M.L. MARTIN, TAMU Newsletter 188, 13 (1974).



Ul. Vavilova, 32  
Moscow V-312  
USSR

August 23 , 1974

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

Title: Detection of Protein  
Stimulated Intermembrane  
Phospholipid Exchange by NMR

Dear Barry,

The dependence of the lanthanide (e.g.  $\text{Pr}^{3+}$ ) ions induced shifts in the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra [1,2] on the phospholipid composition of the vesicles has been used for studying phospholipid exchange stimulated by soluble proteins from rat liver (postmicrosomal supernatant fraction - PSF).

The magnitude of the  $\text{Pr}^{3+}$  induced  $^{31}\text{P}$  signal shift (lowfield) of the outwardly facing phosphatidylcholine (PC) molecules in the co-sonicated PC-phosphatidylinositol (PI) vesicles linearly depends on the PI content (Figure). In this case of co-sonicated mixture the shift does not depend on incubation with PSF. We have also shown that the PI distribution between the outer and inner monolayers is the same.

Now we have prepared a 98:2 mixture of separately sonicated PC (65  $\mu\text{M}/\text{ml}$ ) and PI vesicles. Then it was incubated for 5 hrs at  $50^\circ\text{C}$  with 5 mg/ml of PCF and just before recording the  $^{31}\text{P}$  spectrum  $10^{-3}$  mM/ml of  $\text{Pr}(\text{NO}_3)_3$  has been added. The induced shift shown by filled circle on the Figure is evidently larger than for co-sonicated 98:2 mixture. Thus: 1) the PI molecules are incorporated in the PC vesicles with the help of PSF phospholipid exchanging proteins, 2) the vesicles do not become permeable for  $\text{Pr}^{3+}$  ions during incubation with PSF and 3) the apparent PI concentrations is higher in the obtained PC-PI vesicles than in the co-sonicated sample. The latter demonstrates that an asymmetric bilayer structure has been formed. Simple calculation in the assumption that PC-PI co-sonicated vesicles are symmetrical shows that in the outer monolayer a relative PI content is 2.8 % and in the inner one - only 0.6%. In other words nearly 90% of PI turned to be located at the outer surface of the vesicle bilayer.

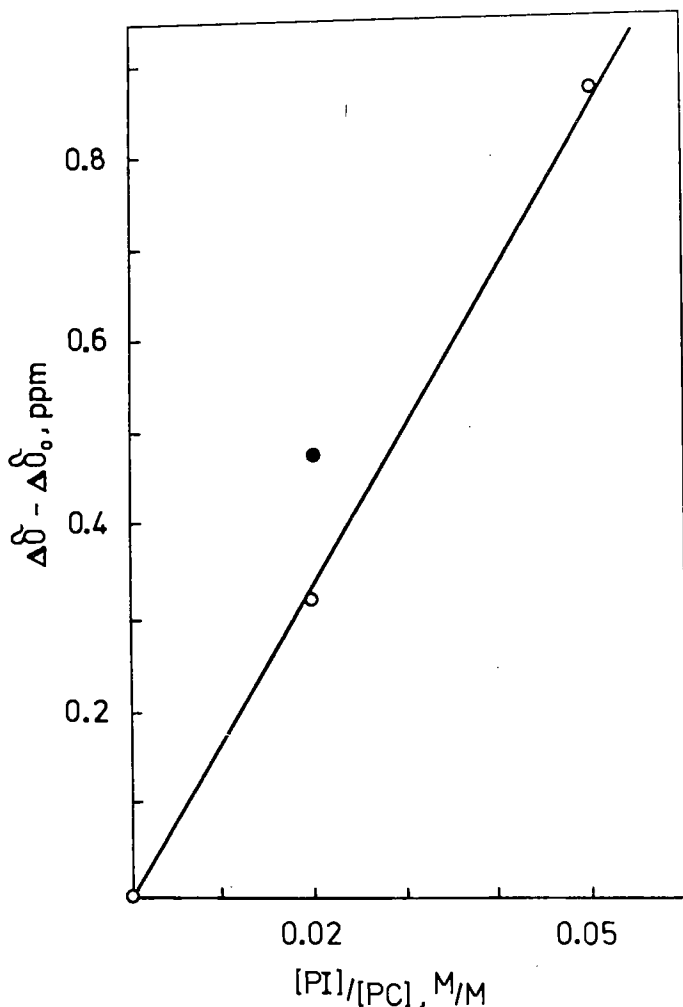


Figure.  $\text{Pr}^{3+}$  "extra", induced shift ( $\pm 0.01$  ppm) of the "outer" phospholipid molecules  $^{31}\text{P}$  signal for co-sonicated PC-PI water dispersion at various PI content (open circles). The shift at  $[\text{PI}] = 0$  is 0.28 ppm lowfield. Filled circle - see text. (Varian XL-100-15, 40.5 MHz, proton noise decoupling,  $^2\text{D}$  heavy water internal lock, 12 mm tubes, FT 1000 scans, pulse interval 9 sec.)

This study is in progress in collaboration with Prof. L.D. Bergelson and Drs. L.I. Barsukov, Yu.E. Shapiro, A.V. Viktorov and V.I. Volkova.

Sincerely yours,

*Vladimir*

1. TAMU NMR Newsletters: 156 -1 (1971), 166 -24 (1972).
2. The above cited teem: Dokl. Acad. Nauk SSSR (Russian) 194, 220 (1970); Chem. Phys. Lipids 6, 343 (1971); FEBS Letters 25, 377 (1972); Biophysika (Russian) 19, 463 (1973).

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: תאריך / DATE August 27, 74: מספרנו / OUR REF.

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

Dear Professor Shapiro,

Coalescence Measurements, Again: A Simple Method for the Evaluation of  
Coalescence Rate Constants of Exchanging AB Systems

We have calculated and plotted (Figure) rate constants at coalescence ( $k_c$ ) against widths at half height ( $W_{1/2}$ ) of the coalescence spectra of exchanging AB spin systems with various chemical shift differences and coupling constants. From this plot  $k_c$  values can easily be interpolated.

The experimental parameters necessary are  $W_{1/2}$ , which is measured from the coalescence spectrum, and  $J_{AB}$ , which is temperature independent and can be measured at the slow exchange limit.  $\Delta\nu_{AB}$ , which cannot be measured at the coalescence temperature, and is usually extrapolated from a rather ill defined plot of  $\Delta\nu$  against temperature, is not used as an experimental parameter in the present method. This method will replace the use of the approximate equation:  $k_c = (\pi/\sqrt{2})\sqrt{(\Delta\nu^2 + 6J^2)}$ , that has been shown (1) to be valid only within certain limits. It is based on complete line shape analysis, and is expected to yield  $\Delta G^\ddagger$  values as accurate as the latter method.

In spite of the many arguments used against coalescence measurements, we feel that the method proposed here can be used satisfactorily in all simple AB exchange experiments. (2)

Yours sincerely,

*Daniel Kost*

Daniel Kost.

(1) D. Kost, E. H. Carlson and M. Raban, Chem. Commun., 656 (1971).

(2) We have used a value  $T_2 = 0.4$  throughout the calculations.

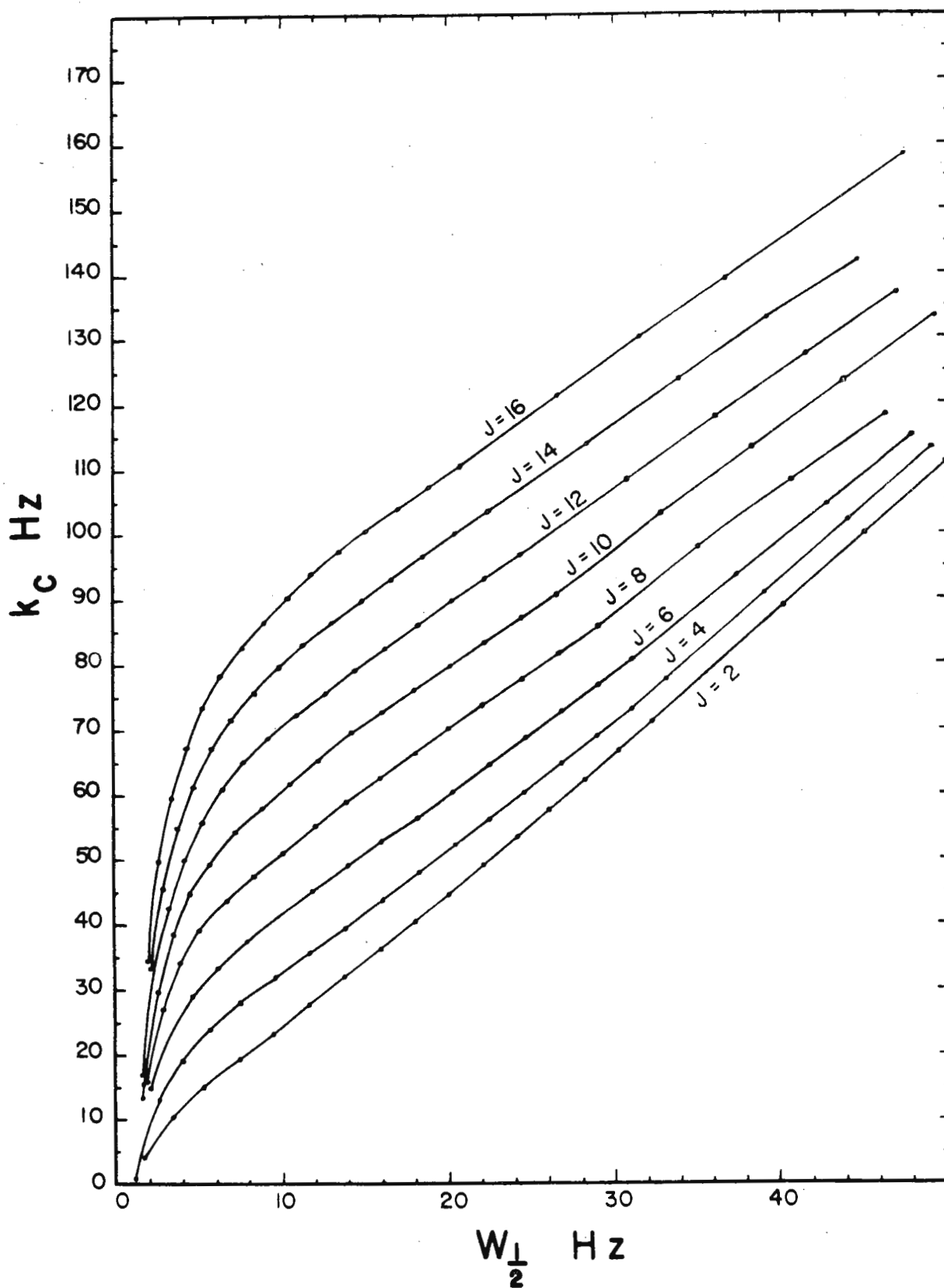


FIGURE: A plot of rate constants against line widths at half height at the coalescence of exchanging coupled nuclei. ( $J_{AB}$  expressed in Hz).

**NTE** NICOLET  
TECHNOLOGY  
CORPORATION

300 Pioneer Way  
Mountain View, California 94041  
Phone: 415/969-2076  
(formerly Transform Technology Inc.)

Title: 75% pure trimethylphosphite

Aug. 28, 1974

Dear Barry,

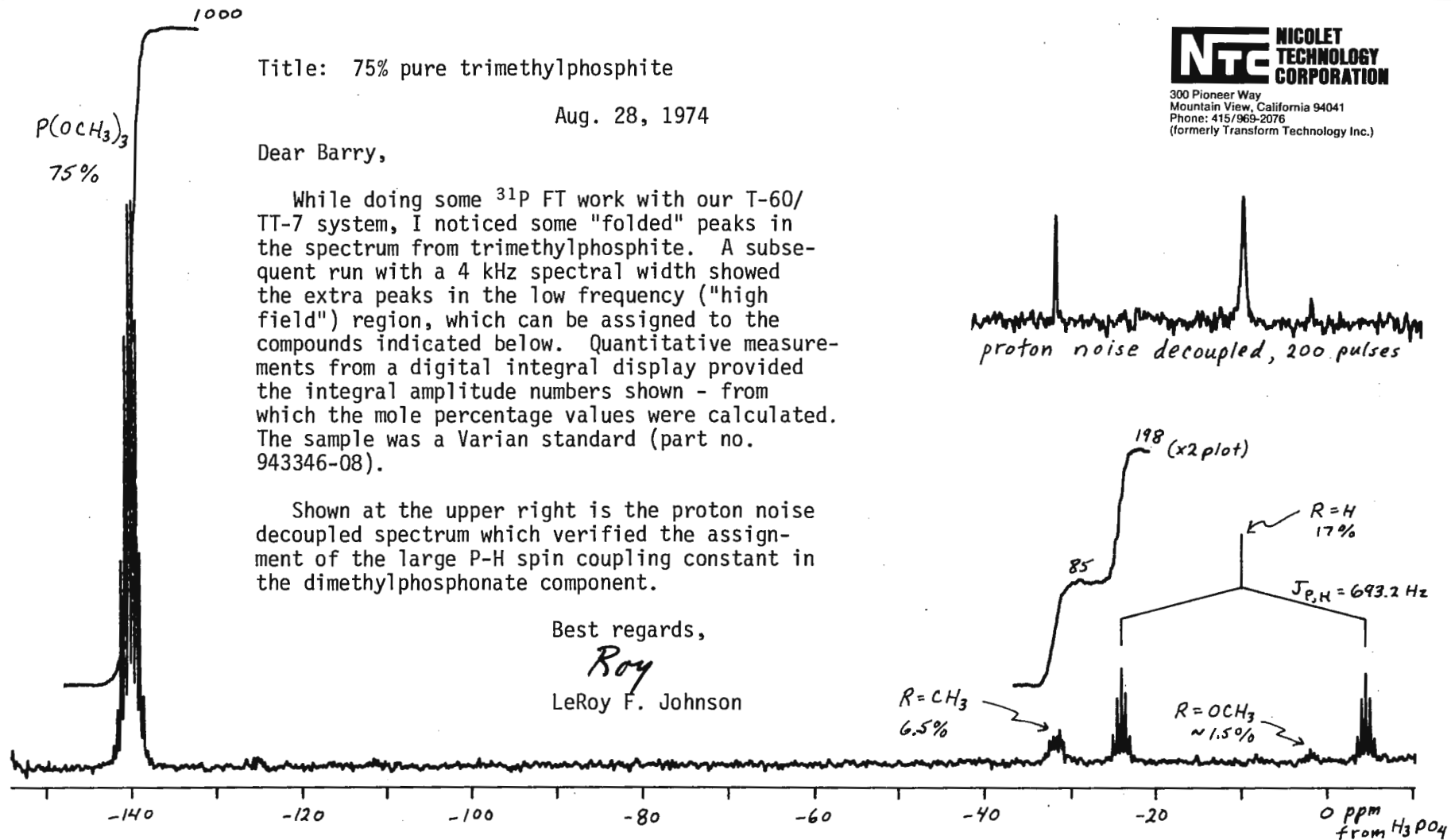
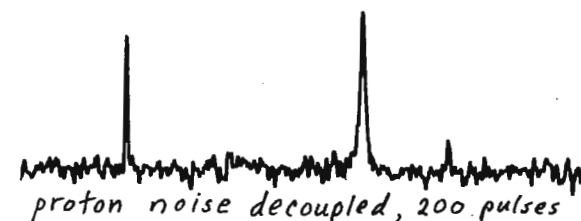
While doing some <sup>31</sup>P FT work with our T-60/TT-7 system, I noticed some "folded" peaks in the spectrum from trimethylphosphite. A subsequent run with a 4 kHz spectral width showed the extra peaks in the low frequency ("high field") region, which can be assigned to the compounds indicated below. Quantitative measurements from a digital integral display provided the integral amplitude numbers shown - from which the mole percentage values were calculated. The sample was a Varian standard (part no. 943346-08).

Shown at the upper right is the proton noise decoupled spectrum which verified the assignment of the large P-H spin coupling constant in the dimethylphosphonate component.

Best regards,

*Roy*

LeRoy F. Johnson



<sup>19</sup>F 56.4Hz PPM

<sup>31</sup>P 24.3Hz PPM

WIDE SWEEP OFFSET	-140	PPM	SWEEP TIME	SEC
SWEEP OFFSET	-14	PPM	SWEEP WIDTH	PPM
SPECTRUM AMPLITUDE			FILTER	
INTEGRAL AMPLITUDE			RF POWER LEVEL	
SPINNING RATE		RPS	NUCLEUS <sup>19</sup> F <input type="checkbox"/> <sup>31</sup> P <input checked="" type="checkbox"/> <sup>11</sup> B <input type="checkbox"/> <sup>13</sup> C <input type="checkbox"/>	

DATE 8 Aug 74 OPERATOR *PJG*

SAMPLE trimethylphosphite  
plus  
 $O=P(OCH_3)_2$   
R R=H, CH<sub>3</sub>, OCH<sub>3</sub>

SOLVENT none

SW = 4000 Hz, Plot = 4000 Hz  
BK f.i.d., LB = 2 Hz, PW = 10 usec  
AT = 1.024 sec, PD = 0.5 sec  
600 pulses (15 minutes)

14.1KG NMR  
SPECTRUM NO.



E. I. DU PONT DE NEMOURS & COMPANY  
INCORPORATED

WILMINGTON, DELAWARE 19898

August 28, 1974

CENTRAL RESEARCH DEPARTMENT  
EXPERIMENTAL STATION

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

Chemical Shift Assignments in the  $^1\text{H}$  Spectra of  
Symmetrical Ortho-disubstituted Benzenes

The proton spectra of symmetrical ortho-disubstituted benzenes are the well known AA'BB' patterns, which can be readily analysed using computer techniques to give chemical shifts and coupling constants. However, since these patterns are centrosymmetric about the mean chemical shift of the A and B nuclei, the chemical shifts cannot be assigned from the proton spectrum alone. This can be done from known substituent effects, but in the case of substituents with unknown effects, an absolute method is needed.

Recently Gunther, Schmickler and Jikeli (2) reported that the splitting patterns for the uncoupled  $^{13}\text{C}$  NMR resonances of such molecules differ characteristically for the  $\alpha$  and  $\beta$  carbon atoms, giving "fingerprints" which can be used for assignment. In the uncoupled spectra, each protonated carbon appears as a doublet ( $J \sim 160$  Hz). Each component of the  $\beta$ -carbon doublet is itself a doublet, while each component of the  $\alpha$ -carbon doublet is more complex. This was observed for several molecules and computer simulations show it is insensitive to small changes in J-values but that the separation between the protons must be at least 10 Hz.

Once the  $^{13}\text{C}$  resonances of a symmetrical orthodisubstituted benzene have been assigned in this manner, selective  $^1\text{H}$  decoupling of the  $^{13}\text{C}$  spectrum can be used to establish connections between the two spectra. This enables the two halves of the AA'BB' pattern to be definitely assigned. This technique was tested out with orthodichlorobenzene and is being used in the analysis of the  $^1\text{H}$  and  $^{13}\text{C}$  spectra of polynuclear aromatics.

*Derick W. Ovenall*

Derick W. Ovenall

1. Contribution No. 2189, Central Research Department
2. H. Gunther, H. Schmickler and G. Jikeli, J. Mag. Res. 11, 344 (1973)

UNIVERSITY OF MINNESOTA  
TWIN CITIES

Department of Chemistry  
139 Smith Hall  
Minneapolis, Minnesota 55455

September 5, 1974

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

Re: POSITION AVAILABLE

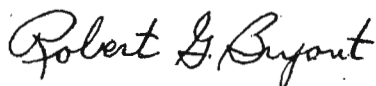
Dear Barry:

A person experienced in high resolution nmr is needed to run an nmr service laboratory as a Research Associate primarily for University users in the Chemistry Department. Experience in chemistry and capability in electronics are desirable. Equipment includes Fourier transform XL-100, several 60 MHz spectrometers and new ESR Equipment when funded. Twelve month salary is negotiable.

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Sincerely,



Robert G. Bryant  
Associate Professor  
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Using the insert, it's possible to run spectra of 50  $\mu\text{g}$  or less of sample. Spectra run thusly are obtained in less than 17 minutes, yet are superior to 8-hour runs in a 5-mm tube. Sensitivity for a fixed amount of sample can improve from 4- to 6-fold when the 1-mm Insert Accessory is used.

The two spectra of  $\Delta^9$ -tetrahydrocannabinol (THC) shown here demonstrate the dramatic results possible using the 1-mm Insert. Spectrum A, of a concentrated sample in a 5-mm tube, serves as a comparison for the other spectra. Spectrum B (20  $\mu\text{g}$  of sample in a 1-mm tube) and Spectrum C (20  $\mu\text{g}$  of sample in a 5-mm tube) were run under identical conditions. Note the well-defined peaks in the spectrum run using the 1-mm Insert.

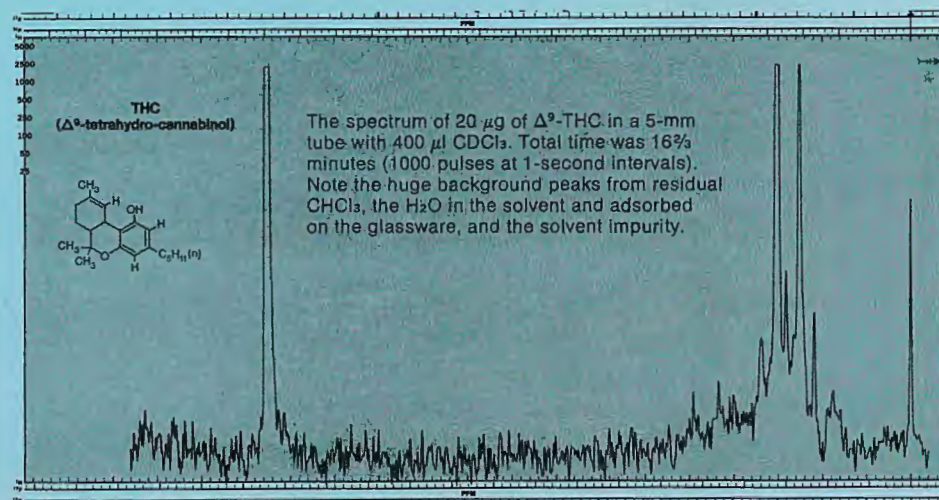
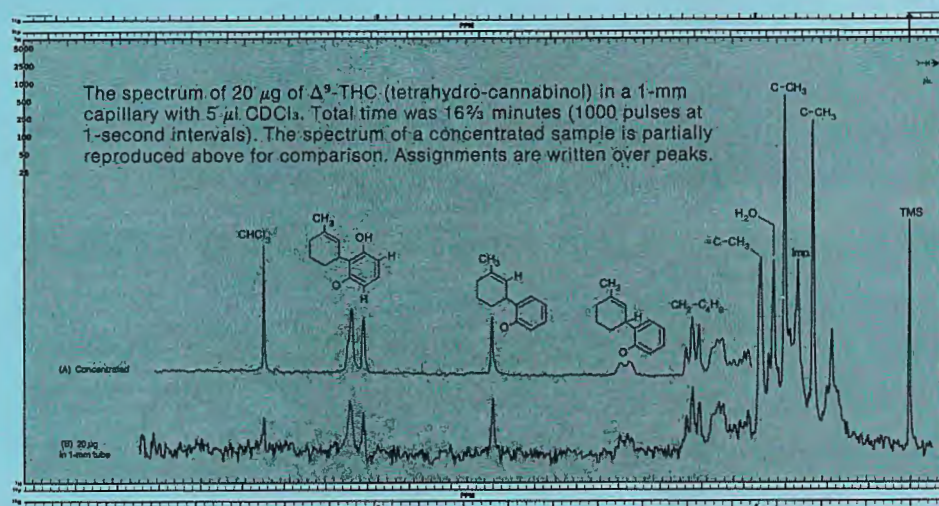
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To interchange the 1-mm Insert with standard XL-100A inserts, merely take one out, put in the other, retune and balance. The sample is dissolved in 5  $\mu\text{l}$  of an NMR solvent containing TMS for a reference. It is then transferred into a 1-mm sample tube by using a drawn out glass pipette or a hypodermic syringe. This eliminates the bubble problems which sometimes arise with the use of microcells in larger tubes. The resulting column length is about 10 mm, assuring freedom from line shape distortion. Since spinning produces no vortex, spinning speed is not a critical factor.

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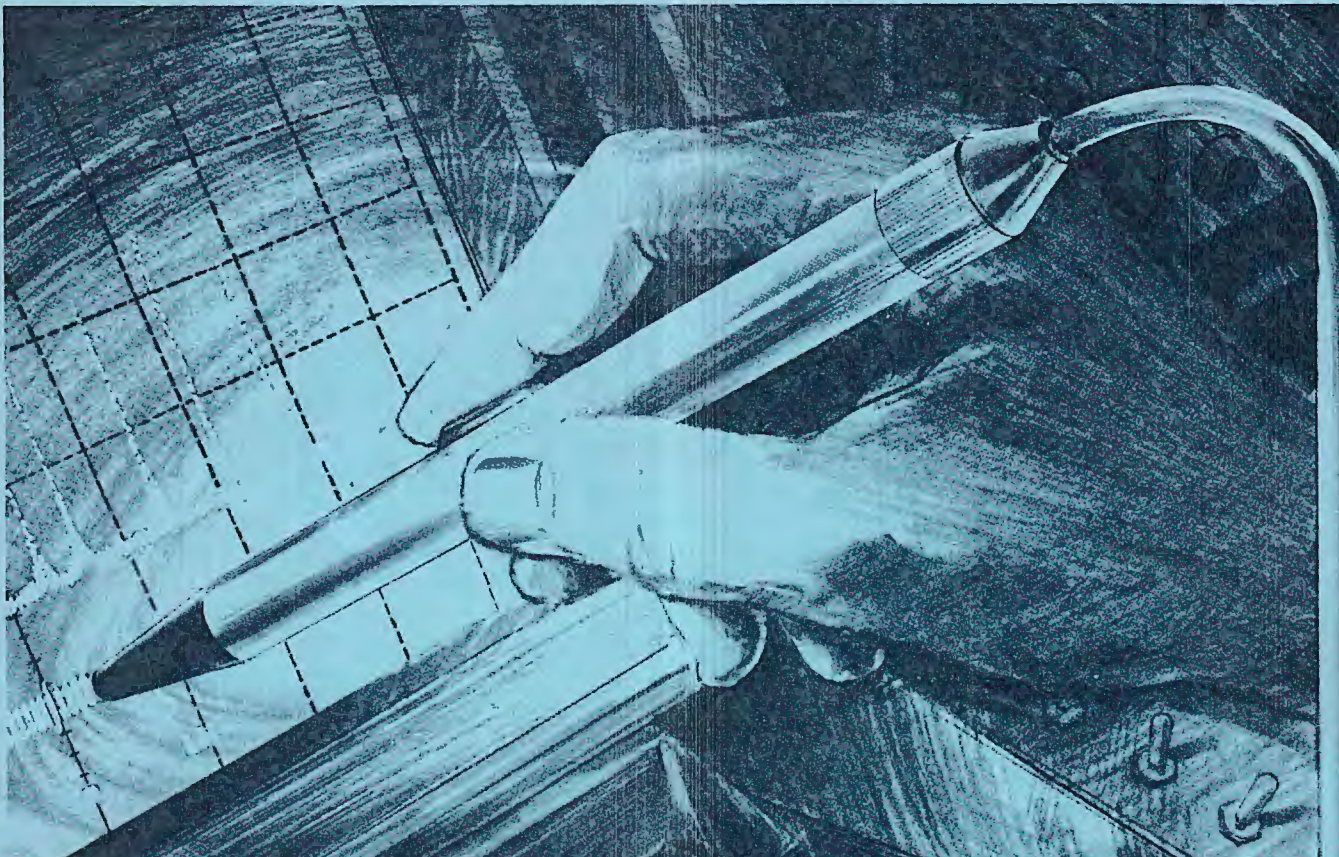
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