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Newsletter

No. 178

July, 1973

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Deadline Dates: No. 179: 6 August 1973 No. 180: 3 September 1973
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All Newsletter correspondence, etc. should be addressed to:

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

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DIVISION OF BIOLOGICAL SCIENCES  
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OUR FILE  
NOTRE DOSSIER

June 13, 1973.

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

THREE CHEERS FOR  $^2\text{H}$  NMR; CALL FOR REPRINTS AND PREPRINTS

Dear Barry,

For the last several years we have been trying to convince our chemical colleagues that  $^2\text{H}$  NMR was well worth doing. In doing so we were merely reiterating the points made by Diehl and Leipert (1). Recently Ed Randall and co-workers have demonstrated this again with some very nice work on  $^2\text{H}$  in natural abundance (2). We would like to report here our own study of a biological system using  $^2\text{H}$  NMR. The details will appear subsequently (3).

Our object is to study biological membranes by biosynthetic incorporation of specifically-deuterated probe molecules. As a test of the viability of the experiment we have looked at a deuterated lauric acid derivative  $\text{C}^2\text{H}_3-(\text{CH}_2)_9-\text{C}^2\text{H}_2-\text{COOH}$  in vesicles of the phospholipids known as egg lecithin. Some spectra are shown in the Figures. In the multilamellar vesicles, Figure A, only the natural abundance  $^2\text{H}$  water resonance is observable. On sonication to single bilayer vesicles, the  $\text{C}^2\text{H}_3$  resonance shows up with a line width of 17 Hz, Figure B. This line narrowing on sonication has already been observed by  $^1\text{H}$  NMR (4). Successive additions of cholesterol, which have been demonstrated by spin label experiments to result in reduced fatty acid chain mobility (5), give successively broader lines, Figures C and D. The derived correlation times for reorientation of the  $\text{C}^2\text{H}_3$  group (no cholesterol,  $1.2 \times 10^{-9}$  sec.; 20 mole % cholesterol,  $4.4 \times 10^{-9}$  sec.) are in nice agreement with those estimated from the spin label results (5). With our recently acquired Fourier transform capability, we can also measure  $T_1$ 's for the probes. This gives us a better estimate of the correlation times.



We are now busily growing microorganisms on media enriched in deuterated lipids, and we hope in our next report to describe the  $^2\text{H}$  NMR spectra of living cells.

We are presently writing a review of  $^2\text{H}$  NMR for Progress in NMR Spectroscopy. In order to be as comprehensive and up-to-date as possible, we would appreciate reprints or preprints of any  $^2\text{H}$  measurements that have been made. The closing date for receipt of this material is September 1, 1973.

Yours sincerely,

*Ian*

Ian C.P. Smith,

*Hazime Saitô*

Hazime Saitô,

*SSM for SSM.*

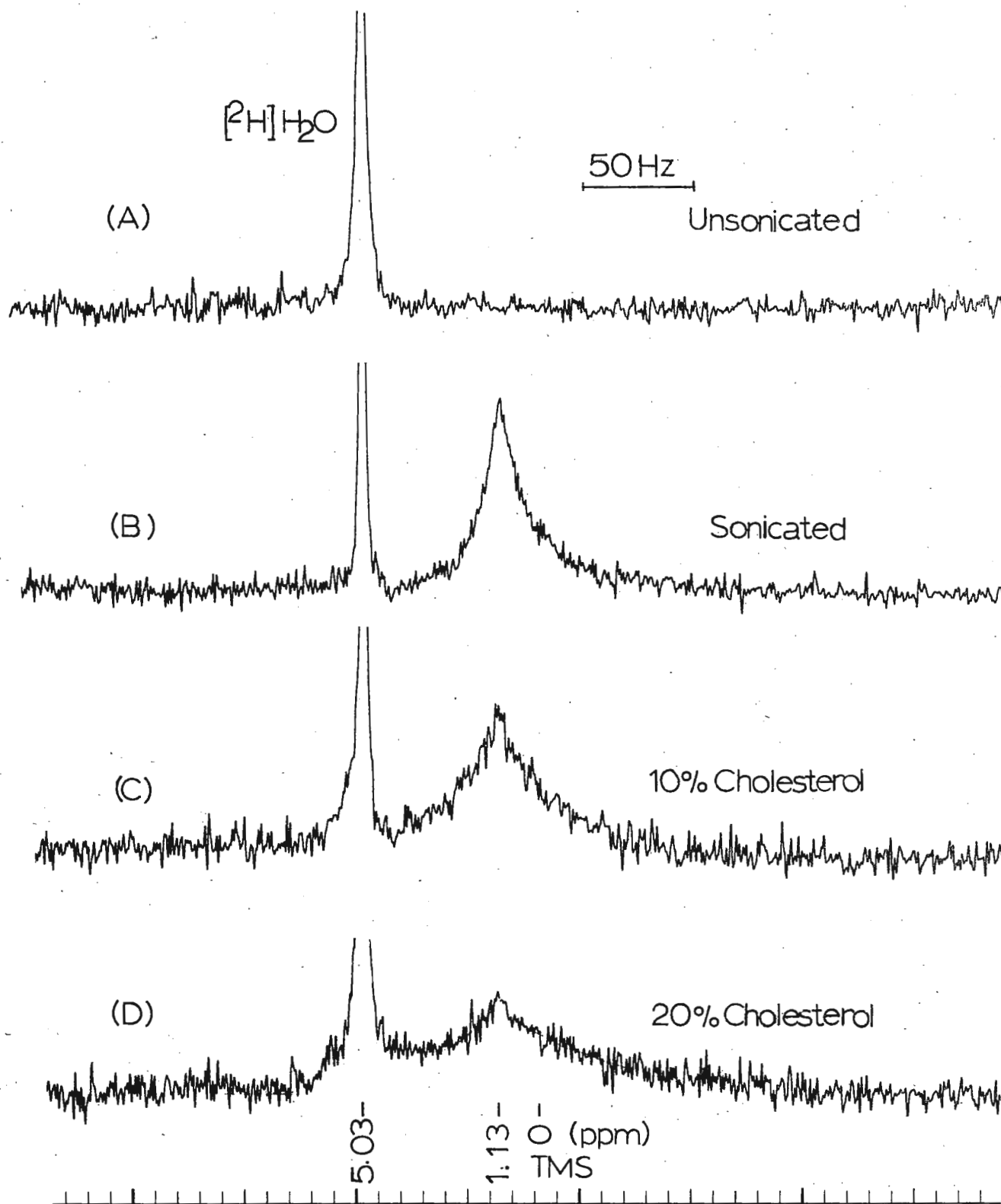
Shirley Schreier-Muccillo.

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Figure captions      Fourier-transformed  $^2\text{H}$  NMR spectra (Varian XL-100) of the  $\text{C}^2\text{H}_3$  group of the lauric acid probe (20mM) in dispersions of egg lecithin (195 mM) in  $\text{H}_2\text{O}$  (3).

- A. Unsonicated; 19,755 transients.
- B. Sonicated; 35,468 transients.
- C. Sonicated, 10 mole % cholesterol; 20,172 transients.
- D. Sonicated, 20 mole % cholesterol; 62,289 transients.





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95125 CATANIA (ITALY) - TEL. 338317

Catania, li June 5, 1973

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

Dear Professor Shapiro:

Conformational study of 2,2'-dipyridyl disulphide

The  $^1\text{H}$  n.m.r. spectra at 60 MHz of the title compound have been registered in MeOH (from  $38^\circ$  to  $-65^\circ$ ) and in  $\text{CDCl}_3$  (from  $38^\circ$  to  $-35^\circ$ ).

The attached table shows that the spectra are markedly affected by the change of temperature in both the solvents used. The listed spectral parameters were obtained by the use of the LAOCN3 computer programme. The complete spectral analysis at the reported temperatures has shown that magnetic equivalence between corresponding protons of the pyridine rings occurs in the disulphide under examination. Such an equivalence, however, cannot be verified at temperatures below  $-50^\circ$ . At these temperatures, in fact, the spectra result as a superposition of spectral patterns which correspond to several different conformations about the C-S bonds.

The above n.m.r. evidence as well<sup>py</sup> as previous dipole moment studies (1) confirm that "free rotation" about these bonds occurs in 2,2'-dipyridyl disulphide.

CNDO/2 type calculations (2) predict as favoured the planar cis-cis (I), cis-trans (II) and trans-trans (III) conformations. The small difference between the energies of these forms and the low barrier to the interconversion among these conformers (about 12 Kcal/mole) evaluated by the method allow us to consider that free rotation is also termodinamicamente possibile for this disulphide.

Sincerely,

*G.C. Pappalardo*

Dr. G.C. Pappalardo

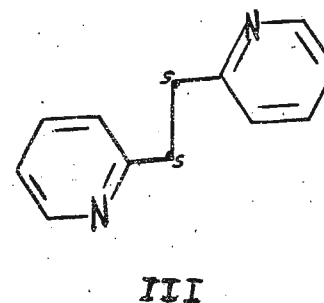
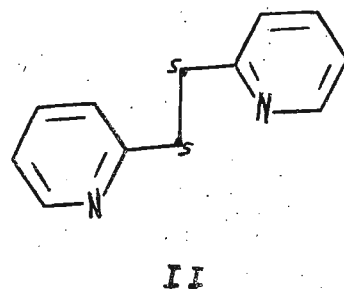
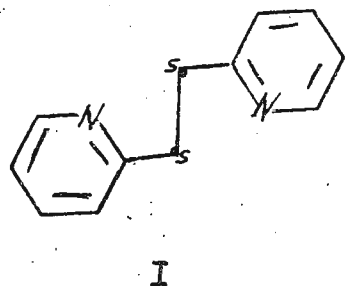
(1) G.C. Pappalardo et al., J.C.S. Perkin II 1973, in print.

(2) " " " " " " , submitted for publication



<sup>1</sup>H N.m.r. spectral parameters for 2,2'-Dipyridyl disulphide at variable temperature.  
The mean square deviations (RMS) for the calculated and experimental lines are given.

Temp.	Solvent	Chemical shifts ( $\delta$ , p.p.m. downfield from TMS)				Coupling constants (Hz)						RMS
		H-3	H-4	H-5	H-6	J <sub>34</sub>	J <sub>35</sub>	J <sub>36</sub>	J <sub>45</sub>	J <sub>46</sub>	J <sub>56</sub>	
38°	MeOH	8.353	7.188	7.676	7.616	4.789	1.652	0.970	7.626	0.726	7.933	0.035
-5°	MeOH	8.379	7.262	7.751	7.655	4.702	1.685	0.938	7.199	1.278	7.797	0.031
-30°	MeOH	8.414	7.305	7.815	7.673	5.525	1.648	0.875	5.321	1.571	7.699	0.043
38°	CDCl <sub>3</sub>	8.361	7.053	7.530	7.558	4.421	1.558	0.744	7.640	1.069	7.571	0.040
-30°	CDCl <sub>3</sub>	8.514	7.224	7.720	7.658	4.735	1.716	0.964	5.844	2.305	7.845	0.042



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43, Bd DU 11 NOVEMBRE 1918  
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TÉL. (78) 52.07.04 ~~et 52.12.29~~

Lyon, le 3 Juin 1973

Cher Professeur SHAPIRO,

{<sup>35</sup>Cl} - <sup>1</sup>H N.M.D.R. observation.

Nous avons modifié la sonde de notre spectromètre HA 100 pour la double résonance hétéro<sup>nucléaire</sup> des noyaux suivants : <sup>2</sup>D, <sup>14</sup>N et <sup>35</sup>Cl. Les tests de découplage du deutérium (dans CHD<sub>2</sub>CN) et de l'azote 14 (dans CHONH<sub>2</sub>) ont été satisfaisants.

Pour tester l'irradiation du chlore 35 nous avons utilisé le trichlorosilane SiHCl<sub>3</sub> dont la raie protonique est élargie par couplage scalaire avec les noyaux de chlore.

En effet le temps de relaxation de Cl-35 ( $T_1 = T_2$ ) obtenu en bande large pour ce produit, est de 125  $\mu$ S à 20°C. C'est un temps relativement long si on le compare aux 35  $\mu$ S mesurées dans le chloroforme à la même température, (W.T. Huntress Jr J. Phys. Chem. 73, 103, (1969)), et c'est ce qui peut expliquer l'élargissement de la raie du proton.

L'irradiation, à la fréquence du chlore 35 (9,7983 MHz) affine la raie protonique, la largeur de raie à mi-hauteur passant de 0,95 Hz à 0,75 Hz. Le champ d'irradiation qui n'est pas rigoureusement constant sur le volume de l'échantillon était en moyenne de 6 Gauss dans cette expérience ( $\gamma_{35\text{Cl}} \cdot H_2 \approx 2500$  Hz).

Nous avons observé que l'effet s'accroissait lorsque la puissance du champ radiofréquence était augmentée.

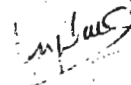
Actuellement nous portons nos efforts sur les points suivants :

- mesure précise de H<sub>2</sub>
- augmentation de l'efficacité de l'irradiation du chlore 35.
- irradiation de l'isotope <sup>37</sup>Cl qui doit être plus délicate à mettre en évidence en raison de la moindre abondance.

Pour toutes ces irradiations nous n'utilisons qu'une seule bobine (6 tours) montée sur un support en porcelaine. cf (G.J. LONG et A.G. MORITZ Molecular Physics 15, 439, (1968)).

Pour chaque noyau un circuit d'adaptation par capacité est fixé à l'arrière de la sonde qui a été percée et munie d'une prise H.F. Le corps de la sonde est refroidi par ~~azote~~ azote détendu, procédé simple et efficace.

Recevez, cher Monsieur, nos sentiments les meilleurs.



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## PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY  
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June 15, 1973

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

Dear Barry:

TITLE: NEW  $^1\text{H}$ -NMR PEAKS IN SPECTRA OF TRYPSIN AND SOYBEAN TRYPSIN INHIBITOR.

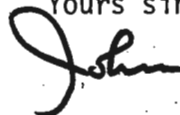
It is always news when those of us who do NMR spectroscopy of proteins find new, assignable peaks to study. We have recently been investigating "virgin" and "modified" (the timid official nomenclature for not-virgin) trypsin inhibitors and their interaction with trypsin. In the case of soybean trypsin inhibitor, we found that cleavage of the Arg<sup>63</sup>-Ile<sup>64</sup> peptide bond (by trypsin modification) raises the pK of a single histidine residue by 0.64 (1). This change is sufficient to explain some puzzling results in the literature concerning the pH dependence of the virgin - modified STI equilibrium and the  $\Delta H$  of the modification reaction. It was reassuring to find that trypsin modification of ovomucoid, another trypsin inhibitor which does not exhibit these anomalies, has little effect on the histidine pK values (2). We are presently assigning these and other protein histidine C2-H peaks (3).

Our latest new peaks are presented in the accompanying figures. Figure 1 shows  $^1\text{H}$ -NMR spectra of soybean trypsin inhibitor at pH 5.5 in D<sub>2</sub>O (a) and H<sub>2</sub>O (b). The two histidine C2-H peaks are labeled H1 and H2. Two broad peaks are visible in the tryptophan N-H region (4) in H<sub>2</sub>O solution. These are labeled W1 and W2. Peak W1 persists (for a while) in D<sub>2</sub>O solution. Soybean trypsin inhibitor has only two tryptophans, in positions 93 and 117 (5). Furthermore, it is known that Trp<sup>117</sup> is reactive whereas Trp<sup>93</sup> is not (6). We thus suspect that W1 = Trp<sup>93</sup> and W2 = Trp<sup>117</sup>. Peak W1 corresponds to an "important" residue in that chemical modification of the buried tryptophan renders soybean trypsin inactive (7).

The recent observation of a low-field D<sub>2</sub>O-exchangeable resonance in spectra of bovine chymotrypsin in H<sub>2</sub>O attributed to the "change relay" His-NH (8) prompted us to look at spectra of trypsin, another serine protease which is believed to have a similar active site. As Figure 2 illustrates, a peak in the histidine NH region ( $\delta$  15.23) of porcine trypsin is observed at pH 2.9 in H<sub>2</sub>O (b) but not in D<sub>2</sub>O (a). However, the peak disappears above pH 4 under the conditions of this experiment (c). The disappearance is probably the result of exchange broadening and seems to indicate, along with the higher chemical shift of the peak, that the hydrogen bond that this trypsin proton participates in is weaker than that of the chymotrypsin proton. The peak at  $\delta$  11.34 shifts upfield as the pH is lowered from 2.8 to 2.0.

probably as a result of a conformational transition. Additional peaks in the histidine NH region of trypsin show up below pH 2.

Yours sincerely,



John L. Markley  
Assistant Professor

JLM:Th  
Enclosure

P.S. Please credit this contribution to the Purdue account in Professor N. Muller's name.

### References

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7. R. F. Steiner, Arch. Biochim. Biophys. **115**, 257 (1966).
8. G. Robillard and R. G. Shulman, J. Mol. Biol. **71**, 507 (1972).

### Captions

Figure 1. 250 MHz cross-correlation spectra of 1.4 mM soybean trypsin inhibitor in 0.5 M KCl containing 0.05 M  $\text{CaCl}_2$ : (a). in  $\text{D}_2\text{O}$ , pH\* 5.51; (b). in  $\text{H}_2\text{O}$ , pH 5.51.

Figure 2. 250 MHz cross-correlation spectra of 2 mM porcine trypsin in 0.5 M KCl: (a). in  $\text{D}_2\text{O}$  pH\* 2.83; (b). in  $\text{H}_2\text{O}$ , pH 2.89 (c). in  $\text{H}_2\text{O}$ , pH 4.08.

### Acknowledgement

The 250 MHz cross-correlation spectra were taken at the NMR Facility for Biomedical Studies, Carnegie-Mellon University, supported by NIH Grant R 00292. I thank Drs. J. Dadok and R. E. Sprecher for their generous assistance in gathering this data.

Figure 1

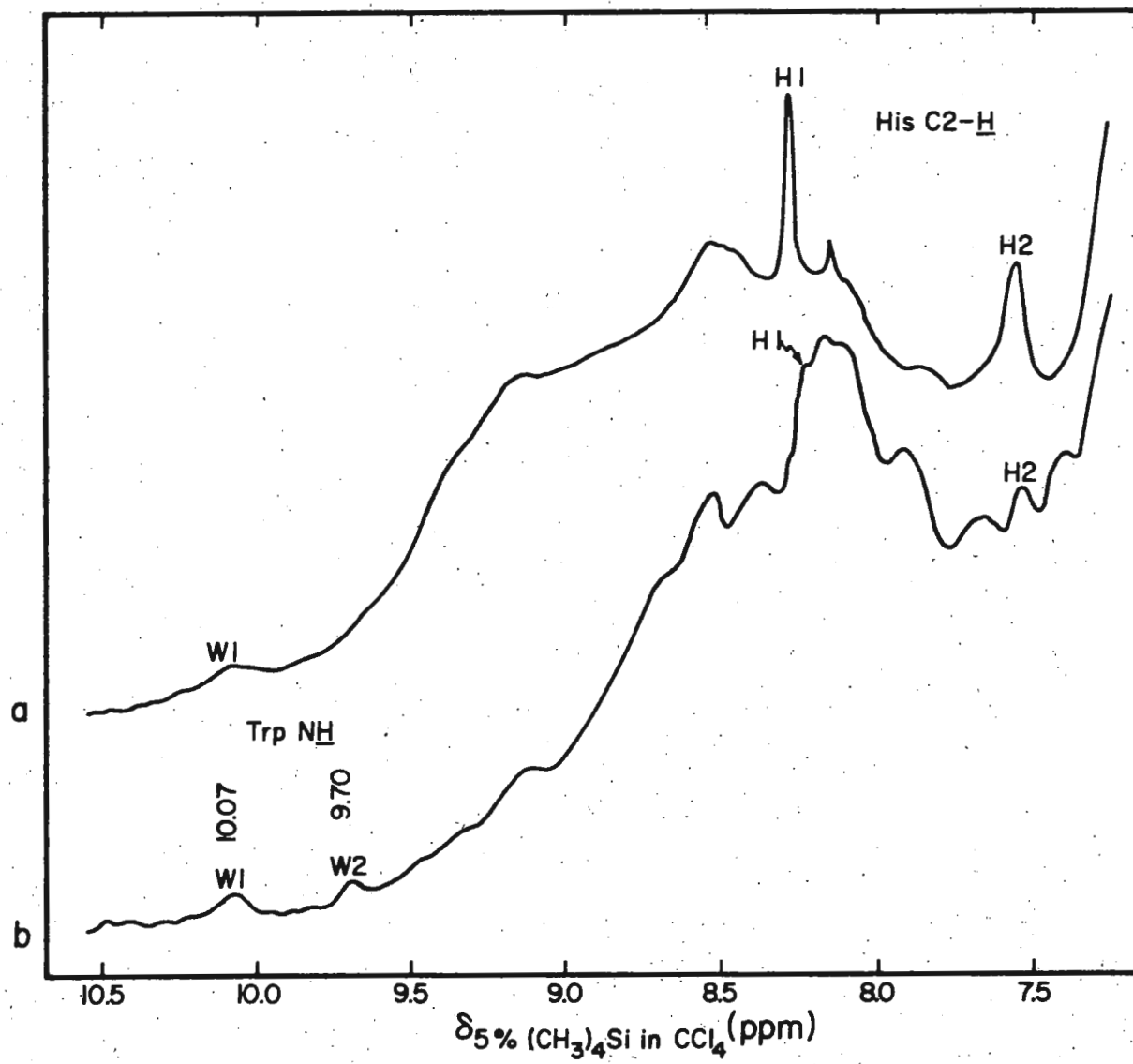
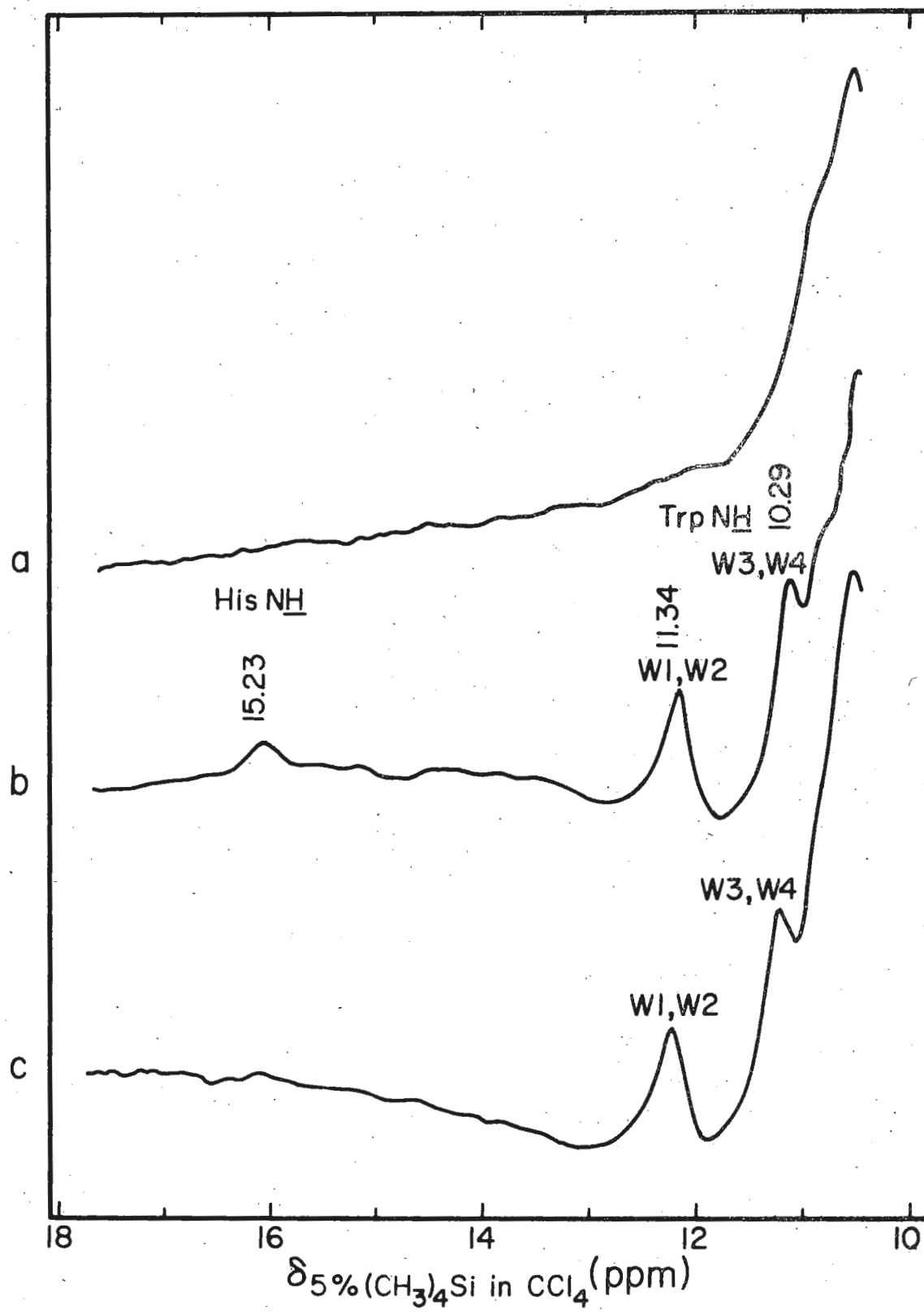




Figure 2





Eidgenössische Technische Hochschule Zürich  
Laboratorium für Organische Chemie

CH-8006 Zürich,  
Universitätstrasse 6/8 7 June 1973.  
Tel. (01) 32 62 11

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

Comments on the Automatic Determination of Carbon Number by C-13 NMR

Dear Prof. Shapiro

We are of the opinion that artificial intelligence programs like the one described by Ochiai and Sasaki in TAMUNMR letter 175-28 work satisfactory in straightforward cases (cf. example given there). It is precisely here that the computer is of little help because the solution is readily found by hand. In complicated cases, however, artificial intelligence programs are prone to the same mistakes as is the analyst who favors off-hand answers; thereby, the machine apparently corroborates false conclusions.

We would like to present an example that cropped up in our routine laboratory work which we think would present insurmountable difficulties to any program along these lines. We have lately come across a compound with the molecular formula  $C_{13}H_{22}O$ . Its spectrum, recorded under routine conditions is given in Fig. 1 (solvent:  $CD_3OD$ ). As it shows only 11 signals (there are no signals above 80 ppm), either 2 signals must correspond to 2 carbons, or 1 signal must correspond to 3 carbons. Another spectrum was recorded with, as far as routine work is concerned, unreasonably long interwalls between successive pulses (Fig. 2). The total accumulation time was about one order of magnitude larger here than with the spectrum presented in Fig. 1. Due to the absence of saturation effects in this second run, it can be conclusively shown that the small signal at 55 ppm in the routine spectrum corresponds to 3 carbons. We seriously doubt that an artificial intelligence program would be capable of extracting this information from spectrum 1.

Yours sincerely

J. T. Clerc

H. P. Meier

E. Pretsch

*J. T. Clerc*

*H. P. Meier*

*E. Pretsch*

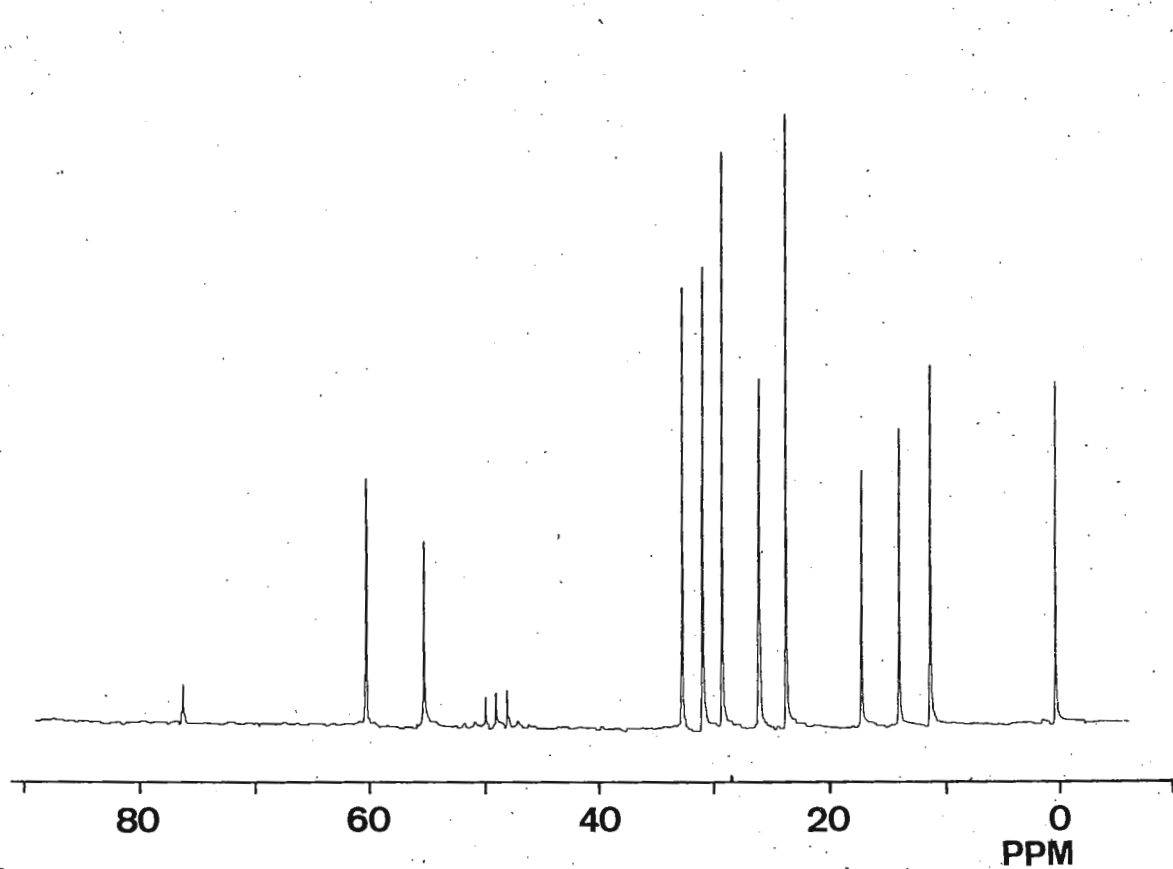


Fig. 1

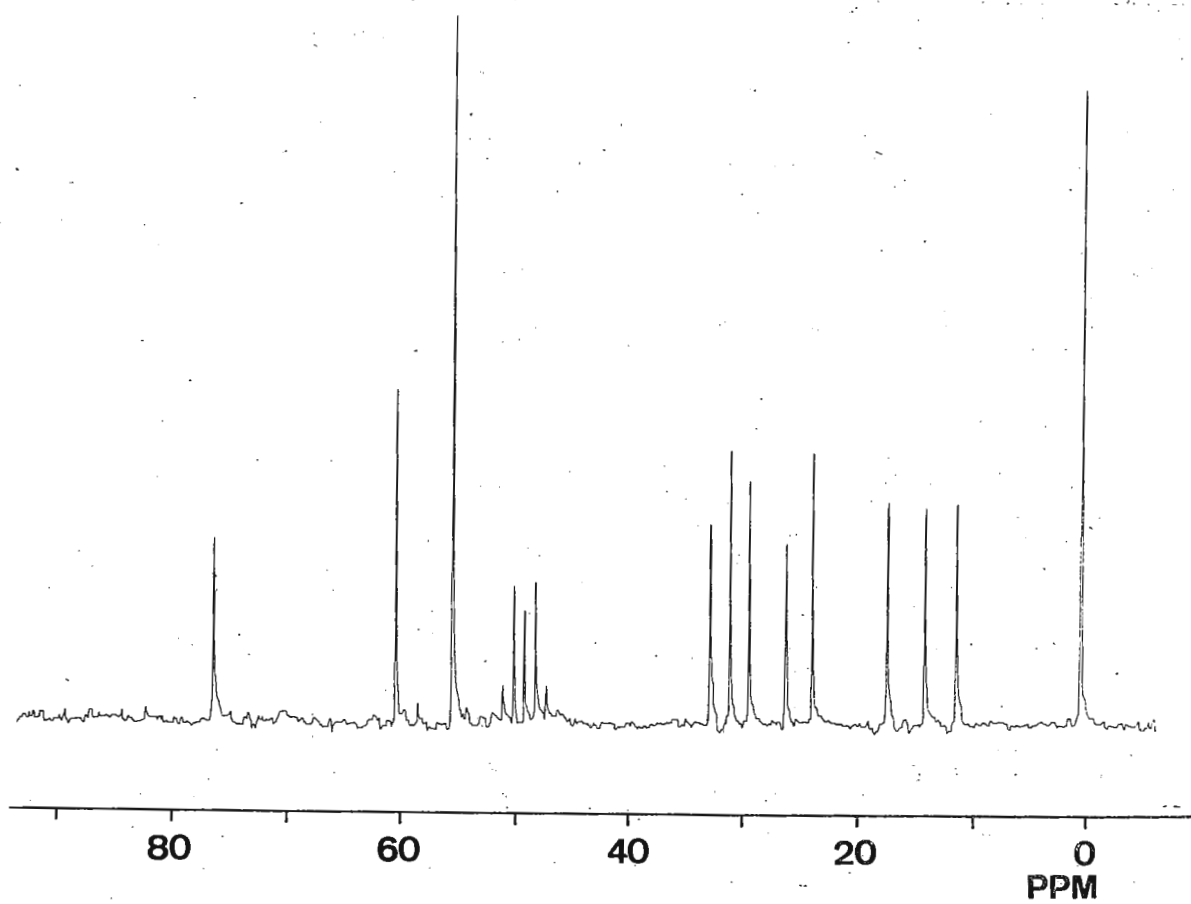


Fig. 2



## UNIVERSITY OF SASKATCHEWAN, REGINA CAMPUS

REGINA, CANADA  
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DEPARTMENT OF CHEMISTRY

June 13, 1973

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

Dear Barry:

TITLE: Now come off it, Pierre! (An ASIS Whodunit)

I was surprised to read Laszlo's comments (1) on my work re the effect of the internal reference on ASIS (2). The reason for my surprise is the fact that Laszlo's statements are totally wrong. It is true enough that when one subtracts two, TMS internally referenced, ASIS data, that the result is then independent of the TMS. Laszlo in his work (3) uses the C10 signal of camphor to reference the C9 and C8 signals. What he is in fact discussing and plotting are  $(\Delta C_{10}-\Delta C_9)$  and  $(\Delta C_{10}-\Delta C_8)$  values, free of TMS influence, but not free from the medium effects of C10. All he has done is replacing one internal reference (TMS) by another (C10 of camphor), but that does not improve the situation one iota.

Once more this shows how one can suffer from optical illusions. It is simply impossible to obtain any reference-free ASIS unless one determines experimentally the medium shifts (gas-to-liquid) of the reference compound.

We are in the process of doing just that by measuring the gas-to-liquid shifts of TMS (and camphor) in a series of solvents and then converting Laszlo's  $\Delta$  data to the reference-free  $\bar{\Delta}$  data. Our preliminary data are rather interesting.

- (a) It does not matter whether one starts from C10 or TMS-referenced  $\Delta$  data; after the corrections are made, the  $\bar{\Delta}$  data are the same for any solvent pair.
- (b) If one plots  $\bar{\Delta}$  (C9) versus  $\bar{\Delta}$  (C8), varying the aromatic solvent, a straight line is obtained with zero intercept and a slope  $\bar{C} = 1.06 \pm 0.02$ . This slope is to be compared with the value  $C = 1.35$  found by Engler and Laszlo for their (C10 referenced) plot of  $\Delta C_9$  versus  $\Delta C_8$ . In their theory this slope is equal to the ratio of "site factors", relating to the position of solute protons relative to an assumed cluster of partially oriented aromatic solvent molecules "draped" around the carbonyl group.

Now it appears that the true ratio is very close to unity. In fact, the difference can now very well be accounted for by the site-effect that even the Van der Waals term has on the medium effects (4).

Incidentally, I have also found the reason for the linearity of such  $\Delta/\Delta$  or  $\bar{\Delta}/\bar{\Delta}$  plots. It has nothing to do at all with complexation or restricted rotation or cluster formation or whatever you call it.



When comparing the ASIS, using two aromatic solvents i and j the slope of  $\Delta$  (proton A in solute X) versus  $\Delta$  (proton B in solute X) as with reference R is given by (2)

$$C_{ij} = (\Delta_{XAm}^{ij} - \Delta_{Rm}^{ij}) / (\Delta_{XBm}^{ij} - \Delta_{Rm}^{ij}) \quad (1)$$

For  $C_{ij}$  to be a constant for all combinations ij there are several possibilities;

- (i) If  $\Delta_{Rm}^{ij} \neq 0$  then  $\Delta_{XAm}^{ij} \neq \Delta_{XBm}^{ij}$

This is the solution I gave before (2). Actually I should have rejected this solution since it implies unity slope and zero intercept, contrary to Engler and Laszlo's findings

- (ii) If  $\Delta_{Rm}^{ij} = 0$  then  $C_{ij} = \Delta_{XAm}^{ij} / \Delta_{XBm}^{ij}$  which could indeed be any constant if  $\Delta_{XAm}^{ij}$  is proportional to  $\Delta_{XBm}^{ij}$ . This solution has been suggested by Engler (5). However, this has to be rejected also since the  $\Delta_{XRm}^{ij}$  are not zero (as now found in my own experiments) and in fact they are always very close to the respective  $\Delta_{XAm}^{ij}$  and  $\Delta_{XBm}^{ij}$  values.

- (iii) The general solution is given by

$$\left. \begin{array}{l} \Delta_{Rm}^{ij} = a \Delta_{XAm}^{ij} \\ \Delta_{Rm}^{ij} = b \Delta_{XBm}^{ij} \end{array} \right\} \rightarrow C_{ij} = \frac{(1-a) b}{(1-b) a} = \text{constant} \quad (2)$$

All that is necessary therefore is a proportionality between the differential (between two aromatic solvents i j) medium shift of the reference and that of the solute proton(s). This seems to be a rather logical condition (in fact borne out by experiment), provided the same medium shift mechanisms are operative on both solute and reference. So again, Engler & Laszlo's  $\Delta C9$  vs.  $\Delta C8$  plots prove the opposite of what they claim. Since it does not matter whether TMS or C10 of camphor is chosen as reference this seems to indicate, if anything, that there are no specific interactions. Working with the  $\bar{\Delta}$  scale leads to the following

$$\bar{C}_{ij} = \frac{\bar{\Delta}_A^{ij}}{\bar{\Delta}_B^{ij}} = \frac{\Delta_{XAm}^{ij}}{\Delta_{XBm}^{ij}} = \frac{b}{a} \quad (3)$$

Using the experimental slopes of eqs. (1) and (3) we obtained  $a=.71$   $b=.76$ , which, considering eqs. (2) and (1) shows that the terms  $\Delta_{Rm}^{ij}$  cannot be ignored. These results are for R=TMS; for R=C10 (camphor) the a and b parameters are closer to unity. We are preparing a note on this matter for J.A.C.S. Hopefully, that will settle this issue once and forever.

Best wishes,

*F. H. A. Rummens*

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

- (1) P. Laszlo TAMU NMR Newsletter 176, 10(1973).
- (2) F. Rummens, R. Krystynak; J.A.C.S. 94, 6914(1972).
- (3) E. Engler, P. Laszlo, J.A.C.S. 93, 1317(1971).
- (4) F. Rummens et al., J.C.P. 43, 2971(1965); J. Phys. Chem 72, 2111(1968); Mol. Phys. 19, 423(1970); Magn. Res 8, 332(1972).
- (5) E. Engler (Princeton) private communication (1972).

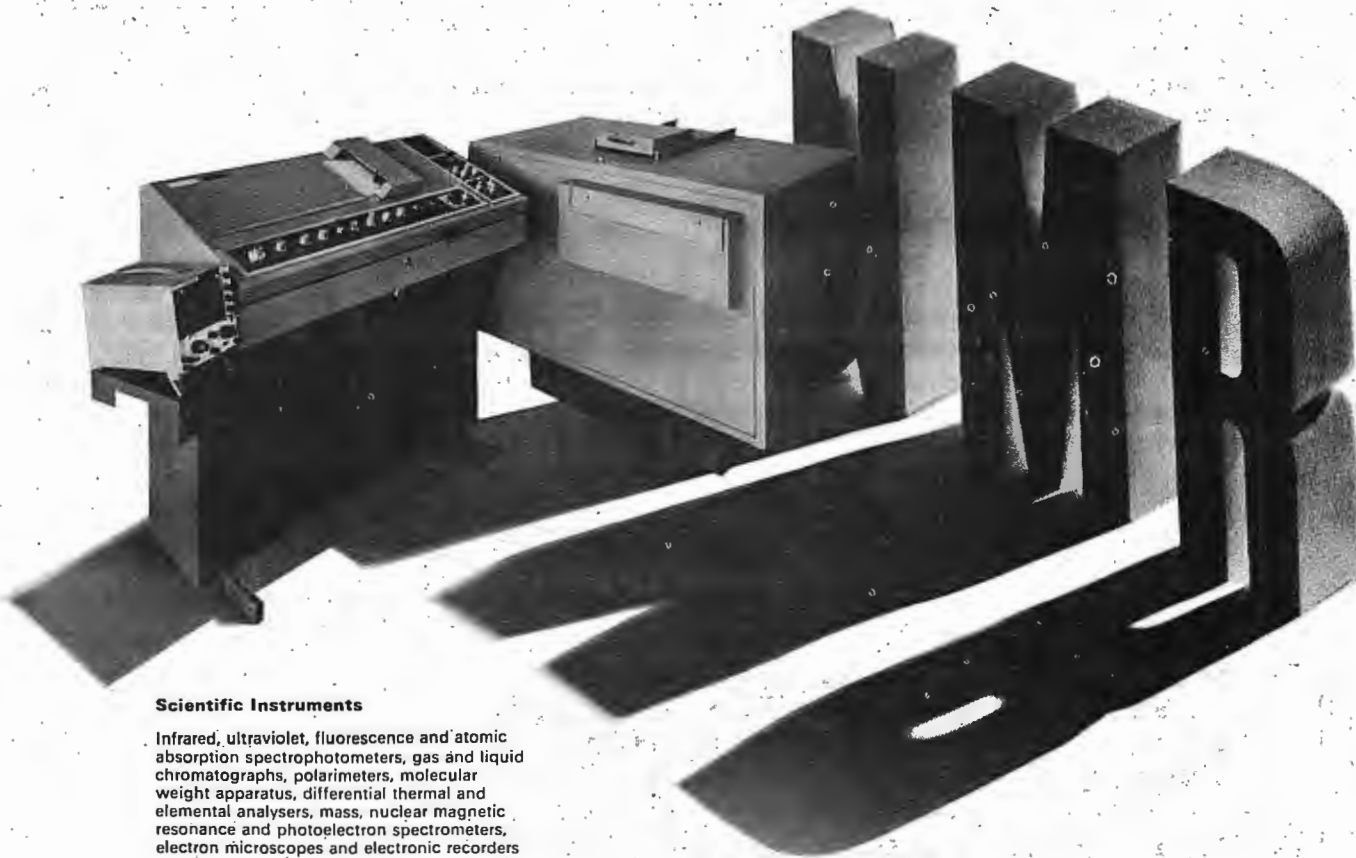
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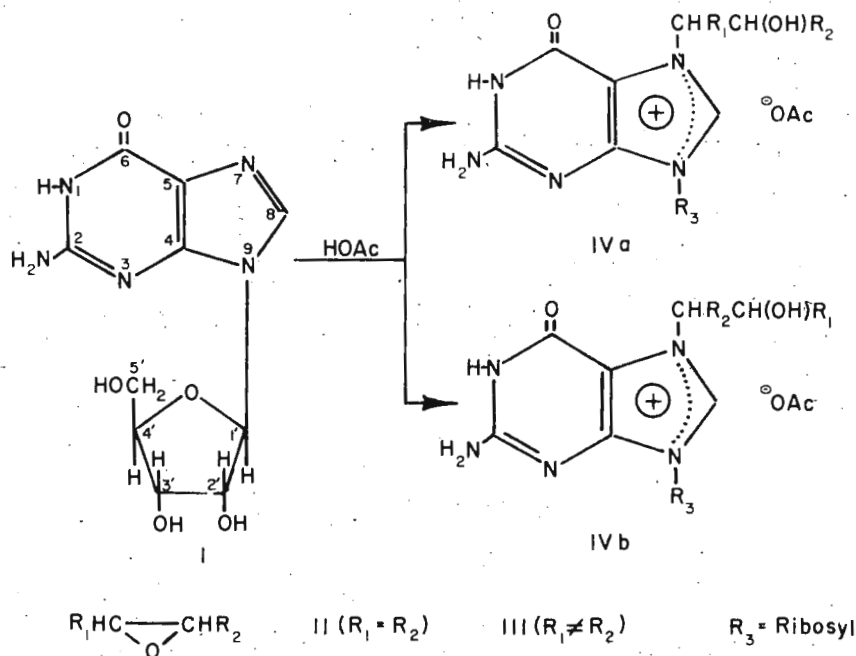
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Dr. B. L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

<sup>1</sup>H NMR SPECTRA OF 7-HYDROXYALKYLGUANOSINIUM ACETATES

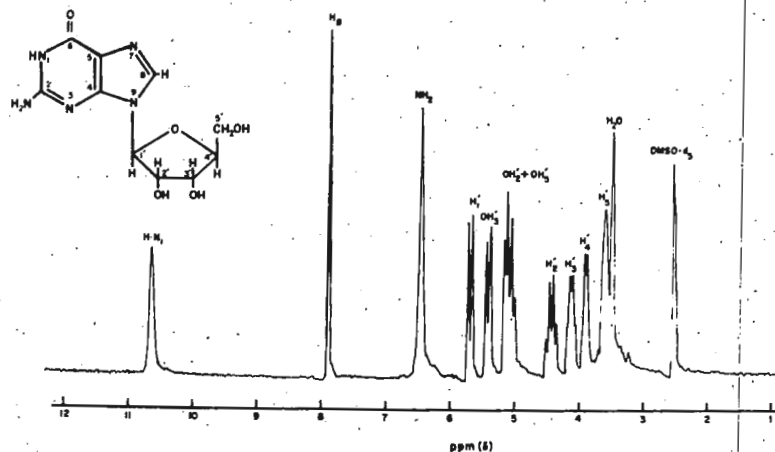
Dear Dr. Shapiro:

We have recently obtained pmr spectra of several previously unreported 7-hydroxyalkylguanosinium acetates (IVa and IVb) from the reaction of guanosine (I) in glacial acetic acid with equally and unequally substituted epoxides (II and III).

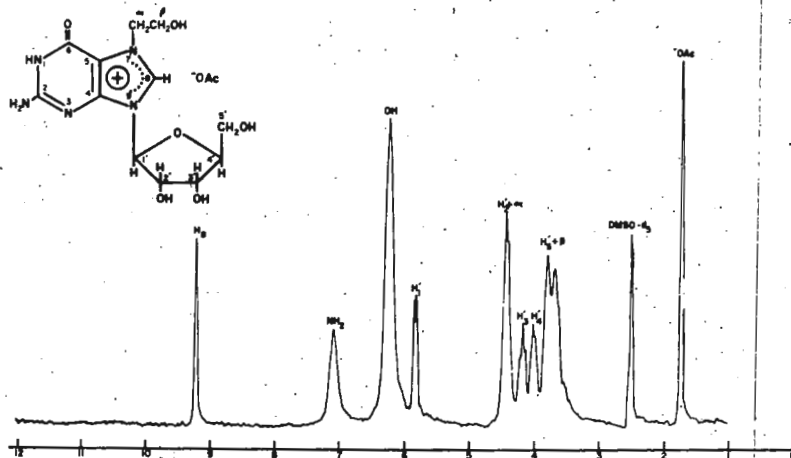


Comparison of the pmr spectra of 7-hydroxyalkylguanosinium acetates in DMSO-d<sub>6</sub> to the spectrum of guanosine reveals that the H<sub>8</sub> and amino group proton absorptions common to guanosine are shifted downfield by approximately 1.2 and 0.8 ppm respectively. Additionally, the H<sub>1</sub> proton absorptions are absent and the H<sub>1</sub><sup>1</sup> - H<sub>2</sub><sup>1</sup> coupling constants are decreased from about 5.7 ± 0.1 Hz in guanosine to about 3.5 ± 0.1 Hz in the hydroxyalkylated products. The pmr spectra of guanosine (I), 7-(2-hydroxyethyl)guanosinium acetate (V) and a mixture of 7-hydroxypropylguanosinium acetate isomers (VIa and VIb) are shown.

GUANOSINE (I)



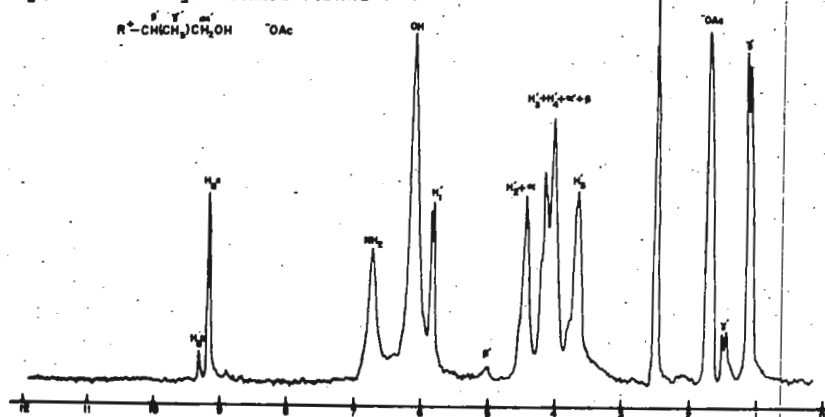
7-(2-HYDROXYETHYL)GUANOSINIUM ACETATE (V)



7-[1-(2-HYDROXYPROPYL)]GUANOSINIUM ACETATE (VIa)



7-[1-(1-HYDROXYPROPYL)]GUANOSINIUM ACETATE (VIb)



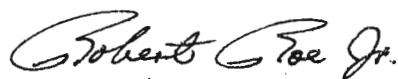
Product V is from the reaction of guanosine in glacial acetic acid with 1,2-epoxyethanol and products VIa and VIb with 1,2-epoxypropane. The above spectra were obtained using solutions which were approximately 10% by weight of the compound in DMSO-d<sub>6</sub>.



Although the downfield shift in the  $H_8$  absorption in V with respect to guanosine (I) might have been expected as a consequence of the deshielding influence of the positive charge in the imidazole ring of V, the relatively large downfield shift of the amino protons was unexpected. Extensive delocalization of the positive charge in V may account for this observation. Presumably, the absence of an  $H_1$  signal in V is due to a rapid exchange involving  $H_1$  and the acetate counter anion. The decrease in the  $H_1 - H_2'$  coupling constant in V in comparison to guanosine (I) is presumably associated with either the effect of the positive charge in the imidazole ring or in a change in the orientation of the purine ring with respect to the ribosyl group due to the rotation about the  $N_9 - C_1$  bond. The  $H_8$  protons of V are exchangeable in  $D_2O$  within a few hours at  $30^\circ$ . This is in contrast with the  $H_8$  protons of guanosine (I) which exchange more slowly under these conditions.

The quality of the recorded spectra of these compounds could probably be improved by nitrogen decoupling and by multiple scans of less concentrated solutions. Problems with the nmr instrument used in this study prevented us from obtaining more highly resolved spectra. Others might be motivated to obtain improved spectra of these compounds. We would be happy to provide samples of several 7-hydroxyalkylguanosinium acetates for this purpose.

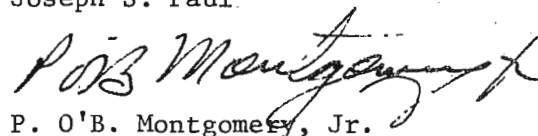
Sincerely,



Robert Roe, Jr.



Joseph S. Paul



P. O'B. Montgomery, Jr.

UNIVERSITY OF DELAWARE  
NEWARK, DELAWARE  
19711

DEPARTMENT OF CHEMISTRY

June 19, 1973

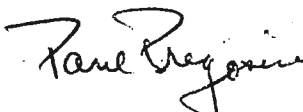
Dr. B. L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843

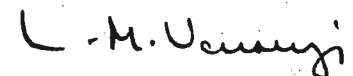
Dear Barry:

Perhaps some recently obtained  $^{195}\text{Pt}$  results will stave off further blue-notes until we are properly set up in Zurich.

Platinum-195 ( $I = 1/2$ , natural abundance 33%) is a nucleus which, surprisingly, has received only scant notice. We find that direct observation of this nucleus using our Bruker HX-90, in FT mode, is not difficult and has much to offer in terms of a chemical shift-molecular structure correlation. Thus, as may be seen from the Table, a change in either oxidation state or substituent induced a large change in the platinum chemical shift. While these data may suggest an electronegativity correlation, other experiments suggest that a number of factors are operative. Preliminary relaxation studies indicate that  $T_1$ 's(undegassed) are quite short.

Best wishes,

  
Paul S. Pregosin

  
L. M. Venzani, Chairman and  
E. I. duPont de Nemours  
Professor of Chemistry

PSP/sma  
Encl.

Platinum-195 Chemical Shifts in Halogen and Amine Complexes

<u>Compound</u>	<u><math>\delta^*</math></u>
$\text{Na}_2\text{PtCl}_6$	0
<u>cis</u> - $[\text{Pt}(\text{CH}_3[\text{CH}_2]_{11}\text{NH}_2)_2\text{Cl}_4]$	- 269 $^{\pm}$
<u>cis</u> - $[\text{Pt}(\text{CH}_3[\text{CH}_2]_{11}\text{NH}_2)_2\text{Br}_4]$	-1,316 $^{\pm}$
$\text{Na}_2\text{PtCl}_4$	-1,647
<u>cis</u> - $[\text{Pt}(\text{CH}_3[\text{CH}_2]_{11}\text{NH}_2)_2\text{Br}_2]$	-2,544 $^{\pm}$

\* Data are reported in ppm upfield from aqueous  $\text{Na}_2\text{PtCl}_6$  and are estimated to be correct to  $\pm 1$  ppm.

$^{\pm}$  Measured as chloroform solutions.



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NATIONAL HEART AND LUNG INSTITUTE

June 18, 1973

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

Dear Barry:

<sup>13</sup>C Characteristics of Phenalenone

In preparation for biogenetic studies of the pigments of Lachnanthes spp. in collaboration with Ulrich Weiss of the Arthritis Institute and Mike Edwards of the University of Connecticut, we are studying the central aromatic system, which is that of phenalenone. The results are tabulated and attached.

The assignments are based largely on selective decoupling experiments. Since H-3 and H-4 both have  $\delta=7.63$  ppm, C-3 and C-4 are differentiated by their coupling, on the assumption that  $J(\text{gen}) < J(\text{vic-cis}) < J(\text{vic-trans})$ . C-9a moved more with a lanthanide shift reagent than the other quaternary carbons, but C-6a and C-3a could be interchanged.

We thought the correlation of the  $T_1$ 's rather interesting. <sup>13</sup>C's on the "points", (2,5,8) have  $T_1$ 's of approximately 1.5 sec., while other protonated <sup>13</sup>C's are about 2 sec. <sup>13</sup>C's on the periphery without protons have  $T_1$ 's of about 40 sec., while the central atom is 71 sec.

Spectra were taken on an XL-100 equipped with Digilab FT equipment.  $T_1$ 's were done by semilog plots from  $180^\circ$ - $\tau$ - $90^\circ$  experiments. We have profited greatly from helpful discussions with Rod Wasylishen.

Very truly yours,

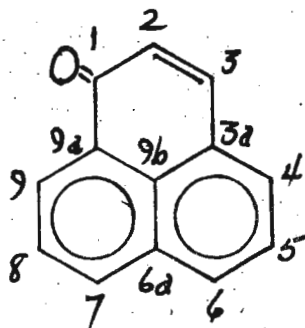
*ES*

E. A. Sokoloski

*Bob*

R. J. Highet  
Laboratory of Chemistry

Attachment



TABLE

C	$\delta_{13C}$	$J_{CH}$	$J_{CCH}$	$J_{CCH}$		$T_1$	$\delta_H^*$
				cis:	trans		
1)	185.0 ppm			4.3Hz(H-9)	10.0Hz(H-3)	39 sec	
2)	128.9	163.2Hz	1.0Hz			1.4	6.66 ppm
3)	141.3	161.3	1.4	5.6 (H-4)		1.9	7.63
3a)	131.9					39	
4)	131.0	160.6	1.2	4.4 (H-3)	4.4 (H-6)	2.0	7.63
5)	126.4	163.2				1.5	7.48
6)	131.6	162.0		4.8 (H-7)	6.8 (H-4)	1.9	7.91
6a)	129.3					40	
7)	134.5	161.2		4.7 (H-6)	7.8 (H-9)	1.9	8.08
8)	126.7	161.9	2.8			1.5	7.67
9)	129.8	161.9	3.5		8.0 (H-7)	1.9	8.52
9a)	127.5					39	
9b)	127.3					71	

\* H. Prinzbach, V. Freudenberger and U. Scheidegger, *Helv. Chim. Acta* **50**, 1087 (1967).

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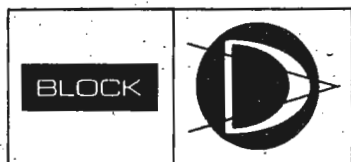
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June 5, 1973

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

Subject: "A Very Large Dynamic Range Phase Detector for  
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Dear Barry:

We have developed a broad-band phase detector (P.D.) capable of detecting high level FTS/NMR type signals without generating objectionable spurious signals. This P.D. will be most useful in <sup>1</sup>H studies at 23 KGauss or higher where the dynamic range of the signals can be very large.

Spurious signals generated by the NMR receiver generally appear at the output P.D. in the form of harmonics, or third order intermodulation products when two or more strong lines are present in the spectrum. Present day broad band receivers show spurious signals between .1% and 1%, that is, 40 to 60db below the stronger lines.

To reduce spurious signals, we must operate it at a signal level much lower than its maximum capability. High level double balance mixers, like the Relcom MLE, come close to fulfilling the requirements. These mixers require having all ports terminated (50Ω) at all pertinent frequencies, which is difficult to achieve in practice, especially when high level outputs are required.

The P.D. we have developed uses an integrated circuit modulator of the 796 type and a differential amplifier.

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June 5, 1973

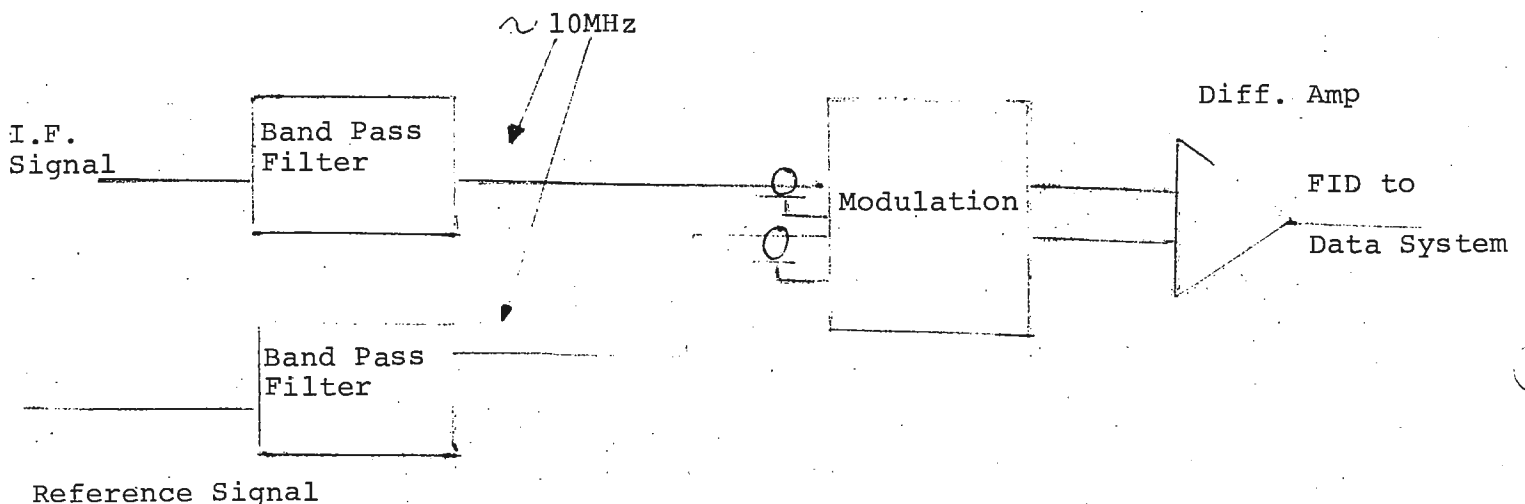
The signal level at the input of the modulator is several orders of magnitude smaller than the maximum capability, which insures linear operation. The differential amplifier provides a low output impedance and allows dc coupled operation near zero volts dc.

The level of spurious signals measured at the bench for this P.D. is below -80db (0.01%) and for some selected IC's, it is below -90db which is all we can measure with reasonable effort.

The critical factors to achieve this performance are:

1. Very clean signals, that is, both inputs to the P.D. must be free of harmonics to at least -80db below the fundamental. In practice, band-pass filters are required to assure this level of signal purity.
2. The electromagnetic coupling between the IF input and the reference input must be kept below -80db, which emphasizes the need for a careful mechanical layout and assembly of the circuitry next to the modulator.

Figure 1 - Large Dynamic Range P.D.

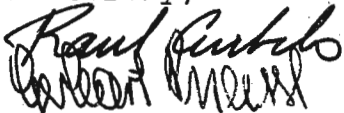


Dr. Bernard L. Shapiro  
Texas A&M University

June 5, 1973

Figures 2A and 2B illustrate the performance of our new receiver. These  $^1\text{H}$  spectra of 130  $\mu\text{g}$  10.4 ml of Adenosine were obtained on an XL-100\* equipped with this new FT receiver. Figure 2A shows a vertical expansion of X10; Figure 2B an expansion of X100. The three (3) strong  $^1\text{H}$  resonances are TMS, residual protons of DMSO and  $\text{H}_2\text{O}$ . The spectrum shows no observable spurious frequencies throughout the entire range of 1000Hz.

Sincerely,



Raul Curbelo  
Gerhart Kneissl

RC&GK/rsm

\* We would like to thank Mrs. Martha Thorpe of SRI, Birmingham, Alabama, for supplying us with these spectra.

Figure 2A

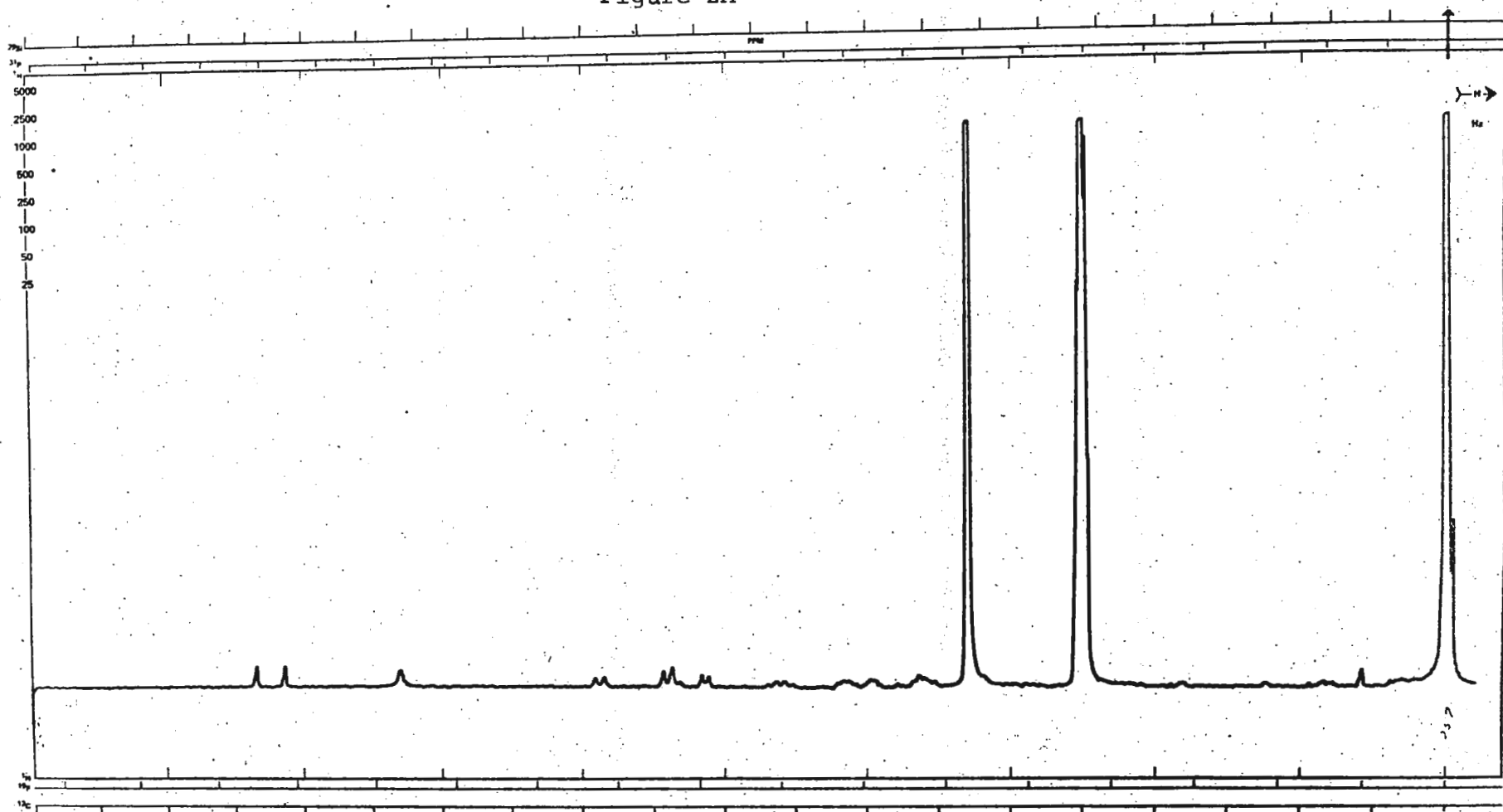
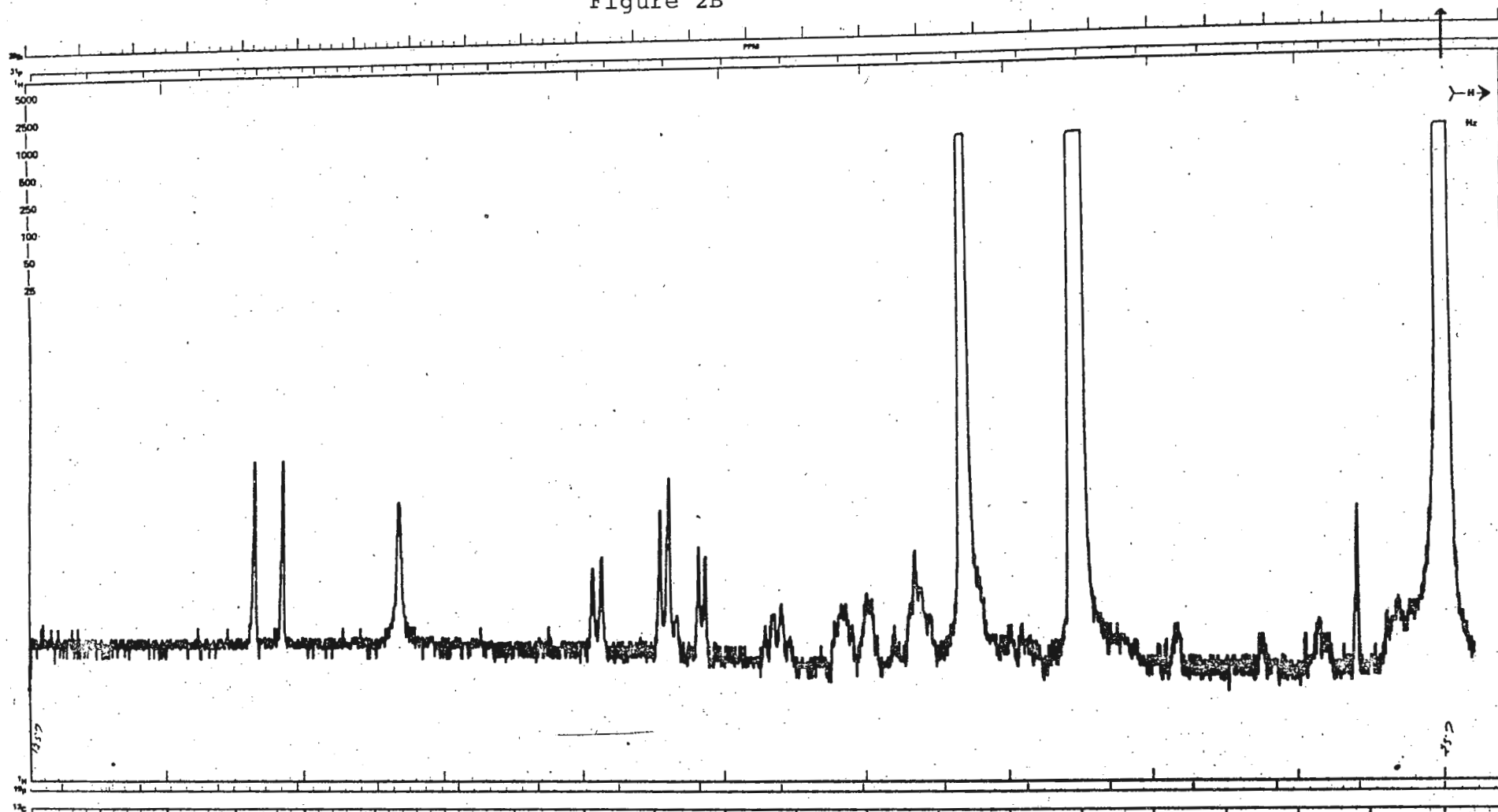


Figure 2B



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Albrecht Mannschreck

Violet Jonas

Bernd Kolb

8400 REGENSBURG, June 1, 1973

Universitätsstraße 31 — Postfach

Telefon (0941) 9431 943-2186

M/S

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

Diastereomeric Association Complexes  
of Rapidly Interconverting Enantiomers

Dear Professor Shapiro,

the nmr signals of a racemate may be split by the presence of an optically active auxiliary compound <sup>1)</sup>. All observations of this kind were made for enantiomers which do not interconvert or which interconvert slowly at room temperature. The latter situation is known for diaziridines, i.e. three-membered rings containing two invertible nitrogen atoms. Recently, we proved the chirality of this class of compounds by means of the nmr of their diastereomeric association complexes <sup>2)</sup>. Although nitrogen inversion occurs somewhat more rapidly in aziridines, the splittings <sup>3)</sup> expected for (R)- and (S)-1,2,2-trimethylaziridine were still observed at 39°. We have now used Pirkle's method <sup>1)</sup> to demonstrate the chirality of diazetidinone (1) (see Figure for formula) which shows fast N<sup>1</sup> inversion at room temperature ( $\Delta G_c^\ddagger = 17.0$  kcal/mole at 48° in CDBr<sub>3</sub> <sup>4)</sup>).

At low temperatures (1) <sup>5)</sup> displays separate <sup>1</sup>H nmr signals for the diastereotopic methyl groups Me<sup>1</sup> and Me<sup>2</sup> and for the N<sup>2</sup> methylene protons H<sub>A</sub> and H<sub>B</sub> (J = 15.5 Hz).

The existence of enantiomers (R)-(1) and (S)-(1) is shown by the splitting of some of the signals when optically active 0<sup>2</sup>,0<sup>3</sup>-dibenzoyltartaric acid, e.g (+)-(2), is added. This is true for Me<sup>1</sup> ( $\delta$ =1.15 and 1.23), Me<sup>2</sup> (1.40 and 1.43), and H<sub>B</sub> (3.60, J=15.5 Hz, and 3.71, J=15.5 Hz) at -55° (Figure). As expected <sup>1)</sup>, these splittings are absent when the auxiliary compound is racemic, i.e (+)-(2). We assume that two complexes, (R)-(1)...(+)-(2) and (S)-(1)...(+)-(2), are formed via hydrogen bonds. The amount of (1) which is protonated by the acid (2) must be small because the  $\delta$ -values of (1) in the presence and in the absence of (2) are very similar.

We have also succeeded in proving the chirality of several other systems comprised of rapidly interconverting enantiomers <sup>6)</sup>. In addition to this work, we are continuing our kinetic <sup>1</sup>H nmr studies on non-planar butadienes <sup>7)</sup> and on acyl shifts in enol esters <sup>8)</sup>, including some <sup>13</sup>C work.

Sincerely yours,

*Albrecht Mannschreck*

Albrecht Mannschreck

*Violet Jonas*

Violet Jonas

*Bernd Kolb*

Bernd Kolb

- 
- 1) M.Kainosho, K.Ajisaka, W.H.Pirkle, and S.D.Beare, J.Amer.Chem.Soc. 94, 5924 (1972) and earlier papers by W.H.Pirkle and coworkers.
  - 2) A.Mannschreck and W.Seitz in: IUPAC (ed.), XXIIIrd International Congress of Pure and Applied Chemistry, Vol.2, p.309, Butterworths, London 1971.

- 3) K.Mislow, Princeton, personal communication 1970.
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- 7) G.Köbrich, A.Mannschreck, R.A.Misra, G.Rissmann, M.Rösner, and W.Zündorff, Chem.Ber. 105, 3794 (1972).
- 8) A.Mannschreck and H.Dvorak, Tetrahedron Lett. 1973, 547.

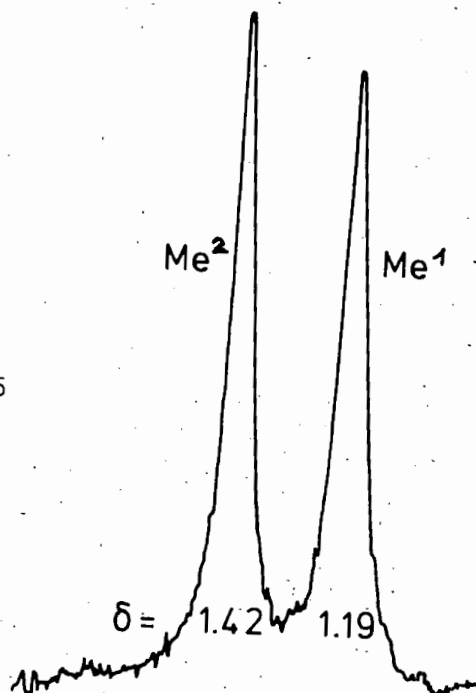
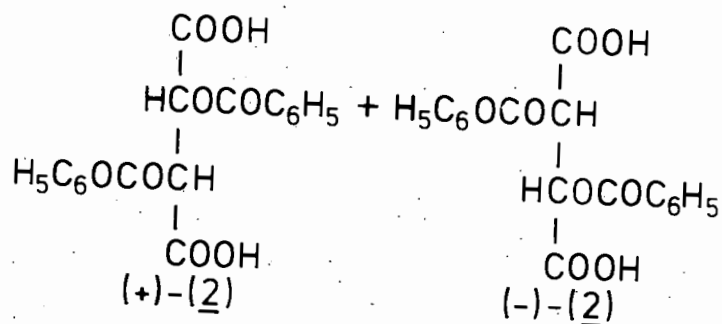
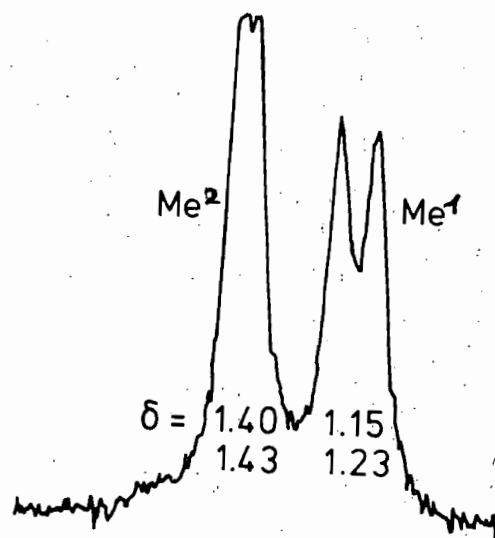
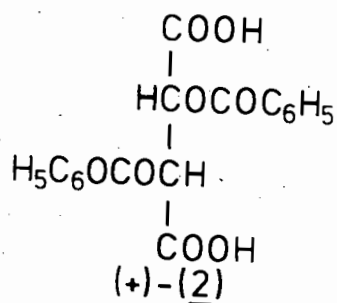
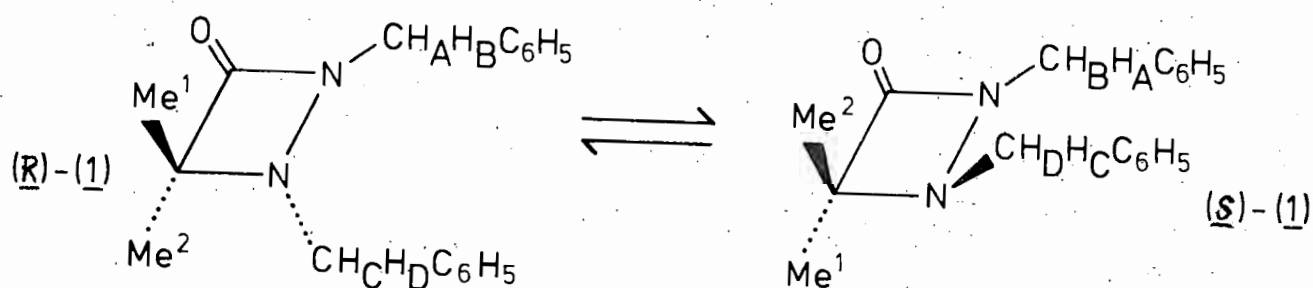
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Legend to Figure:  $^1\text{H}$  nmr methyl signals of (RS)-4.4-dimethyl- $\text{N}^1, \text{N}^2$ -dibenzyl-1,2-diazetidione, (RS)-(1), in  $\text{CDCl}_3$  at  $-55^\circ$  in the presence of an equimolar quantity of the following auxiliary compound:

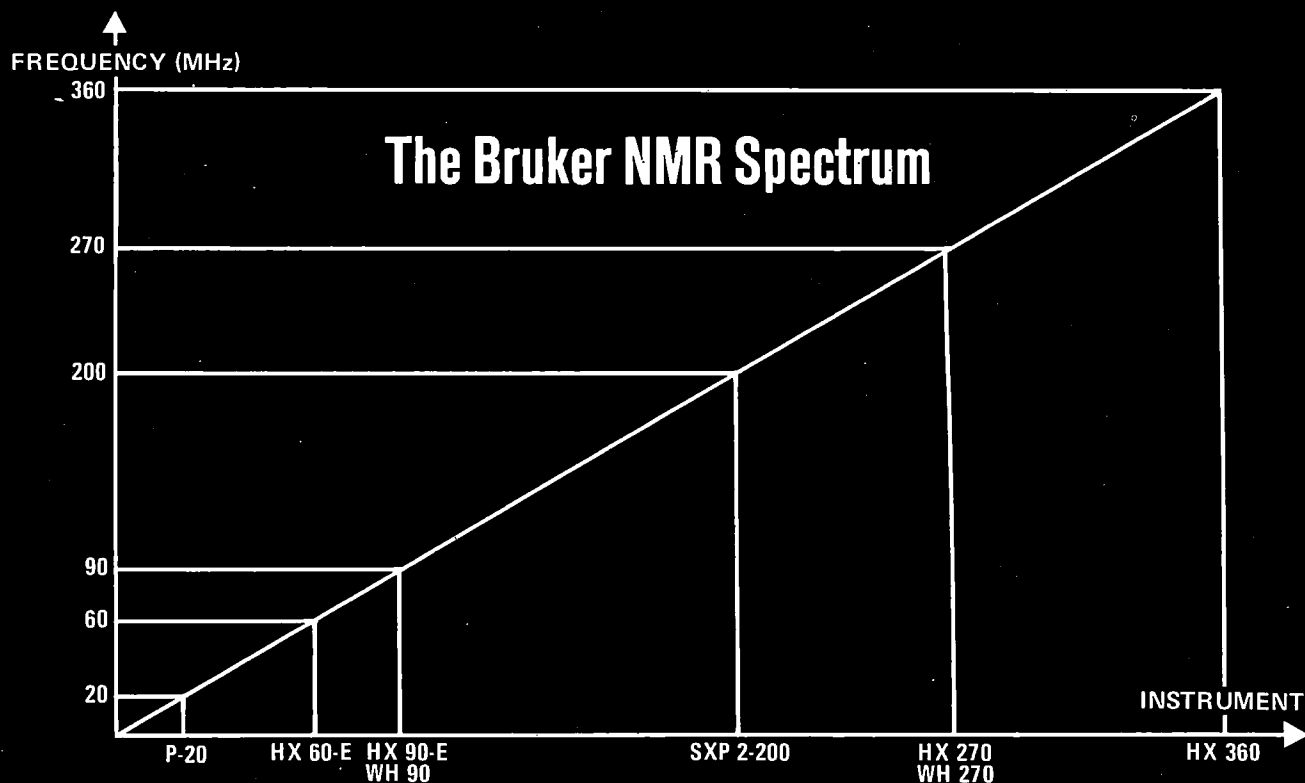
Top: (2R,3R)- $\text{O}^2, \text{O}^3$ -dibenzoyltartaric acid, (+)-(2).

Bottom: (2RS,3RS)- $\text{O}^2, \text{O}^3$ -dibenzoyltartaric acid, (±)-(2).





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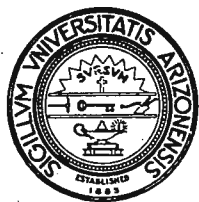
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DEPARTMENT OF CHEMISTRY

June 21, 1973

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

Dear Barry:

## Conformational Dependence of Vicinal $^{15}\text{N}$ -C-C-H Coupling Constants

Vicinal  $^{15}\text{N}$ -C-C-H coupling constants have become of particular recent interest (1,2) because of their relationship to the angle  $\psi$  about  $\text{C}_\alpha$ -C bonds in peptides. Calculated results were based on the self-consistent perturbation method in the INDO approximation with the geometrical model used to examine vicinal H-N-C-H coupling constants (3). The following values were obtained at  $30^\circ$  intervals of the dihedral angle  $\theta$ , for the cis and trans arrangements of the amide bond:

$\theta, \text{deg}$	$^3J_{\text{NH}}(\text{cis}), \text{Hz}$	$^3J_{\text{NH}}(\text{trans}), \text{Hz}$
0	- 1.80	- 2.33
30	- 0.88	- 1.28
60	0.89	0.60
90	0.99	0.90
120	- 1.50	- 1.54
150	- 4.84	- 5.02
180	- 6.53	- 6.23

It is tempting to compare the value of 0.89 Hz for  $\theta=60^\circ$  with the recently measured experimental one of  $\pm 1.02$  Hz in L-Val-Gly- $^{15}\text{N}$ -diketopiperazine (2). A value of  $\pm 1.85$  Hz was reported (2) for L-Ala-L-Phe- $^{15}\text{N}$ -diketopiperazine, which should be rather rigid because of steric effects. Experimental values of  $\pm 1.3$  Hz,  $\pm 1.5$  Hz, and  $\pm 1.2$  Hz have been reported for acetamide (4), N-acetylglycine (1), and some dipeptides (2), respectively. If it is assumed that one of the protons of the methyl group of N-methylacetamide eclipses the double bond, then the average calculated value for the coupling (trans) from the above table is -1.81 Hz. Coupling constants of positive sign in the  $60^\circ$  orientation are substantial in comparison with the negative,  $180^\circ$  values. This is in marked contrast with N-C-C-H coupling in amines (5), and indicates the need for sign determinations in suitable molecular systems.

Sincerely yours,

Mike Barfield

1. S. Karplus and M. Karplus, Proc. Nat. Acad. Sci., U.S., 69, 3204 (1972).
2. J. A. Sogn, W. A. Gibbons, and E. W. Randall, Biochem., 12, 2100 (1973).
3. M. Barfield and H. L. Gearhart, J. Amer. Chem. Soc., 95, 641 (1973).
4. G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, J. Amer. Chem. Soc., 86, 5564 (1964).
5. R. Wasylishen and T. Schaefer, Can. J. Chem., 50, 2989 (1972).

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June 11, 1973

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

Dear Barry:

Re: Analysis of Lanthanide Induced Shifts

Vern Cheney and I have written a program, which we call LISC, for the correlation of lanthanide-induced shifts, LIS, with molecular structures. We make use of the molecular geometry program of B. V. Cheney to enter the proposed structure into the computer from internal coordinates, cartesian coordinates or x-ray data. Provision is made for rotating the molecule as desired, and for adjusting the coordinates of the molecule to give a least squares fit to specified interatomic distances using a subroutine from D. J. Duchamp, also of these laboratories.

We find that getting a good description of the molecule is half the battle. To evaluate the latter we use a conformational analysis program, CONAL, written by D. J. Duchamp, which provides distances, angles and molecule plots.

The calculation is similar to that described by Willcott, Lenkinski and Davis.<sup>1</sup> The position of the lanthanide is varied within specified limits with specified increments. The pseudocontact shifts for the specified atoms are calculated and scaled by a least-squares procedure; the agreement factor, R, is calculated for each lanthanide location; and the best fit is selected. In cases where groups are free to rotate or exchange provision is made to calculate each possible conformation separately, weight them and then average the results. If there are two coordination sites or two species they can both be entered and weighted accordingly.

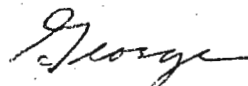
The program was tested on some standard problems. For 4-*t*-butylcyclohexanone the molecule was entered *via* internal coordinates and the shift data for Yb reported by Wolkowski<sup>2</sup> was used with the *t*-butyl hydrogens averaging and the cross-ring hydrogens averaging. The best fit to six observed shifts had an agreement factor of 0.061 in which the Yb was on the symmetry plane of the molecule, 2.5 Å out from the oxygen and oriented upwards (in the axial direction) with a bond angle of 157 degrees.

For *endo*-norborn-5-en-2-one the skeleton was entered from the x-ray data reported<sup>3</sup> for the *anti*-7-norbornenyl p-bromobenzoate and the other atoms were generated in CONAL. The shift data of Willcott, *et al.*<sup>1</sup>, was used. The best fit to nine observed shifts agreed well with their results considering the independent source of molecule coordinates and the shallowness of the fit contours, see table.

When the *endo* data was tested as the *exo* structure the agreement factor was significantly poorer, as was observed previously for borneol.<sup>1</sup>

We are currently working on bicyclo-3,2,1-oct-6-en-3-one using WASER to fit the molecular coordinates to cyclohexanone with the norbornene bridgework.

Very truly yours,



George Slomp  
Physical & Analytical Chemistry Research

ejw

*Endo*-norbornenol

	<u>R-factor</u>	<u>Distances</u>	<u>Bond Angle</u>	<u>Dihedral Angle</u>
Willcott	0.050	3.2 Å	130°	70°
This report	0.036	3.4 Å	127°	53°
<i>Endo</i> as <i>Exo</i>	0.209	1.85 Å	173°	73°

References

1. M. R. Willcott III, R. E. Lenkinski and R. E. Davis, J. Amer. Chem. Soc., 94, 1742, 1744 (1972).
2. Z. W. Wolkowski, Tetrahedron Letters, 821 (1971).
3. A. C. Macdonald and J. Trotter, Acta. Cryst., 19, 456 (1965).



19th June 1973

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

*Roche Products Limited Welwyn Garden City Hertfordshire Telephone Welwyn Garden 28128 Telex 262098*

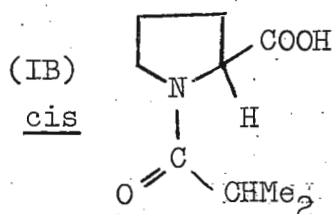
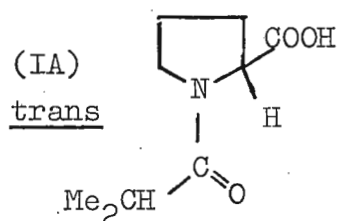
Title - Problems with Proline

Dear Barry

I would like to renew my acquaintance with the Newsletter at my new address with the following contribution. We are well equipped for n.m.r. studies here in a brand-new building, in a laboratory containing a T60 for routine  $^1\text{H}$  spectra, and an XL100/15 instrument for research, the latter being coupled to a 620L computer (16K) and a Sykes cassette. Apart from regular, chronic teething troubles in our first six months of operation, chiefly due to XL hardware problems, we are generally satisfied with the capability of the instrument in  $^1\text{H}$  and  $^{13}\text{C}$  modes.

From some further work by Kevin Williams in Swansea, the following interesting observations have been made:

(a) N-isobutyryl-L-proline (I) in  $\text{CDCl}_3$  ( $^1\text{H}$ ), shows the expected mixture of cis and trans forms (IA and B) in the ratio 1:1. However, in pyridine solution we observe four methyl doublets and two methine septets for the  $\text{Me}_2\text{CH}$  protons, whereas in benzene solution the normal situation is regenerated.



On warming the pyridine solution coalescence of the 4 methyl doublets to 2 and then to 1 doublet takes place as the temperature is raised to 100°C. Although the two methyl groups are intrinsically diastereotopic, we consider that restricted rotation about the Me<sub>2</sub>CH-CO bond is the major cause of the non-equivalence. The methylester of (I) in CDCl<sub>3</sub> shows 4 methyl doublets, but with the intensity of the higher field pair of doublets ca 30% that of the lower field pair. This tends to favour the restricted rotation idea which seems reasonable for the study of models.

(b) Examination of the <sup>13</sup>C spectra of a wide range of di- and tripeptides containing proline has demonstrated a wide range of cis/trans ratios about the amide bond to proline. It seems that if proline is the N-terminal amino acid, far more cis form is present than if the proline is the central amino acid, when the cis/trans ratio approaches zero.

I hope this maintains our contribution for a few months.

With best wishes

Yours sincerely

Tom

W.A. Thomas

WAT/LR





DEPARTMENT OF THE NAVY  
NAVAL WEAPONS CENTER  
CHINA LAKE, CALIFORNIA 93555

IN REPLY REFER TO:

6052/DWM:bjy  
25 June 1973

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

Dear Barry:

In February we installed the world's first Transform Technology/Varian XL-100-15 FT spectrometer. It has come through its initial shake-down with only minor problems and is presently churning out data faster than two humans can assimilate it. Consequently, one topic of this announcement will be the availability of a postdoctoral appointment here. It is offered under the aegis of the National Research Council, and applications for the coming academic year must be in their Associateship Office by January 15, 1974. Research Associates are Federal employees, Grade GS-11, and now receive \$13,300 per year. I will be happy to provide further particulars to anyone interested.

The Varian/TTI XL-100 system is living up to all our expectations. Transform Tech's high-power pulse system is essentially a second-generation Varian design, since it was created by a group of VA alumni who knew all the weaknesses of the original pulser. We are working at only 400 watts for  $^{13}\text{C}$ , since the high-power transmitter matching network (1 kW) hasn't yet arrived. Still we get a  $90^\circ$  pulse at 34  $\mu\text{sec}$  which is generally adequate. Design of the pulse circuitry to include Nicolet's Model 293 I/O Controller makes for a highly versatile system.

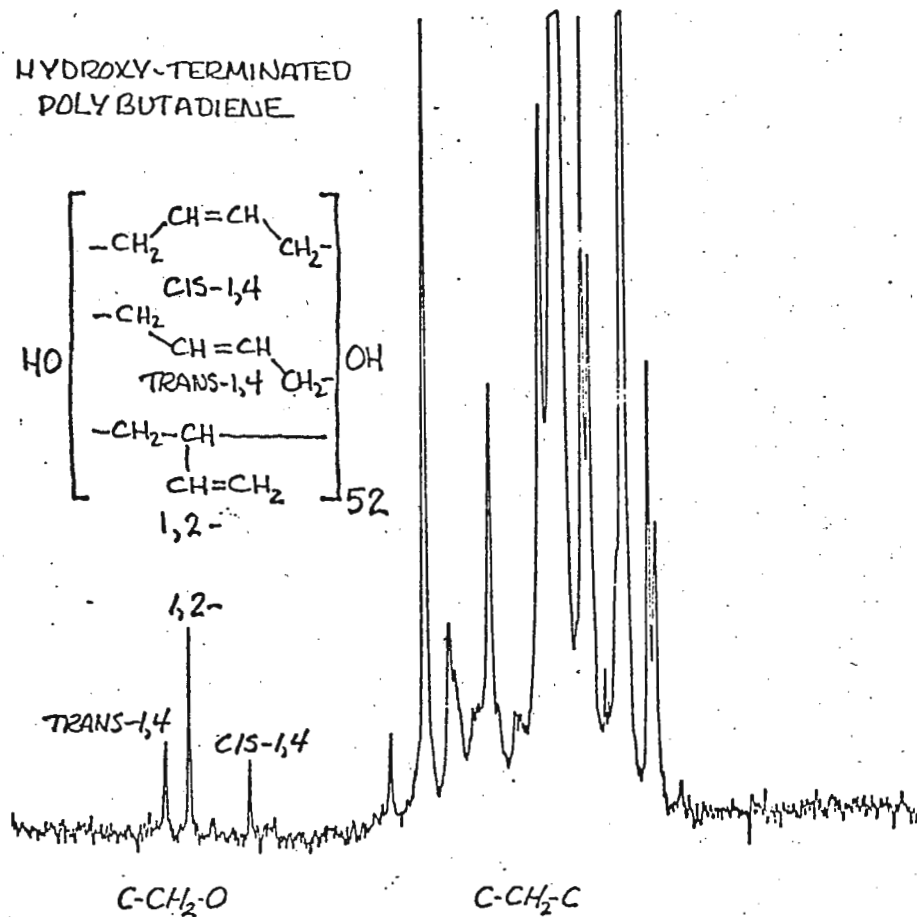
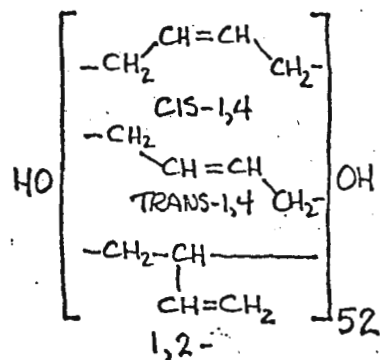
Our computer is a Nicolet 1085 with 20K of core memory and the 600K-word Diablo disk storage system. The latter is truly indispensable, and is in almost constant use, both for scratch storage of data being processed and as our permanent program library. With enough core to handle 16K FID's, there is no need to get data in or out of disk storage during FT calculations, and we are able to exploit the high speed of the 1080 series. Typically, 90% of our  $^{13}\text{C}$  spectra are done with 8K FID's, but the added resolution possible with 16K is sometimes needed - even at the expense of doubling acquisition time. The enclosed spectra of "undecoupled" acetone which Roy Johnson obtained on our instrument show what I mean.

We have found the greater dynamic range of the 20-bit Nicolet data system to be especially useful in one type of problem. Much of our polymer research involves the addition of reactive end-groups to medium-weight pre-polymers, and we hoped that  $^{13}\text{C}$  nmr would make it possible to follow the reactions of the terminal carbons. Enclosed is a spectrum of a hydroxy-terminated polybutadiene ( $\text{MW} \approx 3000$ ) in which we are readily able to discern the three types of end carbons resulting from three possible modes of addition when the polymer was formed.

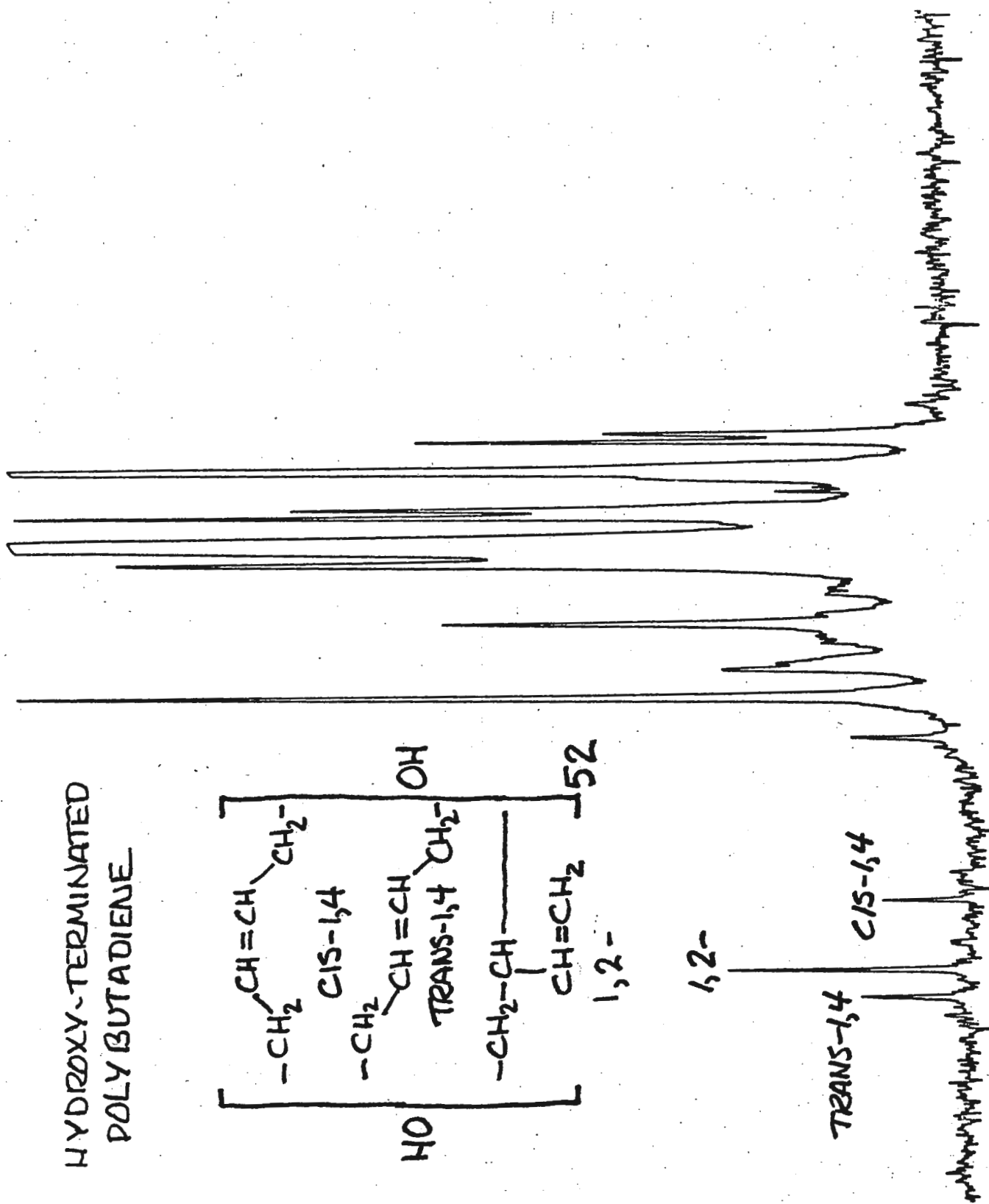
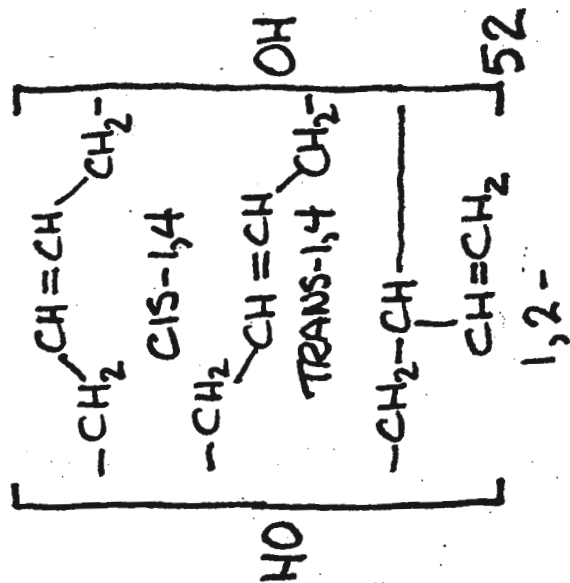
Best regards.

Sincerely,

  
D. W. MOORE

HYDROXY-TERMINATED  
POLYBUTADIENE

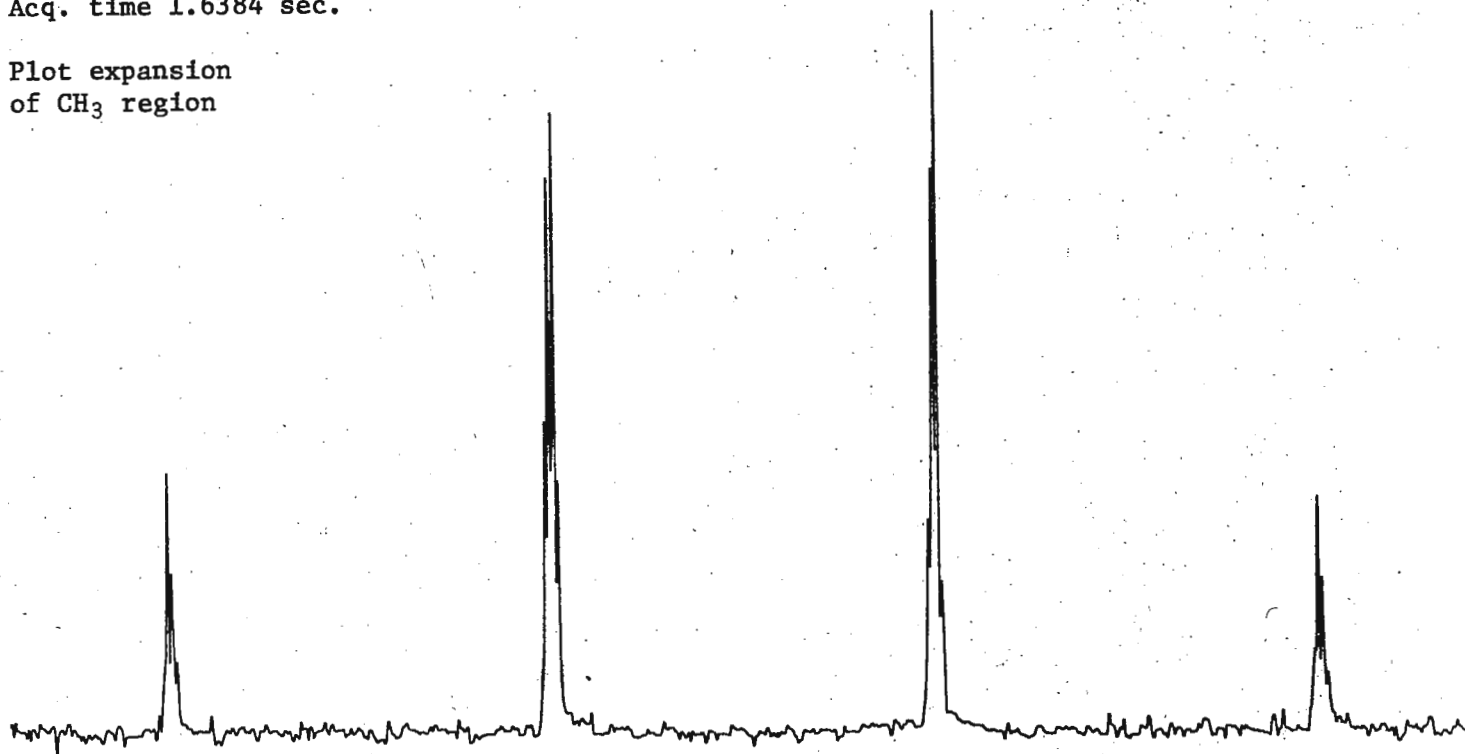
# HYDROXY-TERMINATED POLYBUTADIENE



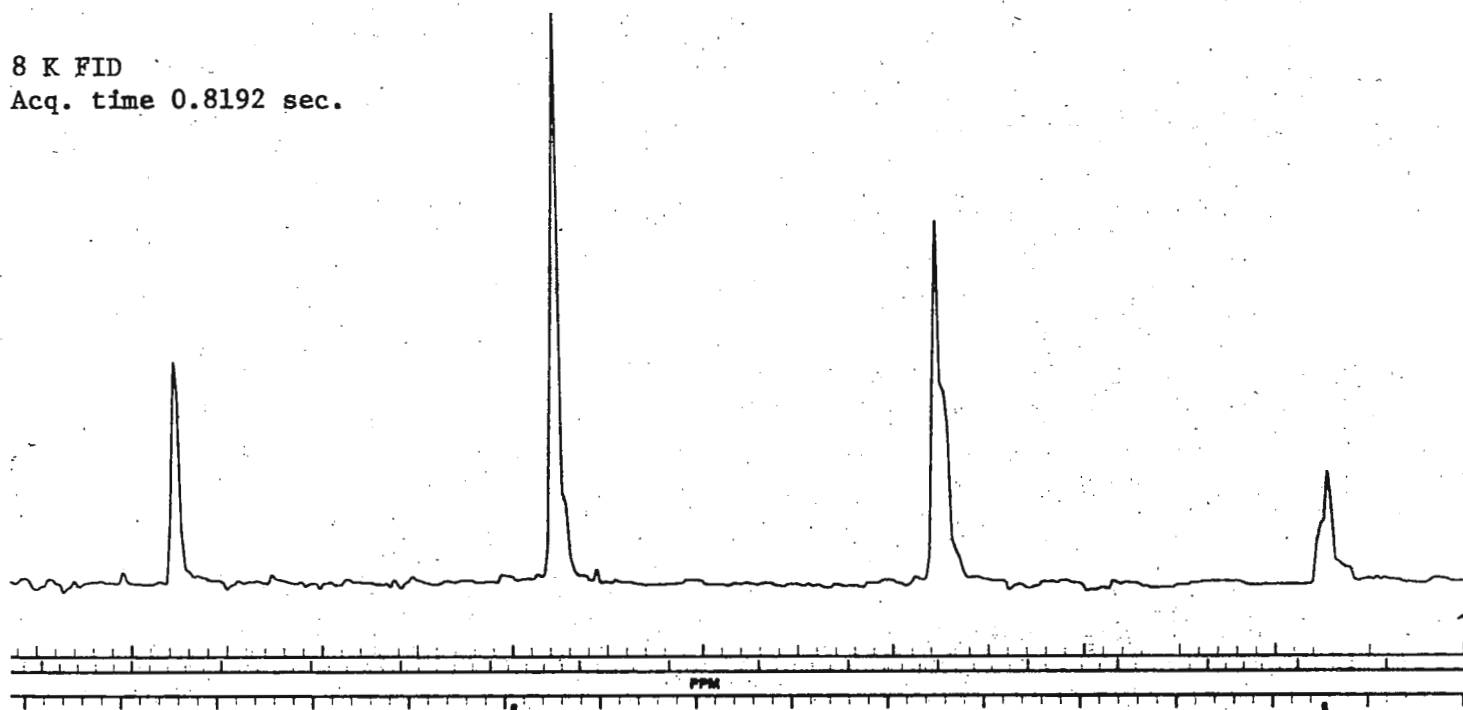
Acetone,  $^{13}\text{C}$  25.14 MHz

16 K FID, Spectrum width 5kHz  
Acq. time 1.6384 sec.

Plot expansion  
of  $\text{CH}_3$  region



8 K FID  
Acq. time 0.8192 sec.



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333 (Prof. Fritz)

Herrn

Professor B.L. Shapiro

Department of Chemistry,

Texas A and M University,

College Station,

T e x a s 77 843

U.S.A.

Lieber Professor Shapiro!

Die Vorbereitung von KMR-Proben in Röhrchen mit  $\varnothing > 8$  mm führt selbst bei der Routinespektroskopie häufig zu Fehlern. Zusätzliche Schwierigkeiten ergeben sich, wenn luft- bzw. temperatur-empfindliche Substanzen vermessen werden. Um die Probenvorbereitung einfacher und sicherer zu machen, haben wir die KMR-Röhrchen in verschiedener Weise modifiziert.

Standardröhrchen mit den bekannten Plastikkappen sind in der Regel kein ausreichender Schutz für Lösungen luftempfindlicher Substanzen. Eine wesentliche Verbesserung läßt sich mit Stopfen aus Silicongummi erreichen (Abb. 1).

Bei diesen Stopfen besteht jedoch die Gefahr, daß der Röhrchenrand ausbricht. Deswegen "stabilisieren" wir unsere Röhrchen durch Rundschmelzen des Randes.

Bei Tieftemperaturspektren schafft der Teflonstopfen Probleme, der üblicherweise zum Vermeiden von Strudeln und Blasen verwendet wird:

Beim Abkühlen zieht sich das Teflon stark zusammen und der Stopfen fällt in die Lösung. Wir führen deshalb einen Nylonfaden durch den Teflonstopfen, fixieren ihn von unten mit einem Knoten und klemmen ihn am Röhrchenrand mit einem

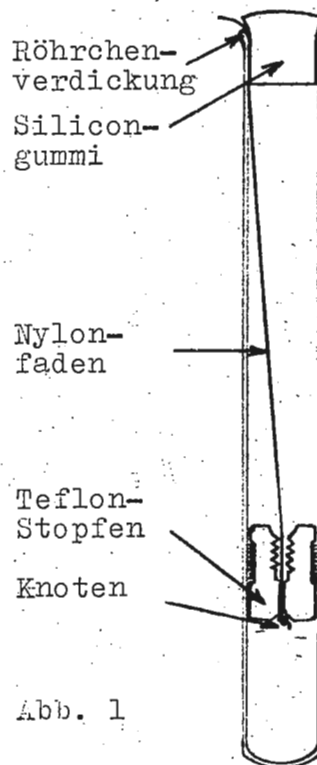


Abb. 1

Silicongummistopfen ein (Abb. 1). Bei höheren Ansprüchen an die Luftdichtigkeit wird der Nylonfaden durch ein sehr dünnes Teflonband ersetzt. Auf diese Weise haben wir ohne Mühe  $^{13}\text{C}$ -Tieftemperaturspektren von Aluminiumalkylen aufgenommen.

Bei längerem Stehen der Proben entweicht jedoch auch durch Silicongummistopfen Lösungsmittel. Hier bewährt sich die Anordnung nach Abb. 2. Wir benutzen sie vor allem für hochsauerstoffempfindliche Substanzen sowie für Hochtemperaturspektren. Dazu wird ein Standardröhrchen am Rand so verschmolzen (Ansetzen eines vorgeschmolzenen Stückes ist vorzuziehen), daß später ein 2 - 3 mm Planschliff angebracht werden kann. Wie Abb. 2 zeigt, fertigt man aus PVC eine Kappe sowie einen Ring mit Gewinde. Durch Verschrauben der Anordnung mit einer Silicongummischeibe sowie einer Teflonhaut wird eine ausgezeichnete Dichtigkeit erreicht: In einem solchen Röhrchen haben wir Benzol tagelang ohne Substanzverlust auf 150 - 160°C erwärmt; eine Lösung von Bis(h<sup>5</sup>-cyclopentadienyl)vanadium ist darin wochenlang ohne Zersetzung haltbar. Der Vorteil gegenüber der Abschmelzmethode ist klar ersichtlich.

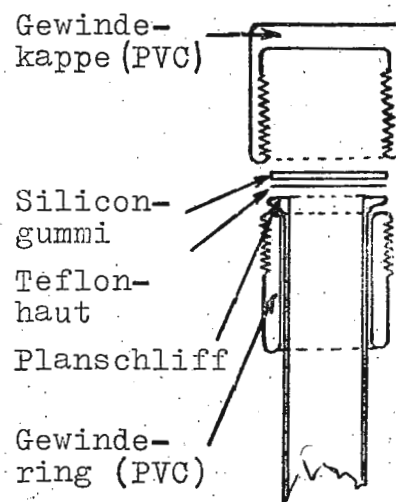


Abb. 2

Bleibt zu erwähnen, daß bei sorgfältiger Ausführung alle Röhrchen regelmäßig "spinnen" und in der Homogenität keine nennenswerten Störungen auftreten.

Bitte vermerken Sie unseren Beitrag zu Gunsten von Prof. H. P. Fritz.

Mit freundlichen Grüßen

*F. H. Köhler*  
F. H. Köhler

*C. G. Kreiter*  
C. G. Kreiter

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

26th June, 1973

Dear Professor Shapiro,

I think your readers may be interested to know that the following advertisement will appear shortly in the London Sunday Times and Chemistry in Britain :-

" Perkin-Elmer are an international company specialising in the manufacture of advanced scientific instruments for analytical use. To cope with current expansion the following vacancies exist in the NMR product line located at Beaconsfield, Bucks.

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A knowledge of NMR techniques, a willingness to travel and the ability to communicate are essential.

A Senior Development Engineer to assist with current development programmes and to assume responsibility for new projects. A top grade experimental physicist with a good knowledge of electronics and an interest in instrumental methods is required. Previous experience in magnetic resonance is not essential.

Salaries offered will be commensurate with qualifications and experience.

Professor Bernard L. Shapiro,  
Texas A & M University

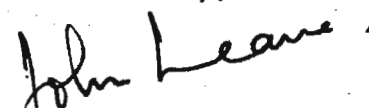
26th June, 1973.

Fringe benefits include 4 weeks annual holiday, Pension and free Life Assurance Schemes, a generous Sick Benefit scheme and subsidised Canteen.

" Assistance will be given to successful applicants in respect of re-location expenses.

I shall be very pleased to hear from anyone who may be interested in these vacancies.

Yours sincerely,



Dr. J. B. Leane  
NMR Product Manager

JBL/ECP



## Secrétariat :

Section de Physique  
de l'Université de Genève

32, boulevard d'Yvoy

CH-1211 Genève 4

Suisse

Téléphone (022) 21 93 55

## GROUPEMENT AMPÈRE

LE SECRÉTAIRE GÉNÉRAL

GJB / el

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

---

Genève, le 26 juin 1973

Cher Docteur Shapiro,

Merci beaucoup de votre lettre de rappel du 8 juin.

## 1) Travaux récents dans le domaine du magnétisme nucléaire:

- Communication à la session d'automne de la Société Suisse de Physique - Lucerne 13-14 octobre 1972:

Echos de Spins en régime permanent

G.J. Béné, Département de Physique de la Matière Condensée,  
Université de Genève.

Les échos de spins peuvent être définis, pour un système quelconque, comme un retour temporaire dans un état ordonné, cet état ayant été antérieurement détruit par une cause réversible, après inversion de l'effet de cette cause. Traditionnellement, cet état ordonné est une aimantation cohérente. Il peut être une simple polarisation. Par une analogie avec la focalisation des jets atomiques ou moléculaires, nous montrons qu'il est possible d'obtenir des échos de spins en régime permanent, en utilisant par exemple comme échantillon un liquide en mouvement: il suffit en effet que l'écho soit obtenu en un endroit différent des zones où sont produites la cohérence initiale, la destruction et le rétablissement de l'état ordonné.

- Communications à la session de printemps de la Société Suisse de Physique - Neuchâtel 4-5 mai 1973:

Echos de spins en gradient alternatif

B. Borcard et G.J. Béné, Département de Physique de la Matière Condensée, Université de Genève

Cette méthode de travail permet de s'affranchir des impulsions de renversement d'un gradient constant pour obtenir des échos de spins. L'emploi d'un gradient pur alternatif,

Prof. B.L. Shapiro, Texas, U.S.A. le 26 juin 1973

---

superposé à un champ constant très homogène facilite considérablement l'emploi de périodes très courtes pour l'inversion du référentiel. Nous discutons quelques applications possibles de cette nouvelle technique.

Effet Overhauser et haute résolution dans le champ magnétique terrestre.

R. Séchehaye, B. Borcard, E. Hiltbrand, G.J. Béné, Département de Physique de la Matière Condensée, Université de Genève.

L'étude théorique et expérimentale de la polarisation dynamique protonique dans le champ magnétique terrestre a porté sur quelques solvants peu visqueux contenant le radical stable tétraméthyle-2, 2, 6, 6-pipéridone 4-oxyde ou tanone. La mesure de la constante de relaxation spin-réseau  $T_1$  et la connaissance des fréquences protoniques et électroniques ont permis le calcul du facteur multiplicatif de la polarisation protonique et sa comparaison avec la valeur mesurée. Cette technique de polarisation a été appliquée à la mise en évidence des couplages des noyaux  $C_{13}$  et  $P_{31}$  avec le proton. Les résultats ont été comparés à ceux de la précession libre.

## 2) Nouvelles du Groupement Ampère:

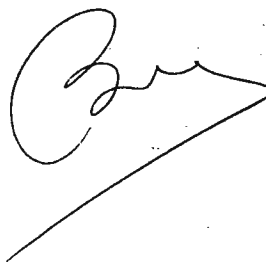
- Nous rappelons le 1er Colloque spécialisé Ampère qui aura lieu à Krakow (Pologne) du 28 août au 1er septembre 1973.
- 18e Congrès Ampère - Nottingham, 9-14 septembre 1974. Magnetic Resonance and Related Phenomena. (Chairman Prof. E.R. Andrew).

The programme of the 18th Ampere Congress will cover the whole range of magnetic resonance and radio frequency spectroscopy as applied in Physics, Chemical Physics and Biophysics. This includes both the experimental and the theoretical aspects of n.m.r., e.p.r., molecular beams and Mössbauer spectroscopy.

More detailed information concerning accommodation, submission of papers and the social programme will be circulated late in 1973. For further information please address all correspondence to one or other of the Local Secretaries: Dr. P.S. Allen and Dr. C.A. Bates, 18th Ampere Congress, Department of Physics, University of Nottingham, Nottingham NG7 2RD, England. (Telephone Nottingham (0602) 56101 extension 2842, Telex 37346.

Meilleurs sentiments,

Prof. G.J. Béné.



## Southern Research Institute

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 TELEPHONE 205-323-6592

June 22, 1973

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

Dear Barry:

The following is a copy of a communication which Dr. W. C. Coburn, Jr., and I have just submitted for publication. Hope this will be in time to keep me from getting a pink notice.

The  $^{13}\text{C}$  Magnetic Resonance Spectrum of Imidazole

In connection with our work on the  $^{13}\text{C}$  magnetic resonance spectra of nitrogen heterocycles, we had occasion to run the  $^{13}\text{C}$  spectrum of imidazole in the solvent  $\text{DMSO}-d_6$ , since no literature data were available for imidazole in this solvent. When we compared our data with those of Weigert and Roberts (1), who had studied this compound in acetone, we found that our value of  $^1J_{\text{C}_4\text{H}_4} = ^1J_{\text{C}_5\text{H}_5}$  was 11 Hz smaller than theirs, a surprisingly large discrepancy. Since our measured chemical shifts,  $^1J_{\text{C}_2\text{H}_2}$ , and long-range C-H coupling constants agreed reasonably well with their values, we decided to remeasure these parameters in acetone- $d_6$  and chloroform- $d$ . Our results, together with comparative data from the literature, are shown in Tables 1 and 2.

As may be seen from the data in Table 2, our value for  $^1J_{\text{C}_4\text{H}_4}$  in acetone- $d_6$  is close to the values determined in other solvents and is also confirmed by the  $^{13}\text{C}$  satellite values measured from CW pmr spectra.

As Weigert and Roberts (1) point out, the coupled  $^{13}\text{C}$  spectrum of imidazole is first order, so the relative signs of the coupling constants cannot be obtained. They also discuss the fact that there is an ambiguity in the assignment of the two long-range coupling constants involving  $\text{C}_4$ , but they assigned the larger of the two to  $^2J_{\text{C}_4\text{H}_5}$  by analogy with the

Professor B. L. Shapiro  
June 22, 1973

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TABLE 1  
CHEMICAL SHIFTS OF IMIDAZOLE

Solvent	Chemical Shift (ppm. downfield from internal TMS)		Ref.
	$\delta_{C_2}$	$\delta_{C_4} = \delta_{C_5}$	
CDCl <sub>3</sub>	135.27+0.02	121.78+0.02	This work <sup>a</sup>
DMSO-d <sub>6</sub>	135.46+0.02	121.92+0.02	This work <sup>a</sup>
Acetone-d <sub>6</sub>	136.14+0.02	122.46+0.02	This work <sup>a</sup>
Acetone	135.7	121.8	(1) <sup>b</sup>
H <sub>2</sub> O	136.4	122.5	(2) <sup>b</sup>

<sup>a</sup>Measured at 25.16 MHz in the pulsed FT mode on a Varian XL-100-15 spectrometer equipped with a Digilab NMR-3 data system. Nearly saturated solutions were employed in each case.

<sup>b</sup>Values quoted by Stothers, Ref. (3), after conversion to the TMS scale.

TABLE 2  
C-H COUPLING CONSTANTS OF IMIDAZOLE

Solvent	$J_{CH}$ (Hz)					Ref.
	$^1J_{C_2H_2}$	$^1J_{C_4H_4}$	$^2J_{C_4H_5}$	$^3J_{C_2H_4}$	$^3J_{C_4H_2}$	
		$=^1J_{C_5H_5}$	$=^2J_{C_5H_4}$	$=^3J_{C_2H_5}$	$=^3J_{C_5H_2}$	
CDCl <sub>3</sub>	205.1+0.3	188.6+0.3	13.4+0.3	9.2+0.3	7.3+0.3	This work
DMSO-d <sub>6</sub>	206.1+0.3	187.7+0.3	13.6+0.3	9.5+0.3	7.5+0.3	This work
Acetone-d <sub>6</sub>	205.7+0.3	188.0+0.3	13.4+0.3	9.2+0.3	7.3+0.3	This work
Acetone	208	199	13.0+0.1	9.4+0.1	7.3+0.1	(1)
D <sub>2</sub> O	208+1	190+1	—	—	—	(4) <sup>a</sup>
Acetone-d <sub>6</sub>	206+1	188+1	—	—	—	This work <sup>a</sup>

<sup>a</sup>These values were determined from the separation of the <sup>13</sup>C satellites in the <sup>1</sup>H magnetic resonance spectra.

Professor B. L. Shapiro  
June 22, 1973

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corresponding coupling constants in 1,2,3-triazole. We have verified this assignment by measuring the  $^{13}\text{C}$  spectrum of a sample of imidazole in  $\text{DMSO-d}_6$  in which  $\text{H}_2$  had been more than 50 percent exchanged for deuterium by heating the solution, to which a few drops of 5-N NaOD had been added, for several hours at  $100^\circ\text{C}$ . The degree of exchange was determined from the pmr spectrum. The smaller coupling assigned to  $^3\text{J}_{\text{C}_4\text{H}_2}$  clearly disappeared in the exchanged imidazole.

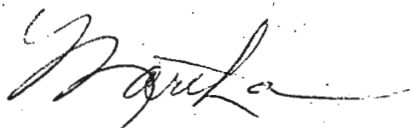
Martha C. Thorpe  
W. C. Coburn, Jr.

Kettering-Meyer Laboratory  
Southern Research Institute  
Birmingham, Alabama 35205

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Sincerely,



Martha C. Thorpe  
Senior Chemist

MCT:bbm

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