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Newsletter

No. 272

May, 1981

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DEADLINE DATES: No. 273 1 June 1981
 No. 274 6 July 1981

All Newsletter Correspondence, Etc., Should be Addressed To:

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

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The University of Western Ontario

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April 2, 1981

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

^{113}Cd NMR of Some Complexes with Model Oxygen, Sulfur, and Selenium Donor Ligands

Dear Professor Shapiro,

The slow-exchange ^{31}P -coupled ^{113}Cd nmr spectra of some cadmium complexes of phosphine oxides, sulfides and selenides, previously studied by low temperature ^{31}P nmr (1), have provided us with some interesting results.

In liquid SO_2 at 213 K, the tetrahedral complexes $[\text{Cd}(\text{EP}(\text{C}_6\text{H}_{11})_3)_4]^{2+}$ have shifts in the sequence $\delta_{\text{O}} \ll \delta_{\text{Se}} < \delta_{\text{S}}, \delta_{\text{Cd}}$ (relative to 4 M $\text{Cd}(\text{NO}_3)_2$ at RT) being 159, 655 and 587 ppm for E = O, S and Se, respectively. The deshielding effect of replacing an oxygen donor to cadmium by a sulfur donor has been amply demonstrated already, eg. Ref. 2, but exact analogs do not seem to have been studied previously, making the separation of the effect of change of donor atom from the effect(s) of other changes difficult.

From data for a variety of complexes $[\text{Cd}(\text{EPR}_3)_n]^{2+}$, again in liquid SO_2 at reduced temperature, the chemical shift sequence is clearly $\delta_{2:1} < \delta_{3:1} < \delta_{4:1}$ as n is varied for E = S or Se. The total spread here is several hundred ppm, eg. 441 ppm for $[\text{Cd}(\text{SP}(\text{O}-\text{C}_6\text{H}_4\text{Me})_3)_n]^{2+}$. The same sequence has been deduced for $\text{CdCl}_n(\text{aq})^{(2-n)-}$ (3,4) from analyses of rapidly exchanging systems. Such analysis, demanding an accurate knowledge of all species formed, with their stabilities, is unnecessary in our work because we are able to observe unambiguous slow-exchange spectra.

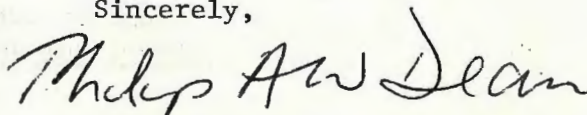
(continued)

Finally, we find that $\delta_{\text{CdO}_6} < \delta_{\text{CdO}_4}$ when a series of octahedral complexes of chelating phosphine oxides is compared with tetrahedral $[\text{Cd}(\text{OP}(\text{C}_6\text{H}_{11})_3)_4]^{2+}$. Further studies to try and separate possible chemical shift chelate effects from the effect of change in coordination number alone are planned.

A full account of this work will appear in Can. J. Chem.

Please credit this contribution to the account of Prof. J.B. Stothers.

Sincerely,



Prof. P.A.W. Dean

1. P.A.W. Dean and M.K. Hughes, Can. J. Chem. 58, 180 (1980); P.A.W. Dean and L. Polensek, Can. J. Chem. 58, 1627 (1980).
2. R.A. Haberkorn, L. Que, Jr., W.O. Gillum, R.H. Holm, C.S. Lui, and R.C. Lord, Inorg. Chem. 15, 2408 (1976).
3. T. Drakenberg, N.-O. Björk, and R. Portanova, J. Phys. Chem. 82, 2423 (1978).
4. J.J. Ackerman, J.V. Orr, V.J. Bartuska, and G.E. Maciel, J. Am. Chem. Soc. 101, 341 (1979).

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Professor B.L. Shapiro,
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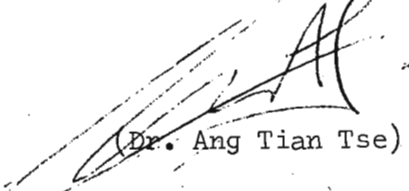
Dear Professor Shapiro,

C-13 nmr spectra of natural
rubber latex and modified NR

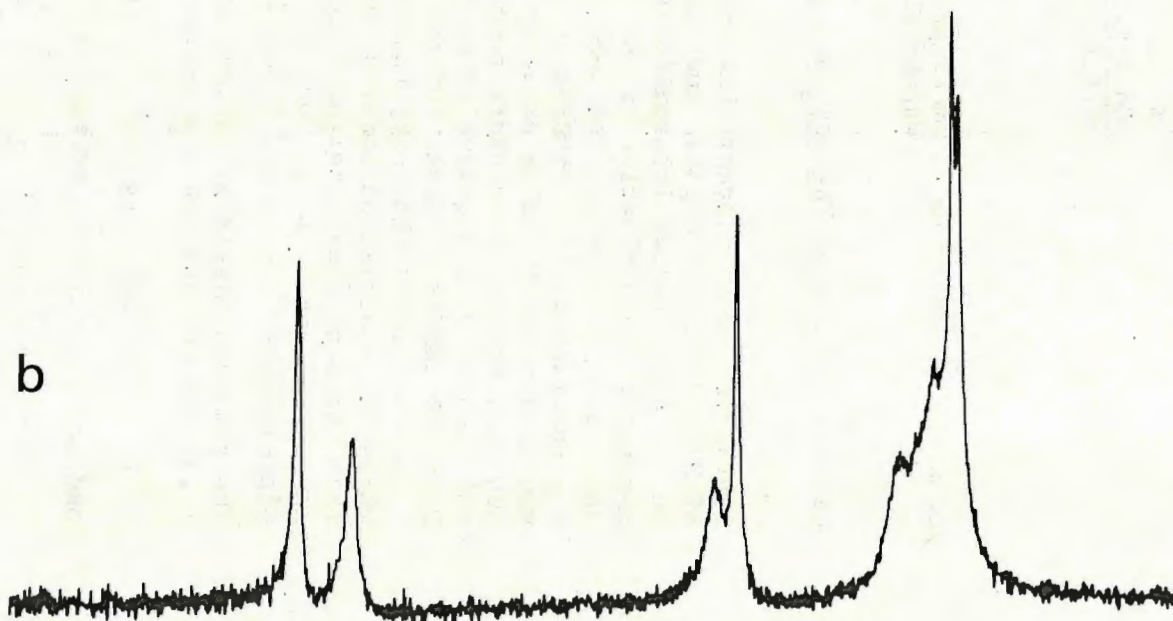
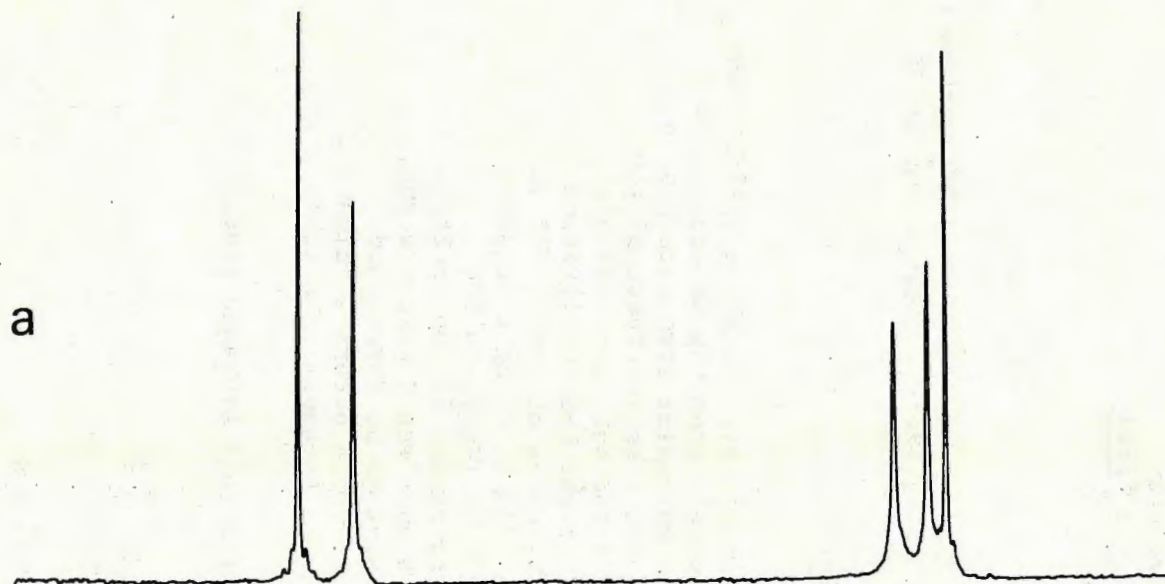
Rubber molecules above glass temperature exhibit fast mobility in the solid state and therefore high resolution C-13 nmr spectra can be obtained without spinning at magic angle.

We have obtained the C-13 nmr spectra for natural rubber latex (a) and epoxidized natural rubber (b) in solid form. The determination of the extent of epoxidization of the natural rubber by C-13 nmr in solid form agrees with the titration method. The C-13 nmr spectra of epoxidized NR in CDCl_3 show that the structure of the epoxidized NR is not $\begin{array}{c} \diagup \text{C} \text{---} \text{C} \diagdown \\ | \quad | \\ \text{O} \quad \text{O} \end{array}$.

Yours sincerely,


 (Dr. Ang Tian Tse)

ATT/nah



C-13 spectra of (a) natural rubber latex (b) epoxidized NR



TECHNISCHE HOGESCHOOL DELFT

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Dr. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
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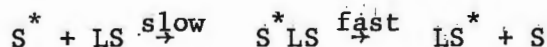
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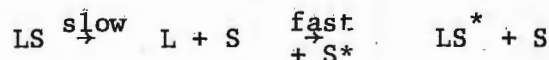
Onderwerp Adducts of Yb(Fod)₃ and quinuclidine

Lanthanide shift reagents have become valuable aids in the simplification of NMR spectra of organic compounds. Moreover, from the pseudocontact shifts quantitative information about the molecular structure can be obtained. The evaluation of these shifts requires knowledge of the equilibria involved in the complexation of the substrate (S) with the Lanthanide shift reagent (L). Therefore the L-S complexation was studied in the slow exchange region by means of proton NMR at 300 MHz, in the temperature range 250 to 330 K, using a degassed solution of 0.23 M quinuclidine and 0.12 M Yb (Fod)₃ in CDCl₃. From the number of peaks and the intensity ratios in the spectrum it was concluded that only the complex LS and free S were present, while the association constant was too large to be determined from the peak areas. Selfassociation of L, which occurs at higher concentrations of L (1), was not observable. Exchange of S takes place between free S and S bound as LS.

The two most likely mechanisms expected for this exchange process (2,3) are the associative mechanism;



and the dissociative mechanism



A linewidth study as a function of the ratio L/S gives the possibility to differentiate between these two mechanisms (2).

By doing so it was concluded that we deal with an associative mechanism.

The average lifetimes τ_S and τ_{LS} of the S and LS species in this case are given by

$$\tau_S^{-1} = k [LS] \quad \tau_{LS}^{-1} = k [S]$$

k is the reaction rate constant for the formation of the S^{*}LS intermediate. Determination of τ_S and τ_{LS} as a function of temperature from the linewidths of S and LS gave the results of the figure. Using the Eyring equation the following data were obtained for the temperature dependence of the rate constant k;

$$\Delta H^\ddagger = -27.4 \pm 2.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = -54 \pm 7 \text{ J mol}^{-1} \text{ K}^{-1}$$

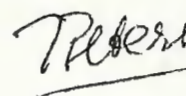
A manuscript of the complete results is in preparation.

Please credit this contribution to professor J. Smidt.

J.H. Alberts

W.M.M.J. Bovée

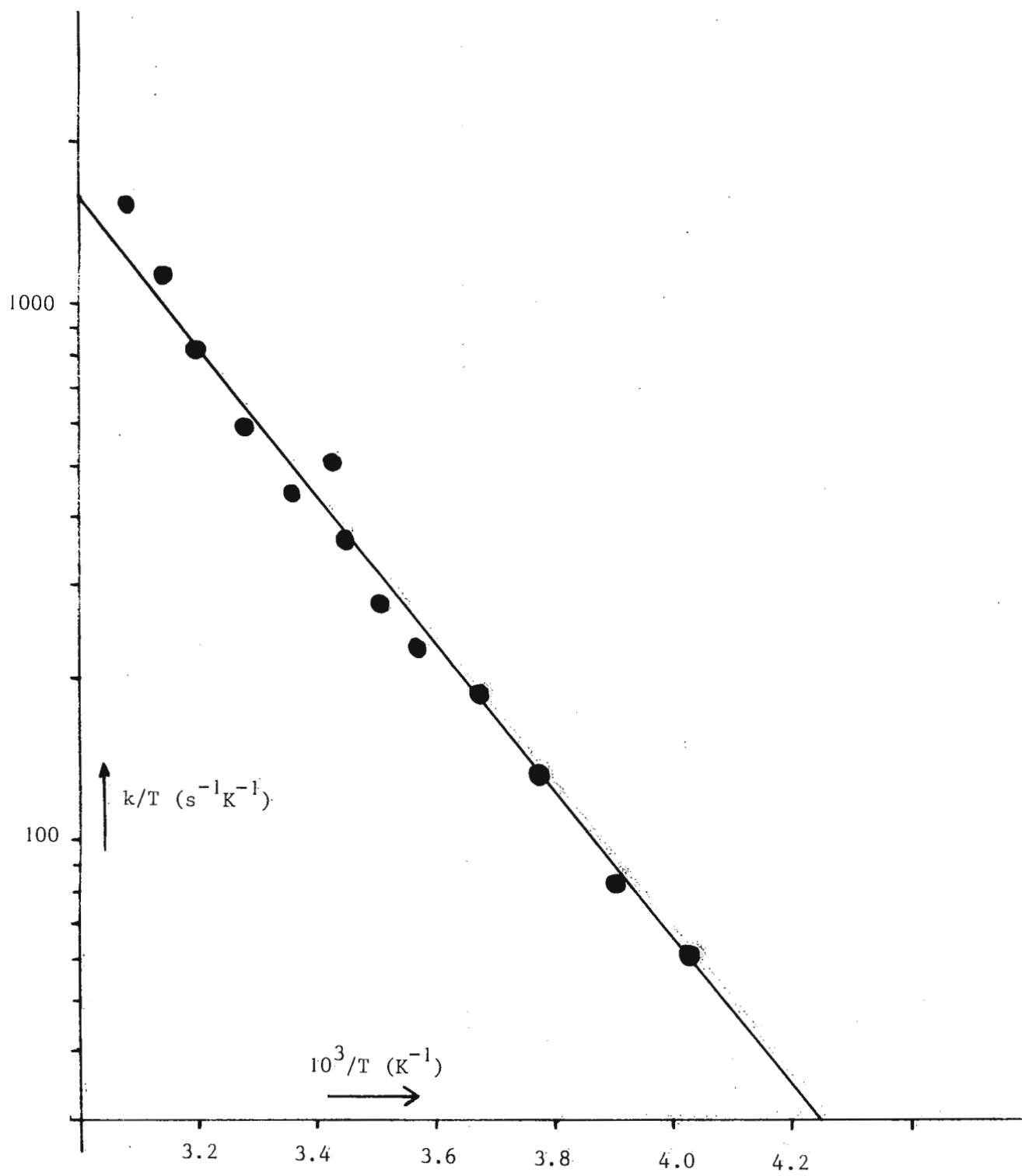
J. Peters^{*}



^{*} Chemistry Department

References:

- 1) J.A.Peters, P.J.W. Schuyt, W.M.M.J. Bovée, J.H. Alberts and H.van Bekkum
J. Org. Chem. May 1981, in press.
- 2) L.F. Lindoy, H.W. Louie,
J.Am. Chem.Soc. 101, 841, 1979
- 3) J.W.M. de Boer, Thesis Nijmegen, 1977.



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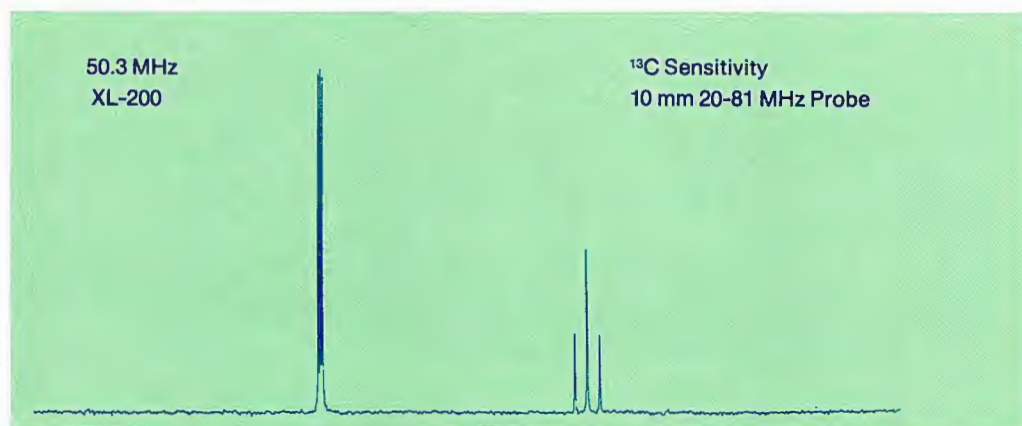
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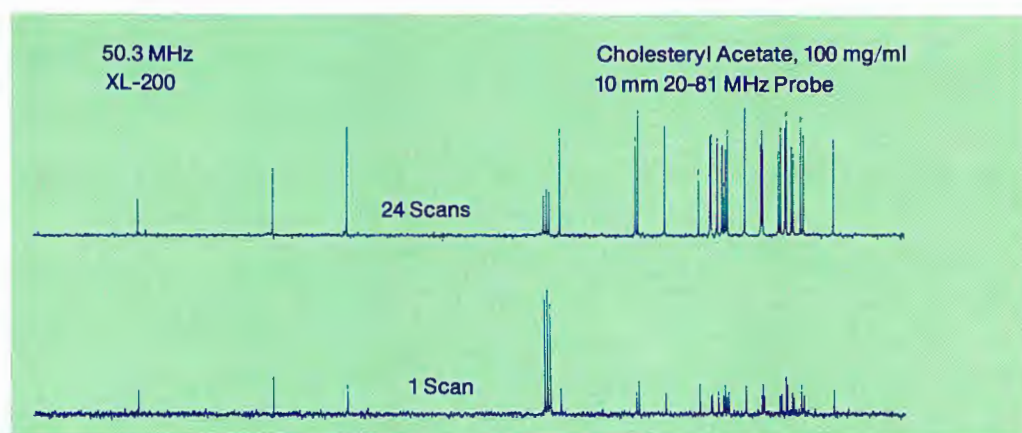
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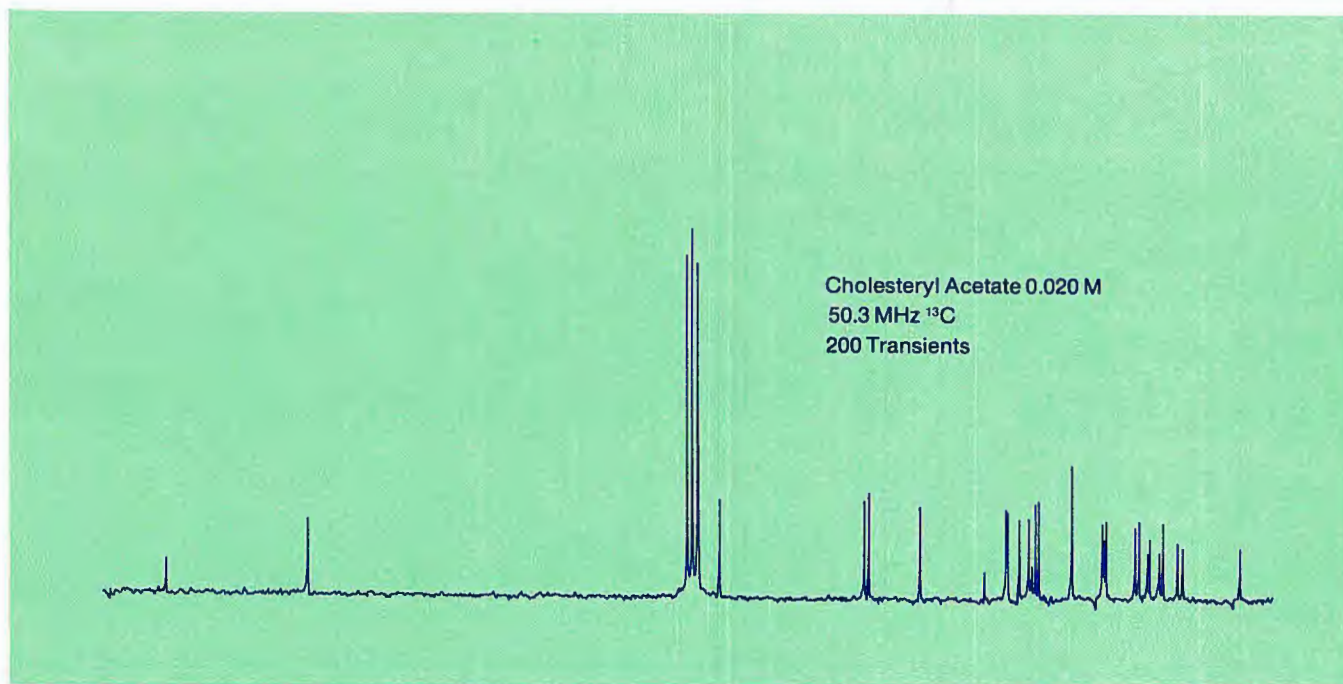
^{13}C Sensitivity Test: Single transient following 90° pulse on 60% C_6D_6 /40% dioxane using the 10 mm 20-81 MHz broadband probe.



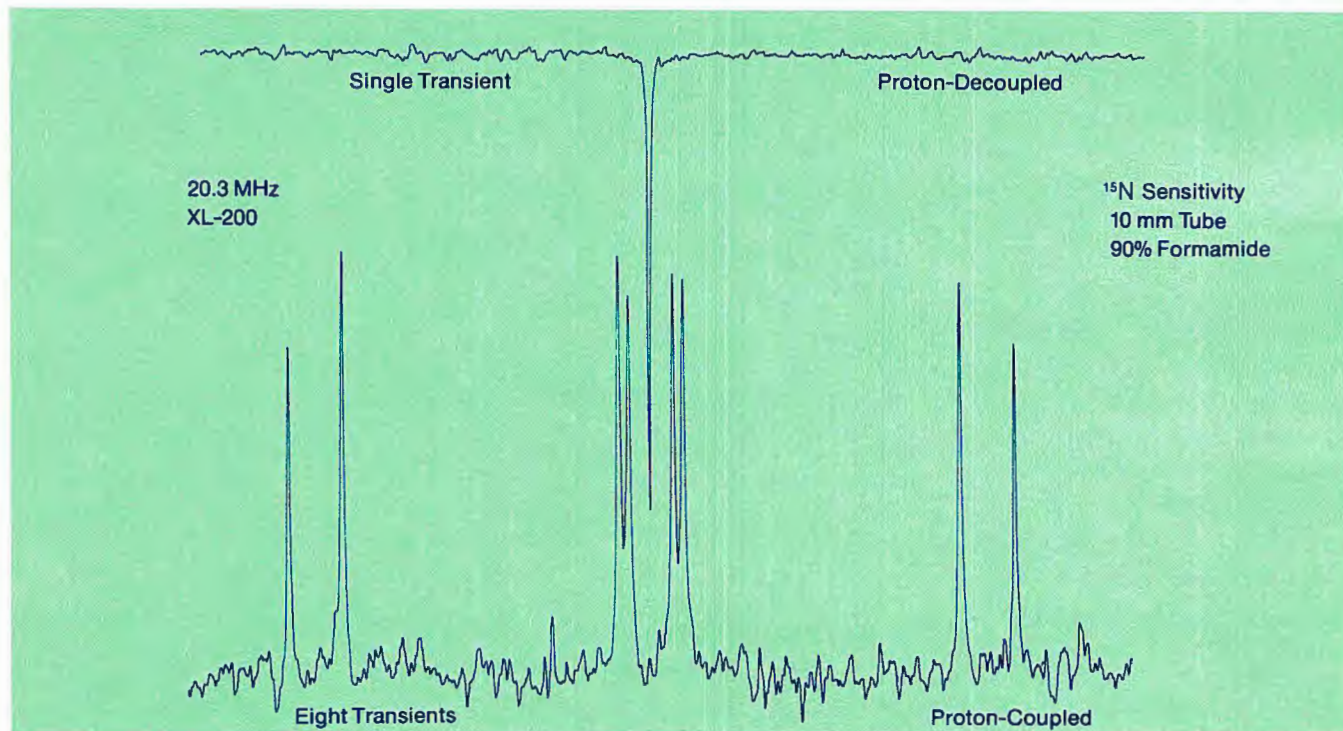
^{13}C Sensitivity Test: Cholesteryl acetate, 100 mg/ml, 10 mm broadband probe. Transients accumulated using 90° pulses every 2.28 seconds with 0.5 Hz line-broadening.

**Additional spectra appear
on the following page**





¹³C Sensitivity Test: 0.02 molar cholesteryl acetate in a 16 mm tube, 200 transients.



¹⁵N Sensitivity Test: 90% Formamide in dms_o-d₆, 10 mm 20-81 MHz broadband probe. Upper trace: single-transient (with NOE) proton-decoupled. Lower trace: eight transients, coupled (with NOE) 8-second acquisition time, 20-second delay time.

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IN REPLY
PLEASE QUOTE:

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

March 31, 1981

Dear Barry,

NMR AT THE UNIVERSITY OF SYDNEY

It may be of interest to readers of TAMUNMRN (especially for travellers) to get an overview of NMR work at this institution.

Most of the activity centers on the School of Chemistry, although Professor P. Küchel (Biochemistry) studies whole cells, Dr Ros Remedios (Anatomy) is working on actin and several workers in the Department of pharmacology and the School of Pharmacy rely heavily on NMR in their synthetic, metabolism and biogenesis work.

Within the School of Chemistry, a group under the leadership of Professor W.J. Moore (Physical Chemistry) is working on peptides and proteins in connection with fundamental studies of multiple sclerosis. A group connected with Dr P.W. Wright (Inorganic Chemistry) is involved in the study of structure and dynamics of metalloproteins, while my own group in Organic Chemistry is largely involved in DNMR and structure/parameter relationships.

In addition, the very large and active research groups in various aspects of organic and organometallic chemistry are prodigious users of ^1H and ^{13}C NMR for structural and synthetic problems.

The instrumentation comprises WM-400, HX-90, XL-100-12/FT, HA-100-D, CFT-20 and FX-60-Q instruments as well as student-operated PE 24-B and EM-360. We largely rely on in-house maintenance of instruments, although Bruker, Varian and JEOL are all represented in Sydney. The School of Pharmacy runs an FX-90-Q and PE-12.

Sincerely

S. Sternhell
Professor of Chemistry (Organic)

UNIVERSITÉ D'OTTAWA

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CANADA K1N 6N5

UNIVERSITY OF OTTAWA

DÉPARTEMENT DE CHIMIE

DEPARTMENT OF CHEMISTRY

March 30, 1981.

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

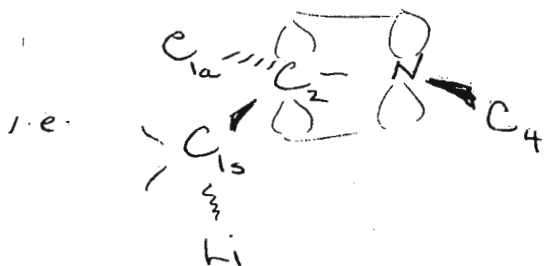
Dear Barry,

This response to your repeated reminders for an overdue contribution only became feasible with the approaching termination of classes and the increase in time available to describe some recent results.

Lithiation Shifts in Aldimines and Ketimines

Our studies (1-3) on the stereochemistry of lithiated imines has inferred a knowledge of the stereochemistry of the organometallic intermediate resulting from reaction of an imine with LDA $\{Li-N[CH(CH_3)_2]_2\}$, by a rapid alkylation with methyl iodide, benzyl bromide, etc., then examination of the stereochemistry of the alkylated product.

The observation of syn products only has led us to conclude that the anionic intermediate is also syn. We have now measured the ^{13}C spectra of a number of lithiated aldimines and ketimines and the results are given in the table for compounds 1 to 11 and their alpha-lithio derivatives (Li at C_1).



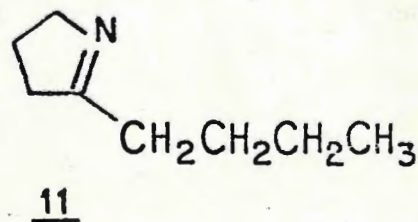
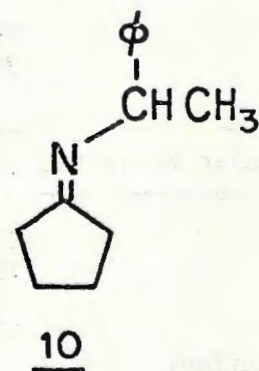
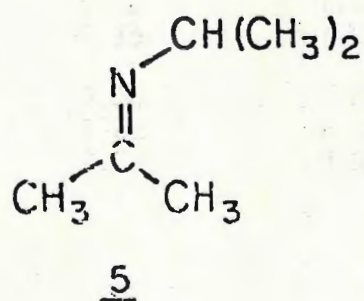
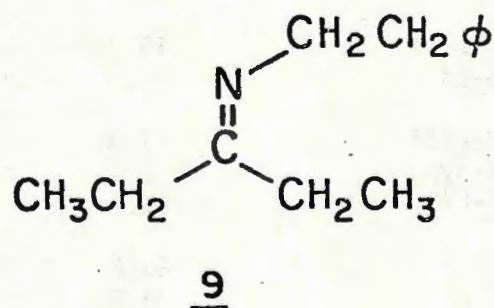
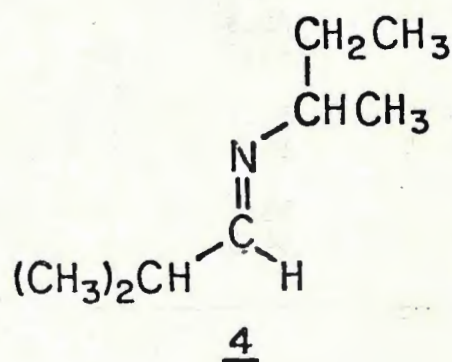
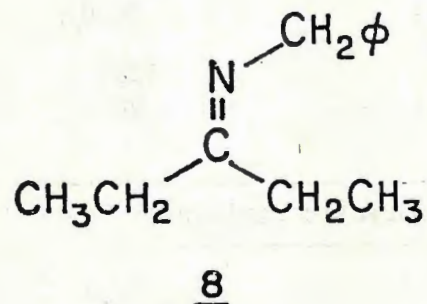
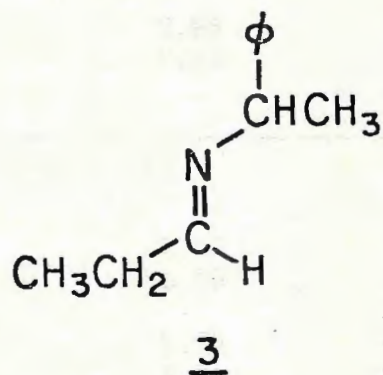
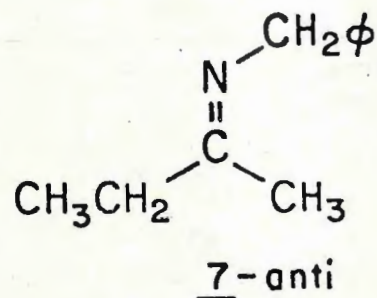
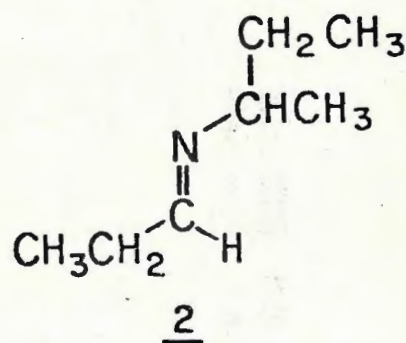
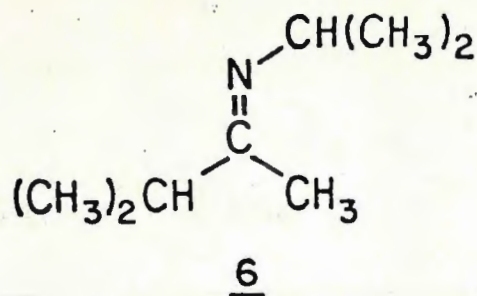
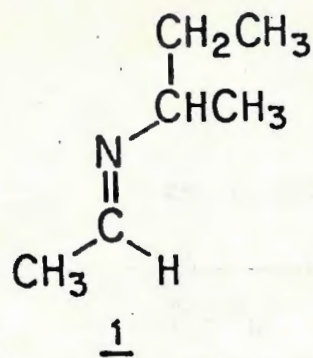


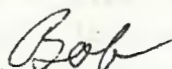
TABLE 1: ^{13}C Shieldings in Imines and Lithiated Imines

Compound	$\text{C}_{1\text{s}}$	$\text{C}_{1\text{a}}$	$\text{C}_2(=\text{N})$	$\text{C}_4(-\text{N}=)$
<u>A - Aldimines</u>				
<u>1</u>	(17)	23.1	157.9	69.5
<u>1</u> -Li	67.0		155.2	61.5
<u>2</u>	(23)	30.4	163.1	69.4
<u>2</u> -Li	76.8		152.0	60.5
<u>3</u>	(23)	30.5	164.4	71.5
<u>3</u> -Li	80.0		151.5	62.4
<u>4</u>	(28)	35.3	167.2	69.2
<u>4</u> -Li	90.7		145.1	60.9
<u>B - Acyclic Ketimines</u>				
<u>5</u>	17.8	30.1	163.6	50.5
<u>5</u> -Li	67.9		160.7	50.0
<u>6-anti</u>	15.3	41.0	169.9	51.3
<u>6</u> -Li	61.3		171.1	49.2
<u>7-anti</u>	17.8	36.2	-	55.7
<u>7-syn</u>	27.2	26.4	-	55.3
<u>7</u> -Li	64.5	33.8	-	55.7
<u>8</u>	25.6	33.1	-	54.7
<u>8</u> -Li	74.9	30.1	-	55.8
<u>9</u>	25.6	33.2	174.2	53.8
<u>9</u> -Li	76.6	30.4	159.8	54.3
<u>C - Cyclic Ketimines</u>				
<u>10</u>	29.6	37.9	178.1	63.7
<u>10</u> -Li	79.5	37.7	162.1	61.0
<u>11</u>	37.2	33.6	178.2	60.9
<u>11</u> -Li(major)		74.6	165.4	56.2
<u>11</u> -Li(minor)		78.3	162.5	57.2

As the data in Table 1 shows, the shifts for C_4 - the sp^3 carbon attached to nitrogen-provides clear evidence of a syn configuration in the lithiated aldimines 1-4 in exhibiting a large (8-9 ppm) upfield shift on lithiation which is attributable to the δ effect introduced by the change in configuration at the C_2 -N bond from anti imine to syn lithio derivative. No such effect is seen in the ketimines as there is no γ effect introduced on lithiation. The other shifts at C_1 and C_2 show clear similarities to those reported by House for the analogous enolates (4,5).

We have also detected an unusually high rotational barrier about the N- C_4 , bond (~ 12 kcal/mole) in these lithiated imines and these results which confirm the syn stereochemistry have recently appeared in print (6).

Yours sincerely,



Robert R. Fraser

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6. R.R. Fraser, N. Chuaqui-Offermann, K.N. Houk and N.G. Rondan. J. Organometal. Chem., 206, 131 (1981).

C. N. R.

Centro di Studio per le
Sostanze Organiche Naturali
presso

Istituto di Chimica del Politecnico

20133 MILANO - Piazza Leonardo da Vinci, 32
Tel 230845-6-7-8-9

April 14, 1981

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

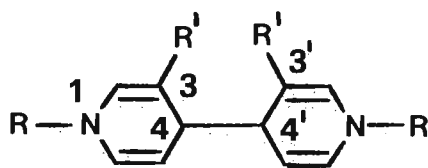
Dear Barry,

An NMR evidence for the structure of dimers of NAD⁺

Recently we succeeded in analysing by ¹H and ¹³C NMR the complex mixture obtained from the electrolysis of NAD⁺ (nicotinamide adenine dinucleotide).

The basic electrochemical reduction pathway of NAD⁺ has been well established and extensively reviewed. It has been consistently found that the uptake of one electron leads to the formation of a radical, that undergoes irreversible dimerization. However neither the structure of the dimeric products, nor the number of the isomers obtained has been proved yet.

The complete analysis of the ¹³C spectrum of the reaction mixtures, together with the parallel measurements at 270 MHz of the proton spectra, led to the conclusion that the dimerization occurs at the 4,4' positions. We could also exclude the presence of dimers 4,6' or 6,6' linked, for the mixture in our hands, by comparison with the model compounds **2**, **3** and **4**.



- 1** R = ribose-phosphate-phosphate-ribose-adenine
R' = H
- 2** R = C₆H₅
R' = CONH₂
- 3** R = CH₃
R' = CN

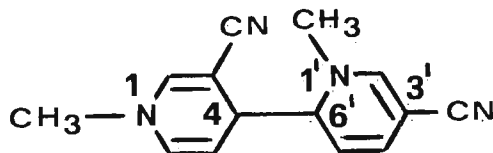


Table 1. ^{13}C NMR Chemical Shifts Assignments for Dimers 1 and NADH.⁽⁺⁾

	Dimers 1	NADH
N-7	174.9, 174.1, 173.5, 172.9	173.3
A-6	155.8	156.1
A-2	153.3	153.4
A-4	149.3	149.6
A-8	140.3	140.4
N-2	141.2, 135.9, 135.0, 130.2	139.1
N-6	129.1, 124.8	124.7
A-5	119.0	119.3
N-5	106.1, 104.1, 103.0	106.1
N-3	105.0, 103.6, 102.1, 101.3	100.8
N-1'	97.1, 95.6	95.9
A-1'	88.1, 87.9	88.0
A-4'	84.3	84.4
N-4'	83.1, 82.8	83.1
A-2'	75.2	75.3
N-2'		
N-3'	72.9, 72.4, 71.2	71.6, 71.3, 71.0
A-3'		
N-5'	66.7	66.7
A-5'	66.1	66.0
N-4	40.0, 39.8, 39.7, 39.6	22.7

(+) A and N are the carbon atoms of adenine and nicotinamide respectively; A' and N' are the sugar carbon atoms of the adenine and nicotinamide nucleoside respectively.

Taking account that in 4,4'-linked dimers two additional chiral centers must be considered and that the configuration of the adenosine diphosphato ribose moieties is retained, evidence has been given for the presence in our reaction mixture of the three diastereoisomers **1a-1c** :

dimer 1a	A, R, R, A	(where A is the adenosine
dimer 1b	A, S, S, A	diphosphato ribose moiety)
dimer 1c	A, R, S, A	

For dimer **1a** and **1b**, corresponding groups in the two halves are stereochemically equivalent by internal comparison, and must show chemical shift equivalence, whereas for dimer **1c** the corresponding groups are diastereotopic and may give different NMR signals. Consequently the NMR spectrum of a mixture of the above three diastereoisomers can exhibit a maximum of four signals for each proton and carbon of a certain structural type.

Actually the ^{13}C NMR spectrum (table 1) shows the quadrupling of the signals of the dihydropyridine carbon atoms, whereas the adenine and ribose carbons give broader signals (width ca 10 Hz). The assignment was performed by the multiplicity of the signals and on the basis of the

assignments given for NADH.^{a)}

Although the possibility of slow conformational processes cannot be completely excluded for the dimers, we can reasonably conclude that the quadrupling of the NMR signals is due to the presence of the three diastereoisomers **1a-1c**, because the ^{13}C spectrum of NADH in the same conditions shows one single resonance for each carbon atom.

An interesting result is the biological activity shown by the NAD^+ dimers that we have prepared: a liver cytoplasmatic preparation stimulates the oxygen uptake by the dimeric product as well as by NADH, to yield NAD^+ .

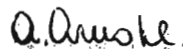
The oxygen consumption is in favour of H_2O_2 formation. This not only leads to a re-evaluation of the claimed lack of biological activity of these compounds, but also stimulates new ideas in corrent theories of electron transfer by pyridine coenzymes.

a) B. Birdsall and J. Feeney, J. Chem. Soc. Perkin Trans. 2, 1643 (1972).

Sincerely yours,



R. Mondelli



A. Arnone.



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ISOTOPE DIVISION

April 27, 1981

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

Subject: Letter from Gruppo LePetit, Research Labs., Via Durando, 38, 20158 Milano.
RE: Water in Deuterated DMSO

Dear Prof. Shapiro:

A copy of Drs. Martinelli and Ripamonti's paper entitled "Water in Deuterated Dimethyl Sulphoxide" as submitted to you August 1980 has been referred to us by Mr. Suraj Manrao. In turn, I have asked both the synthesis labs and our quality control labs for their independent comments on the findings reported. Their comments follow.

First, we must point out that the "Merck" referred to as source is probably not MSD Canada, but rather E. Merck, Darmstadt, Germany, a separate, independent company that also sells NMR solvents and who have most of the business in Italy. (Our distributorship in Italy have no record of selling DMSO-d₆ to Gruppo LePetit.)

Comments from our laboratories are as follows:-

From Dr. Grant Reader, Manager, NMR Solvents Production Lab:

"The most likely explanation is that the two peaks for water are due to the presence of both H₂O and HOD. The lower field, smaller peak is H₂O and the higher field, larger peak is HOD. HOD is expected at higher field than H₂O because deuterium substitution causes an upfield shift of other nuclei in the molecule - this fact is known and published in the literature.

"The concentrations of H₂O and HOD are sufficiently low so that exchange between them is sufficiently slow - on an NMR timescale - that two peaks are seen. Raising the temperature, raises the rate of exchange, leading to coalescence of the peaks - as observed by these researchers."

From Mr. S.C. Ho, Supervisor, Quality Control laboratory:

"The two peaks referred to by the customer are due to H₂O and HOD @ 20°C.

The fact that the rate of exchange between the H & D atoms increases with increase in temperature explains the customer's observation that the two peaks coalesce at 80°C. At this temperature, the rate of exchange is so rapid that the resonance signals average out to a singlet."

Yours very truly,

C.P. / P.O. BOX, 899 POINTE-CLAIRE - DORVAL, QUÉBEC H9R 4P7 TELEPHONE 514-697-2823

Cable: ISOMERCK / Telex: 05-821-533

Maureen Kallos
Manager, Technical Sales Service,
Stable Isotopes.

cc: Mr. S. Manrao

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

April 15, 1981

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

Dear Dr. Shapiro:

"A Versatile Computer Interface for a Pulsed NMR"

In our letter of May 2, 1978, we described our home-built pulsed NMR spectrometer, which we use primarily for relaxation-time measurements of bulk water protons in biochemical solutions. Briefly, the spectrometer consists of a magnet from a Varian DA-60, and a two-channel pulse programmer and r.f. circuitry built by SEIMCO of New Kensington, Pa.

As useful and versatile as this instrument has been, we realized that a computer interface could enhance the capabilities even more. We have now constructed an interface to a DEC LSI-11-based computer (specifically, a Heath H11-A) which allows the computer to set pulse intervals, sweep the field, and digitize FID's. It thus became possible to have relaxation times determined quickly and automatically, freeing the operator from staring at a flashing oscilloscope and automating the laborious data reduction which is sometimes necessary. Additionally, a fitting routine is employed to determine best values for relaxation times; this routine can also correct for improperly set pulse widths. The computer can also detect a drift in the field (by counting the "beats" in an FID) and corrects it accordingly. This is important because we operate the instrument without a lock.

It recently occurred to us that we can use the computer and pulse programmer together to implement pulse sequences not possible with the programmer alone. (This is similar to firing a 21-gun salute with only two guns; it can be done if the guns can be reloaded quickly enough.) When channel A of the programmer is "firing", the computer loads new pulse-interval values into channel B, and so on. Thus pulse sequences with more than two distinct delay times are possible. Furthermore, data acquisition and reduction of the Carr-Purcell and Meiboom-Gill pulse sequences are facilitated. The ability to set pulse widths and phases by computer, which we will soon implement, will allow virtually any pulse sequence to be generated.

Perhaps the most impressive feature of this interface is that it can be built for about \$2500, including the computer. (The actual interface is about \$600.) We believe this interface is general enough to be used with other pulse programmers, and almost any reasonably powerful microcomputer could be substituted for the LSI-11. We would be happy to provide more details to interested readers.

Please credit this to the account of Mr. Bill Hutton.

Sincerely,

Thomas Spraggins

Thomas Spraggins
Graduate Student

Charles M. Grisham

Charles M. Grisham
Associate Professor

Postdoctoral Position Available

A postdoctoral position will be available beginning June 1, 1981. Research is directed at elucidating the structural, permeation and transformation properties of vesicular lipid membranes. Nuclear magnetic resonance techniques are used extensively in this research. Yale will be well equipped to carry out this research with facilities that include 4.7, 6.3, and 11.7 Tesla superconducting spectrometers.

Preference will be given to applicants who have experience in one or more of the following areas: 1) nuclear magnetic resonance, 2) lipid biochemistry, 3) isolation of vesicular organelles. Applicants should send a resume and 3 letters of recommendation to:

Dr. J. H. Prestegard
Chemistry Department
Yale University
225 Prospect Street
P. O. Box 6666
New Haven, CT 06511



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DEPARTMENT OF CHEMISTRY

May 1, 1981

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

Dear Barry:

"On the Sign of $^5J(H-C_\alpha-C(O)-N-C_\alpha-H)$ Coupling Constants: A Second Try"

Our previous contribution to the Letters [261, 26 (1980)], which was also submitted under the pressure of expulsion, presented some results for the signs of the five bond H-H coupling constants in cyclo-[Gly-Tyr]. Based on the spin tickling results, it was concluded that the syn and anti values were of the same sign. Our guess was that they were both negative, but that we were waiting for a more suitable model compound. Since that time, we received a sample of cyclo-[Gly-Phgly] from F. A. Al-Obeidi in Victor Hruby's group. At 250 MHz the spectrum in D₂O at pH 3 is of the ABX type. Spin tickling of every line in the spectrum shows that the two five bond coupling constants (1.37 and 1.59 Hz) are also of the same sign but they are opposite in sign to the geminal H-H coupling constant (-18.53 Hz). Although coupling constants of the type $^5J(H-C_\alpha-C(O)-N-C_\alpha-H)$ are exceedingly solvent dependent, becoming too small to be observed in certain mixed solvents, it seems unlikely that there would be a sign change between the two compounds. Therefore, it now seems more likely that the five bond H-H coupling constants in cyclo-[Gly-Tyr] are both positive in contradiction to our previous guess.

As noted previously, the calculated INDO-FPT molecular orbital results for several orientations of cyclo-[Gly-Gly] correspond to syn and anti coupling constants of opposite sign. Not only are these results in disagreement with the experimental data, we have been unable to determine the mechanisms which are implicit in the theoretical model and which lead to values of opposite sign.

Sincerely yours,

Mike

Mike Barfield
Steve Walter

UNIVERSITÄT DES SAARLANDES

Fachbereich 14 - Organische Chemie

66 Saarbrücken, den 16.4.81-bi

Telefon: (0681) 302.3409

Herrn

Professor Dr. B.L. Shapiro

Department of Chemistry

Texas A and M University

College Station

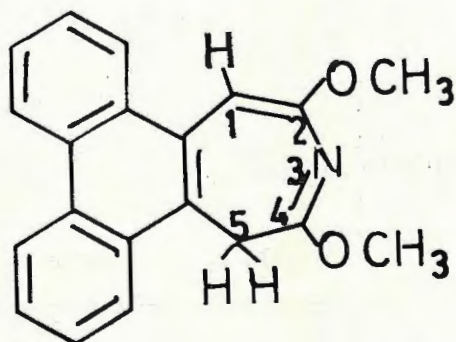
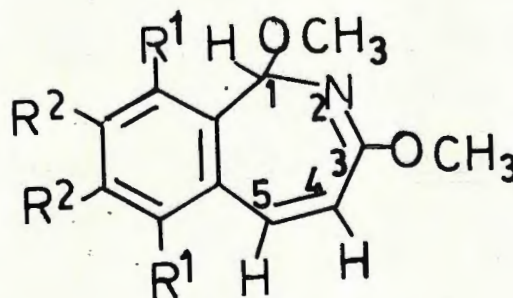
Texas 77843

USA

Dear Professor Shapiro,

Proton NMR Spectra of some Benzazepines

Recently we prepared the benzazepines 1 and 2 whose ^1H NMR are presented in this paper.

12

	R ¹	R ²
<u>a</u>	Benzo	
<u>b</u>	Ph	Ph
<u>c</u>	Ph	H
<u>d</u>	Cl	Cl

Table 1: ^1H -NMR spectrum of the benz[d]-3H-azepine 1

5-H	1-H	OCH_3	aromat. H
2.84/3.03 ($^2J = 7.6$)	7.09 s	3.63/3.67	7.3-7.9

1 shows similar chemical shifts as 4-amino-2-bromo-benz[d]-3H-azepine ¹⁾. The 2J coupling of the methylene protons is relatively small compared with the corresponding values measured for azepines at low temperature ²⁾. This may be due to the electronegative substituents. The fact that we can observe two separated signals for the C-5-methylene protons demonstrates that the inversion of the azepine ring is too slow considering the NMR scale at 300 K.

Table 2: ^1H NMR data of benz[c]-2H-azepines 2

Cpd	1-H	4-H	5-H	OCH_3	arom.a.olef.H
<u>2a</u>	5.47 s	6.07 d ($^3J = 7.9$)	6.75 d	3.91 s 4.09 s	7.1- 8.4 m
<u>b</u>	5.31 s	5.89 d ($^3J = 7.9$)	6.78 d	3.79 s 3.81 s	7.0- 7.2 m
<u>c</u>	4.64 s	6.24 d ($^3J = 7.6$)	6.70 d	3.78 s 3.84 s	7.0- 7.6 m
<u>d</u>	6.48 s	6.30 d ($^3J = 8.2$)	7.39 d	3.92 s 4.04 s	

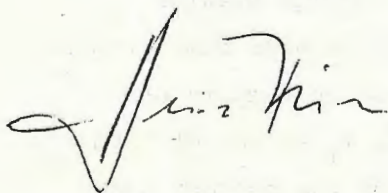
The chemical shifts of the C1 protons of 2 are remarkably depending upon the substituents at the benzene ring. C1 deshields 1-H whereas the phenyl groups shift this signal to higher field probably due to their anisotropy effect. Similar effects can be observed at the 5-H signal which is shielded by phenyl groups in 2a-c.

The 3J coupling between 4-H and 5-H is nearly unchanged in all compounds showing that the geometry of the heterocyclic ring is not much affected by the substituents at the benzene ring.

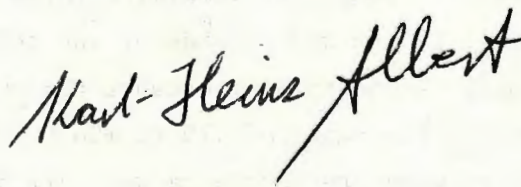
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- 1) F. Johnson and W.A. Nasutavicus, J. Heterocycl. Chem. 2, 26 (1965).
- 2) a) T.J. van Bergen and R.M. Kellogg, J. Org. Chem. 36, 978 (1971);
b) A. Mannschreck, G. Rissmann, F. Vögtle and D. Wild, Chem. Ber. 100, 335 (1967).

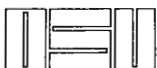
Yours sincerely



Prof. Dr. H. Dürr



Dr. K.-H. Albert



Oklahoma State University

Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74074

April 16, 1981

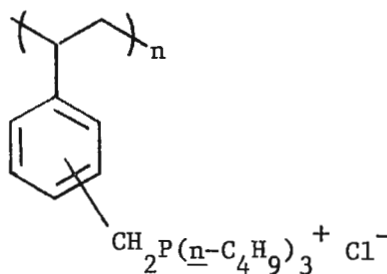
Dr. B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Title: ^{13}C Relaxation of Solvent Molecules in Polymer Gels

Dear Dr. Shapiro:

Interest in mechanisms of polymer-supported catalyst action prompted us to examine ^{13}C NMR spectra of insoluble, crosslinked polystyrene gels in swelling solvents. In DCCl_3 , many samples give a triplet of doublets for the DCCl_3 signals. We attribute the doublets to DCCl_3 molecules inside and outside of the polymer beads. Both halves of each doublet are broadened to 4-8 Hz linewidth because of sample heterogeneity.

Many of our catalysis experiments employ toluene as a solvent, so we chose to examine in more detail the effects of insoluble catalysts containing quaternary phosphonium groups on ^{13}C NMR spectra of toluene. Again all of the toluene ^{13}C signals are split into doublets whose peak separation is



largest for the methyl carbon. The peaks are 4-8 Hz wide and always overlap at 25.2 MHz. Attempts to determine rates of exchange of toluene between environments inside and outside of the polymer beads from variable temperature spectra have failed to date because the spectra show almost no temperature dependence in the range of +10 to +90°C. However, the ^{13}C T_1 values of both peaks for toluene are shortened markedly by the presence of the polymer beads as shown in the Table. All experiments were done on our XL-100(15)/Nicolet TT-100 system at ambient temperature. In bulk liquid ^{13}C relaxation of toluene

April 16, 1981

occurs by a combination of spin rotation and direct dipolar mechanisms. Our T_1 data agree well with literature results. The short T_1 values and the heterogeneous polymer samples indicate that rotational diffusion of solvent molecules is slowed markedly both inside the polymer network and in the spaces between beads of a tightly packed sample. Since bead sizes in these experiments were as large as 100-200 μm , the influence of the bead surface on rotational diffusion must extend tens of microns out into the surrounding liquid. Experiments designed to factor out the direct dipolar contributions to the T_1 s, and hence the rotational correlation times of toluene in the various environments, are in progress.

Sincerely,

Warren T. Ford

Warren T. Ford
Associate Professor

Table

¹³C NMR Spin-lattice Relaxation Times of Toluene in Gel Polystyrene Beads

Carbon Sources	T_1 Values (sec)		
	Neat Liquid	Inside Beads	Outside Beads
H_3C	16	4.9	7.4
<u>ortho</u> carbon	24	3.5	4.9
<u>meta</u> carbon	23	3.7	4.8
<u>para</u> carbon	19	2.6	3.6



File Référence

1 April 1981

Professor B.L. Shapiro,
Texas A and M NMR Newsletter,
College Station, Texas 77843,
USA

Dear Barry,

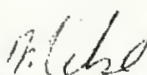
LIPID POLYMORPHISM
CHECKING UP ON ^{31}P BY ^2H NMR

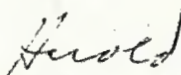
The phase behaviour of a large number of phospholipids has been investigated by ^{31}P NMR (1). This nucleus is well suited to such studies since the ^{31}P NMR chemical shift anisotropy is sensitive to the symmetry of the lipid phase. We have recently used a specifically-deuterated phospholipid in examining lipid phase transformations (2). Deuterium labelling allows examination of a specific lipid in mixtures (some of which may not contain phosphorus), and provides a control for the ^{31}P experiments. One of the interesting observations reported in some ^{31}P studies of lipids and membranes is the presence of relatively narrow lines at the isotropic ^{31}P chemical shift (1). Rapid, isotropic reorientation in the large, highly anisotropic membrane structure is unexpected, and Cullis and coworkers proposed (1) that the narrow resonances arise from phospholipids in small, isotropic "lipidic particles" in the membranes. We have examined, by ^{31}P and ^2H NMR, a system which exhibits such an isotropic feature in the ^{31}P spectrum. The sample consists of 15 mole% egg lecithin in a phosphatidylethanolamine which is deuterated at the two methylene groups of the ethanolamine moiety (see Figure). The low temperature spectra (Figures A and B) are typical for the bilayer phase for this compound. In the higher temperature spectra of both nuclei a resonance attributable to an isotropic phase is observed, superimposed on the lineshape due to the bilayer phase. Further heating leads to an increase in the intensity of this component, and eventually to the appearance of a component due to an hexagonal phase.


We propose an alternative to an isotropic phase as the source of the narrow spectral component occurring at the isotropic chemical shift. The lipids responsible for the isotropic features may be in a region of the membrane which is rapidly interconverting between bilayer and hexagonal phases, over a path which provides isotropic averaging. The rate of motion must be sufficiently great to average the quadrupole splitting for the α -deuterons of PE (9.8 kHz in the bilayer phase). An estimate of the motional time scale could be achieved using labels at positions with greater inherent anisotropies.

With best personal regards,

Yours sincerely,


Michael G. Taylor


Harold C. Jarrell


Ian C.P. Smith

References

1. B. de Kruijff, P.R. Cullis and A.J. Verkleij, Trends in Biochemical Sciences, March, 1980, pp. 79-81.
2. M.G. Taylor and I.C.P. Smith, Chem. Phys. Lipids 28, 119-136 (1981).

Figure Legend

^{31}P (121.5 MHz, upper) and ^2H (46.1 MHz, lower) spectra of the indicated phosphatidylethanolamine, containing 15 mole% egg lecithin, fully hydrated in aqueous Tris acetate buffer (25 mM, pH 7.0) at 42°C (left spectra) and 52°C (right spectra). The spectra were obtained on a Bruker CXP-300 spectrometer, using solenoid coil detection, in tubes of 10 mm outside diameter.

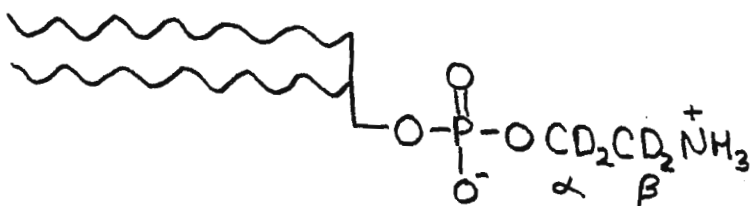
272-29

42°

52°

A

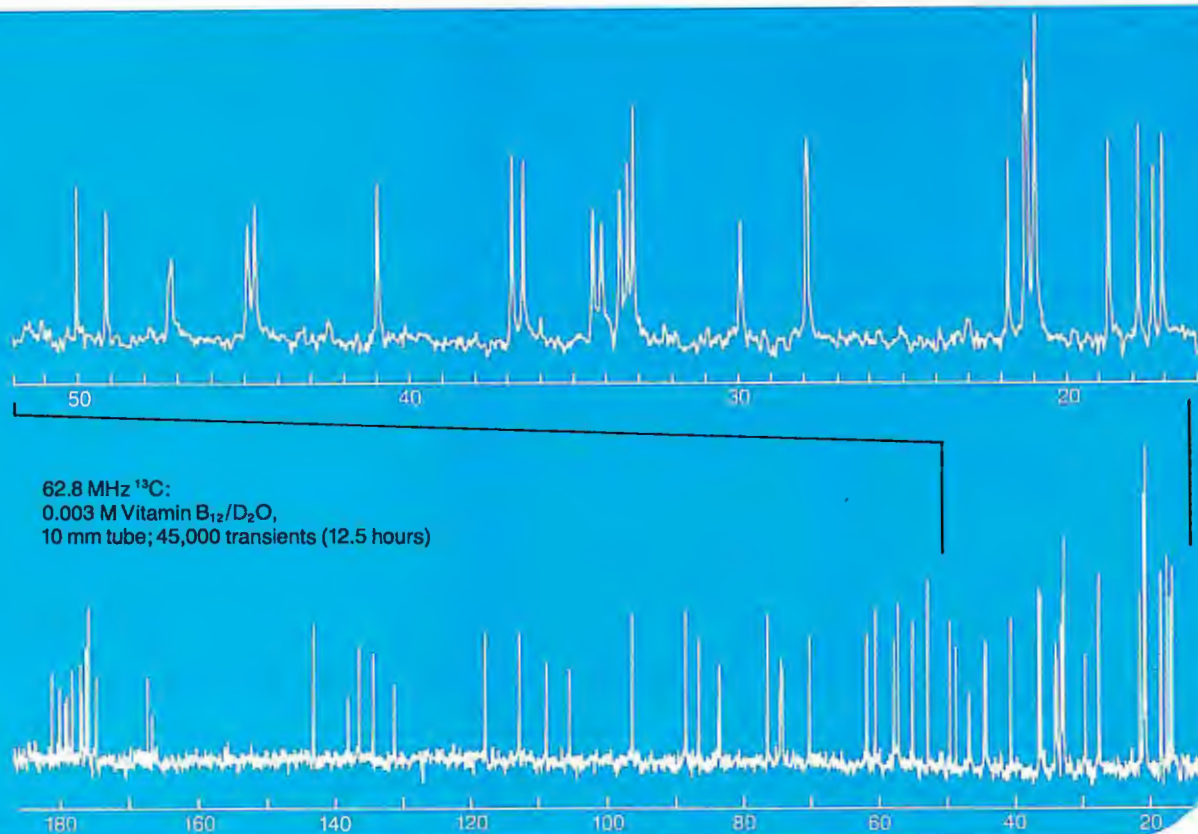
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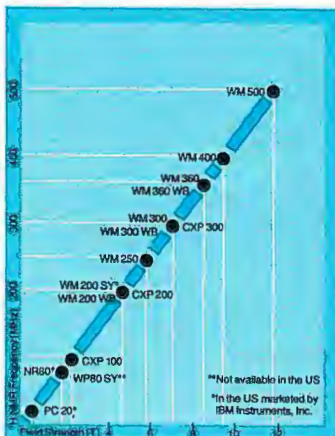
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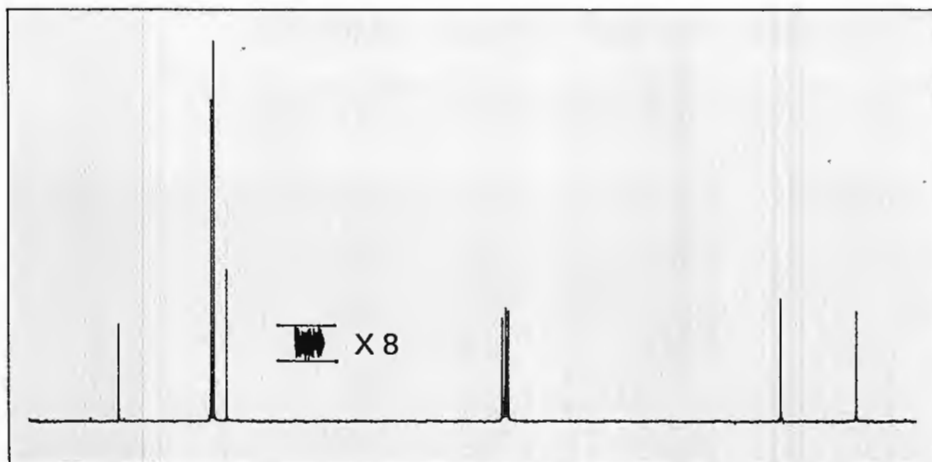
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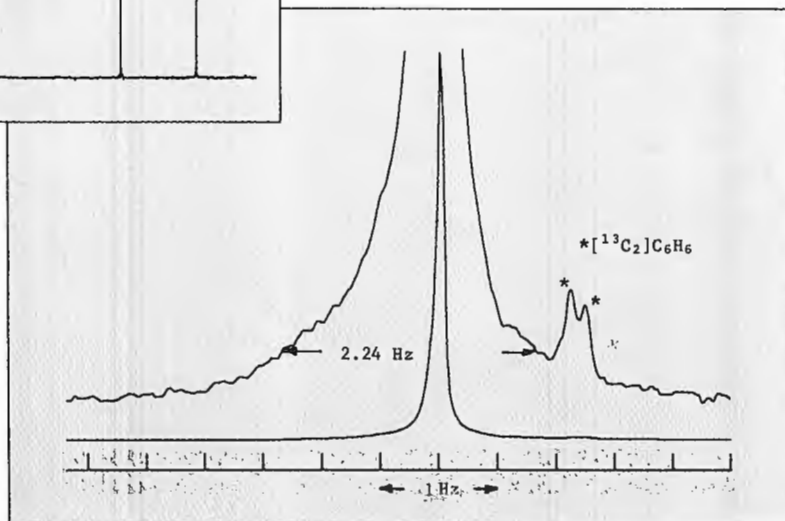


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62.8 MHz ^{13}C lineshape:
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(quod erat demonstrandum)

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University of Melbourne
Department of Inorganic Chemistry

Parkville, Victoria 3052
Australia
April 20th 1981

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

Dear Professor Shapiro,

Gallium-69 and -71 N.M.R. studies of tetrahalogallates

We are interested in halocomplexes and we have used n.m.r. of both gallium-69 and -71 to investigate the halocomplexes of this metal. All measurements were made using tetrabutylammonium tetrahalogallates (and mixtures thereof) in dichloromethane solution at room temperature.

Both gallium-69 and -71 n.m.r. spectra were easily observed for concentrated solutions of $(\text{Bu}_4\text{N})(\text{GaX}_4)$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The chloro complex, at highest frequency had the narrowest line and the iodo complex at lowest frequency, the broadest. Equimolar mixtures of pairs of GaX_4^- anions gave reasonably sharp spectra due to the mixed halide species; in each case the five possible species were observed in the statistical distribution. It was noticed that several minutes were needed for the distribution reaction to reach equilibrium, so the exchange is quite slow on the preparative time scale and obviously slow on the n.m.r. time scale. However, an equimolar mixture of GaCl_4^- and GaBr_4^- in aqueous acid solution gave an exchange averaged signal indicating rapid halogen exchange on the n.m.r. time scale and therefore different exchange mechanisms must be operating in the two solutions,

An equimolar mixture of all three $(\text{Bu}_4\text{N})(\text{GaX}_4)$ in dichloromethane was examined. All 15 possible species were observed in the gallium-71 n.m.r. spectrum in the statistical distribution although only three (those containing three halogens) were new species not previously observed in the pairwise mixtures. The signals in the gallium-69 n.m.r. spectrum were significantly

broadener because of its larger electric quadrupole moment and only 12 separate resonances were observed, as shown in the Figure. It can be seen, for example, that $\text{GaCl}_2\text{BrI}^-$ and GaBr_4^- which occur at -181 and -187ppm respectively are easily resolved in the gallium-71 spectrum but appear as one peak in the gallium-69 spectrum.

The chemical shifts of the mixed halocomplexes are predicted very well by the pairwise additivity model of Vladimiroff and Malinowski as shown in the Table.

Yours sincerely,



R. Colton



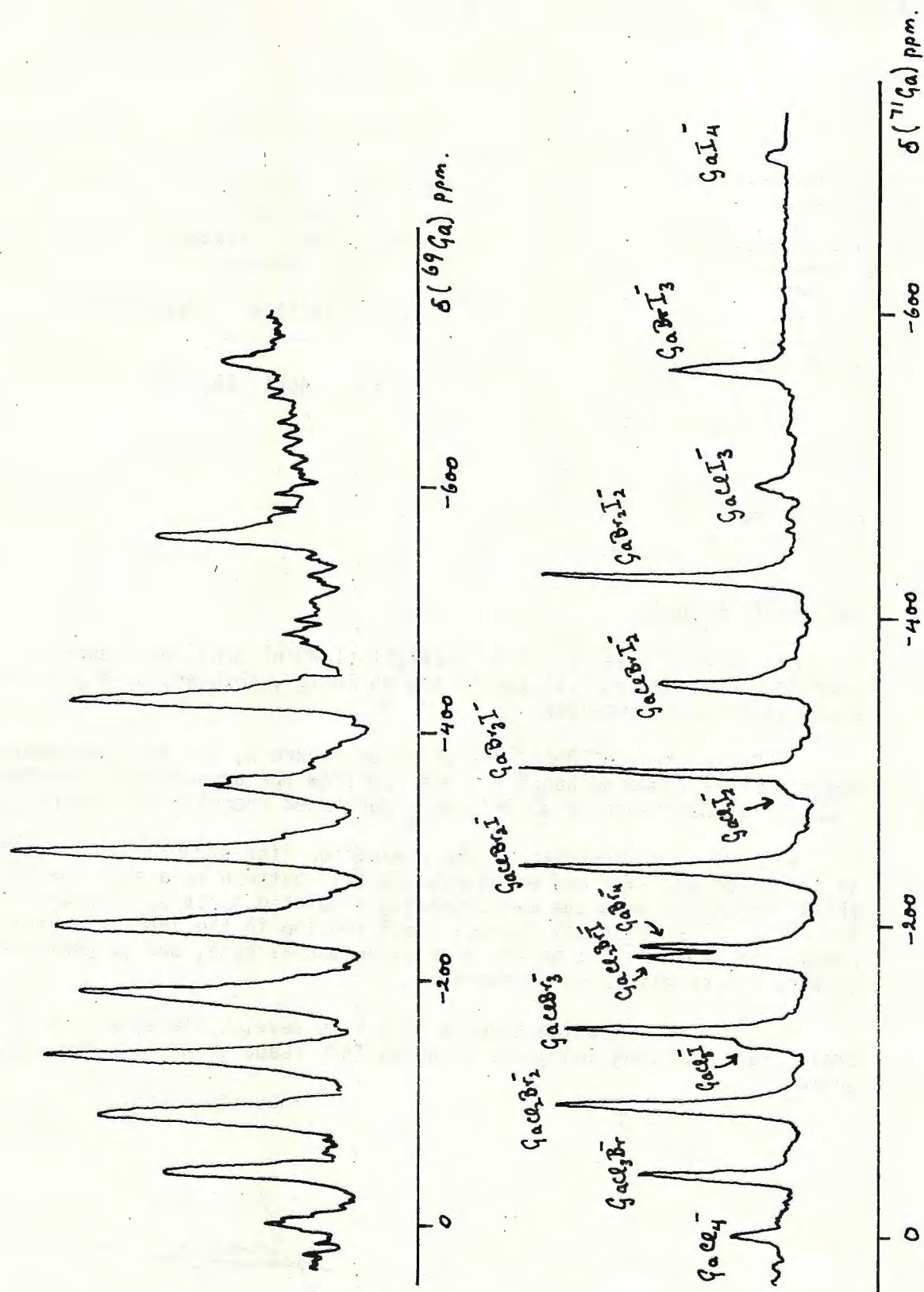
D. Dakternieks

P.S. Please credit this contribution to the subscription of Dr. D.P. Kelly of the Department of Organic Chemistry in this University.

Table Comparison between observed and calculated gallium-71 chemical shifts (ppm) in the tetrahalogallates.

All chemical shifts relative to GaCl_4^- (± 2 ppm), high frequency positive convention used. Interaction parameters at 30°C: Cl-Cl 0.0, Br-Br -31.2, I-I -117.5, Cl-Br -13.0, Cl-I -43.2 and Br-I -69.2ppm.

	$\delta(\text{Ga})$ Expt.	$\delta(\text{Ga})$ Calc.		$\delta(\text{Ga})$ Expt.	$\delta(\text{Ga})$ Calc.
GaCl_4^-	0	0	$\text{GaCl}_2\text{I}_2^-$	-289	-290
GaCl_3Br^-	-38	-39	GaBr_3I^-	-299	-301
$\text{GaCl}_2\text{Br}_2^-$	-83	-83	GaClBrI_2^-	-356	-355
GaCl_3I^-	-126	-129	$\text{GaBr}_2\text{I}_2^-$	-424	-425
GaClBr_3^-	-132	-132	GaClI_3^-	-485	-482
$\text{GaCl}_2\text{BrI}^-$	-179	-181	GaBrI_3^-	-560	-560
GaBr_4^-	-186	-187	GaI_4^-	-705	-705
$\text{GaClBr}_2\text{I}^-$	-237	-239			



Tallium-69 and -71 n.m.r. spectra of a mixture of three GaX_4^- species.

Départements :

Spectrométries de Résonance Magnétique
Spectrométrie Infra-Rouge Fourier
Polarographie
Aimants & alimentations stabilisées
Mesures de Susceptibilité magnétique
Recherche Océanographique

SADIS BRUKER SPECTROSPIN. Boîte Postale N 67160 WISSENBURG

Prof. B.L. SHAPIRO
Dpt of Chemistry
Texas A and M University
College of Science

COLLEGE STATION Texas 77 843

N./Réf. 81 04 221 CB/MCH
V./Réf.

Wissenbourg, le April 16, 1981

Rhodium again

Dear Prof. Shapiro,

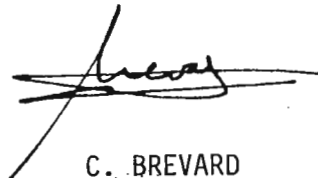
Following the letter of M. Albright (TAMU n° 270), we present a puzzling result we got six months ago on RhCl_6^{3-} , obtained during a ^{103}Rh study of Rhodium aqua-ions.

^{103}Rh spectrum of RhCl_6^{3-} is shown on figure 1, the Rhodium chemical shift of this compound being $\delta + 7\,974$ ppm from the accepted (?) reference $\delta = 3.16$ MHz, close to $\delta \text{Rh}(\text{acac})_3$ published recently by Schwenk (1).

We were much surprised by the unexpected fine structure (figure 1a) of the resonance line and we attributed this pattern to a chlorine isotope shift. Figure 1c show the corresponding simulated spectrum according to the $^{35}\text{Cl}/^{37}\text{Cl}$ statistical isotopic distribution in the ion. It is not very conclusive although not so far from experimental data, but we preferred to keep the result in our drawers.

Perhaps these Rhodium spectra will help developing some kind of brain storming among inorganic oriented TAMU readers. Any comments welcomed.

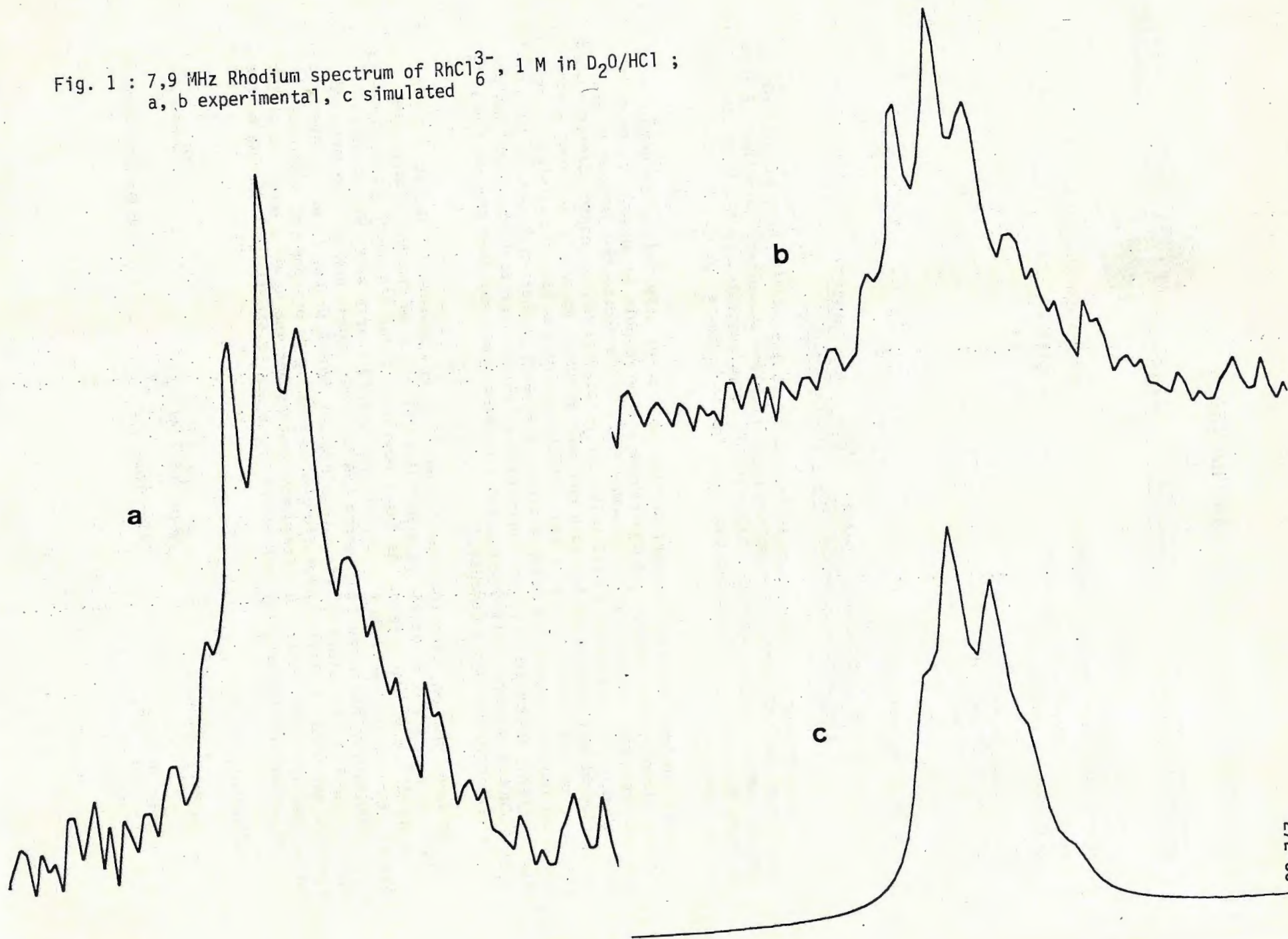
Sincerely yours,


C. BREVARD

(1) Schwenk and al : J. Magn. Res. 41, 354 (1980)



Fig. 1 : 7,9 MHz Rhodium spectrum of RhCl_6^{3-} , 1 M in $\text{D}_2\text{O}/\text{HCl}$;
a, b experimental, c simulated



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SCHOOL OF PHARMACY
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

NMR Laboratory, T. L. James and
I. D. Kuntz, curators.

April 17, 1981

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

Dear Dr. Shapiro:

FIELD LOCKING AND SHIMMING ON BIOLOGICAL SAMPLES:
A PROTON LOCK ACCESSORY FOR A VARIAN XL-100.

We have been involved recently in a high resolution ^{31}P study of rat kidneys using implanted RF coils. One of the major problems encountered was that of locking and shimming of the field. Following a scheme suggested by Ray Nunnally (TAMUNN No. 267-35), we adapted the deuterium lock channel of our XL-100 to lock on protons.

For our experiments, however, we were able to greatly reduce the complexity of our circuit, as indicated in the Figure. We were able to accomplish this for several reasons. First, the pulse power required to excite the protons is quite low. Hence, the few hundred millivolts one obtains from a standard mixer combined with a eight millisecond pulse width has been adequate to excite a strong proton signal from the kidney. Second, the lock channel of the XL-100 contains its own internal gating. Third, by using a mixing frequency higher than that of the proton frequency we obtain a better conversion efficiency for both the pulse and the free induction decay. Furthermore, the low pulse power employed removes the need for a filter in the probe circuit.

We have obtained linewidths as low as 20 Hz for protons (8 Hz for ^{31}P) on a phantom sample and 80 Hz for protons (45Hz for ^{31}P) on the rat kidney after shimming on the proton signal. As the linewidths of our ^{31}P spectra are generally greater than 45 Hz, we obtain good homogeneity with a very short set-up time. Lock sensitivity for these experiments has been very good, and we have employed this scheme with our standard 12mm multinuclear (MONA) probe, as well. The spectrometer was used to observe deuterium while locking on protons. To eliminate noise from the lock pulses, the frequency synthesizer was used to move the field (and therefore the observe window) out of the range of the fixed deuterium source.

Sincerely yours,

Vladimir J. Basus

Vladimir J. Basus

Alan Koretsky

Alan Koretsky

Joseph Murphy

Joseph Murphy - Boesch

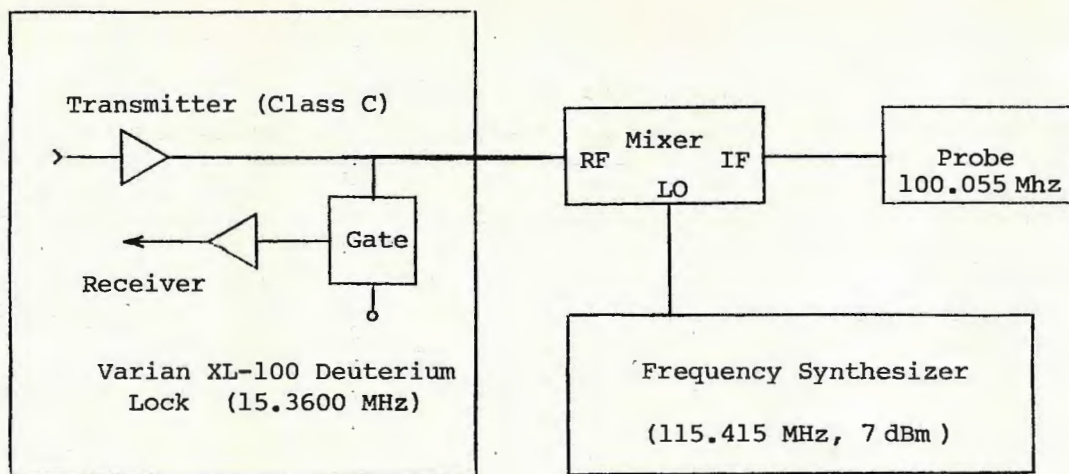


Figure. Proton Locking Scheme.



DEPARTMENT OF CHEMISTRY

1101 UNIVERSITY AVENUE
MADISON, WISCONSIN 53706

April 3, 1981

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

Re: Director of University of Wisconsin
NMR Laboratory

Dear Barry,

The University of Wisconsin-Madison has a career position available in the Department of Chemistry Instrumentation Center. The position is that of Director of the NMR Laboratory and is available 1 June 1981 or as soon thereafter as possible. Responsibilities include operation, research, and teaching graduate students and post-docs the operation of a wide variety of NMR instruments. Primary qualifications for the position are state-of-the-art expertise and experience in NMR spectroscopy and the ability to teach, communicate, and relate well with other faculty members and students in the department. Experience in electronics is preferred but not required. Salary is dependent upon ability and experience. Anyone interested should contact me at the above address. The University of Wisconsin-Madison is, of course, an equal opportunity affirmative action employer.

Please add me to the mailing list.

Regards,

Tom.

Thomas C. Farrar
Professor of Chemistry

Research Resources Center

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Location:
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April 24, 1981

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

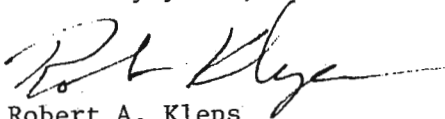
Dear Dr. Shapiro:

The figure below shows the effects of pH on the P-H coupling constant and chemical shift of 50mM phosphorous acid, H_3PO_3 , in 0.1M NaCl. The J_{PH} is represented by x's and the chemical shift relative to 85% H_3PO_4 is represented by O's. This work is a pursuit for NMR probes that can be distinguished from naturally occurring phosphate compounds in cells and model systems.

These last few months have been particularly hectic at our NMR laboratory as our 1H , 5mm, and ^{13}C , 20mm, have just completed their initial shakedown periods on our Bruker CXP-180 and are starting to yield high resolution spectra from both standard samples and intact tissue.

I hope that this contribution will sustain my subscription and I certainly intend to avoid the crashed heads and exploding capacitors that contributed to my delinquency.

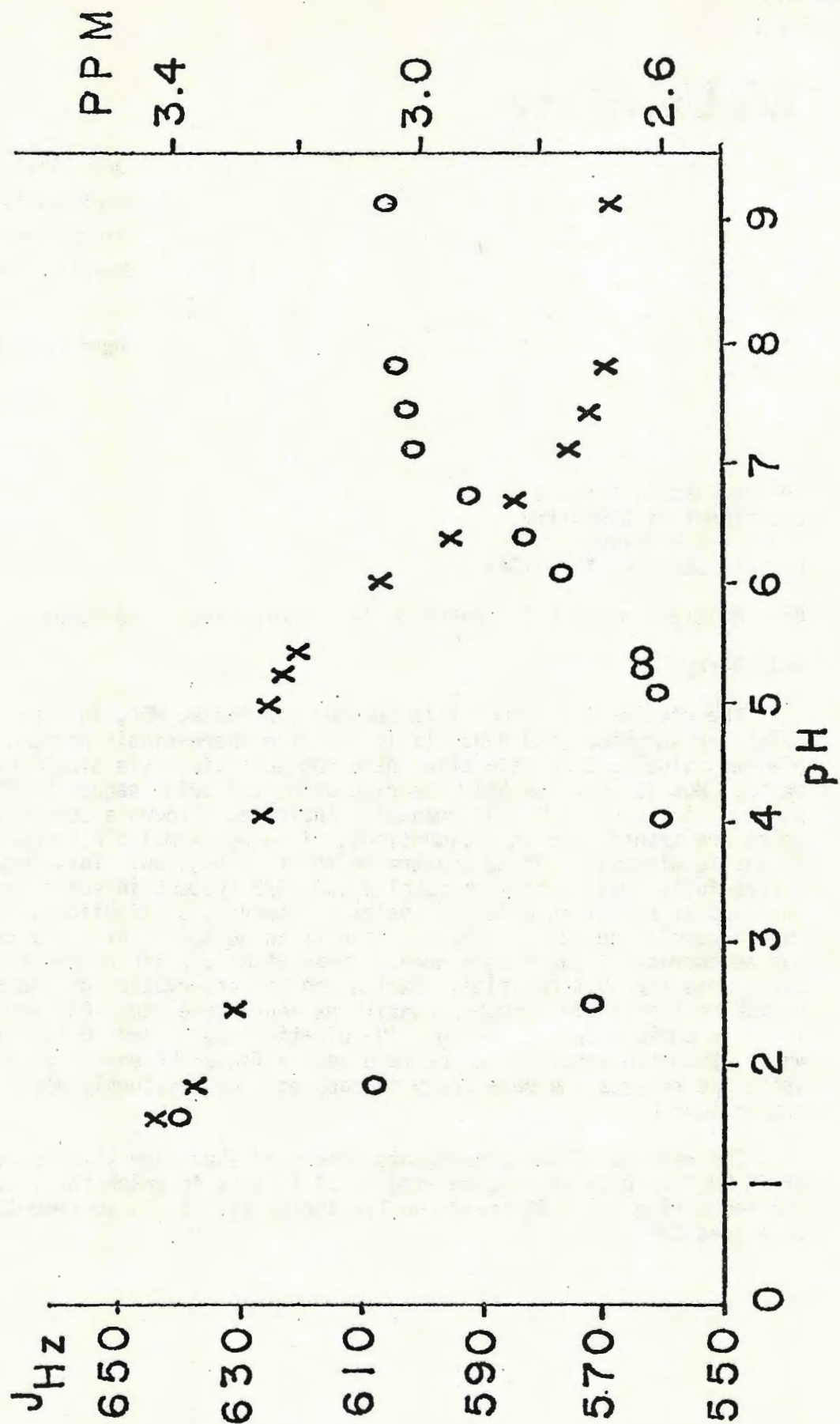
Sincerely yours,



Robert A. Kleps
Senior Spectroscopist

RAK:kam

Enclosure



Yale University

DEPARTMENT OF CHEMISTRY

225 Prospect Street

P.O. Box 6666

New Haven, Connecticut 06511

April 30, 1981

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

Re: Multiple Quantum Coherence of Quadrupolar Nuclei in Solution

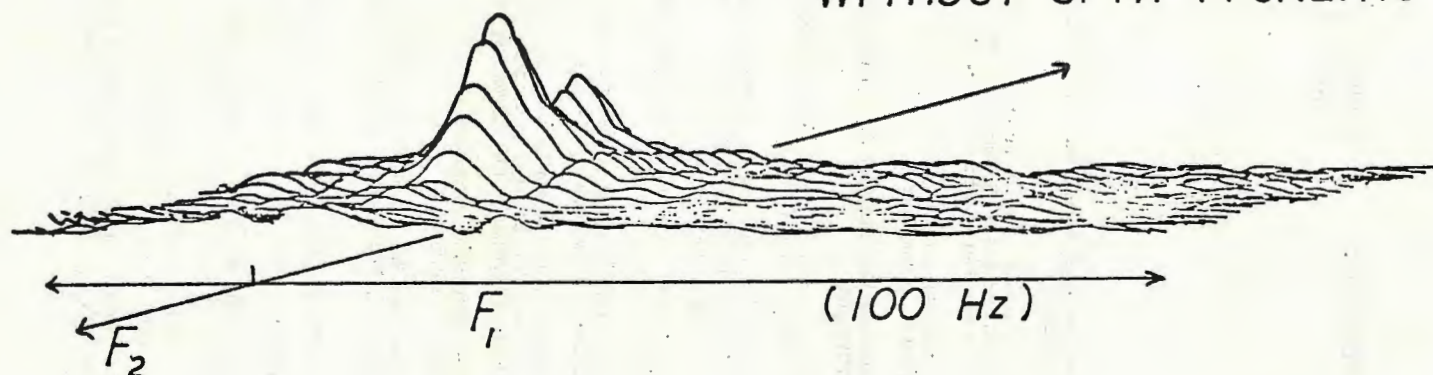
Dear Barry:

The utilization of multiple quantum coherence, MQC, in experiments probing molecular structure and dynamics is becoming increasingly common, and has yielded valuable spin-relaxation data not accessible via single quantum experiments. MQC is most commonly observed using the pulse sequence $90^\circ - \tau - 90^\circ - t_1 - 90^\circ - \text{AQ} (t_2)$, in which t_1 is incrementally increased through a series of spectra which are transformed in 2 dimensions, yielding normal single quantum spectra in the f_2 dimension and MQ spectra in the f_1 dimension. This sequence has been successfully applied to spin-coupled spin-1/2 systems in solution as well as to quadrupolar nuclei in oriented systems. However, straightforward application to quadrupolar nuclei in solution results in no MQC. This is a consequence of the degeneracy of the single quantum transitions, which cancel one another when mixed into the MQ transition. Excitation and observation of MQC can be restored by making the single quantum transitions non-degenerate. One way of accomplishing this employs spin-tickling. ^1H spin-tickling of one ^1H transition, in cases where spin-spin coupling can be resolved, affects the energy of only one ^{14}N state and removes the degeneracy in each pair of previously degenerate ^{14}N transitions.

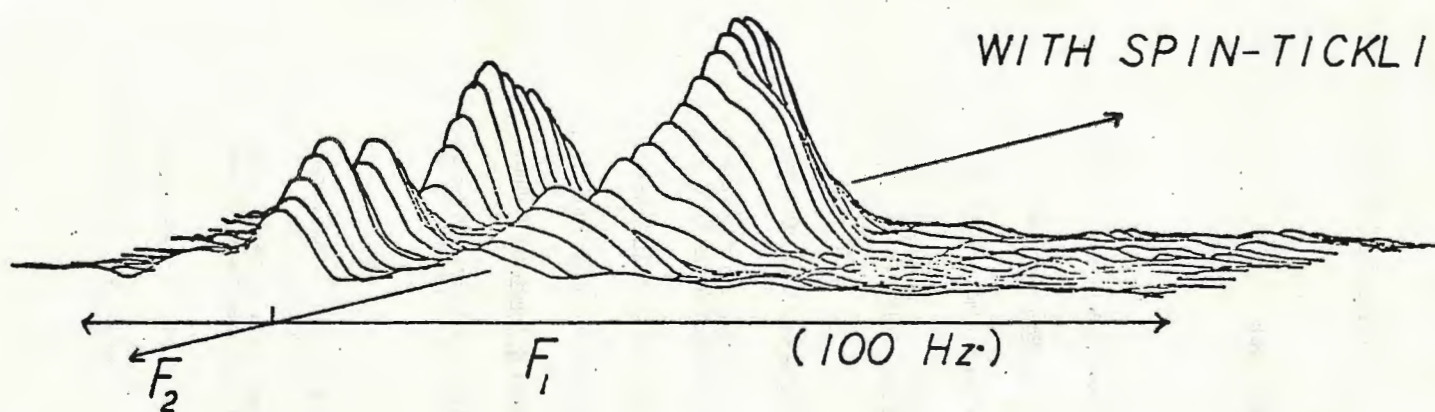
The results of the experiments described above are illustrated for a sample of $6\text{M NH}_4\text{Cl}$. Data are accumulated in 64 1K sets in which the system is spin-tickled during τ and AQ and decoupled during t_1 . t_1 is incremented by 3.9 msec in successive spectra.

Although spectral appearance is complicated by spin-tickling, it is important to note that decoupling during t_1 results in a simple spectrum when viewed in the f_1 direction. Sections of 2-D plots are shown below. The presence and absence of spin-tickling clearly results in the appearance and disappearance of the double quantum transition, and from the f_1 direction, these appear as single, well-resolved resonances.

WITHOUT SPIN-TICKLING



WITH SPIN-TICKLING



Yours sincerely,

V. W. Miner *J. H. Prestegard*
V. W. Miner J. H. Prestegard

Please credit this contribution to Dr. Ian M. Armitage's subscription.

VWM, JHP/sk

P.S. We have a postdoctoral position available. Those interested should respond to the following announcement.

23rd ROCKY MOUNTAIN CONFERENCE

(Denver, Colorado
August 3-6, 1981)

272-43

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

F. Miknis, Chairman

MONDAY MORNING, AUGUST 3 NMR Session I - Solids

Robert Vaughan Plenary Lecture, "NMR in Solids: A Study in Anisotropy", J. S. Waugh, Massachusetts Institute of Technology.

"Recent Developments in Multiple Quantum NMR", A. Pines, University of California, Berkeley.

"Geometry of Molecules in the Amorphous State by NMR Nutation Spectroscopy", C. S. Yannoni and R. D. Kendrick, IBM Research Labs.

"¹³C NMR in Oriented Polymeric Solids", D. L. VanderHart, G. G. A. Bohm, and V. O. Mochel, National Bureau of Standards and Firestone Tire and Rubber Co.

MONDAY AFTERNOON, AUGUST 3 NMR Session II - Solids

"Elimination of Severe Magnetic Susceptibility Broadening in Solid State NMR", M. Stoll, Sandia National Labs.

"²⁷Al NMR Characterization of Aluminum Sites in Amorphous and Crystalline Silica-Aluminas", E. G. Derouane, J. B. Nagy, J. P. Gilson, and Z. Gabelica, Facultes Universitaires De Namur, Belgium.

"CP/MAS Studies of Surface Adsorbed and Surface Attached Species", G. E. Maciel and I. S. Chuang, Colorado State University.

"Characterization of Zeolite Molecular Sieves by Magic Angle Silicon-29 NMR", M. J. Melchior, Exxon Research and Engineering Company.

"Spin 1/2 Nuclei in Catalytic Environments", W. Dawson, R. Inners, and P. Ellis, University of South Carolina.

"Solid State High Resolution ¹³C NMR of Organometallics; Correlations with X-Ray Crystallography", N. Zumbulyadis, D. L. Smith and S. Gross, Eastman Kodak Research Labs.

TUESDAY MORNING, AUGUST 4 NMR Session III - Biopolymers

"¹³C NMR Studies of Lipid-Lipid and Lipid Protein Interactions in Phospholipid Vesicles", J. H. Prestegard, Li-da Ony, and M. A. Fuson, Yale University.

"¹H NMR Study of the Location and Motion of Ubiquinones in Perdeuterated Phosphatidylcholine Bilayers", P. B. Kingsley and G. W. Feigenson, Cornell University.

"³¹P NMR Studies of the Phospholipid-Protein Interface in Cell Membranes", P. L. Yeagle, SUNY at Buffalo.

"C-2H Bond Order Parameter Distributions for Partially Ordered Systems with Axial Symmetry", J. H. Davis, University of Guelph.

"NMR Studies of Bilayer Membranes at 500 MHz", S. Chan, California Institute of Technology

"Studies of Molecular Dynamics Using ¹³C NMR", R. E. London, R. L. Blakley, J. P. Groff, L. Cocco, J. M. Stewart, M. H. Phillippi, and G. Kwei, Los Alamos National Lab, University of Iowa and University of Colorado Medical Center.

TUESDAY AFTERNOON, AUGUST 4 NMR Session IV - Biopolymers

"Solid State NMR Studies of Protein and DNA Dynamics", S. J. Opella, University of Pennsylvania.

"Structure and Interaction of Specifically Carbon-13 Labeled Transfer RNAs", M. P. Schweizer, University of Utah.

"CP-MAS ¹³C NMR of Carbohydrates Containing Glucose", W. L. Earl and P. E. Pfeffer, National Bureau of Standards, Los Alamos National Lab and U.S. Department of Agriculture.

"Laser Photo CIDNP Studies of Alpha-Lactalbumins", L. J. Berliner, Ohio State University.

"¹¹³Cd and ³¹P NMR of Metallo-Alkaline Phosphatase", P. Gettins and J. E. Coleman, Yale University.

"Application of ¹⁵N NMR Spectroscopy to Biological Systems", K. Kanamori, W. W. Bachovchin, T. L. Legerton, B. L. Vallee, R. L. Weiss, and J. D. Roberts, California Institute of Technology, Tufts University, UCLA, and Harvard University.

WEDNESDAY MORNING, AUGUST 5 NMR Session V - Polymers

"Structurally Specific Proton Relaxation Studies on Solid Polycarbonates", A. A. Jones, J. F. O'Gara and P. T. Inglefield, Clark University and College of the Holy Cross.

"Solid State NMR of Polycarbonates", D. R. Holocek, Shell Development Co.

"Molecular Motion in Substituted Polystyrene", M. Sefcik, Monsanto Company.

"A ¹³C NMR Investigation of Polymers Prepared by Glow Discharge Techniques", S. Kaplan and A. Dilks, Xerox Corporation.

"³¹P Shift Anisotropies and Molecular Motion in Polyphosphazene Elastomers", J. Ackerman, University of Cincinnati.

"Determination of Dihedral Angles in Substituted Polybiphenyls by ¹³C NMR Spectroscopy", J. R. DeMeister, Polaroid Corporation.

WEDNESDAY AFTERNOON, AUGUST 5
NMR Session VI - Polymers

"¹³C NMR Studies at Poly (vinylchloride): New Information on Structural Defects and the Mechanism of Vinyl Chloride Polymerization", W. A. Starnes, Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, F. A. Bovey, G. S. Park, and A. H. Saremi, Bell Laboratories and University of Wales Institute of Science and Technology.

"Sequence Distribution in Ethylene-1-Butene Linear Low Density Polyethylenes", E. T. Hsieh and J. C. Randall, Phillips Petroleum Company.

"Quantitative Analysis of the Microstructure of Dicyclopentadiene/Cyclopentene Copolymers using 20 MHz ¹³C NMR Spectroscopy", D. H. Beebe and R. C. Hirst, Goodyear Tire and Rubber Co.

"¹³C, ²⁹Si and ¹⁹⁹Hg NMR of Polymers and Model Systems", E. A. Williams, P. E. Donahue and J. D. Cargoli, General Electric Corporate R&D Company.

WEDNESDAY AFTERNOON, AUGUST 5
Poster Session

"¹H NMR of Paramagnetic Complexes", M. Luciano, University of Milan, Italy.

"²⁷Al NMR Studies of Concentrate Basic Aluminum Chlorides", J. Fitzgerald, South Dakota School of Mines.

"Hydrogen NMR Spin Diffusion in Epoxy Polymers", A. Lind, McDonnell Douglas Corporation.

"Carbon-13 NMR Study of Syn-Anti Isomerism in 2-Phenylimino-1,3 Dioxolanes", J. E. Over, Mobay Chemical Corporation.

"Carbon-13 NMR and Other Spectroscopic Studies of Chemically Modified Silica Surfaces", D. S. Kendall and D. E. Leyden, University of Denver.

"Determination of the Relative Concentration of Carbohydrate Groups in Fulvic Acid by ¹³C NMR", R. L. Wershaw, C. Steelink, K. Thorn, D. J. Pinckney, and M. A. Mikita II, U.S. Geological Survey and University of Arizona.

"Aqueous Relaxation Reagents for Carbon-13 and Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy", T. J. Wenzel, M. E. Ashley and R. E. Sievers, University of Colorado.

"Silicon-29 NMR Chemical Shifts: Additive Relation in Alkylhalo Silanes", D. Cory, A. Wong, and W. M. Ritchey, Case Western Reserve University.

THURSDAY MORNING, AUGUST 6
NMR Session VII - Fossil Fuels

"Solid State NMR Studies of Coalified Logs and Sapropelic Coals", P. Hatcher, L. W. Dennis, N. A. Szeverenyi, and G. E. Maciel, U.S. Geological Survey and Colorado State University.

"Characterization of Carbon Deposits in Coal Conversion Catalysts", H. R. Retcofsky, S. S. Pollack, and G. E. Maciel, Pittsburgh Energy Technical Center and Colorado State University.

"Quantitative Aspects of ¹³C CPMAS Spectroscopy in Coals: Relaxation Effects and Experimental Requirements", J. Lee and K. Zilm, University of Utah.

"Spin Dynamics and CP/MAS Experiments on Fossil Fuels", G. E. Maciel, M. Sullivan and N. A. Szeverenyi, Colorado State University.

"High Resolution NMR and Selective Derivatization of Solid Fossil Fuels", K. D. Rose and M. J. Melchior, Exxon Research and Engineering Company.

"An NMR Investigation of Eastern and Western Shale Oils", D. A. Netzel and F. P. Miknis, Laramie Energy Technical Center.

INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

Chaired by E. R. Eaton and S. S. Eaton

MONDAY AFTERNOON, AUGUST 3 - G. R. Eaton, Presiding
EPR SESSION I

INTRODUCTORY REMARKS - G. R. Eaton

Plenary Lecture "EPR Studies of Multi-Protein Complexes", B. J. Gaffney, The Johns Hopkins University.

"Advantages of ¹⁵N and Deuterium Substituted Spin Labels for Quantitative Simulation of EPR and ST-EPR Spectra in Biological Studies", A. H. Beth, K. Balasubramanian, R. T. Wilder, S. D. Venkataramu, B. H. Robinson, L. R. Dalton, D. E. Pearson, C. R. Park, and J. H. Park, Vanderbilt University.

"Anisotropic Motional Models in ST-EPR at 9 and 35 GHz", L. Lee, L. Fung, Wayne State University, and M. E. Johnson, University of Illinois at the Medical Center.

"Ca(II) and Mn(II) Binding to α -Lactalbumin", K. Murakami, H. Nishikawa, P. J. Andree, and L. J. Berliner, Ohio State University.

"A Probe of Differential Covalency of Metal-Ligand Bonds in Metalloenzymes", M. W. Makinen, A. C. Kuo, and M. B. Yim, University of Chicago.

"Use of Methylmercury as a Spin-Orbit Probe in Optically Detected Magnetic Resonance to Distinguish Between Single-Stranded and Duplex DNA", C. K. Ott and A. H. Maki, University of California at Davis.

"Spin Labeled Crown Ethers", M. Eastman, University of Texas at El Paso.

TUESDAY MORNING, AUGUST 4 - I. B. Goldberg, Presiding
EPR SESSION II

Plenary Lecture "Paramagnetic Defect Species in Silicon Dioxide", J. A. Weil, R. H. D. Nuttall and J. Isoya, University of Saskatchewan.

"Photochemical Studies of Defect States in Inorganic Solids by EPR", R. S. Eachus, Eastman Kodak Company.

"Optically Detected Magnetic Resonance of the Triplet States of Thiouracils", M. R. Taherian, and A. H. Maki, University of California at Davis.

"EPR Investigation of U.V.-irradiated RDX Single Crystals at 77 K", M. D. Pace and W. B. Moniz, Naval Research Laboratory.

"The Varied Guises of Alkoxy Radicals", H. C. Box, Roswell Park Memorial Institute.

"Spin Diffusion in Single Crystals of Alkali Biphenyl", E. de Boer and O. Takizawa, University of Nijmegen.

"An EPR Study of the Free Radical Processes Occurring in the Reaction of AsF₅ with a p-Terphenyl Single Crystal", L. D. Kispert and K. Ezell, The University of Alabama.

TUESDAY AFTERNOON, AUGUST 4- J. R. Pilbrow, Presiding
EPR SESSION III

Plenary Lecture "Structure and Reactivity of Simple Alkane Cations and Characterization of Hydrogen Atom Reactions with Alkanes in Low Temperature Solids", M. Iwasaki, Government Industrial Research, Nagoya.

"EPR and ENDOR Studies of Hydrogenated and Deuterated Coal", I. Goldberg, Science Center, Thousand Oaks, California, L. Dalton and H. Tomann, SUNY at Stony Brook.

"Electron Paramagnetic Resonance of Whole P.R. Spring Tar Sand and Its Various Fractions", V. M. Malhotra and W. R. M. Graham, Texas Christian University.

"An EPR Study of a Bituminous and a Sub-bituminous Coal and Their in Situ Oxidation", V. M. Malhotra and W. R. M. Graham, Texas Christian University.

"EPR Spectra of Stable Free Radicals Adsorbed on Metal Surfaces", R. D. Allendoerfer and J. B. Carroll, Jr., SUNY at Buffalo.

"Spin-Trapping of Phosphorus Centered Free Radicals", R. Sridhar, Oklahoma Medical Research Foundation.

"NMR and ESR Evidence of Molecular Aggregates in Sodium Dibutylphosphate Aqueous Solutions", S. Belaid and C. Chachaty, C.E.N. de Saclay.

"Electron Transfer Between Distant Weakly Interacting Functional Groups - Evidence for a Non-adiabatic Process", S. Mazur, V. M. Dixit, and F. Gerson, The University of Chicago and the University of Basel.

WEDNESDAY MORNING, AUGUST 5 - L. Kevan, Presiding
EPR SESSION IV

Plenary Lecture "Contemporary Issues in Field-Swept EPR in some High and Low Symmetry Systems", J. R. Pilbrow, Monash University.

"EPR and Chemistry in Single Crystals of Nitrosylhemoglobin", D. C. Doetschman and S. G. Utterback, SUNY at Binghamton.

"EPR Study of Fe^{3+} and Cr^{3+} in Different Forsterite Crystals", J. M. Gaité, Université d'Orléans, S. S. Hafner and H. Rager, Universität Marburg, and L. V. Bershov, IGEM, USSR.

"Superposition-Model Analysis of Gd^{3+} Spin Hamiltonian Parameters Doping Rare-earth Trifluoride Single Crystals", S. K. Misra, P. Mikolajczak, and N. R. Lewis, Concordia University.

"A 9.3 GHz EPR Study of Dynamical Interactions in Gd^{3+} : $\text{Eu}(\text{OH})_3$ Single Crystals at 10-300 K", V. M. Malhotra, W. R. M. Graham, Texas Christian University, and H. A. Buckmaster, the University of Calgary.

"An EPR Investigation of Gd^{3+} in Single Crystal and Powder Specimens of $\text{Y}(\text{OH})_3$ at 10-300 K", J. M. Boteler, V. M. Malhotra, and W. R. M. Graham, Texas Christian University, and H. A. Buckmaster, The University of Calgary.

"EPR of Heavily Doped $\text{CaF}_2:\text{R}_3^+$ Crystals (Pr, Eu, Tb)", J. Chrysochoos, V. S. Fivakankar, P. W. M. Jacobs, and M. J. Stillman, University of Western Ontario.

"EPR Spectroscopy at Zero Magnetic Field", S. J. Strach and R. Bramley, Australian National University.

WEDNESDAY AFTERNOON, AUGUST 5 - S. S. Eaton, Presiding
EPR SESSION V 1:30-5:00

POSTER SESSION

"EPR Study of the Binding of CuL^+ to Cat and Normal Human Hemoglobins", W. E. Antholine and F. Taketa, The Medical College of Wisconsin.

"EPR and Quantum Chemistry Studies of Adenosylcobalamin", R. E. Coffman and V. D. Ghanekar, University of Iowa.

"A Comparative Study of the Active Sites of Atropinesterase and Other Esterases by using Spin Labeling Techniques", B. A. C. Rousseau, E. van der Drift, Technical University of Delft, and A. C. M. van der Drift, T.N.O. Rijswijk.

"High Resolution ENDOR Studies of Flavin and Flavin Analog Free Radicals", H. Kurreck, M. Bock and W. Lubitz, Freie Universität Berlin.

"ENDOR Investigations of an Organic Quintet State Tetradical", B. Kirste, H. Kurreck, and W. Harrer, Freie Universität Berlin.

"EPR Studies on the Effects of Ethanol on Phospholipid Bilayer Membranes", J. D. Zimbrick and J. A. McFaul, University of Kansas.

"Light-Induced Transients of Spin Label Signal Amplitude in Spinach Thylakoids", S. P. Berg, University of Denver.

"Examination of Epoxy Morphology Using Nitroxide Free Radicals", T. C. Sandreczki and I. M. Brown, McDonnell Douglas Research Laboratories.

"ENDOR on Biradicals Randomly Oriented in Frozen Solution", H. van Willigen and C. F. Mulks, University of Massachusetts at Boston.

"Effect of an Added Electron upon the Viability of a Hydrogen Bond Acceptor: an EPR and NMR Study", G. R. Stevenson and M. Pourian, Illinois State University.

"EPR Studies of the Photophysics of Silver Chloride and Silver Bromide", R. S. Eachus and M. T. Olm, Eastman Kodak Co.

"CIDEP and Heisenberg Spin Exchange in Two Mixed Radical Systems", J. P. Hornak and R. W. Fessenden, University of Notre Dame.

"The Reactions Between DPPH and Surface Active Sites of Metal Oxides - Surface Properties", T. Kawaguchi, S. Hasegawa, and K. Yasuda, Tokyo Gakugei University.

"EPR Studies of Surface Mobility", J. Lopata, W. Timmer, S. Abdo, and R. F. Howe, University of Wisconsin-Milwaukee.

"Location and Movement on Dehydration of Cations in Zeolites from Electron Spin Echo Modulation Analysis", M. Narayana and L. Kevan, University of Houston.

"Superparamagnetic Effects in the EPR Investigation of a Silica Supported Nickel catalyst", V. K. Sharma, ETH-Zentrum, Zurich.

"Spin-Spin Interaction Through Saturated and Unsaturated Linkages", K. M. More, G. R. Eaton, University of Denver, and S. S. Eaton, University of Colorado at Denver.

"Spin-Labeled Pyridine Adducts of Copper and Vanadyl β -Diketonates", B. M. Sawant, A. L. W. Shroyer, G. R. Eaton, University of Denver, and S. S. Eaton, University of Colorado at Denver.

"Collision Broadening of Nitroxyl Radical EPR Spectra by Transition Metals", G. R. Eaton, D. Reddy, D. Dalal, University of Denver, and S. S. Eaton, University of Colorado at Denver.

"Exchange Interactions in tropylium bis [1,2-dicyanoethylenedithiolato] nickelate(III) $\{\text{C}_7\text{H}_7\}^+ \{\text{Ni}(\text{mnt})_2\}^-$ ", E. de Boer, P. T. Manoharan, J. H. Noordik, and C. P. Keijzer, University of Nijmegen.

"The Electric Quadrupole Moment of Niobium-93", D. Attanasio, C. Bellitto, and A. Flamini, ITSE, Italy.

"Superposition Analysis of Zero Field Splittings (ZFS) for Mn^{2+} . Results and Applications", M. Heming and G. Lehmann, Institut für Physikalische Chemie, Münster.

"EPR of Binuclear Vanadyl(IV) Complexes", R. E. Tapscott, E. Duesler and R. Ortega, University of New Mexico.

"Computer Simulations of Quantum Mixed-Spin and High-Spin EPR Signals of Ferric Heme", T. Lutton and M. M. Maltempo, University of Colorado at Denver.

"Generalized EPR Parameter Refinement for $S = 5/2$ Ions in Low Symmetry Sites", W. C. Tennant, DSIR, Petone.

"High Spin Fe^{3+} in Low Symmetry Sites: Analysis of Polycrystalline EPR Spectra", W. C. Tennant, DSIR, Petone.

"Triplet-State Spin Coherence in Photoexcited Benzil Crystals at 77 K: Optically Detected Transient Nutation and Adiabatic Rapid Passage", R. Gillies and A. M. Ponte Goncalves, Department of Chemistry, Temple University.

THURSDAY MORNING, AUGUST 6 - M. Eastman, Presiding
EPR SESSION VI

Plenary Lecture "Measurement of Electron and Nuclear Spin Lattice Relaxation Times by Magic Angle Spin Locking", J. M. McNally and R. Krellick, University of Rochester.

"Digitally Controlled ENDOR Spectrometer", R. B. Clarkson, Varian Associates.

"ENDOR Detected NMR (EDNMR) Studies in Single Crystals", A. Reuveni and A. L. Kwiram, University of Washington.

"Pulsed EPR of Electron Dynamics in Organic Conductors", L. Dalton, SUNY at Stony Brook.

"Application of Combined Fourier Transform and Time Domain Simulation of Electron Spin Echo Modulation Data to Ion Solvation Geometry", P. A. Narayana and L. Kevan, University of Houston.

NMR SYMPOSIUM

Fran Miknis
Laramie Energy Technology Center
Laramie, WY 82071
307-721-2307

EPR SYMPOSIUM

Gareth R. Eaton
Sandra S. Eaton
Department of Chemistry
University of Denver
Denver, CO 80208
303-753-2507, 2436

BIOLOGICAL NMR SPECTROSCOPIST

The Purdue Biological Nuclear Magnetic Resonance Laboratory is seeking an OPERATIONS MANAGER for its regional facility. Qualifications should include a Ph.D. or equivalent achievement with experience in NMR spectroscopy of biological or organic systems using high-field superconducting solenoid spectrometers, NMR electronics, and computer programming. Duties include routine scheduling and maintenance of spectrometers, assisting users in designing and carrying out experiments, and instrument development. Independent as well as collaborative research will be encouraged. The salary will be based on the level of experience. Write enclosing curriculum vitae, a summary of research interests, and the names of three references to: Dr. Robert E. Santini, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Purdue University is an Equal Opportunity/Affirmative Action Employer.*

The University of Manitoba

Department of Chemistry
Winnipeg, Manitoba
Canada R3T 2N2



April 21, 1981

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

Dear Dr. Shapiro:

RE: 1) Bruker/Nicolet Interface Modifications;
2) Disc wanted

Users of Bruker WH/WP/HX series spectrometer equipped with Nicolet 1180/293A computer systems and NTC software (NTCFT) may have noted several problems with control of the decoupler. Specifically, the Nand F pulse program suffixes generate interrupts to the 1180 and are restricted to intervals of greater than 100 μ s, thus making it very difficult to use the decoupler as a pulse transmitter. Furthermore, there is no provision for switching the decoupler between the broadband (BB) and continuous wave (CW) modes during a pulse sequence.

To circumvent these problems we have connected some of the unused 293A timer outputs to the Bruker/1180 interface. Details are given on the enclosed schematics. With this arrangement an A suffix will enable the decoupler output and a B suffix will enable the broadband modulator during the intervals in which they are included. A T suffix activates, via 293A-SP3, a homebuilt 90° phase shifter in the decoupler (details of which are available upon request). These suffixes generate no interrupts and may be used in intervals in any length. The broadband modulator is activated by a small relay in the decoupler and should be activated in the interval prior to the one requiring broadband decoupling. The N and F suffixes can still be used, if desired, as can the keyboard DF and DN commands. The following experiment illustrates the use of these suffixes.

NAME: PTRAN2

TITLE: POLARIZATION TRANSFER WITH REFOCUSING

#1	D3,A,S	(90° ¹ H pulse)
#2	D4	(delay, (4 J) ⁻¹)
#3	D6,A	(180° ¹ H pulse)
#4	P1/0	(180° ¹³ C pulse)
#5	D4	(delay, (4 J) ⁻¹)
#6	D3,T,A	(90° ¹ H pulse, 90° phase shift)
#7	P2/0	(90° ¹³ C pulse)
#8	D1	(delay list)
#9	D6,A	(180° ¹ H pulse)
#10	P1/0	(180° ¹³ C pulse)
#11	D1,B	(delay list, prepared for BB decoupling)
#12	A,A,B	(acquisition trigger, BB decoupling)
#13	D2,A,B	(acquisition delay, BB decoupling)
#14	D5,X	(post acquisition delay, restart)

(D.M. Doddrell and D.T. Pegg. J. Amer. Chem.Soc. 101, 6388 (1980)).



UNIVERSITY OF DENVER

An Independent University

University Park, Denver, Colorado 80208

Department of Chemistry / 303-753-2436

April 13, 1981

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

Dear Barry:

We are acquiring an XL-100 and retiring an HA-100. We offer for sale the HA-100D, in whole or in parts. We acquired the HA-100D in 1973. The 12-inch magnet comes with V2608 power supply and V3508 solid state flux stabilizer. We have two V4311 RF units (¹H, ¹¹B) and three probes. Anyone interested in the equipment should call as soon as possible (303-753-2507).

We are moving into a new research laboratory this summer, and hope to sell the HA-100 before then.

Sincerely,

Gareth R. Eaton
Professor

Sandra S. Eaton
Associate Professor

GRE:rd

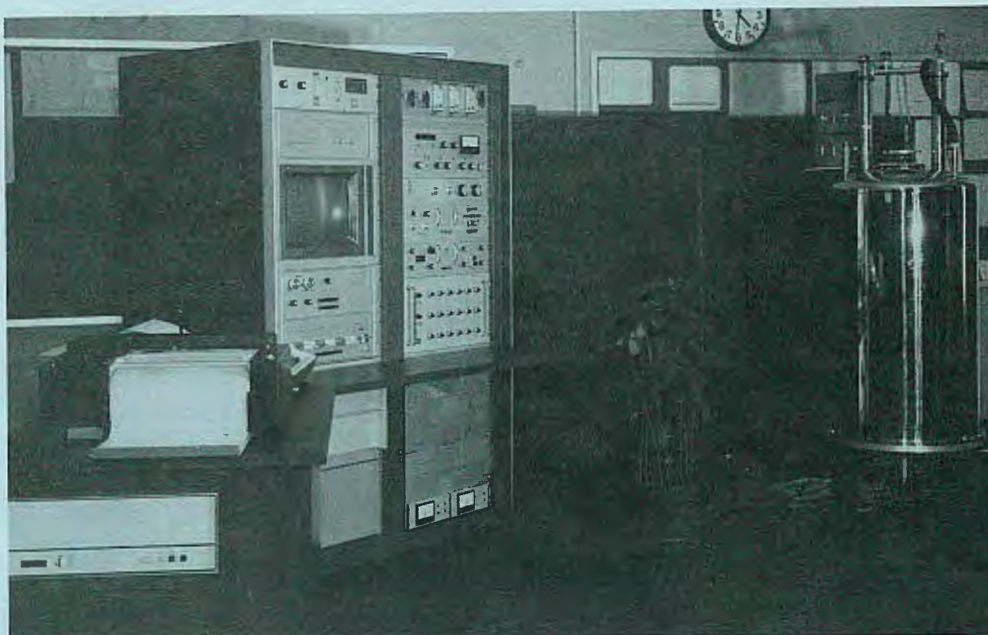
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- A full range of superconducting magnets from 4.7T to 11.7T (200MHz to 500MHz proton frequency range), in both wide-bore and narrow-bore configurations.
- Multinuclear observation with a wide variety of fixed-tune and broadband probes.
- Simultaneous acquisition, processing, and plotting for greater sample throughput.
- Simplified control of spectrometer operations and parameters by using easy keyboard commands.



- Advanced Nicolet 1180E Data System with 128K/20-bit memory, 256-step pulse programmer, and the most comprehensive FT-NMR software package available.

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- An expandable pulse-sequence library, including T_1 , T_2 , Redfield, INEPT, homo- and hetero- 2D-FT, etc.

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- Temperature-programmed experiments.
- ^{31}P experiments on living organs.

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- Broad-Band Probes
- "Tilt" Micro Probe

FX-90Q:

- OMNI Probe™ System
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- Wide Band (^1H to ^{103}Rh)

FX-200:

- Dual Frequency Probes
- Broad-Band Probes
- CP/MAS Extension



JEOL

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235 Birchwood Ave., Cranford, NJ 07016
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