Texas A & M University

No. 173

N - M - R Newsletter

February, 1973

(Cont'd. inside on p. (i))

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All Newsletter correspondence, etc. should be addressed to:

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

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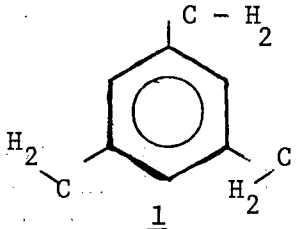
January 16th, 1973.

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

Dear Barry:

Hindered rotation in nonachloromesitylene

This compound exists as 1 and 2 in solution (positions of chlorine are



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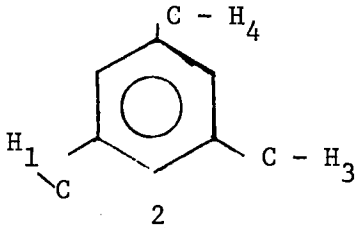

2

obvious). Rotation of one of the dichloromethyl groups in 1 by π radians converts 1 to 2 but only rotation of $H_3 - CCl_2$ in 2 converts 2 back to 1. Rotation of either of the other two groups in 2 produces 2. But note that any one of these rotations interchanges the chemical shifts of some or of all of the protons and one may determine the activation parameters for the conversion from 1 to 2 as well as from 2 to 2.

Jim Peeling has done a proper lineshape study of this system in various solvents (1 more stable than 2) and finds, for example, that a 1.5 mole % solution in CH_2Cl_2 is characterized by $\Delta G^{\ddagger}$ (2 → 1) = 16.09 ± 0.10 kcal / mole, $\Delta G^{\ddagger}$(2 → 2) = 16.47 ± 0.11 kcal/mole at 304.6° K. Furthermore, the entropies of activation do not deviate appreciably from zero, perhaps as negative as - 2 e.u.

We have studied a series of halogenated toluenes (Can. J. Chem. since 1970) and tend to think that entropies of activation in these systems are very near zero. Has anybody an example where hindered rotation about a single bond is clearly characterized by a nonzero activation entropy?

Yours sincerely,

Ted Schaefer.

varian AG / Steinhauserstrasse / 6300 Zug / Switzerland / Tel. (042) 23 25 75 / Telex 78841

Zug, January 10, 1973

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

POSITION AVAILABLE

Dear Barry,

We are expanding our Magnetic Resonance Laboratory in Zug, Switzerland, and are looking for an NMR scientist to join our existing staff. The successful candidate should have a PhD in Chemistry and Physical Chemistry, a strong background in High Resolution NMR and interest or experience in computer applications. Fluency in English and German is required.

Further details can be obtained by writing to me at the above address.

Sincerely yours,
VARIAN AG

Dr. Ulrich Scheidegger

LAWRENCE LIVERMORE LABORATORY

January 22, 1973

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

Dear Dr. Shapiro:

^{81}Br-NMR Studies of Carbonic Anhydrase

We have continued our investigations of the zinc metalloenzyme carbonic anhydrase by means of the very sensitive relaxation properties of the quadrupolar halogen ions. Although it was at first thought that the large increase in the relaxation rate of Cl^- in the presence of this enzyme was due to a quadrupolar mechanism, it has since been found that the dominating factor in the line broadenings is the lifetime of halogen bound to the zinc ion.[1] The relaxation mechanism for Cl^- in the presence of aqueous Zn, however, is quadrupolar in nature. The lifetime of Cl^- bound to the Zn of carbonic anhydrase is therefore related, in some unknown fashion, to the three dimensional structure of the protein at the active site.

Carbonic anhydrase exists in multiple forms, isoenzymes, in mammalian erythrocytes. An examination of the isoenzymes by ^{35}Cl nmr has been reported in the literature.[2,3] It was found that the high and low activity forms of the enzyme could be readily differentiated by the ^{35}Cl line broadening as a function of pH. Furthermore the Cl^- broadening was completely removed by the addition of one equivalent of CN^- or acetazolamide, a potent sulfonamide inhibitor.

We have now extended our halogen probe studies to include ^{81}Br nmr. We have examined the bovine (high activity form), human B (low activity form), and a chemical modified form of the human B enzyme (a carboxamidomethyl group attached to His 204, located near the active site). The bovine enzyme exhibits a "normal" ^{81}Br line broadening which, in many ways, agrees with the ^{35}Cl nmr results.[2] The human B enzyme, however, does not exhibit a Br line broadening under similar conditions of concentration, pH, etc. These results are shown in Fig. 1.

Competitive binding studies using ^{35}Cl nmr demonstrate that Br^- and Cl^- compete for the zinc site in the human B enzyme. Cyanide and acetazolamide binding studies indicate that Br^- does bind to the zinc ion of the bovine enzyme. Since the lifetime of Cl^- bound to the zinc ion is the determing factor in the ^{35}Cl nmr line broadenings, it is expected that this same mechanism applies to Br^-. ^{81}Br/^{79}Br line width ratio measurements substantiate that the lifetime of Br^- bound to the zinc is the determining factor in the line broadening for the bovine enzyme. The failure to observe a Br^- line broadening by the human B enzyme is thus attributed to an increase in the lifetime of the zinc bound Br^-. An increase in this lifetime by a factor of 10-100 over that exhibited by the bovine enzyme is sufficient to abolish the line broadening.

Interestingly we have observed that the modification of the human B enzyme at His 204, by reacting the enzyme with iodoacetamide, allows the zinc ion to be probed by Br^-. The ^{81}Br line broadening, in the presence of the modified human B enzyme, responds to pH, cyanide, and acetazolamide in a very similar fashion to that of the bovine enzyme. Estimates of the lifetime of zinc bound Br^-, τ_m, are 1×10^{-7} sec. for the bovine enzyme at pH 7 and 4×10^{-7} sec. for the chemically modified human B enzyme at pH 8. The lifetime for Br^- bound to the human B enzyme is estimated to be $\geq 10^{-6}$ sec.

Please credit this note to the account of Dr. B. E. Holder.

Sincerely,

Raymond Ward

Raymond L. Ward

---

(1) R. L. Ward and M. D. Cull, Arch. Biochem. Biophysics 150, 436 (1972).
(2) R. L. Ward, Biochemistry 8, 1879 (1969).
(3) R. L. Ward, Biochemistry 9, 2447 (1970).

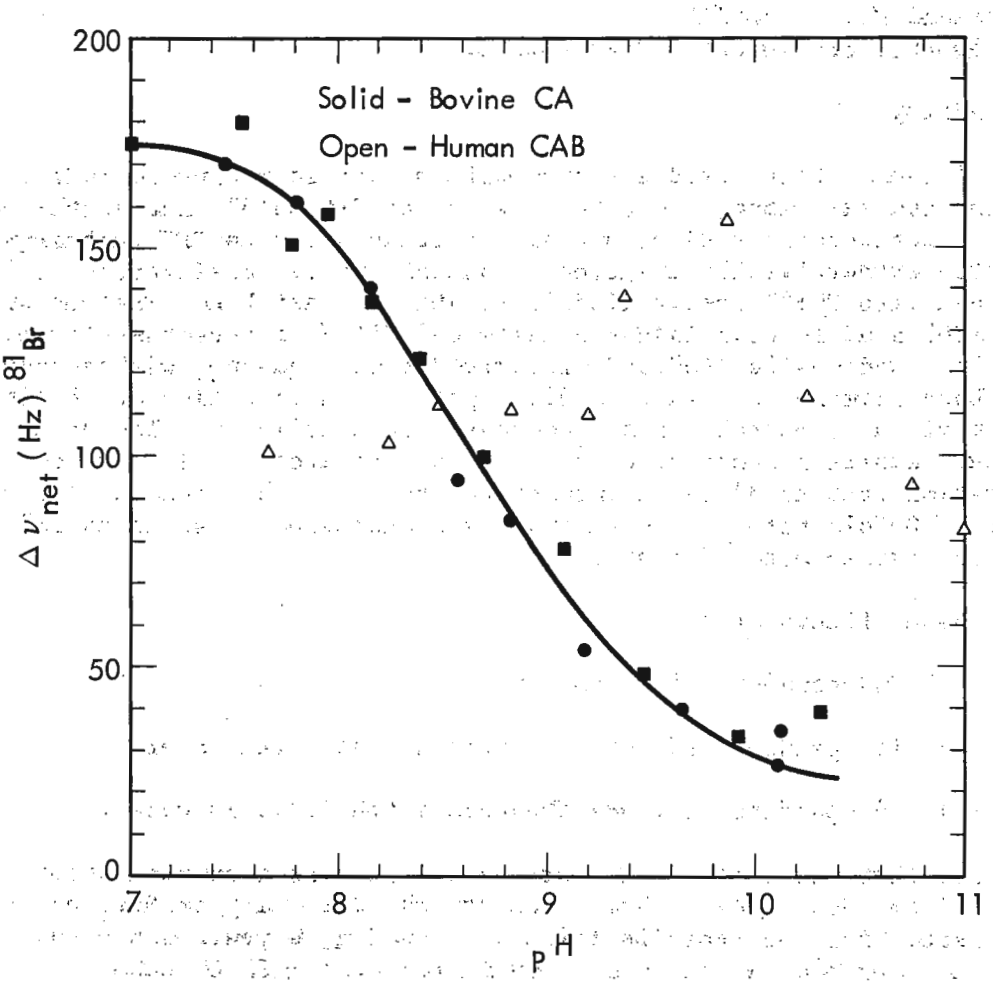

Fig. 1 Net line width, $\Delta\nu_{net}$, i.e., $\Delta\nu_{obsd} - \Delta\nu_{Br^-}$, vs. pH for solutions of bovine carbonic anhydrase (solid symbols), 0.8 mg/ml, and human carbonic anhydrase B (open symbols), 4 mg/ml, in 0.5 M NaBr. The pK_a for the bovine enzyme is 8.6.

173-6

University of Waterloo

Waterloo, Ontario, Canada

Faculty of Science
Department of Chemistry

January 3, 1973.

Professor Barry L. Shapiro,
Department of Chemistry,
Texas A/andM. University,
College Station, Texas, 77843, U.S.A.

Dear Barry,

It seems that relatively few workers are active now outside the routine nuclei, amongst which we now count Carbon-13. Many other nuclei, which can be considered essentially routine using the FFT techniques, seem to attract little attention. One of our rewards for not following the rush into C-13 spectra is illustrated in the table. The measurements of Tl-203 and Tl-205 relaxation times of Tl(-I) in aqueous solutions have been made using 180°/90° or Carr-Purcell sequences with accumulation for about 15 minutes. Accessible ranges on concentration of the ion in water with a 10 mm tube can be decreased to 0.03 molar. The main feature of the results is an incredible and unprecedented sensitivity of the relaxation rate to dissolved molecular oxygen. The rates increasing about 10 0 fold between deoxygenated solutions and those in equilibrium with one atmosphere of oxygen.

These effects are:-

(a) Independent of the anion.

(b) Independent of isotopic composition of the water.

(c) Independent of concentration of the Tl(I) in water.

A fuller account of this work will appear as a communication in the J. Am. Chem. Soc. Mark Bacon, now at the University of Nevada was responsible for the experimental work, during a year of post-doctoral work at Waterloo. Work is now continuing with Dr S. O. Chan.

A Happy New Year.

Kind Regards,

L. W. Reeves.

LWR/jr

Table. Relaxation Rates of Aqueous Solution of Tl^+

Solute	Solvent	Conc(mole-l^{-1})	R_1^a(sec^{-1})	R_2^b(sec^{-1})
$TlNO_3$	$H_2O(N_2)^c$	0.0803	0.54	0.83
	H_2O(air)^d		8.3	9.6
	$H_2O(O_2)^e$		38.0	---
	f	f	5.8[f]	17.5[f]
	$D_2O(N_2)^c$	0.0839	0.44	---
	D_2O(air)^d		8.3	---
	$D_2O(O_2)^e$		41.0	---
	$H_2O(N_2)^c$ 8×10^{-5}M $Fe(CN)_6^{-3}$	0.080	15.3	13
	$H_2O(N_2)^c$ 7×10^{-3}M Cu^{++}	0.15	9.9	19

a. $R_1 = 1/T_1$, the longitudinal relaxation rate, measured from plots of log of free-induction decay amplitude vs pulse spacing (ref. 13), from standard 180º - -90º pulse sequences. Estimated precision ± 4%.

b. $R_2 = 1/T_2$, the transverse relaxation rate, measured from standard Carr-Purcell spin-echo sequences (ref. 13). Estimated precision ± 8%. A Fabritek (Nicolet) 1074 signal averager was used to enhance repetitive signals in both R_1 and R_2 measurements. Probe temperature 26.0ºC.

c. The sample was thoroughly purged with N_2, and less than 10^{-6} mole of $N_2H_4.H_2O$ was added to reduce any remaining O_2.

d. The sample was saturated with air.

e. The sample was saturated with O_2 at 1 atm.

f. From Table IV of Ref. 5. The sample consisted of 0.10M $TlNO_3$ and 0.05M cacodylate buffer.

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toestel:

Uw kenmerk	Uw brief van	Ons kenmerk
	2 february 1973	

Onderwerp

Dear Professor Shapiro,

Your blue reminder of 15-12-'72 arrived at my desk on 23-1-'73.
I wonder what the reason for this time-lag can be.
You activated us to the following title:

A proton-free crossed-coil system for the DP/60

When trying to measure the proton signal of a solid polymer with our Varian DP/60 we saw the signal of figure a, which clearly is due to protons inside as well as outside the receiver coil. So we suspected the probe; rightly, as can be seen from figure b. This prompted us to develop a new system, as protonfree as possible. The new system has the following main features:

a. Instead of a receiver coil, glued to the inner tube of a Dewar, we use a glass capillary with a well-cleaned copper wire inside, put in the shape of a coil and fitting tightly on the inner tube of the Dewar.
b. Instead of the Varian-Faraday shield (the main cause of the false signal) we use a copper grid in the shape of a comb, clamped between two coaxial glass tubes.
c. Instead of a transmitter coil,glued to the outside of the Varian-shield, we use a coil which is etched on the outside of the new Faradayshield.

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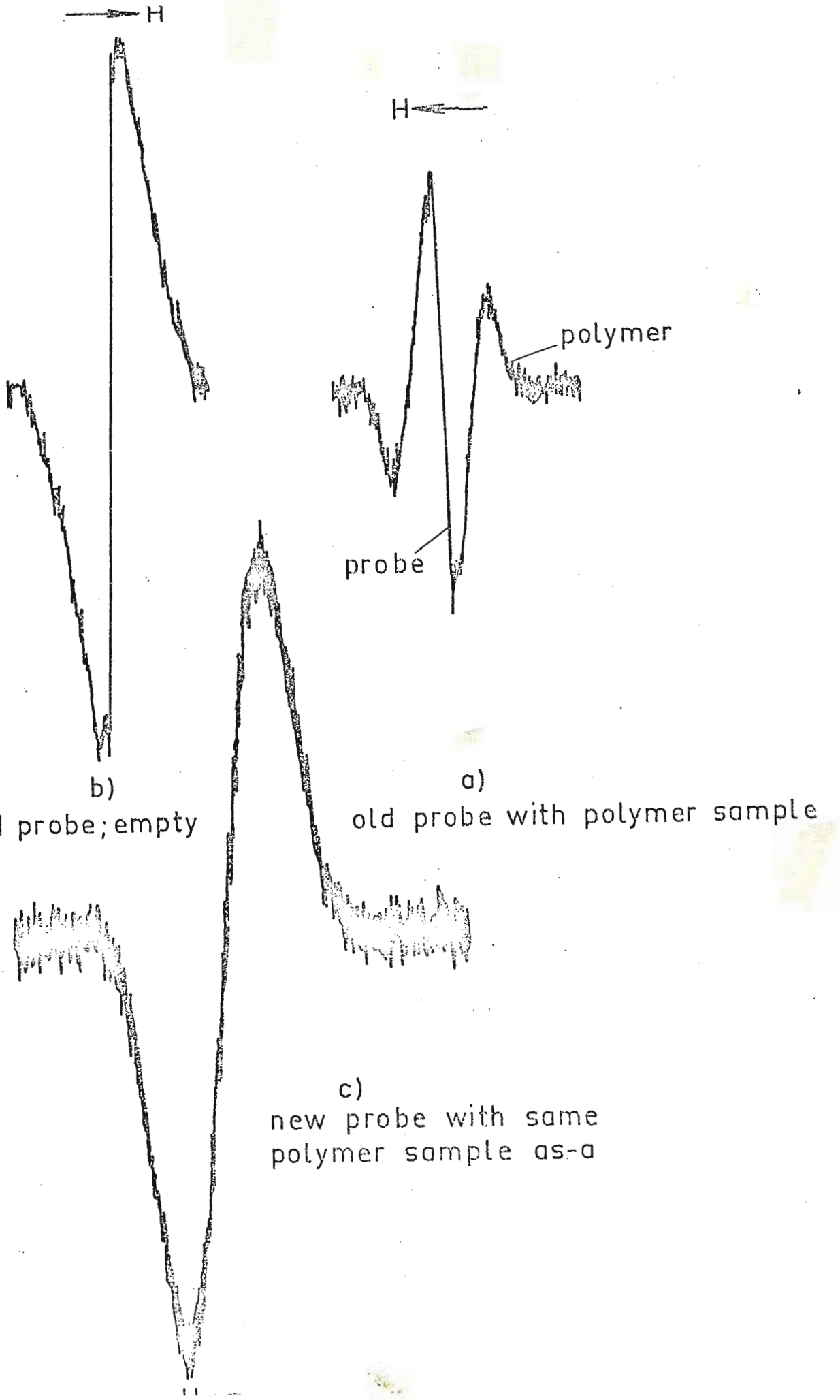
Prof. B.L. Shapiro
Texas A&M University

d. The Dewar is not glued to a ceramic plug, but clamped in a Teflon plug.
The result is a coil-system which has no detectable false signal (figure c.).

We will be pleased if anyone who is interested in more technical details, writes to Mr. J. Vriend, who did the work.

J. Vriend

Prof.Dr.Ir. J. Smidt



b)
old probe; empty

a)
old probe with polymer sample

c)
new probe with same
polymer sample as-a

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January 12, 1973

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

Dear Barry:

I thought that I would briefly discuss two areas we are working in that may be of interest to readers of the TAMU-NMR Newsletter.

Silicon-29 Spin-Lattice Relaxation

As reported in preliminary communications[1,2], ^{29}Si T_1's are generally unfavorable for FT nmr studies, commonly 50-100 sec (the full T_1 range observed to date is 17-135 sec for some 15 kinds of compounds over the temperature range -70^{o} to $+130^{o}C$). ^{29}Si-^{1}H dipole-dipole interactions and the spin-rotation interaction largely dominate ^{29}Si relaxation but minor contributions are observed at 23 kG from chemical shift anisotropy with non-protonated ^{29}Si nuclei.

Some major differences were noted between ^{13}C and ^{29}Si relaxation. In particular, long-range <u>intramolecular</u> as well as <u>intermolecular</u> ^{29}Si-^{1}H dipole-dipole interactions can be non-negligible contributions - even for <u>protonated</u> ^{29}Si nuclei!! We have recently submitted a manuscript detailing ^{29}Si relaxation processes. On request copies will be supplied.

Electron-Nuclear Dipole-Dipole Relaxation

We are currently evaluating the <u>quantitative</u> relaxation effects produced on ^{13}C nuclei in various small and intermediate sized molecules upon addition of paramagnetic relaxation reagents such as $Cr(acac)_3$. Some phenomena were anticipated but we have also

observed some interesting surprises.

For totally inert substrates T_1^e (the ^{13}C T_1 due to DD relaxation with the $Cr(acac)_3$) follows Abragam's hard-shell sphere model,[3] even for ^{13}C nuclei buried inside the molecule, such as C-2 in isooctane (2, 2, 4-trimethylpentane) and the carbon in CCl_4.

On the other hand, weakly interacting groups or electrostatic considerations result in preferential "solvation" between substrate and $Cr(acac)_3$ molecules. These effects may be examined giving insight into solution structure and specific molecular interactions. Such studies are in progress.

Meanwhile: A practical tip. To shorten ^{13}C T_1's to ca. 1 sec (the shortest T_1 not leading to any line broadening) use $Cr(acac)_3$ concentrations of ca. 5×10^{-2} Molar in non-viscous solutions (use proportionately lower conc. of $Cr(acac)_3$ where the solution viscosity is more than 0.5 to 1 centipoise).

My best regards.

Yours sincerely,

George C. Levy

George C. Levy
Materials Characterization Operation
MATERIALS SCIENCE AND ENGINEERING

1. G. C. Levy, J. Am. Chem. Soc., 94, 4793 (1972).
2. G. C. Levy, J. D. Cargioli, P. C. Juliano, and T. D. Mitchell, J. Magn. Resonance, 8, 399 (1972).
3. A. Abragam, "The Principles of Nuclear Magnetism", Oxford Press (1961), p. 304.

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January 15, 1973

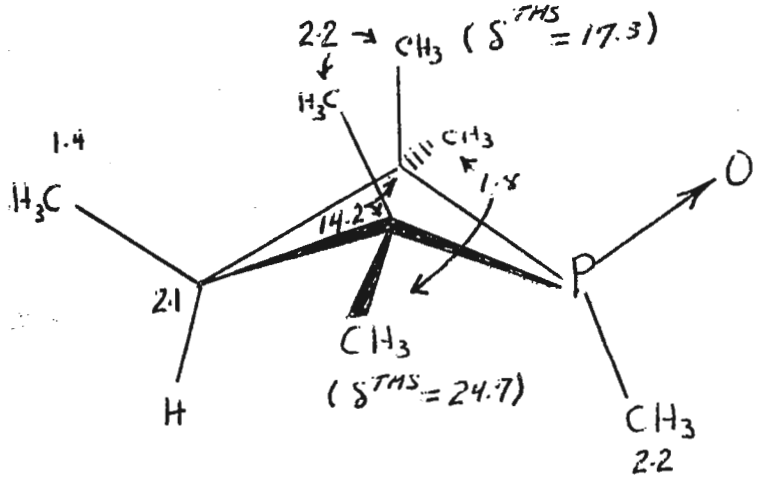
Dr. Barry L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry: Steric Crowding and ^{13}C T_1's

As the determination of ^{13}C T_1's becomes more and more popular it becomes increasingly important for people to interpret their data correctly in terms of the various relaxation mechanisms. Putting aside any confusion as to dipole-dipole vs. spin rotation etc. and focusing only on the dipole-dipole mechanism, danger can arise in interpretation even within this mechanism. The relaxation time is usually given by

$$\frac{1}{T_1^{CH}} = \sum_{\substack{\text{all} \\ \text{protons}}} \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{r_{CH}^6} \tau_c$$

This form is valid for an isotropic tumbler in normal solutions. Given no significant change in r_{CH} between various alkyl carbons, changes in T_1^{CH} can be related to changes in τ_c, the effective molecular reorientational correlation time. The danger of misinterpretation comes when one deduces severe steric "crowding" from a shortened T_1. It is very easy to interpret shorter T_1's and therefore longer τ_c's as resulting from the placing of the C-H fragment into a region of considerable "steric compression", to use a fashionable term. This can be incorrect, as evidenced by the data below



Dr. Barry L. Shapiro

January 15, 1973

From x-ray results the pseudoaxial methyl with T_1 of 2.2 sec. is sterically very crowded while the pseudoequatorial (1.8 sec.) methyl is relatively uncrowded, perturbed only by the geminal methyl group. Note that the more crowded methyl has the longer T_1. Spin-rotation contributions should be negligible in view of the very short T_1's. The pseudoaxial methyl must have a longer τ_c - in direct conflict with intuitive prediction. Of course, the fallacy lies in equating "steric crowding" with longer τ_c, i.e. locking up methyl rotation. Some perusal of the literature coughs up an ideal example - 1,2,3 trimethylbenzene. Alger, Grant and Harris (J. Phys. Chem., 76, 281(1972)) determined T_1's and found that the central methyl was essentially a free rotor (low 6-fold barrier) while the outer methyls were severely hindered in their rotation (higher 3-fold barrier). Thus, the secret is that the barrier to rotation, which controls τ_c, can be low, even in a "crowded" environment. Hence, the pseudoaxial methyl above, although more "crowded" has a lower barrier to rotation than the less "crowded" pseudoequatorial methyl. This is nothing new and is obvious when thought about. However, if not considered it is all too probable that someone will take two experimental T_1's and say that the carbon possessing the shorter T_1 is obviously in a more "crowded" environment. This can be particularly dangerous in a situation where the molecular structure is not known. Careful attention must be paid to the value of the ^{13}C shift and in particular whether an upfield shift is observed relative to the value expected before conformational or steric effects are considered. An upfield shift occurring simultaneously with a shortened T_1 is a much safer indicator of "steric compression" and restricted rotational freedom.

Sincerely yours,

George

George A. Gray
Senior Applications Chemist

GAG/dp

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KRIJGSLAAN [redacted] Tel. (09) [redacted]
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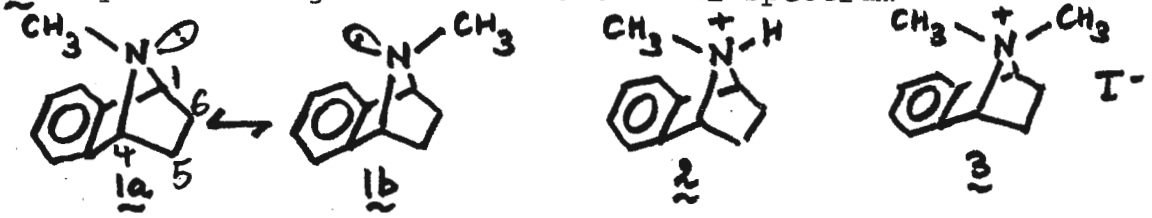
GENT, January 8th 1973.

Assoc. Prof. B.L. SHAPIRO,
TAMU-NMR-Letters
Texas A and M University,
College Station,
TEXAS 77843. U.S.A.

Dear Barry,

We are currently involved in a ^{1}H-NMR study of 7-azabenznorborene (1) for which the two forms (94 % : 6 % at -60°C) 1a and 1b may be distinguished in the 300 MHz spectrum



at T < 0° ($CDCl_3$: CH_2Cl_2 30:70). Also, the protonated species (2) ($CDCl_3$: CF_3COOH 80:20) shows the same distribution of syn- and anti-7-methyl isomers. Finally and most interestingly, the quaternised derivative (3) reveals stereospecific coupling between $N^{\oplus}$ and either exo or endo H-5 and H-6 protons [1], (hetero N-decoupling experiments). From the SIMEQ-analysis of the parent compound 1a we know that the endo H-5(6) protons are at highest field (as expected), for which ^3J (5n,4) ≃ 0.
Further work in progress is concerned with obtaining direct proof of the equilibrium 1a ⇄ 1b being in favour of 1a (presumed from relative shift considerations of both isomers observed at t < 0°). We are also searching for other examples which show the same stereospecific coupling phenomenon in quaternary amine derivatives.

During our NMR experiments, however, we found some interesting but also puzzling results which we would like to mention and for which we feel the need of help from any of your readers.

(a) In the neutral amine (1a ⇄ 1b), there is a specific broadening for the low field absorptions for H-5(6), (exo-protons as follows from ^3J(5x,4)≃4.5 Hz which is not due to coupling with other protons, as follows from line width considerations). We must therefore ascribe this broadening to a stereospecific interaction with N. However, we are then left with the conclusion that this stereospecific interaction (between N and exo-5,6 protons) is the opposite of what was found for the quaternary salt, 2 (for which a stereospecific interaction between N^+ and the endo-5,6 protons was observed).

(b) The less stable isomer (believed to be 1b) shows a shift-differentiated absorption for H-1(4) (at lower field), suggesting a change in electronic character in the bridgehead C-H bonds when passing from one isomer into the other. Alternatively this may simply reflect changes brought about by the fluctuating spatial orientation of the $N^{\oplus}_{CH_3}$ moiety in traversing the equilibrium 1a ⇄ 1b.

(c) A NOE experiment (in C_6D_6-degassed) on 1a is most puzzling. Irradiation of Me (having almost identical shift width as the (broad) pattern for H-5e(6e)(!) shows a specific positive effect (15-20 %) for H-5n(6n)(sic), but none for all other intensities (internal check). Can any of the TAMU-NMR readers suggest any explanation for this phenomenon ? Even accepting that 1b should be the most preponderent isomer, these results make no sense in light of a through-space interaction.

Table

NMR parameters for 1a ⇄ 1b in C_6D_6 (300 MHz, TMS internal). Linewidths : 0.75 Hz except for H-5' (6') : 1.3 Hz. Shifts in δ, J in Hz.

	H-5	H-6	H-5'	H-6'	H-1	H-4	H-ar	Me
H-5	1.034							
H-6	8.6	1.03_4						
H-5'	-11.2	4.0	2.01_7					
H-6'	4.0	-11.2	10.0	2.01_7				
H-1	0.0	0.0	0.0	4.4	3.81			
H-4	0.0	0.0	4.4	0.0	0.7	3.81		
H-ar							7.09_5	
Me								1.97_4

[1] Stereospecificity in $J(\overset{+}{N}CC\underline{H})$ has been suggested by Anna Laura Segre (private communication to Prof. Alan Marchand), but it was known for some time that coupling to β-protons could occur : C.C. Culvenor and N. Ham; Chem. Comm., 537 (1970) reported broadening by ca 2 Hz for β-H in acetylcholine.

Yours sincerely,

Alan P. Marchand
(on sabbatical leave from The University of Oklahoma, 1972-73)

M. Anteunis.

Alan Marchand

I '3-18

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

January 10, 1973

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

Dear Barry:

There will be a postdoctoral position available in my group as of next September. The research problems will be in the area of organic conformational analysis. The applicant should have experience in organic synthesis as well as in nmr spectroscopy.

Sincerely,

Joe

Joseph B. Lambert

JBL/kp

Short title: Postdoctoral position available

THE UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
RIVER STATION
ROCHESTER, NEW YORK 14627

DEPARTMENT OF CHEMISTRY

January 31, 1973

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

Postdoctoral Position Available

Dear Barry:

I will have funds available for a postdoctoral position beginning March 1, 1973 (or later). The research will involve the investigation of drug-DNA interactions, using nmr, optical, and fluorescence spectroscopies. We have available a JEOL PFT-100 nmr spectrometer with an EC-100 computer (20K of memory), a Cary 14, and a Perkin-Elmer fluorescence spectrophotometer.

Interested individuals should forward a curriculum vitae, transcripts, and arrange to have three letters of recommendation sent to me at the address below. I would also appreciate an estimate of the approximate date of availability.

Sincerely,

Thomas R. Krugh
Department of Chemistry
University of Rochester
Rochester, New York 14627

TRK:lcb

מכון ויצמן למדע
THE WEIZMANN INSTITUTE OF SCIENCE
REHOVOT · ISRAEL רחובות · ישראל

ISOTOPE DEPARTMENT מחלקת איזוטופים

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

30th January 1973

Dear Barry,

The Shift Reagent Program for the 10th Rare Earth Research Conference to take place at Carefree, Arizona, April 30 - May 3, 1973, has been finalized. It includes formal presentation of the following papers:

Lanthanide Shift Reagents, C.C. Hinckley.

The Stoichiometry of Shift Reagent Substrate Interactions, T.J. Marks, D.F. Shriver, and R. Porter.

Shift Reagents in Polyfunctional Systems, J.K.M. Sanders.

The Lanthanide Cations as NMR Probes: A Novel Approach to Organic Shift Reagent Studies and Amino Acid Sequence Determination of Simple Peptides, E. Nieboer, B. Flora, M. Podolski, and H. Falter.

Magnetic Anisotropy and Dipolar Shifts in Shift Reagent Systems, W. DeW. Horrocks, Jr., J.P. Sipe, III, and D. Sudnick.

Determination of the Structure of Organic Molecules by Lanthanide Induced Shifts in Theory and in Practice, M.R. Willcott, and R.E. Davis.

Determination of Molecular Conformation using Lanthanide Induced Shifts, B.L. Shapiro.

Analysis of Dipolar Shifts in the NMR Spectra of Organic Molecules with the Aid of a Digital Computer, J. Barciszewski, A.J. Rafalski, and M. Karonski.

CABLE ADDRESS: WEIZINST (Israel) :מען למברקים PHONE: 951721 :טלפון

Professor Bernard L. Shapiro

30th January 1973

The Biochemistry program (not parallel) also includes at least five papers describing NMR work. In addition, arrangements are being made to have an informal discussion, which will be devoted to ironing out some of the controversies in the field. Suggestions as to subjects for the discussion are welcome, and should be directed to me so as to reach me before April 1, 1973.

I am sure that we will have an interesting and fruitful meeting.

Those wishing to attend the Conference should write at their earliest convenience to the Conference Chairman, Prof. Therald Moeller, Department of Chemistry, Arizona State University, Tempe, Arizona 85281.

Sincerely yours,

Jacques Reuben

JR:dr

BROWN UNIVERSITY *Providence, Rhode Island • 02912*

DEPARTMENT OF CHEMISTRY

6 February, 1973

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

Non-exponential Relaxation of CIDNP in Methyl Groups ?

Dear Dr. Shapiro:

We have recently been applying nuclear relaxation theory to the problem of predicting the decay of non-thermal populations generated by CIDNP. Although there are now several examples of CIDNP multiplets distorted by relaxation[1], it was surprising to find that dipolar relaxation of even the single line from an A_3 spin system, such as a methyl group, should be modified if it has been enhanced by a chemical reaction.

It has been known for 15 years that relaxation of three equivalent dipolar coupled protons in liquids is properly described by two exponentials[2]. This is essentially a consequence of the coupling of the $I=3/2$ and $1/2$ irreducible components of the spin system by the dipolar hamiltonian. In the presence of both chemical reaction and dipolar relaxation the magnetization, M_I^z, of the two subsystems is described by the equations

$$(1a)\quad \dot{M}^z_{3/2} + 46WM^z_{3/2} + 30WM^z_{1/2} = r[3(\gamma_{3/2} - \gamma_{-3/2}) + (\gamma_{1/2} - \gamma_{-1/2})] = r\Delta_{3/2}$$

$$(1b)\quad \dot{M}^z_{1/2} + 6WM^z_{3/2} + 30WM^z_{1/2} = r[2(\gamma_{1/2} - \gamma_{-1/2})] = r\Delta_{1/2}$$

where r is the rate of the chemical reaction, in $sec.^{-1}$, and $W = (9/160)T_c h^2\gamma^4 R^{-6}$, the spin-lattice relaxation time in the absence of correlated proton relaxation being $[(80/3)W]^{-1}$. According to the radical pair theory[3] the probability, γ_m, of product formation for a set of equivalent protons in spin state m is given by

$$(2)\quad \gamma_m = G_1 - G_2 T_D^{1/2} \left|(g_1-g_2)\beta\hbar^{-1}H_o + Am\right|^{1/2}$$

where G_1, G_2 and T_D are constants, g_1 and g_2 are g-factors of the two radicals and A is the hyperfine coupling between the nuclei and one of the electrons.

In a typical experiment a CIDNP signal is generated by a photoinduced chemical reaction and rapidly reaches a steady state intensity determined by equations (1). Relaxation of the system is then observed after shutting off the light, i.e. r=0. Solution of equations (1) with these boundary conditions gives the following expression for the time dependence of the decay of the total magnetization, $M^z = M^z_{3/2} + M^z_{1/2}$

(3) $M^z(t) = M^z(0)[\ (a - d)e^{-\alpha t/T_1} + (b + d)e^{-\beta t/T_1}\ ]$

where the equilibrium contribution to M^z has been ignored and a=0.008, b=0.992, α= 0.42, β= 1.005 and d= $(0.107)(3\Delta_{3/2} - 13\Delta_{1/2})/(3\Delta_{3/2} + 2\Delta_{1/2})$. Except for the factor d, which depends on the CIDNP populations, equation (3) is identical to the expression previously derived[2] in which the first, slower decaying exponential has a negligible weight. This need not be the case, however, when the populations have been established by CIDNP. Indeed, in the limit where γ_m is dominated by the hyperfine splitting, substitution from equation (2) gives d = -0.156 and the first exponential contributes about 20% of the second. While this would still be difficult to observe, it is nevertheless 20 times larger than in the case of relaxation from a population distribution describable by a spin temperature (d = 0).

Among other things, the population dependence of the weighting factors for the two exponentials also complicates the interpretation of the magnetic field dependence of CIDNP even for nmr singlets, since the "relaxation time" becomes field dependent.

Sincerely your,

Ron Lawler

Ronald G. Lawler

Associate Professor
of Chemistry

1. K. Muller and G. L. Closs, J. Amer. Chem. Soc., 94, 1002 (1972); K. Schaffner, H. Wolf, S. M. Rosenfeld, R.G. Lawler and H. R. Ward, ibid, 94, 6553 (1972); M. Lehnig and H. Fischer, Zeit. Naturforsch., 27a, 1300 (1972).

2. P. S. Hubbard, Phys. Rev., 109, 1153 (1958); A Abragam, The Principles of Nuclear Magnetism, Oxford Press, 1961, p. 293

3. F. J. Adrian, J. Chem. Phys., 54, 3912 (1971)

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DEPARTMENT OF CHEMISTRY DAVIS, CALIFORNIA 95616

January 11, 1973

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

Proton Relaxation in Paramagnetic Metallo-porphyrins

Dear Barry:

We have extended our investigation of the mechanism of proton relaxation in paramagnetic metallo-porphyrins, (TAMUNMR Newsletter 163-12), to manganese (III) as well as some complexes of an unusual spin state of iron (III).

Using the high-spin complex p-CH_3-TPPMnX, (p-CH_3-TPP = tetra-p-tolylporphyrin, X = halide or azide), we find that the methyl proton linewidths are 32, 52, 44, 34 and 29 Hz at 100 MHz, for X = I, Br, Cl, N_3 and F, respectively. For X = Br, Cl and N_3, the linewidth data closely parallel the previously reported[1] trend in the zero field splitting, ZFS, parameter, D, confirming that electron spin lattice relaxation is dominated by modulation of the ZFS levels by tumbling in solution.

In the case of X = I, for which D was not obtainable by far IR, it has been suggested[1] that D changes sign. Our observation that the trend on linewidths has a turning point at X = Br agrees with this prediction. Similar linewidth trends with experimental[1] D values are observed for the unusual S = 3/2 state of $(Et_2\text{-dtc})_2$ FeX, (Et_2-dtc = diethyldithiocarbamate, X = Br,I).

Sincerely,

Gerd N. La Mar

1. G. C. Bracket, P. L. Richards and W. S. Caughey, J. Chem. Phys. 54, 4383 (1971).

Faculté
des sciences

UNIVERSITÉ
DE SHERBROOKE

Sherbrooke, Qué.

February 6th, 1973.

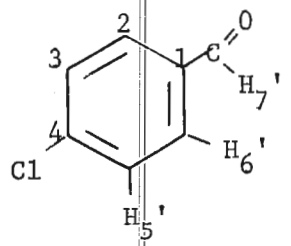
Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A&M University,
College Station, Texas 77845
U.S.A.

Substituent Effects on the J_{CCCH} coupling constants

Dear Professor Shapiro:-

In connection with some other work we decided to look at the effect of substituents on the coupling constants in some substituted benzaldehydes. We were particularly interested to see these effects on the coupling between the aldehydic proton and the ortho carbons and between the aldehydic carbon and the ortho protons.

Unfortunately, this did not exactly turn out as hoped as the coupling between the aldehydic proton and the ortho carbons proved in general to be 1.5 Hz or less. As the corresponding coupling constant in H-H coupling is of the order of 8 Hz this result was quite puzzling. However further investigation of other coupling constants in these molecules threw some light on the situation. If we study as an example p-chlorobenzaldehyde the values obtained



are $J_{3,5'}$ = 5.0 Hz and $J_{4,6'}$ = 10 Hz. This infers that for a -I substituent attached to the observed carbon, the magnitude of the coupling constant is greater than that of benzene (7.4 Hz) whereas if the substituent is in the coupling path a value less than that of benzene is observed. This appears reasonable until one regards the values $J_{1,5'}$ and $J_{2,6'}$ which are both of the order of 7.0 ± .03 Hz. Thus it appears that there is no correlation with simple electronegativity theory e.g. Hammett σ constants although it is possible that the σ_R value may at least explain the results where the substituent is attached to the observed carbon.

The values for $J_{7,6'}$ are between 4.0 Hz and 5.0 Hz with the smallest being for the p NO_2 compound, 4.4 Hz, and the largest being for the p OCH_3, 4.9 Hz. We are presently engaged in determining the data for other similar systems.

Many apologies for the late arrival of this article.

Yours sincerely,

John K. Saunders,
Department of Chemistry,
Université de Sherbrooke.

JKS/sb

173-28

14TH
EXPERIMENTAL
NMR
CONFERENCE

February 2, 1973

14TH ENC FINAL PROGRAM

Dear Barry:

I would like to announce the final details for the 14th ENC, to be held this year at the University of Colorado in Boulder,Colorado.

Registration begins at 4:00 P.M. on Sunday, April 15, 1973 at the Royal Inn Motel. The conference itself begins at 8:45 A.M. on Monday, April 18, 1973. Details including registration forms and a full program are being sent to all attendees of the 11th, 12th, and 13th ENC's. Anyone not on this list, or anyone who, due to the vagaries of the U.S. Postal System (or other reasons), does not receive this information may obtain it and/or further details by writing:

Professor M. Hanna
Department of Chemistry
University of Colorado
Boulder, Colorado 80302
Telephone Number: 303/443-2211, Ext. 6623

Attendance will be accepted on a first come, first serve basis. The final program is attached. Anyone wanting to present a paper should contact me at the above address. We still have room for one or two short ten-minute talks.

Best regards,

Thomas C. Farrar
Chairman, 14th ENC

TCF/rmh
Attachment

14TH ENC 15 - 18 APRIL, 1973

TIME	SUNDAY	MONDAY	TUESDAY	WEDNESDAY
8:45 - 9:00 9:00 - 10:30		Introduction and Welcome SCM-NMR (E.D. Becker)	Educational Aspects in Pulse & FT (P. Bender)	Other Nuclei (G. Levy)
10:30 - 11:00		COFFEE	COFFEE	COFFEE
11:00 - 12:30		Bio-Applications (J. Glasel)	General Instrumentation (R. Lundin)	General Instrumentation (K. Williamson)
12:30 - 2:00		LUNCH	LUNCH	Adjournment
2:00 - 3:30		Multi-Pulse in Liquids (R. Vold)	Other Nuclei (G. Levy)	
3:30 - 4:00		COFFEE	COFFEE	
4:00 - 5:30		Multi-Pulse in Solids (R. Vold)	New Instrumentation and Methods (T. Farrar)	
6:00 - ?	Registration & Mixer	OPEN	Cocktail Party	

173-30

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
9000 ROCKVILLE PIKE
BETHESDA, MD. 20014

February 1, 1973

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77845

^{14}N NMR TITRATION CURVE BY $\{^{14}N\}$ - ^{1}H NMDR

Dear Dr. Shapiro:

We have recently modified the HA-100 probe to enable the performance of double resonance experiments($\{X\}$-^{1}H NMDR) for the following nuclei: X=^{2}H, ^{13}C, ^{14}N, ^{15}N, or ^{31}P. Initial tests of the modification have been highly satisfactory.

One example of a typical $\{^{14}N\}$ - ^{1}H experiment is shown in Figure 1 for an imidazole-D_2O system. The ^{1}H spectrum of a 0.5M imidazole solution shows two broad peaks with the H-2 peak appearing at lower field than the H-4(or H-5) peak(H-4 and H-5 are equivalent due to tautomerism). The broadening of the peaks is due to coupling of the ^{1}H's to the ^{14}N. A ^{14}N decoupling experiment sharpens up the ^{1}H peaks and the ^{1}H spectrum becomes a simple AX_2 spectrum.

In analogy to a ^{1}H nmr titration curve, a plot of ^{14}N chemical shift v.s. pH is obtained with a pK_a calculated to be 6.97(Fig. 2). In contrast to the ^{1}H shift, an upfield shift of 33 ppm is observed for ^{14}N as the imidazole is protonated.

A detailed description of the probe modification will be presented elsewhere.

Sincerely,

Herman J. C. Yeh

Herman J. C. Yeh
Laboratory of Chemistry
NIAMDD, NIH

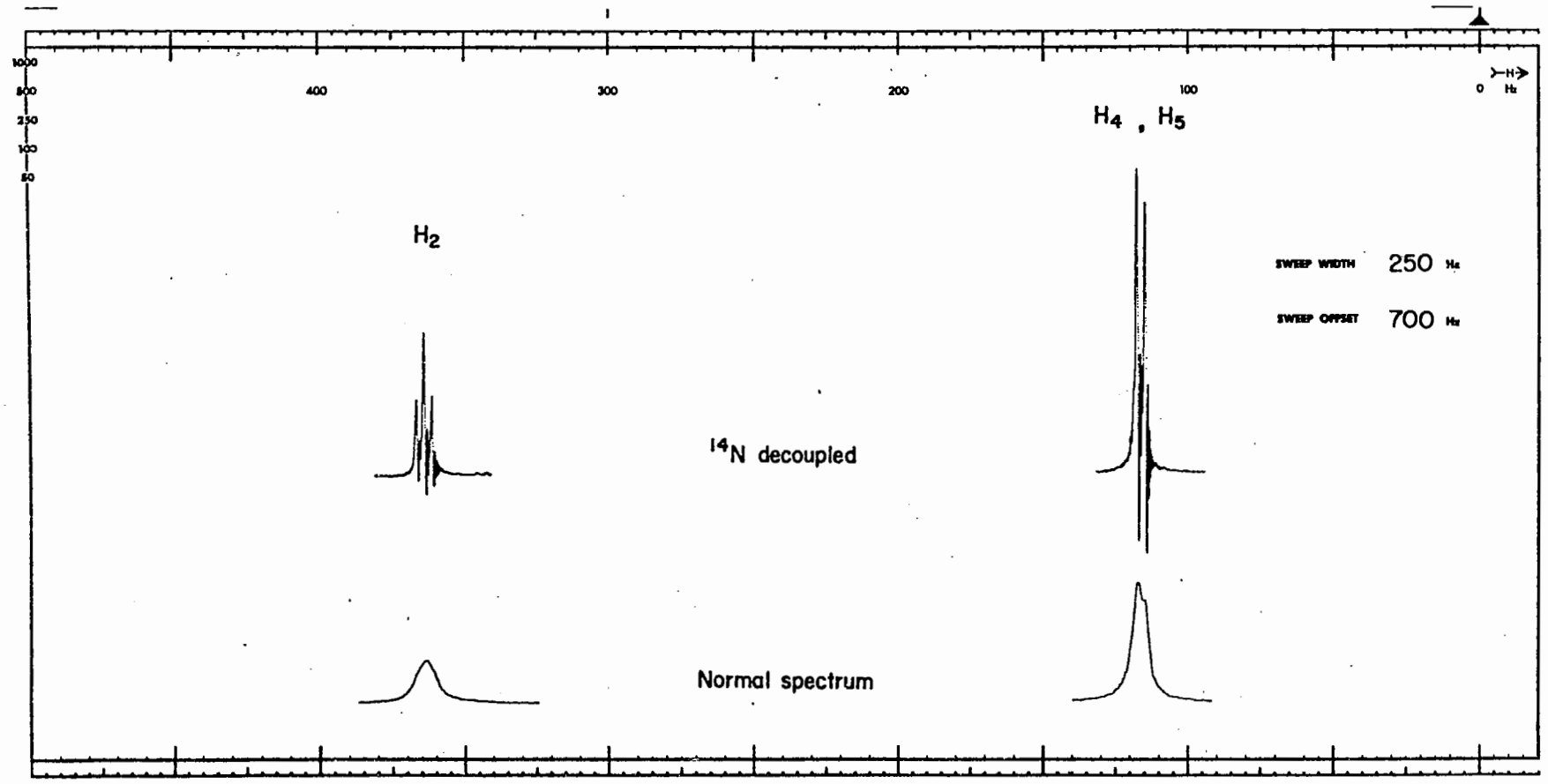

1000
800
400
300
200
100
0 Hz
250
100
50
H4 , H5
H2
SWEEP WIDTH 250 Hz
SWEEP OFFSET 700 Hz
14N decoupled
Normal spectrum

Figure 1.

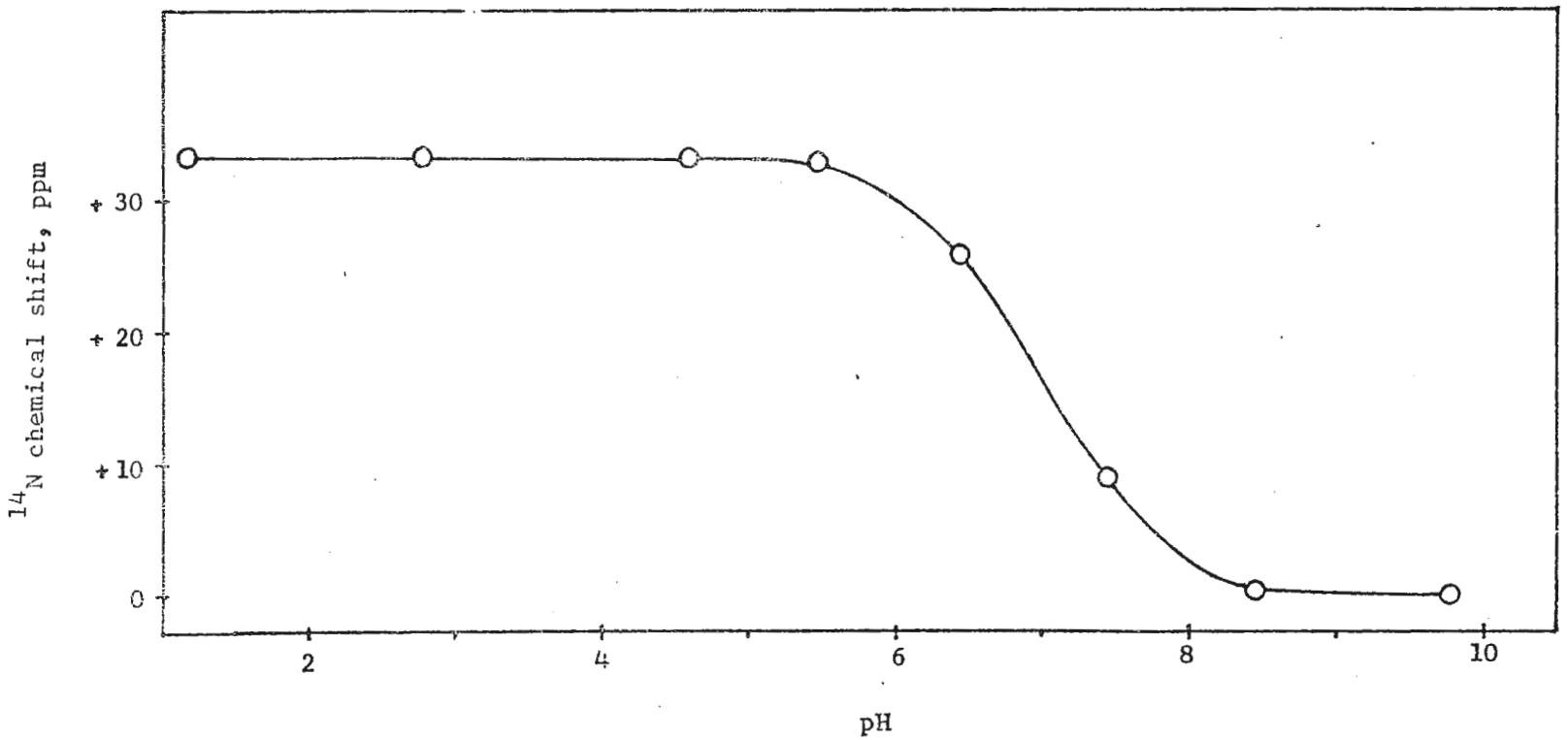


Figure 2.

AUTHOR INDEX

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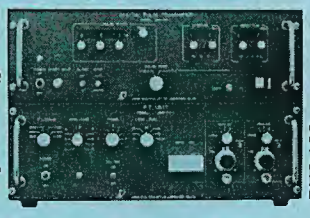

PFT-100

Information and demonstrations are available through our offices in Tokyo, London, Paris and Sydney. As well as the newest laboratory in the United States devoted to NMR research at JEOL, 235 Birchwood Avenue, Cranford, N.J. 07016.

NMR Spectrometers/Mass Spectrometers/ESR Spectrometers/Laser Raman Spectrophotometers/Laboratory Computers/Scanning Electron Microscopes/Electron Microscopes/X-ray Diffractometers/Amino Acid Analyzers.

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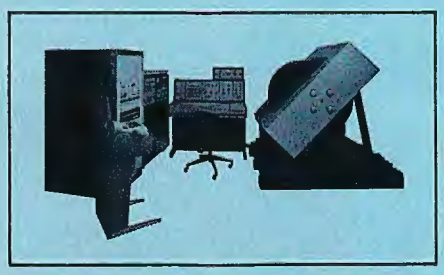
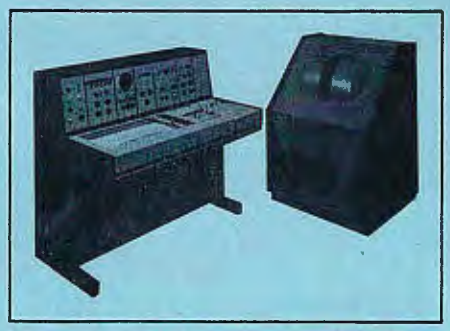
XL-100



A pulsed-Fourier transform or frequency swept high resolution 23.5-kG spectrometer. It features observing capability from 7 to 100 MHz, and decoupling range from 2.9 to 58 and 94 to 100 MHz for continuous wave, noise decoupling or INDOR experiments. Locking flexibility for homo- or heteronuclear internal lock on ^{1}H, ^{19}F, and ^{2}H, and external lock on ^{1}H and ^{19}F are provided. Fourier transform operation, T_1 measurements, homonuclear decoupling and solvent elimination techniques are also routine XL-100 operations. The XL-100 can be tailored to meet single purpose or multi-departmental NMR needs.

NV-14



A moderately priced 14-kG, ^{13}C research spectrometer offering the highest performance per dollar of any NMR system now available. Accessories include Fourier transform for ^{13}C, and other nuclei such as ^{1}H, ^{19}F and ^{31}P. It is a solid state, frequency swept spectrometer ideal for either high performance routine tasks, or for those research requirements demanding state-of-the-art capabilities along with versatile lock, spin decoupling, and variable temperature capability using 8mm sample tubes.

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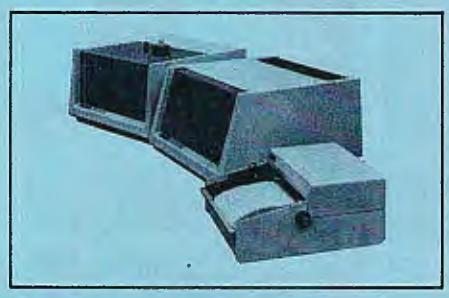
EM-300



A rugged, low priced 30-MHz spectrometer giving excellent results with minimum effort. The EM-300 can easily handle routine proton applications. The instrument's ability to offset, expand or integrate have made it the preferred system in hundreds of teaching laboratories. Other owners have found the EM-300 to be just as useful in simple, routine control applications.

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