DEADLINE DATES: No. 237:   5 June 1978
                  No. 238:   3 July 1978

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.

April 3, 1978

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

Dear Prof. Shapiro:

Of Micelles and Modified Receivers

In the course of our work on magnetic resonance studies of
photoreceptor membranes [Proc. Natl. Acad. Sci. U.S.A., 74,
5222 (1977)], we are attempting the synthesis of deuterium
labelled lipids. A "routine" deuterium-NMR assay of the
first intermediate, 2,2-dideuteropalmitic acid, in $CHCl_3$
solution revealed quite unexpectedly a powder pattern as
shown in the accompanying spectrum. It appears that the
palmitic acid micelles tumble slowly enough to retain
residual quadrupolar coupling. The chloroform solution
looks perfectly transparent to the unaided eye. We are
wondering if other workers in the field have made similar
observations.

On another subject, we are approaching the multinuclear
operation of our Bruker HX-90 spectrometer from a slightly
different point of view than other colleagues. We have
built a broad band receiver (5-200 MHz) capable of detect-
ing at the Larmor frequency. The receiver is fashioned
more or less after Bob Vaughan's published scheme for
multiple pulse experiments. Our only tuned components are
the custom-made Bruker inserts and the band-reject filters
to suppress the lock and decoupling frequencies. Please
credit this contribution to the subscription of
Dr. P. M. Henrichs, of our Laboratories.

Sincerely,

N. Zumbulyadis
S. Gross
Analytical Sciences Division

NZ/SG:mhl
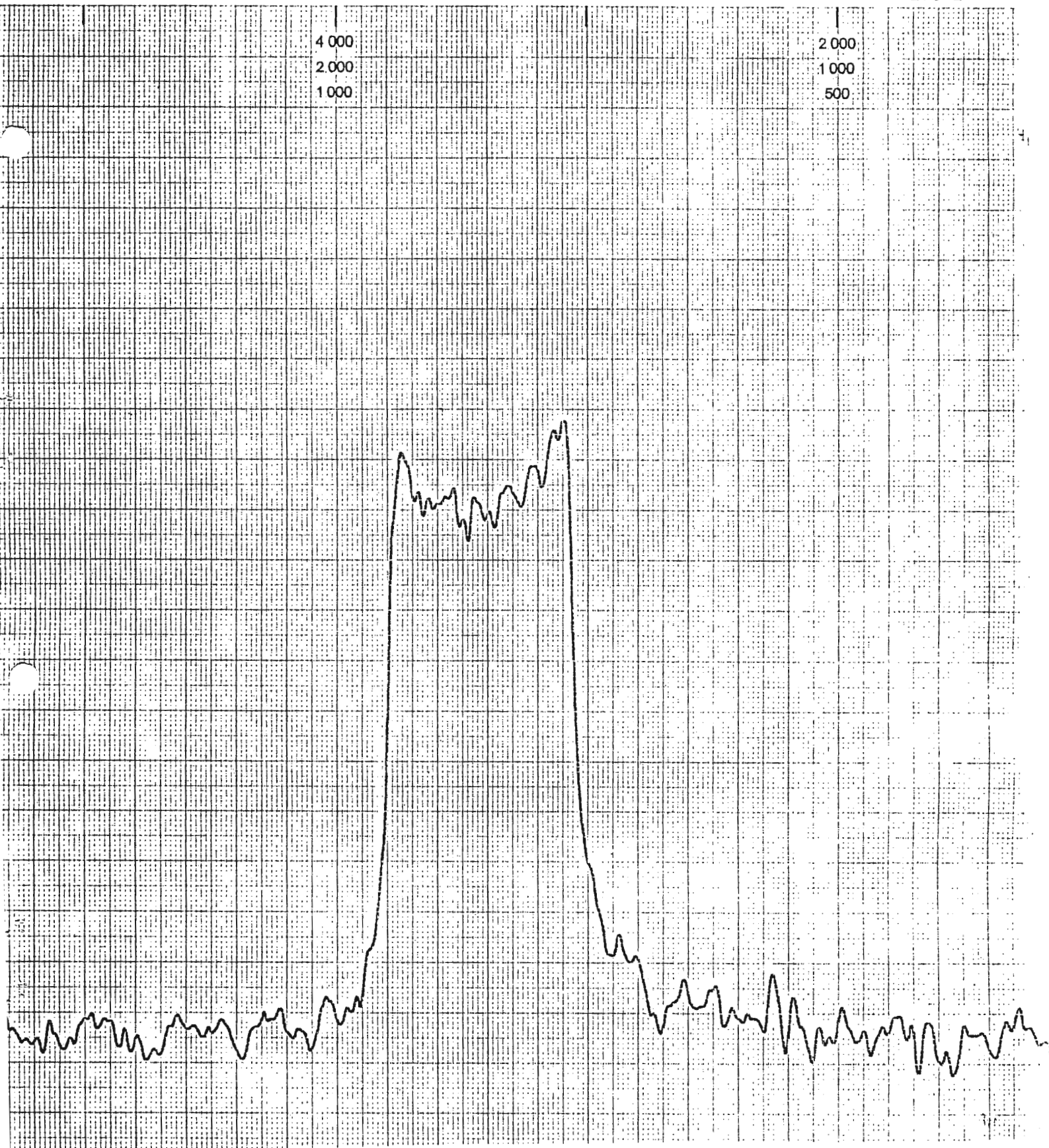
41.46 MHz deuterium NMR spectrum of 2,2 palmitic acid-d_2 in
CHCl$_3$ (5% by weight); 1000 scans; doublet separation 550 Hz;
quadrature detection employed.

CHEMICAL CENTER

PHYSICAL CHEMISTRY 2

April 10, i978

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

Dear Barry,

Title: ^{35}Cl NMR at sub-physiological concentrations

In the study of anion and cation binding to biological macro-
molecules using NMR quadrupolar relaxation techniques (1) it is
desirable to obtain spectra from solutions with low ion concen-
trations. In previous NMR studies in our laboratory using a
wide-line spectrometer the practical lower concentration limit
in the case of chloride has been about 0.2 M. Using our modi-
fied XL-100-15 FT spectrometer we have for some time been able
to obtain good chloride spectra at much lower concentrations.
As an example we wish to describe some experiments on cyto-
chrome c.
Cytochrome c is a small protein (MW= 12000) which transports an
electrone between two protein complexes in the mitochondrial
respiratory chain. There is a wide variety of data indicating
that the interaction between cytochtome c and mitochondrial ox-
idoreductases is primarily mediated by complementary charge int-
eractions (2). 35-Cl NMR offers a direct and sensitive method
to probe changes of the surface charges. Figure 1 shows a 35-Cl
spectrum of 24 mM NaCl in the presence of 1.2 mM oxidized cyto-
chrome c. Figure 2 gives the line broadening due to cytochrome c
as a function of the total chloride ion concentration for both
oxidation states. This figure clearly illustrates the different
ion binding properties of the two species. It is also seen that
important information was lost when the low chloride ion concen-
tration region could not be observed.

Yours sincerely,

Thomas Andersson   Jan-Erik Norne   Sture Forsén

— — — — — — — —

(1) Lindman, B. and Forsén S." Chlorine, Bromine and Iodine
    NMR. Physico-Chemical and Biological Applications ",
    Springer-Verlag, 1976.
(2) Salemme, F. R. Ann. Rev. Biochem. <u>46</u>, 299 (1977).

100 Hz
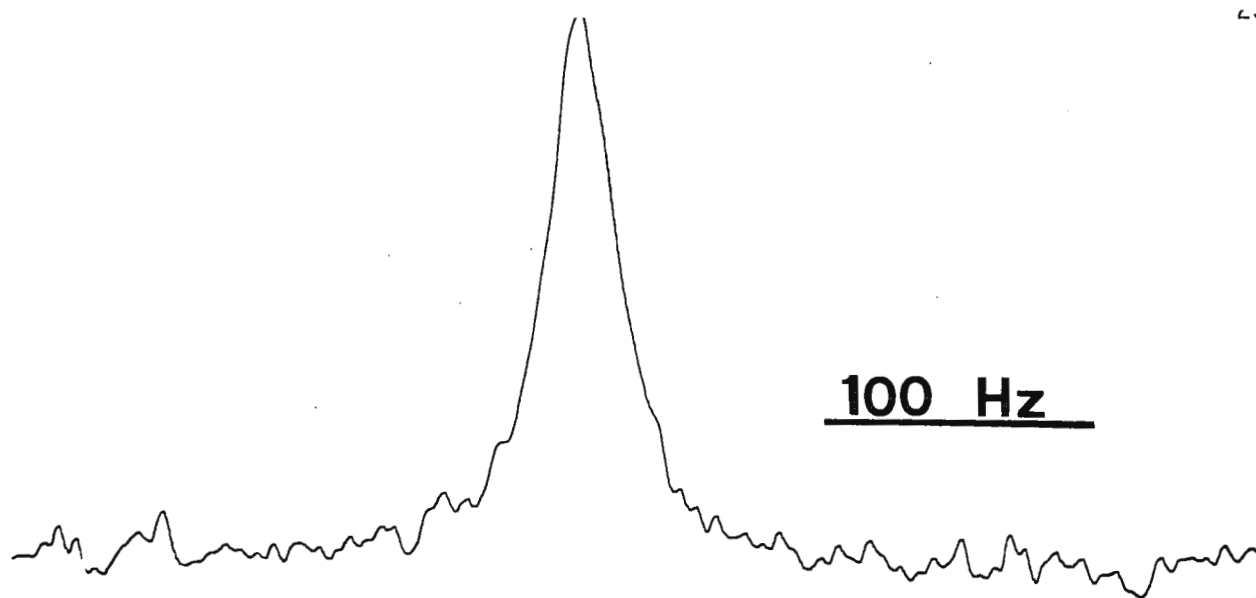
Figure 1   The ^{35}Cl signal of 24 mM NaCl in the presence
of 1.2 mM oxidized cytochrome c. This signal
is the result of 8 hours of accumulation
$(1.5 \cdot 10^5$ transients)
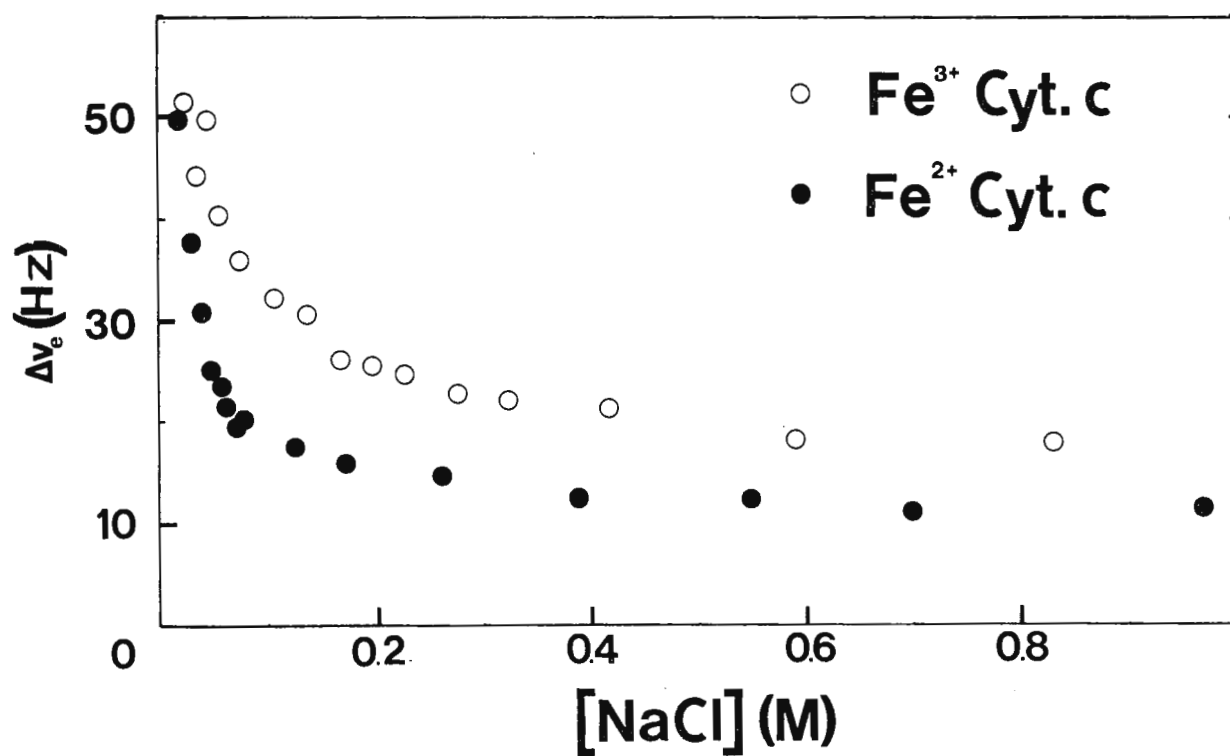
Figure 2   The excess line width of the ^{35}Cl signal as a
function of the total Cl^- concentration, in
the presence of oxidized (Fe^{3+}) and reduced
(Fe^{2+}) cytochrome c at neutral pH. The data
is normalized to 3.0 mM protein concentration
and the linewidth is taken at the half height.

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION
WASHINGTON, D.C. 20204

200 C St., S.W. (HFF–146)

March 21, 1978

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

Interactions of Amines with Nitro-Substituted
Aromatic Compounds in Dimethyl Sulfoxide-d_6

Dear Barry:

We have been examining for some time now nucleophilic
aromatic substitution reactions involving various trinitroaromatic
compounds and a wide variety of amines. Initial reactions involving
primary amines and trinitrobenzene gave rise to very broad proton
spectra. Esr experiments showed no evidence of radical species;
interactions with bulkier secondary amines indicated that the
observed line broadenings were due to slower rates of intercon-
version between the starting materials and the sigma-complex when
amine nucleophiles were employed relative to the well-characterized
alkoxide and alkyl sulfide nucleophilic substitutions.

A wide range of secondary amines have been found to undergo
addition at the methoxyl carbon in trinitroanisole and at a meta-
carbon in dimethyl picramide. Further studies are currently
underway to determine the positions of attack of various secondary
amines upon hindered picryl ethers. Work is rather slow as picryl
chloride is, alas, no longer commercially available for preparation
of the above ethers.

Sincerely,

Eleanor J. Fendler

Eugene P. Mazzola

THE
UNIVERSITY
OF UTAH

March 22, 1978

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

Re: Improved performance of the 22 mm probe

Dear Barry:

We have recently improved some of the performance aspects of our 22 mm probe for the XL-100-15 (227-19). Enclosed are some more recent spectra taken from the Z-22 probe system. We hope that these results will encourage those who own these outdated beasts to take heart. Listed below are the conditions under which the ^{13}C spectra were taken.
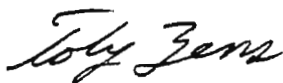
a-Coupled 80% dioxane, 1-90° pulse with 1.6 Hz linebroadening (NOE = 1).

b-^{13}C natural abundance spectrum of 2 atmospheres of allene. 20,000 scans with 3.2 Hz linebroadening.
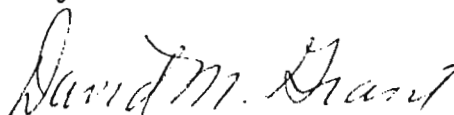
c-0.010 M sucrose 4,000 90° pulses with a repetition rate of 1 sec and 1.0 Hz linebroadening.

d-0.004 M HEW lysozyme 46,000 90° pulses with a repetition rate of 2.1 seconds with 1 Hz linebroadening.

Best wishes,

Toby Zens

Toby Zens

David M. Grant

David M. Grant

a

212mm

$\dfrac{S}{N} = \dfrac{212 \times 2.5}{6.5} \times 4 = 326$

NOISE X 4
6.5mm

b

ΗΑΝS J. JAKOBSEN

AARHUS UNIVERSITY
DEPARTMENT OF ORGANIC CHEMISTRY

8000 AARHUS C, DENMARK March 30, 1978
HJJ/ATL

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

Dear Barry,

SIGNS OF ^{13}C-X COUPLINGS FROM ^{13}C SATELLITES IN ^{13}C SPECTRA

The development of experimental techniques for determination of relative signs of ^{13}C-X coupling constants from observation of ^{13}C NMR spectra has been one of the interests in our group for a long time. These methods include selective or off-resonance ^{1}H decoupling [1], π-pulse selective population transfer (SPT) experiments [2], and spectral analysis of second order coupled ^{13}C spectra [3]. Of course these methods also apply to FT NMR studies of several other nuclei (e.g. ^{29}Si [4]).

We wish to draw attention to an alternative method that should be considered for determination of signs of ^{13}C-X couplings (X different from ^{1}H, e.g. X = ^{31}P) from observation of ^{13}C spectra. The method involves spectral analysis of complete proton decoupled natural abundance ^{13}C-^{13}C satellite spectra (i.e. ^{13}C satellites in ^{13}C NMR spectra) which constitute the AB part of an ABX spin system (A = B = ^{13}C and X = ^{31}P). Thus, provided the AB spectrum is sufficiently second-order, the relative signs of J_{AX} and J_{BX} (i.e. the sign of the product $J_{AX} \times J_{BX}$) may be determined from complete spectral analysis (e.g. using the LAOCN3 program) of the AB part of the spectrum. The ^{13}C satellites observed in the proton decoupled ^{13}C NMR spectrum of triphenylphosphine (figure 1) serve to illustrate the determination of relative signs for $^{1}J_{C1-P}$, $^{2}J_{C2-P}$, and $^{3}J_{C3-P}$ in this compound. Two ^{13}C satellite spectra corresponding to the isotopomers 1a and 1b have been analyzed. In figure 1 the spectra
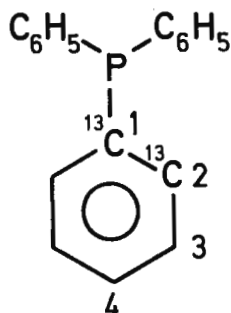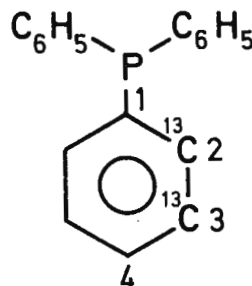
1a   1b
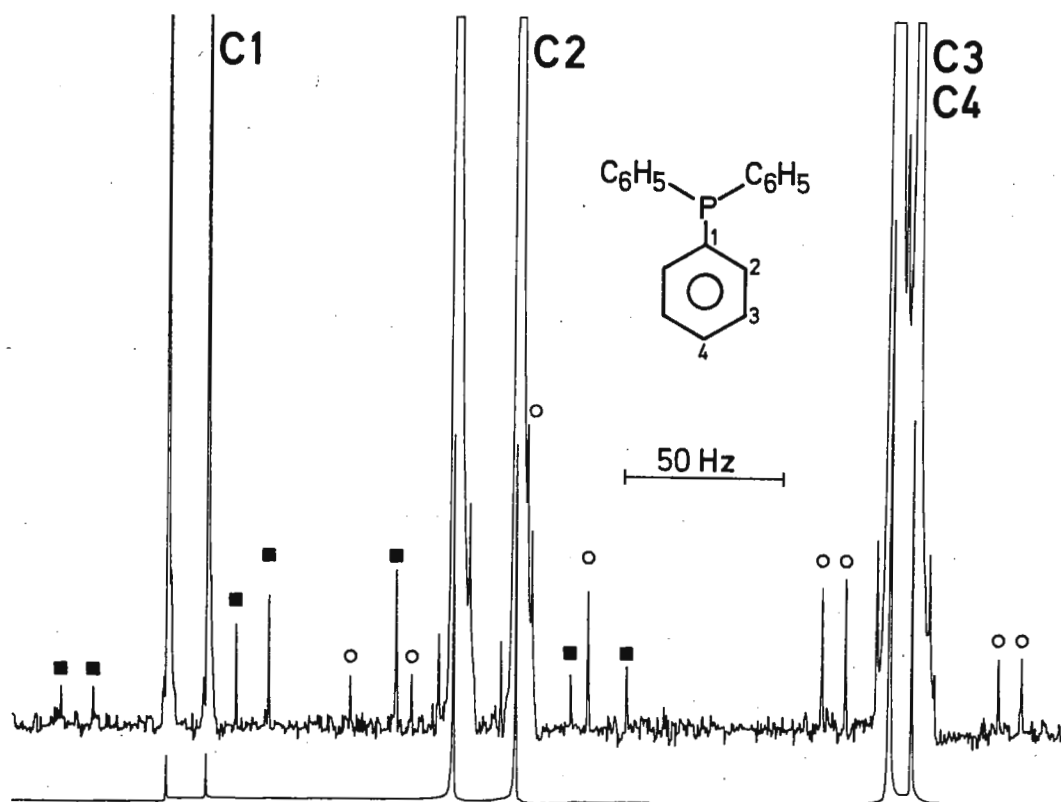
Figure 1. ^{13}C Satellite spectra observed in the proton decoupled ^{13}C FT NMR spectrum of triphenylphosphine. The satellite spectra corresponding to the isotopomer 1a and 1b are marked ■ and O, respectively.

corresponding to 1a and 1b are marked ■ and O, respectively. In the iterative analysis (LAOCN3) of the spectra for 1a and 1b using different relative signs for the J_{C-P}'s, all spectral parameters were allowed to vary. For each spectrum the correct sign combination was determined from the case which gives magnitudes of the J_{C-P}'s similar to those obtained from the "normal" proton decoupled ^{13}C spectrum. The results for the isotopomers 1a and 1b appear from the data summarized in the Table. Thus, it follows that $^1J_{C1-P} \times {}^2J_{C2-P} < 0$ and $^2J_{C2-P} \times {}^3J_{C3-P} > 0$ in accordance with the results ($^1J_{C-P} < 0$, $^2J_{C2-P} > 0$, and $^3J_{C3-P} > 0$) obtained by means of $^{13}C-\{^1H\}$ double resonance techniques [5].

Similarly, analysis of the ^{13}C satellite spectra observed in the proton decoupled ^{13}C spectrum of fluorobenzene gave the following signs: $^1J_{C1-F} \times {}^2J_{C2-F} < 0$, $^2J_{C2-F} \times {}^3J_{C3-F} > 0$, and $^3J_{C3-F} \times {}^4J_{C4-F} > 0$.

Best regards,

Hans J. Jakobsen   *Torben Lund*

Hans J. Jakobsen   Torben Lund

Table 1. Comparison of NMR Parameters Determined from Analysis of the ^{13}C NMR Spectrum of Triphenylphosphine and Its Isotopomers 1a and 1b.[a]

		I[b]	II[c]	III[d]
1a	$^1J_{C1-P}$	12.48	9.63	-12.46
	$^2J_{C2-P}$	19.67	17.95	19.63
	$^1J_{C1-C2}$	-	55.01	55.01
	ν_{C1}	3457.83	3457.48	3457.31
	ν_{C2}	3364.21	3363.63	3363.80
	Rms error	-	0.028	0.028
1b	$^2J_{C2-P}$	19.67	19.62	20.27
	$^3J_{C3-P}$	6.82	6.82	-8.48
	$^1J_{C2-C3}$	-	55.32	55.32
	ν_{C2}	3364.21	3363.70	3363.65
	ν_{C3}	3233.36	3232.87	3232.92
	Rms error	-	0.008	0.008

[a] Coupling constants are in Hz with errors within at least ±0.05 Hz. Chemical shifts on the TMS-scale (internal) are in Hz at 25.1605 MHz; the errors in relative chemical shifts are estimated to be less than ±0.1 Hz.

[b] Parameters determined from the "normal" proton decoupled ^{13}C spectrum, i.e. only the magnitudes, $|J_{C-P}|$, of the $^{13}C-^{31}P$ couplings are determined.

[c] Parameters obtained from the $^{13}C-^{13}C$ satellite spectrum assuming similar signs for the two J_{C-P}'s.

[d] Parameters obtained from the $^{13}C-^{13}C$ satellite spectrum assuming opposite signs for the two J_{C-P}'s.

REFERENCES

[1] H.J.Jakobsen, T.Bundgaard, and R.S.Hansen, Mol.Phys. 23, 197 (1972).

[2] References cited in H.J.Jakobsen and H.Bildsøe, J.Magn.Resonance 26, 183 (1977).

[3] M.Hansen, R.S.Hansen, and H.J.Jakobsen, J.Magn.Resonance 13, 386 (1974).

[4] S.Aa.Linde, H.J.Jakobsen, and B.J.Kimber, J.Amer.Chem.Soc. 97, 3219 (1975).

[5] T.Bundgaard and H.J.Jakobsen, Acta Chem.Scand. 26, 2548 (1972).

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19174

School of Medicine G3

DEPARTMENT OF
BIOCHEMISTRY AND BIOPHYSICS

April 14, 1978

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

Title: Broadband Transmit/Receive Circuit

Dear Professor Shapiro:

How did other people design their T/R circuits for multinuclear probes?
Is the transmitter power efficiently coupled into the probe at all frequencies?
Is the noise figure of the receiver unimpaired? Does one avoid having to
change little matching boxes, quarter wavelength lines or what have you? I
don't know, but at any rate this circuit satisfies the above conditions. What
are the principles?
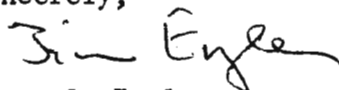
During the Receive time 5 MADC is divided between the two PIN diodes,
making them practically an RF short circuit so that one end of the trans-
mission line transformer is grounded. The probe signal flowing through the
two transformers is twice impedance transformed, so that the broadband pre-
amplifier sees a 50 ohm generator resistance. The transmitter output cir-
cuitry is isolated by the crossed 1N914 diodes.

During the Transmit time a peak detector using two more diodes biases
the PIN diodes off. The first transformer presents a high impedance to the
transmitter, so almost all of the energy goes into the probe.

The frequency range tested here was 5 to 60 MHz, but the principles
should work for higher frequencies. The preamplifier input transistor is
an NC921, which has a good noise figure when it is driven by a 50 ohm source.
The noise figure of the whole arrangement (as measured using a hot and cold
resistor in place of the probe) is never higher than 3 dB. The twisted pair
transmission line in the transformers has an Ro of 100 ohms. 8 turns on a
Stackpole 57-9322 toroid were used for this frequency range.

This report may be appearing later in RSI. Please credit this to Dr.
M. Cohn's account.

Sincerely,

James L. Engle

IE/cls
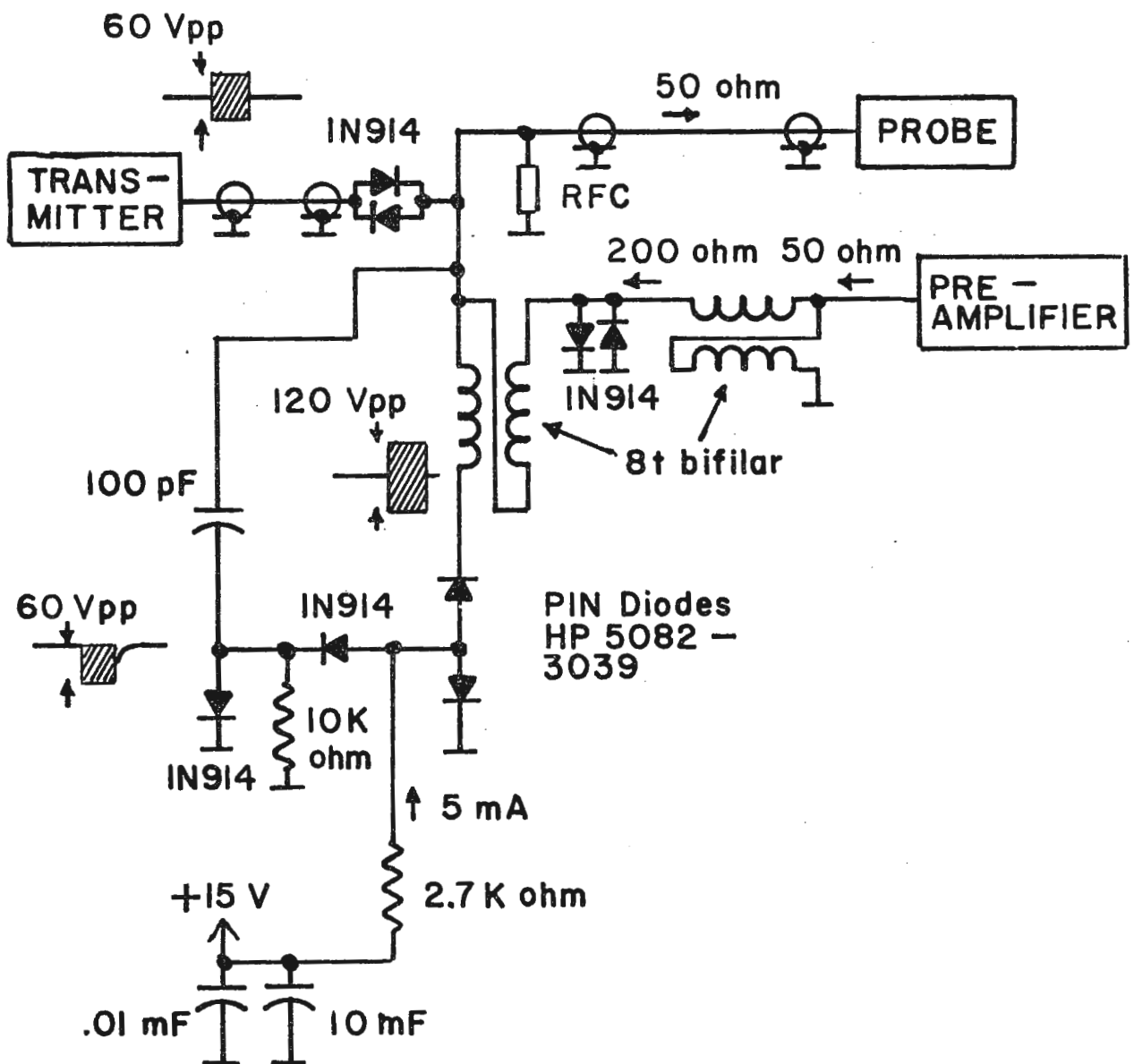
Carnegie-Mellon University   NMR Facility for Biomedical Studies
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213
[412] 6~~XXXXXXXXXX~~ 578-3149

April 1, 1978

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

Dear Barry:

It is some time since we sent in a report on the activities at the NMR Facility for
Biomedical Studies in Pittsburgh, so we thought there might be some interest to
TAMUNMR readers to hear about an approach to broad-band homonuclear decoupling we
have been working on.

One elegant approach to broad-band homonuclear decoupling is the 2D FT spin echo
method demonstrated by Richard Ernst in recent publications.[1,2] We have thought of
a second way which seems conceptually simple, though reduction to ultimate practi-
cality may require some time. We are thinking of calling this method the Results
In Proton Observation at Fearful Fields (RIPOFF). The problem, and our approach
may be appreciated by looking at spectra 1, 2, and 3.

Spectrum 1 is the spectrum of ethyl alcohol at 14,090 gauss, and illustrates the
problem: the coupling of CH_2 and CH_3 is a prominant feature of the spectrum,
amounting to slightly more than 0.11 ppm at this field. If the homogeneity of the
field is reduced to $\Delta H > 0.11$ ppm, the splitting disappears, and effective homo-
nuclear decoupling has been achieved. However an equivalent alternate approach
is to increase the static field H_o.

Theory suggests that J in ppm will be reduced by this procedure, and may eventually
disappear into the inhomogeneity broadening. A spectrum at 58,700 gauss (spectrum
#2) appears promising. J has been reduced to 0.029 ppm and is smaller than in Fig. 1.
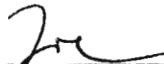
To test the validity of this approach, we have conducted some experiments at 140,900
gauss (spectrum #3). It is clear that the theoretical expectation is satisfied:
J has now been reduced ten fold to 0.011+ppm. A close-up view of the CH_3 triplet
(fig. 4) demonstrates that we still have not achieved sufficiently high field to
cause the splitting to disappear into the inhomogeneity. In order to do this, it
will be necessary to go to a field H_o given by

$$H_o \approx \frac{2\pi J}{\gamma d}$$

where J = coupling constant in Hz, γ, the gyromagnetic ratio, and d the inhomogeneity
in the static field. For $d = 1 \times 10^{-9}$, ethanol will require an H_o of 1.64×10^6 gauss.
We are thinking about ways to move toward this goal.

Best wishes,

Aksel A. Bothner-By
Professor of Chemistry

Josef Dadok
Professor of Chemical
Instrumentation

1. W. P. Aue, E. Bartholdi, and R. R. Ernst. J. Chem. Phys. 64, 2229 (1976).

2. W. P. Aue, J. Karhan, and R. R. Ernst. J. Chem. Phys. 64, 4226 (1976).

1. 14,090 Gauss

2. 58,700 Gauss

3. 140,900 Gauss

PPM From TMS

4.

PPM From TMS
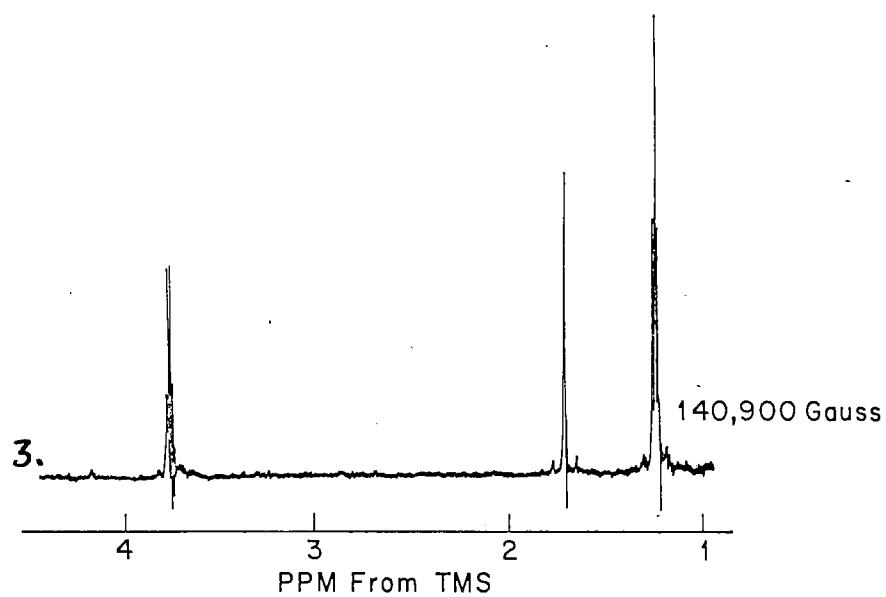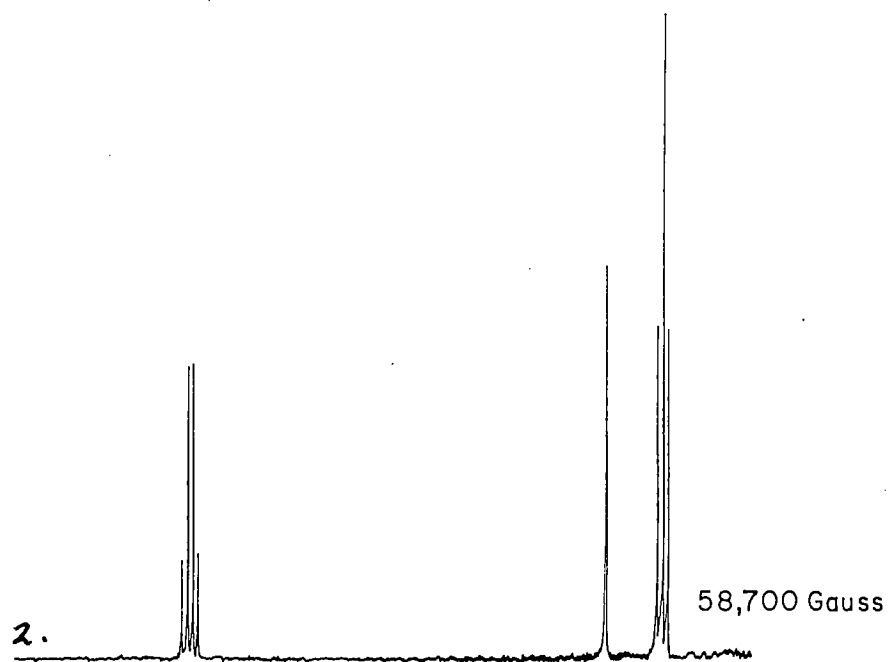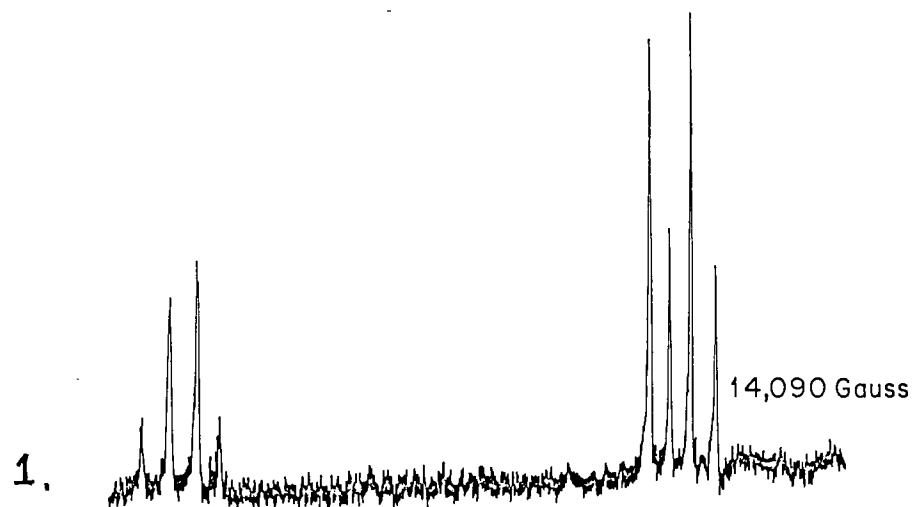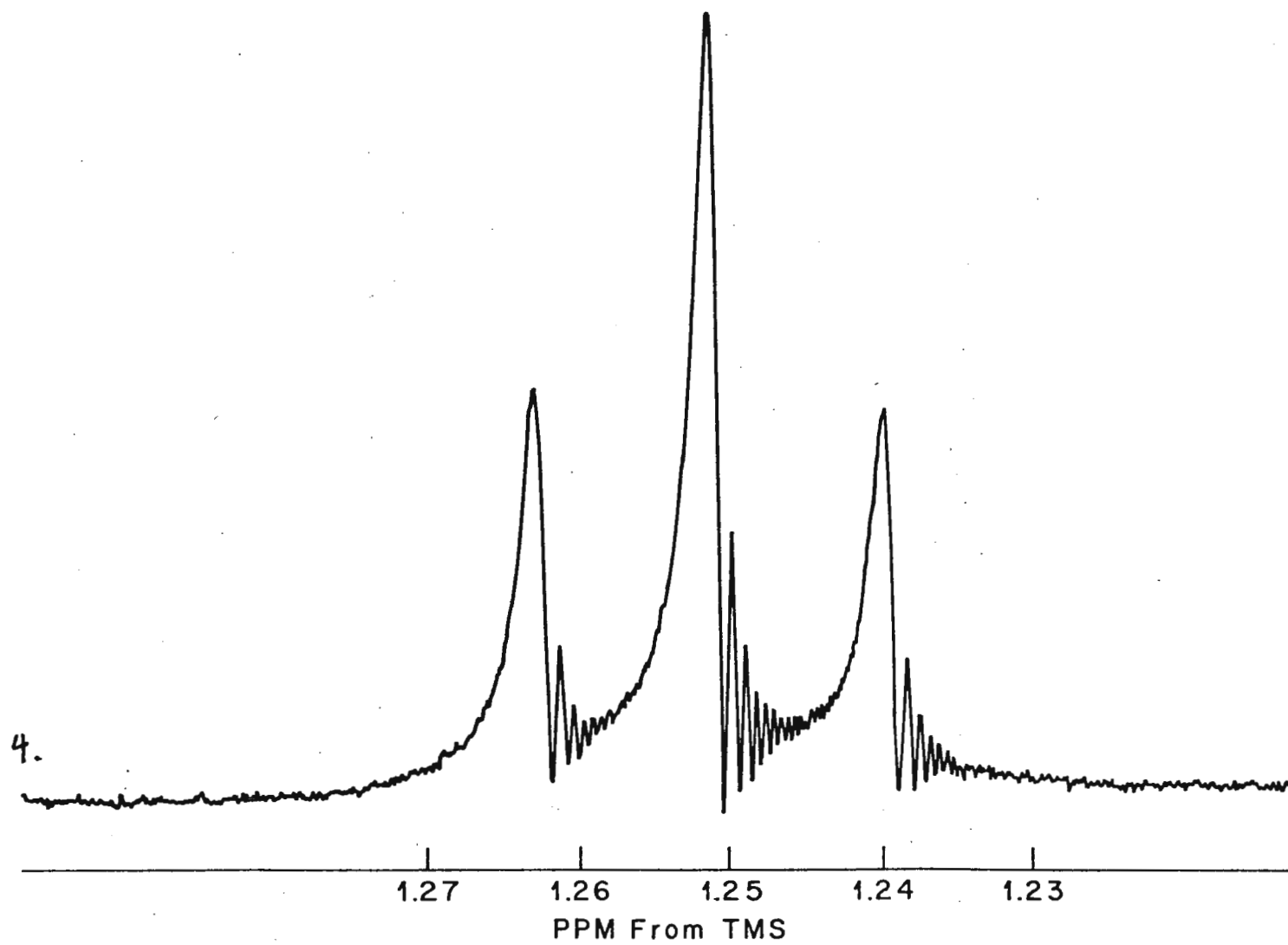
NUCLEAR MAGNETIC RESONANCE

The R-600 control panel is simple to operate, easy to understand.
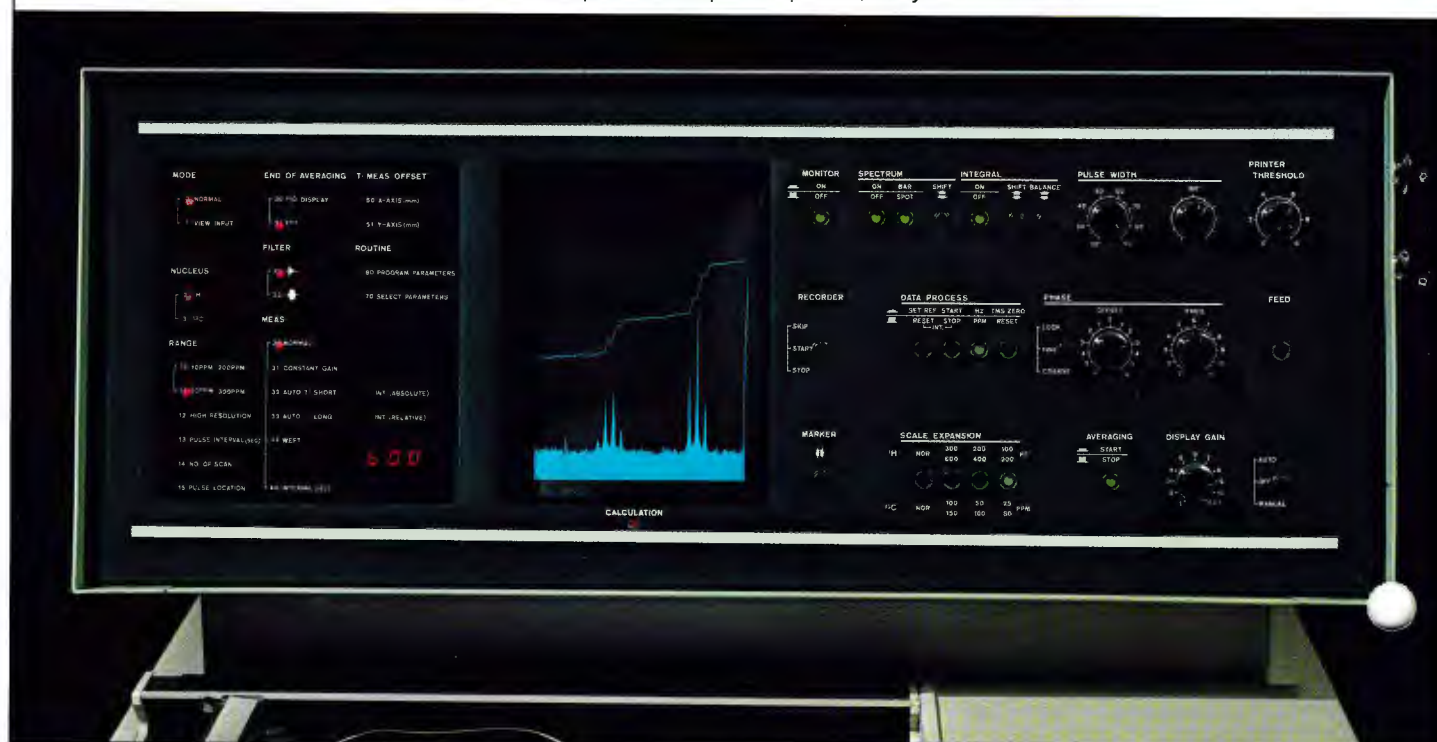
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EFFORTLESS
FT NMR

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So it's easy to operate, easy to install. And with an extremely low price tag and operating cost, it's also easy on your budget.

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Even if you have a complex FT NMR spectrometer now, you still need the Model R-600. Your large unit is usually tied up with time-consuming ^{13}C experiments. Besides, adapting it to proton capability would be tedious or costly. Adding a Model R-600 will give you the extra NMR you need, save money, and get your work done on time.

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DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE

NATIONAL INSTITUTES OF HEALTH

BETHESDA, MARYLAND 20014

April 4, 1978

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

Ligand effect on the ^{15}N and ^{111}Cd NMR
Spectra of doubly labeled ^{111}Cd meso-
tetraphenylporphyrin($^{15}N_4$)

Dear Professor Shapiro:

As part of our continuing interest in the ^{15}N and metal nuclides NMR studies of metalloporphyrins, we have recently made an investigation on the effect of ligands (a series of substituted pyridines) on the ^{15}N and ^{111}Cd chemical shifts and the one-bond Cd-N coupling constants of the titled compound using the $\{^{111}Cd\}$ -^1H and $\{^{15}N\}$ -^1H INDOR experiments (TAMUNMR 225-54). The results of our investigation are listed in the Table. A relatively large ^{111}Cd chemical shift differences were observed (~17 ppm) for the series of ligands, whereas for the same set of ligands the ^{15}N chemical shifts varied over a range of only 0.45 ppm. The ^{111}Cd chemical shifts are correlated nicely with the basicity of the coordinating ligand, with the observation that stronger bases cause ^{111}Cd chemical shifts to higher shielding. The effect on the ^{15}N chemical shift is, however, in the opposite direction as that observed for ^{111}Cd and appears significantly less sensitive to changes in pyridine substituent. These results suggest that ^{111}Cd NMR (and probably the other metal nuclides) is more suitable than ^{15}N NMR for probing the interaction of ligands with metalloporphyrins.

A good correlation is also noted for the trend in the ^{111}Cd-^{15}N coupling constants which decrease with an increase in ligand basicity.

Sincerely,

Herman J. C. Yeh

Herman J. C. Yeh

NMR parameters of ^{111}Cd meso-tetraphenylporphyrin($^{15}N_4$) in $CDCl_3$ (8-10 mg/0.5 ml) with ring-substituted pyridines.

Substituent	pK	$\delta(^{111}Cd)$, ppm*	$\delta(^{15}N)$, ppm*	^1J(Cd-N), Hz
4-CN	1.90	9.31	-0.13	147.6
3-Cl	2.84	5.94	-0.17	146.4
4-CH$_3$OOC	3.26	6.08	-0.16	146.3
4-CH$_3$CO	3.51	6.84	-0.19	146.0
4-H	5.17	0.00	0.00	142.5
4-CH$_3$	6.02	-0.35	0.15	141.0
4-NH$_2$	9.12	-7.86	0.26	137.4

* A positive value denotes a downfield shift relative to the pyridine complexed ^{111}Cd-TPP(^{15}N).

University of Illinois at Urbana-Champaign

School of Chemical Sciences
DEPARTMENT OF CHEMISTRY
Roger Adams Laboratory
Urbana, Illinois 61801

April 11, 1978

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

Title: ^{23}Na Relaxation in Molten Sodium Chloride

Dear Barry:

We hope to make the deadline!

In connection with our studies of compressed supercritical steam we developed a furnace which is well suited for NMR work because it does not affect the homogeneity of the magnetic field. We have recently built several variable temperature probes which operate at atmospheric pressure up to 1000°C and fit into a standard Varian DP-60 electromagnet. Our exploratory relaxation experiments look quite promising. As we show in Table I we have measured T_1 of ^{23}Na (15.87 MHz) using the standard 180-τ-90° sequence in molten sodium chloride at several temperatures. After 64 scans the S/N was about 15:1 but we feel that with some additional effort we could improve it. What is even more interesting is the possibility to increase the maximum temperature to 1500°C with different heating elements and do high resolution spectroscopy.

Table I. ^{23}Na   Spin Lattice Relaxation in Liquid NaCl

T°C	T_1 (msec)
860	97.2 ± 0.7
910	105 ± 1.6
960	111 ± 4.8

Best regards.

Sincerely yours,

Tim DeFries
Graduate Research
Assistant

Walt Lamb
Graduate Research
Assistant

Jiri Jonas
Professor of
Chemistry

JJ/ss

THE UNIVERSITY OF BRITISH COLUMBIA
2075 WESBROOK MALL
VANCOUVER, B.C., CANADA
V6T 1W5

DEPARTMENT OF CHEMISTRY

13 April, 1978

Professor Barry Shapiro
TAMU Newsletter
Department of Chemistry
Texas A & M University
College Station, TX 77843 U.S.A.

POSTDOCTORAL POSITION:
BIOPHYSICAL CHEMISTRY

Dear Barry,

This letter is to announce a postdoctoral position available in my laboratory, beginning 1 September, 1978. The term would be for one year, renewable for one year, at current salary of $11,100 (this may increase by September).

The Work. We have recently shown (TAMU 231, 9 (1977); Anal. Chem. 50 (May, 1978)) that a simple plot of dispersion versus absorption (DISPA) can provide a means for distinguishing and quantifying several different line-broadening mechanisms in NMR, based on data from a single spectrum. The method has been confirmed experimentally for systems involving distributions in chemical shift (polymers; adsorbed species) or line width (ribosomes); chemical exchange; and in resolving closely-spaced peaks. We propose to examine a number of broad NMR signals, including water in biological sources, polymers, and aggregates (micelles, bilayers).

The Locale. Vancouver is a large Canadian city which combines the usual metropolitan advantages with Pacific Northwest mountains and ocean. Although little snow reaches the city, skiing is only an hour away.

Qualifications. The successful candidate should have a Ph.D. involving either NMR or biochemistry (or both), and should submit a curriculum vitae and three recommendations to me at this letterhead. All complete applications will be acknowledged. Our Departmental NMR facilities are strong, machine time is available for research, and a serious researcher should be able to produce a large volume of good work in the proposed term.

Further questions can be answered by phone (call 604-228-3266, and leave a message). Thank you.

Sincerely,

Alan G. Marshall
Associate Professor

Rijksuniversiteit Utrecht

Organisch chemisch laboratorium

Croesestraat 79
Utrecht 2503
Telefoon 030—882311

Datum 4-14-78
Uw kenmerk
Ons kenmerk
Onderwerp

Poly-(iminomethylenes); Structural Studies by ^{1}H- and ^{13}C-NMR

Dear Professor Shapiro,

Just about to leave for the US. Dr. de Bie received your final notice from the US. He was faced with the problem that responding to the pink sheets of his flight-ticket would bring him to a conditioned vacuum, whereas not responding to your pink note would bring him to an un-conditioned TAMU-letter vacuum. Since, however, I have recently been appointed as permanent staff-member of the NMR-department, we request to accept the present contribution as our renewal for the subscription.

Part of our research is concerned with NMR-studies on the title products, which are synthesized and studied by Prof. W. Drenth and co-workers (ref. 1a-d). The compounds, which are obtained by Ni-complex polymerization of the isocyanides, possess a rigid, helical structure with either clockwise or counter-clockwise helix-form each of which possess optical activity. Each turn of the helical rods consists of four isocyanide-units (I a and b; one turn of the polymer drawn with the longitudinal axis perpendicular to the plane of the paper).
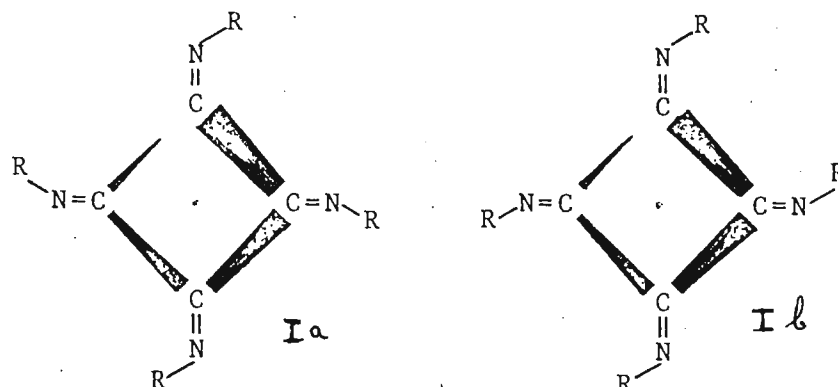
A wide variety of compounds has been synthesized with groups-R as alkyl, aryl and biologically interesting substituents as sugars and amino-acids for the immunological field.
Models of the tightly pact, rigid polymers reveal that orientation of the groups R can be either according to Ia or to Ib. Their precize orientation is of importance for the understanding of their behaviour in several respects. We applied NMR for our study. The typical polymer broad-line ^{1}H-NMR spectrum (Fig. 1a) shows -in the case of most aryl-substituted products- double signals for the substituents attached to the phenyl-ring (e.g. OMe). The high-field position of one OMe-signal suggests a strong anisotropy effect of phenyl-rings upon only one species of OMe's. The doubled resonances are also observed for certain carbon-atoms in the ^{13}C-spectra (Fig. 1b).. As possible cause for these observations, we first assumed association of helices through the

π–systems of the phenyl-groups. Dilution effects, increase in temperature
nor solvent change from $CDCl_3$ to C_6D_6 caused significant spectral changes,
although very slight alterations were observed.
Our present assumption is that structures Ia and b result in a difference
in relative orientation of aryl-substituents in helices organized according
to Ia versus Ib. This could result in a considerable difference in accessibility
of substituents at the phenyl-rings towards large ligands and hence
differences in association or complexation with lanthanide-shift reagents.
In anLSR-experiment,using para-methoxyphenyl-substituted polymer, slight,
but as yet insignificant spectral changes in the OMe region could be observed.
However, it is known from other experiments that single aromatic-OMe groups
are poorly complexing groups and we are presently in the process to
synthesize more suitably substituted polymers for further study.

Dr. Robert J.J.Ch.Lousberg

Fig 1a

Fig 1b
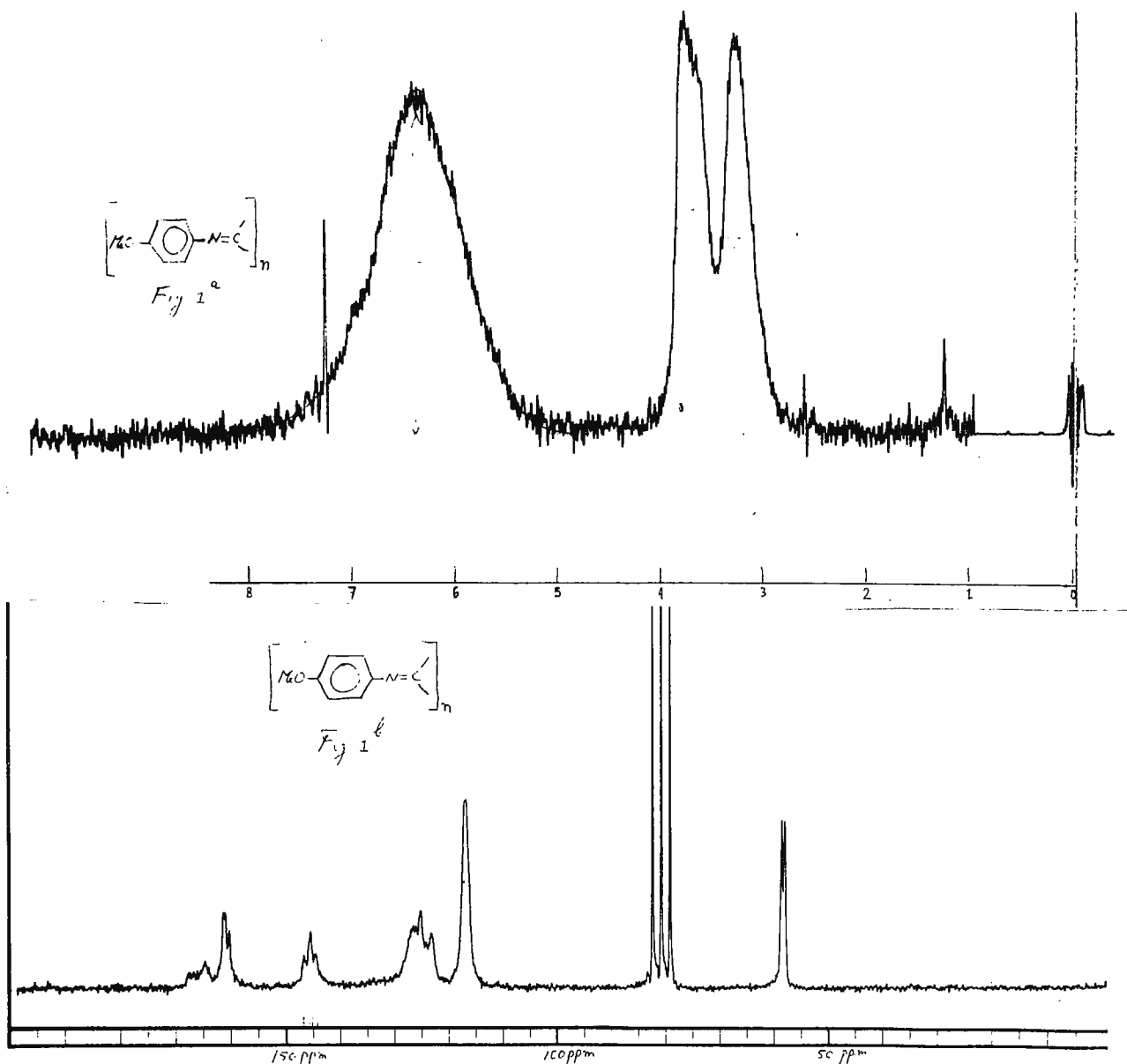
1a) J.W.Zwikker, R.J.M.Nolte and J.S.J.van Zomeren, J.Org.Chem.,43,(1978);b)
A.J.Naaktgeboren, R.J.M.Nolte and W.Drenth,Recl.Trav.Chim.Pays-Bas,97,112,(1978);
c)J.M.van der Eyk, R.J.M.Nolte and W.Drenth,ibid,97,46,(1978) and references
quoted there.

UNIVERSITY OF REGINA

REGINA, CANADA   S4S 0A2

DEPARTMENT OF CHEMISTRY

April 19, 1978

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

Dear Barry:

RE: Recorder-plotting of lock channel signal

in HX-90-type instruments

We have found that with very minor modifications the lock-channel (f_0) signal can be recorded on the instrument's X-Y chart recorder. Two possible applications are:

(i) Fine-shimming. Particularly when the observed signal (f_1) is very weak, the entire shimming process can normally only be done by using the f_0 signal, employing field-sweep mode on the scope. Better homogeneity can be obtained by observing the same f_0 signal on the recorder paper.

(ii) Temperature calibration of non-proton inserts. Perhaps the most universally used T-calibration is that using the ^{1}H signals of glycol or methanol as a means for calibrating the Variable Temperature Control Unit. But such calibration is no longer valid if another insert (be it ^{13}C or [3]He) is used. It is now possible to directly calibrate such non-proton inserts, by using a glycol or methanol sample and recording the ^{1}H spectra of these compounds from the proton f_0 channel.

Such applications all employ a field-sweep un-locked mode, so that magnet field drift will form the limiting factor.

The required modifications are minor, since most of the hardware is already in place. In the shim sub-channel of the f_0 channel there exists already a connection between its 4kHz detector and one of the sections (S2) of the 5-step f_0 attenuator on the front panel. (S2 is not used, at least in our configuration; its output is open.)

Since this portion of the f_0 channel is identical to the f_1 channel, all that is needed is the installation of an SPDT switch connecting recorder Y-input to either the output of S2 of the f_0 attenuator (pin 15) or to the output of the f_1 attenuator (S1). In addition pin 10 of the shim attenuator board has to be grounded.
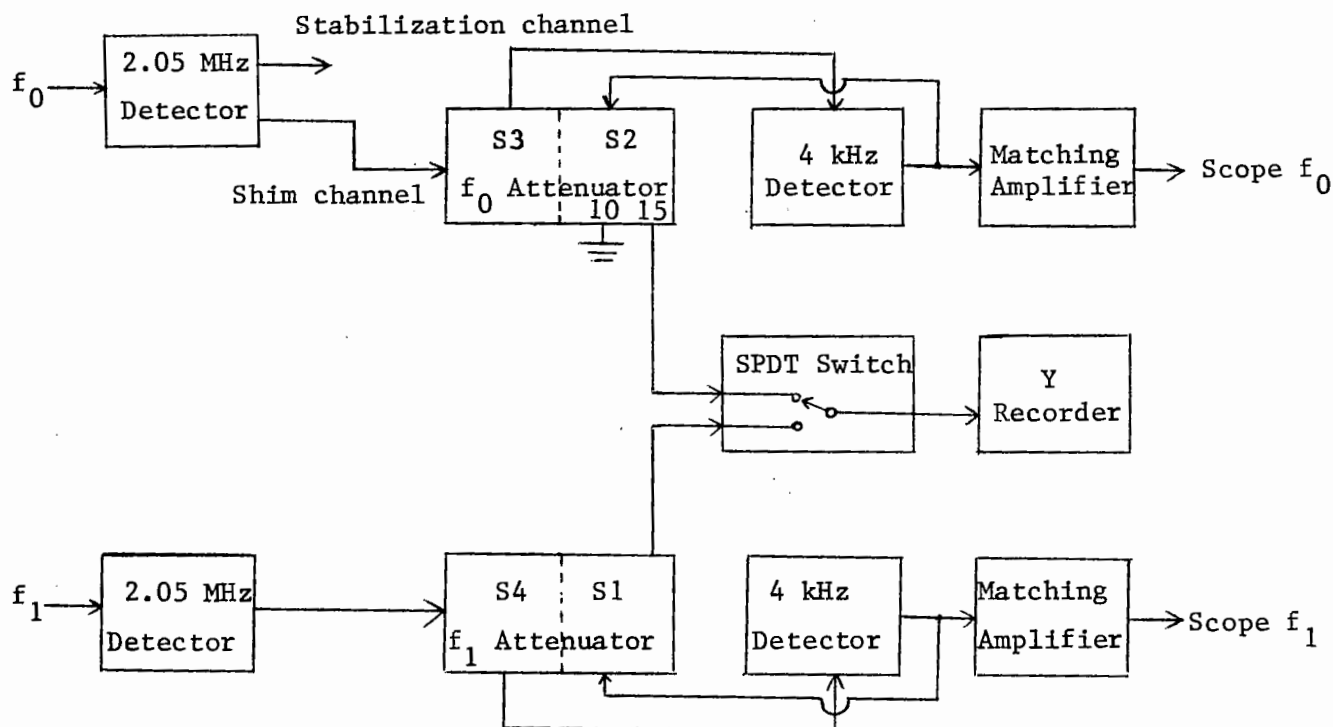
Sincerely

F.M. Mourits   T.C. Ng

P.S. Credit this contribution to Frans Rummens' account.

FHAR/ss

Unilever Research

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Merseyside L62 4XN

Telephone 051-645 2000
Telex 627235

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

Our ref: GJTT/EJS/JL

18 APR 78

Dear Professor Shapiro

For several years' it has been known that some surfactants in micellar solutions give broad nmr resonances ($\Delta \nu \frac{1}{2} > 10 Hz$) as opposed to the sharp lines usually observed ($\Delta \nu \frac{1}{2} < 5 Hz$). This broadening is attributed to the formation of large micelles (probably rod-shaped), and is associated with the large τ_c values required for diffusion around the micelle. Recently, studies of ^{14}N nuclear relaxation[2] and proton line-shapes[3] have been reported for lage micelles in hexadecyltrimethyl ammonium bromide solutions. Both papers include theoretical descriptions relating the observed relaxation rates/line shapes to the long τ_c values.

Frequently, micelle sizes are estimated by the use of a light scattering technique. Two well known examples, where from light scattering and other evidence it is suggested that surfactants from large micelles, are for nonionic surfactants $[C_nH_{2n+1} (OCH_2CH_2)_m OH]$ at temperatures just below the cloud point, and sodium dodecylsulphate ($C_{12}H_{25}SO_4Na$ SDS) in the presence of added octanol[4] and/or sodium chloride[5]. Recently, it has been proposed for nonionic surfactant solution that the large entities 'seen' by light scattering are secondary aggregates of small micelles[6]. Using proton nmr it is easy to distinguish between secondary aggregation of small micelles and large micelles, because the former will give sharp nmr lines while the latter give broad nmr lines.

We have used the approach of Henriksson et al[2] to calculate line-widths as a function of τ_c. Value of proton T_1 and $\Delta \nu \frac{1}{2}$ for the nonionic surfactant $C_{12}H_{25}(OCH_2CH_2)_6$ OH (2% in D_2O with 0.1 MNaCl) show little change on increasing the temperature through the cloud point, indicating that the large entities are formed by secondary aggregation of small micelles. On the other hand, broad resonances are observed for D_2O solutions of SDS in the presence of octanol and/or salt. For the latter solutions, changes in $\Delta \nu \frac{1}{2}$ are consistent with estimates of micelle size obtained from quaisi-elastic light scattering data[5]. Thus the nmr results provide strong evidence for the formation of large micelles in the latter case.

Yours sincerely

E J STAPLES and G J T TIDDY

REFERENCES
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2. U Henriksson, L Öberg, J C Eriksson & L Westman, J.Phys. Chem., 1977, 81, 76.
3. J Ulmius & H Wennerström, J. Magn. Resonance, 1977, 28, 309.
4. D E Clarke & D G Hall, Colloid Polymer Sci., 1974, 252, 153.
5. N A Mazer, G B Benedek & M C Carey., J. Phys. Chem., 1976, 80, 1075.
6. C Tanford, G Nozaki & M F Rohde, J. Phys. Chem., 1977, 81, 1555.

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DEPARTAMENTO DE QUIMICA

April 3, 1978.

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

Carbon magnetic resonance as an identity criterium for orga-
nic molecules.

Dear Professor Shapiro:

It is actually accepted that the identification of samples
arising from different sources, as the same compound is mainly
based on comparison of infrared spectra and on mixed melting
points for solids or adequate chromatographic measurements for
liquids.

In the case of molecules with close structural analogy
very small differences have to be found in the infrared spectra,
thus making final conclusions quite difficult. In contrast cmr
spectra are extremely sensitive to small structural changes and
provide therefore a much more objective comparison criterium.

To illustrate these points we describe here the definitive
stereochemical assignment of α-(I) and β-pipitzol (II). Their
structures were established more than a decade ago[1], but their
stereochemistries remained only tentative due to the lack of
adecuate models for optical rotatory dispersion and circular
dichroism comparisons. We now proof the validity of the origi-
nal assignments.

I   II   III
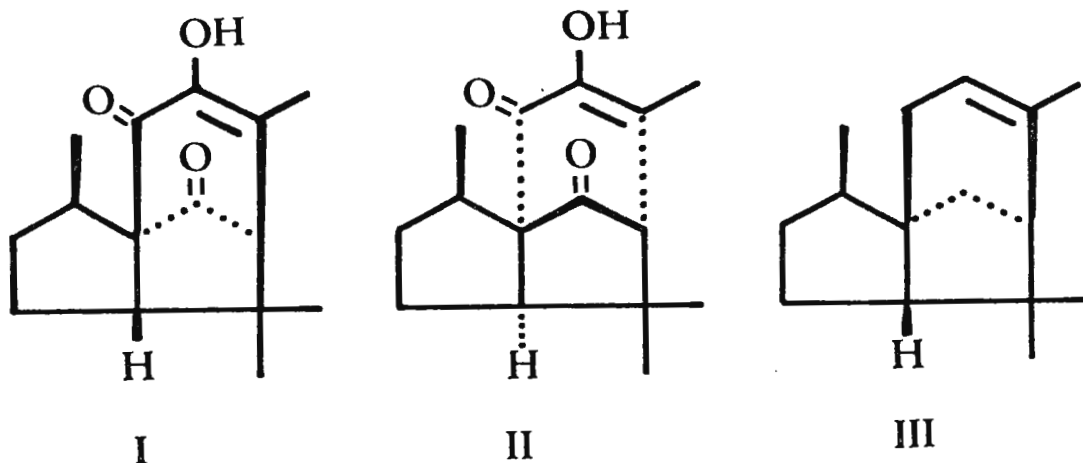
The benzoate of each pipitzol was treated with ethaneditiol and the resulting ditioketal was desulfurized with Raney-nickel. This yielded desoxicompounds in which the conjugated carbonyl disappeared in the ir. Formation of a second ditioketal followed again by desulfurization gave α- and β-bis-desoxipipitzol. A molecule with the same gross structure was prepared from cedrene (III), whose stereochemistry is well defined[2]. Epoxidation of the double bond followed by BF₃ rearrangement gave 2-cedranone[3] which in turn was transformed into the enolbenzoate.

The ir spectra of the three samples are shown in Figure 1, where it can be seen that the identity of two of the compounds is hard to asses. In contrast, the cmr spectra shown in Figure 2, clearly demonstrate that the lower spectrum corresponds to a different compound than the other two and therefore α-pipitzol (I) possesses the same stereochemistry as cedrene (III).

If the secondary methyl group of β-pipitzol (II) would have opposite configuration, then the two pipitzols would be enantiomers and their cmr spectra in achiral media would be identical. However, the differences in stereochemistry (all centers except one or in other words one center prevents that they are enantiomers) produce significant changes in the cmr spectra.

There are some advantages of cmr comparisons in which one is more concerned about chemical shifts, over ir comparisons, since solutions having different concentrations can be compared and even the purity of the molecules is not so serious as in ir. This last point is clearly illustrated in the upper spectrum of figure 2 which corresponds to a crude reaction product.

Sincerely yours,

Pedro Joseph-Nathan   Urania Román   Juan D. Hernández
Professor of Chemistry   Graduate Student   Graduate Student

1.- F. Walls, J. Padilla, P. Joseph-Nathan, F. Giral and J. Romo, Tetrahedron Letters, 1577 (1965).

2.- G. Stork and F.H. Clarke, Jr., J. Amer. Chem. Soc., 83, 3114 (1961); G. Büchi, R.E. Erickson and N. Wakabayashi, Ibid, 83, 927 (1961).

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PJN/psp
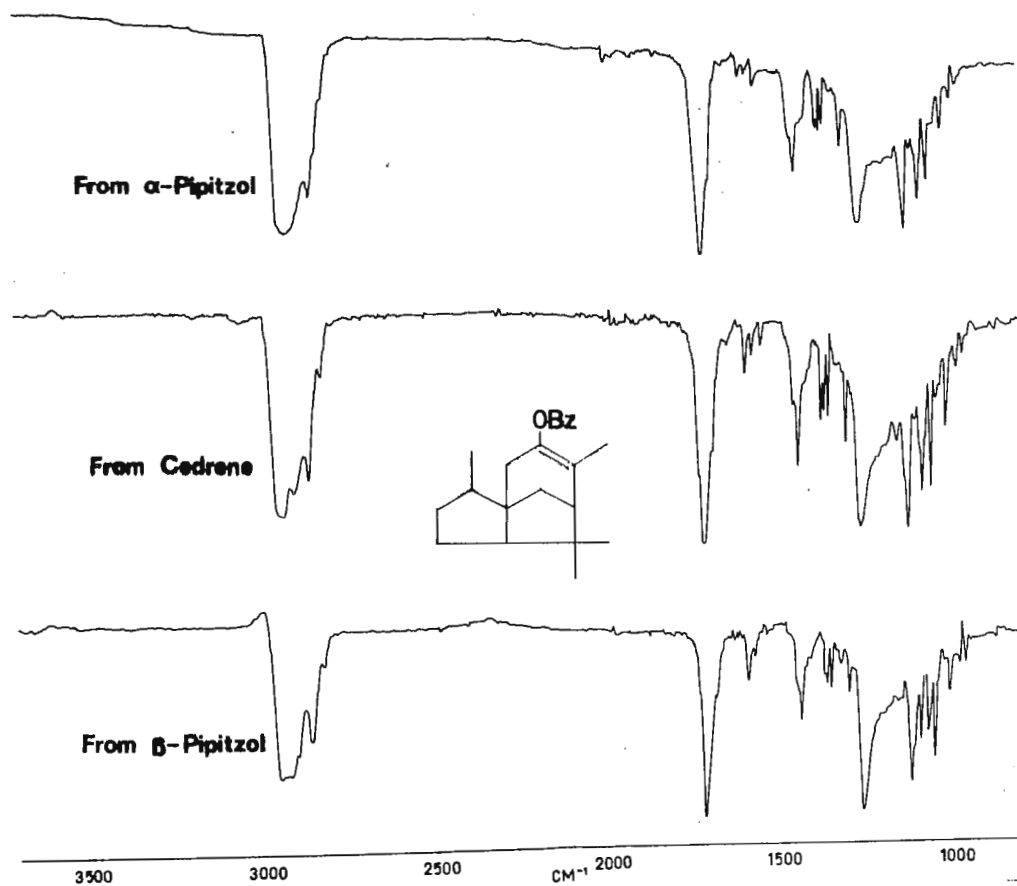
Figure 1.

Figure 2.
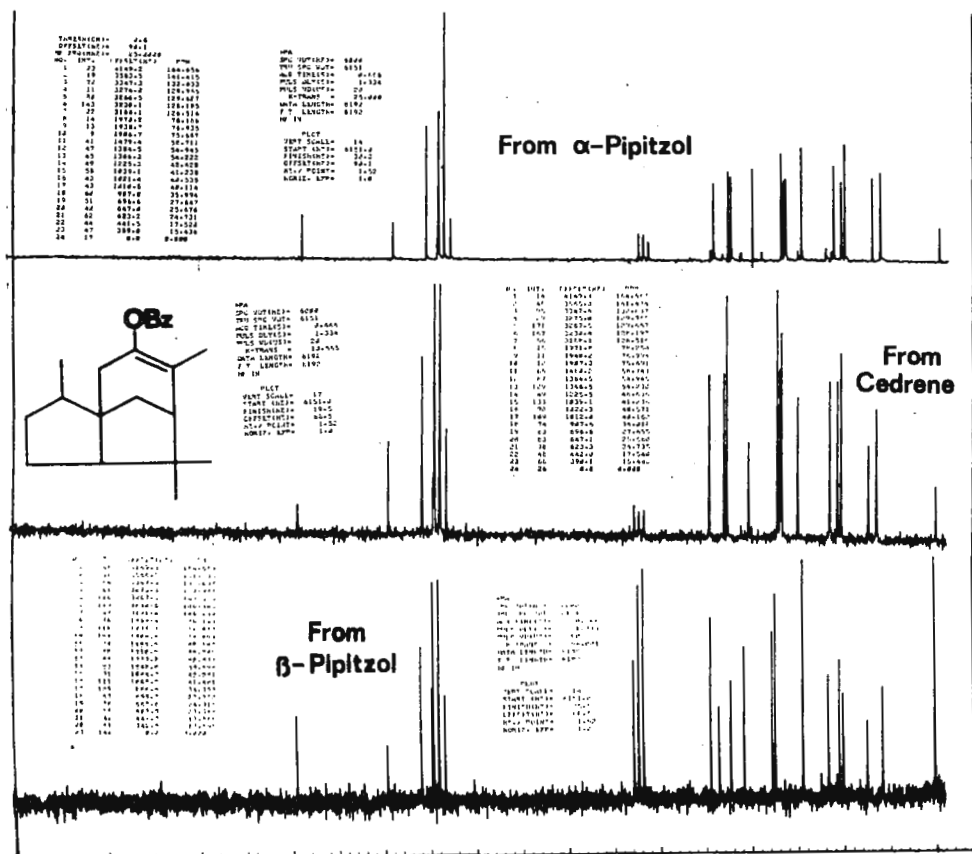
UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

DEPARTMENT OF CHEMISTRY
(803) 777-5263

April 4, 1978

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

RE: Permanent Position Available for an NMR Laboratory Supervisor

Dear Barry:

The Department of Chemistry at the University of South Carolina is seeking qualified applicants for an NMR laboratory supervisor. This position is a line item within the Chemistry Department's budget, and hence the position can become a permanent one. The individual must have extensive experience in the area of nmr spectroscopy and have a working knowledge of small computers. The main responsibility of the applicant will be to maintain and develop the departmental facilities. The nmr instrumentation within the Department includes four ^{1}H spectrometers, CFT-20, and a highly modified XL-100. In addition, the Department has been recommended for funding of an NSF proposal for a 200 MHz superconducting nmr spectrometer. The salary of the applicant will be competitive and commensurate with the individual's experience. The applicants should send their resumes and the names of three references to:

Professor J. D. Odom
Department of Chemistry
University of South Carolina
Columbia, South Carolina 29208

The University of South Carolina is an equal opportunity/affirmative action employer.

Warmest regards,

Paul D. Ellis
Associate Professor

PDE/scc

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London   NW7 1AA

telegrams Natinmed LondonNW7
telex 922666 (MRCNAT G)
telephone 01-959 3666

reference

10th April 1978.

XL-100 Cassette Dump Modification

Dear Barry,

In the standard Varian Fourier Transform 16k computer program (994100-D) as used on the XL 100 the number of data points used for free induction decays, normal spectra or block averaged spectra is variable up to a limit of 8k points. The cassette dumping routine does not take this into account and always stores the full data table with a record length of 8k. Consequently only about 20 fids or spectra can be written onto a cassette. Since we rarely use the whole 8k points this seemed to be an inefficient use of cassette space. Therefore I have written a modification (CRUNCHER) which allows variable length records to be written such that only the points actually used are dumped. With this modification the file capacity of the cassette has increased from 20 to 35 (for 4k data points) and 66 (for 2k data points). I estimate it should be possible to get 115 1k data files per cassette. Of course files of varying length may be stored on the same cassette; the above numbers should therefore be taken as a guide. I will be happy to supply a listing of the modification to anyone who is interested.

Please credit this contribution to Gordon Roberts' subscription.

Yours sincerely,

Barry Kimber.

B.J. Kimber.
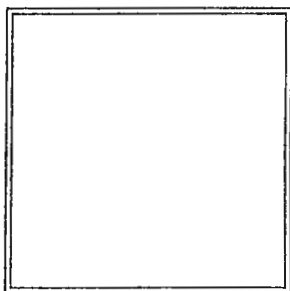
April 10, 1978

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

Title: Supression of Resonance in C-13 Spectra of Co-polyers

   A First Look at the Solid State Version of the NT-150 Spectrometer

Dear Barry:

   Since it took several reminders from you to prompt me to send a contribution
to TAMU I thought it only fitting that perhaps I should include several contri-
butions at the same time. We've been studying the sequence distribution and
microstructure in acrylic nitrile based polymers and relating these properties
to the chemical and physical properties that the polymers display. Using re-
sonance supression we were able to obtain good interpretable spectra including
quantative measurements of the sequencing and microstructure. Figure 1A rep-
resents the C-13 NMR spectrum in the 50 to 23 ppm range of an acryl-nitrile-
methacrylo nitrile copolymer (68%/32% composition) with an acquisition time AT
of 0.800 seconds in CD_3NO_2 at 75%C on a Varian XL-100 spectrometer. A 3 second
delay was used between pulses. One major region of resonance results in the
overlap ov the methylene and the quatinary carbon and the upper field region of
resonance results from the overlap of the methine and methyl resonance. We were
able to selectively observe the resonance of each species by using a supression
technique of $(180°-T -90° -AT)_n$ spectrum B was obtained with T = 0.600 seconds
and resulted in the supression of the quatinary carbon. Spectrum C was obtained
using a T of 0.250 seconds which resulted in the supression of the methyl carbon.
Spectrum D was obtained with T = 0.165 seconds and resulted in the supression of
the methylene carbon and is shown with phase inversion. Spectrum E was obtained
with T = 0.100 seconds resulting in the methylene carbons being supressed, also
the spectrum is shown with its phase inverted. While the conditions for supres-
sing the various carbons were obtained by trial and error, the net result made
it all worthwhile. For example, it is clear that the same information is being
displayed in the methine resonance in spectrum C as with the quatanary carbon
in spectrum E, thus we were able to get quantitative values from each of these
which improved the overall level of quantitative accuracy in our sequence meas-
urements.

   We acquired a Nicolet NT-150 spectrometer last fall, and just a few weeks
ago we had installed the cross polarization gear and a probe capable of spinning
solids at the magic angle. Figure 2 shows one of our spectra of adomantane dis-
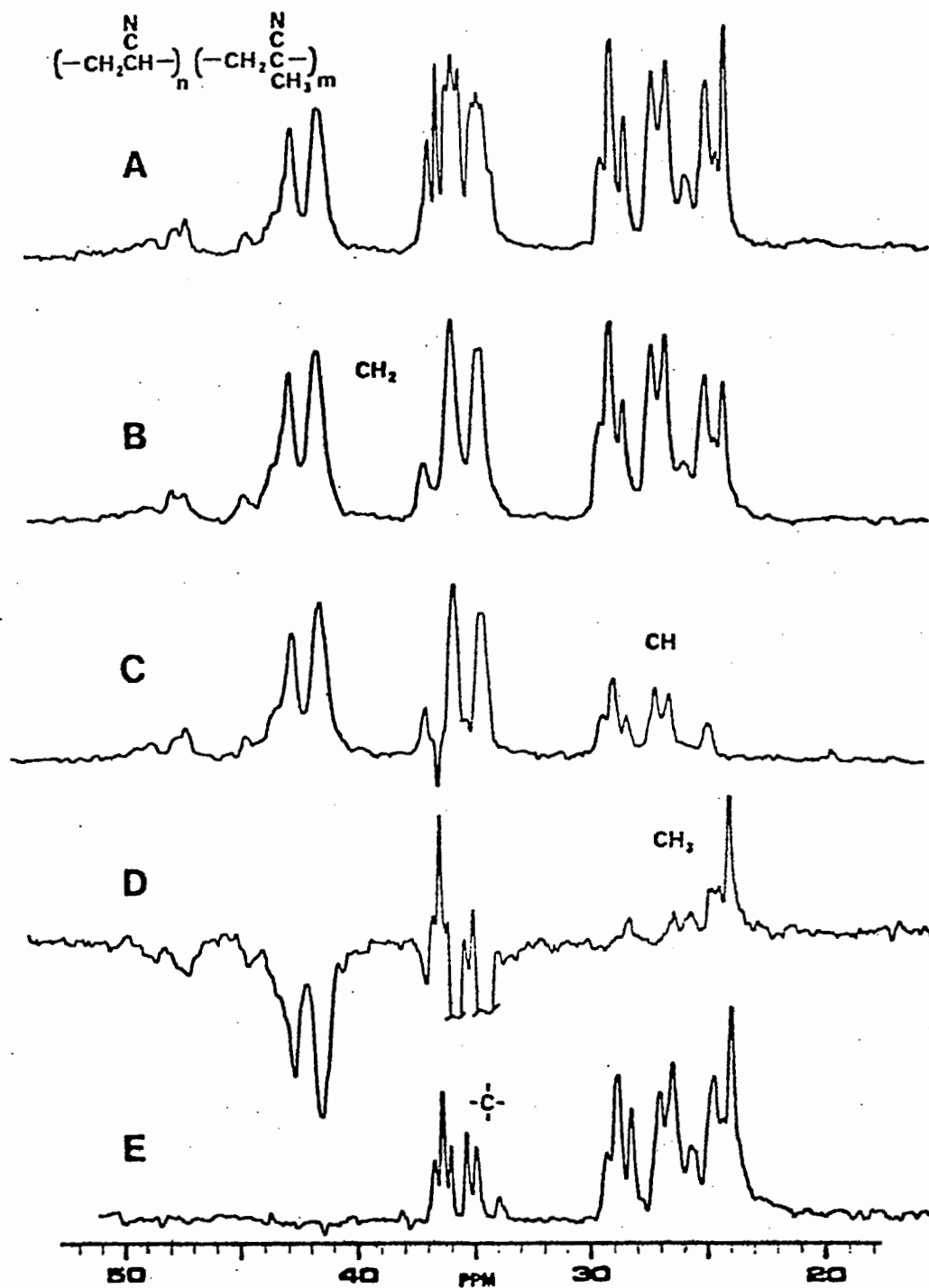
Figure 1. Suppression of Resonance in C-13 spectra in a copolymer system.

playing about 2 Hz resolution. This was obtained utilizing the cross polariz-
ation mode and magic angle spinning with a rate of rotation of approximately
1000 Hz. We also ran dehydroadamantane with comparable resolution and observed
all types of carbon. In general, we have no problems obtaining good quality
spectra of elastameric material, however, with the more rigid materials we are
not currently able to get adequate resolution. This is in part due to our de-
coupling power being inadequate, which we hope to correct very soon. If anyone
is interested in more details, they should feel free to contact me.

                                                Sincerely yours,

                                                Bell

                                                W. M. Ritchey
                                                Associate Professor
                                                of Chemistry

Figure 2. "Solid state" spectrum of adamantane.

200   150   100   -150   -200   Hz
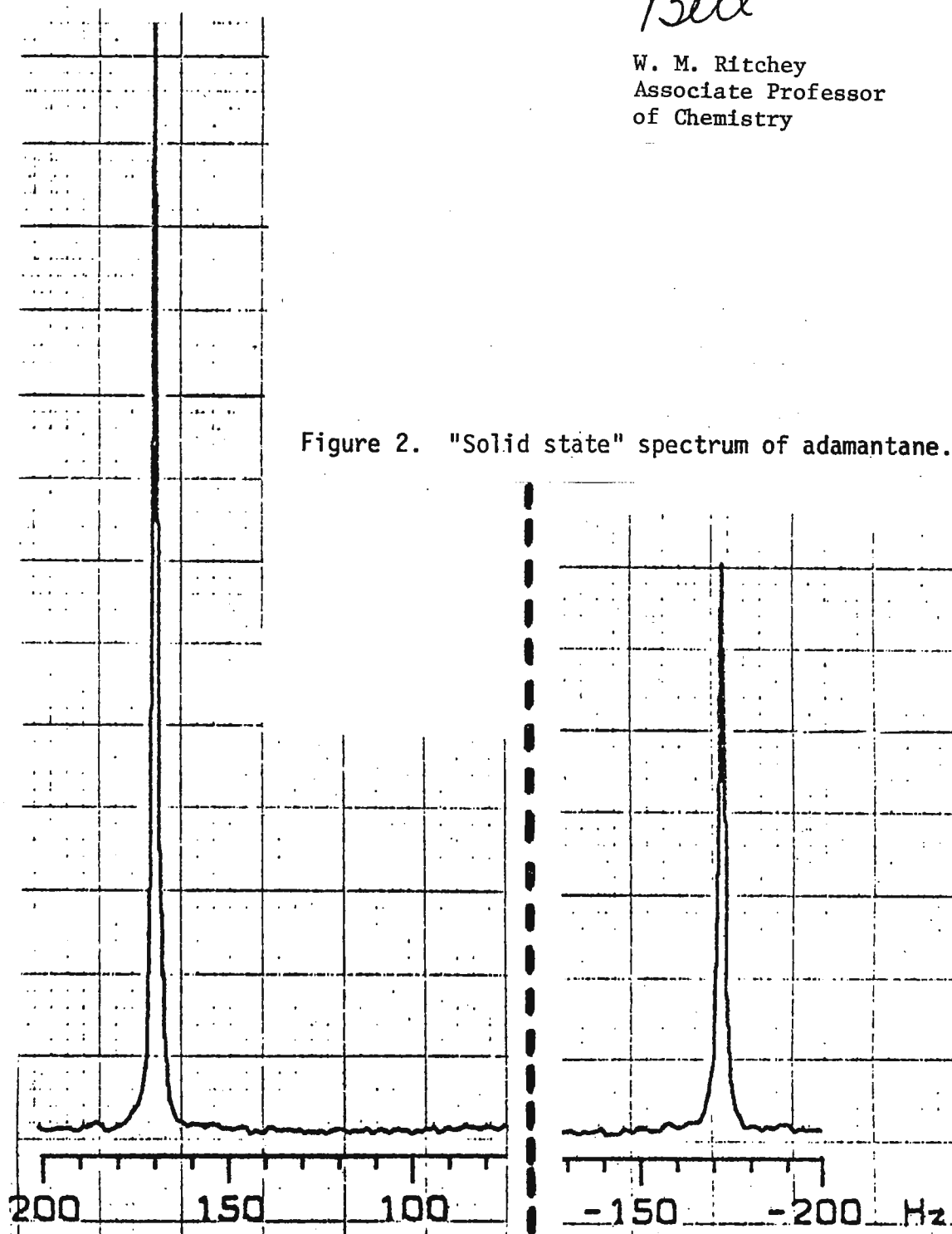
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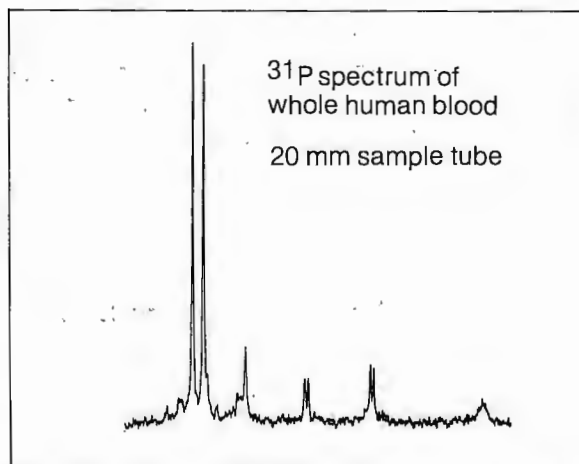
For more information or to discuss your applications, please telephone or write.

NTC
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145 East Dana Street
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NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

April 25, 1978

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

Dear Barry:

Before long, a paper will be coming out in the Journal of the American Chemical Society about the protonation of 1,3-dithiane (1) in FSO_3H. As the observations were rather surprising, I thought I would describe more recent results that corroborate our earlier findings.
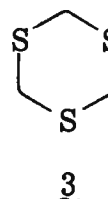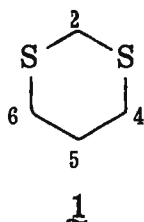
We found that 1,3-dithiane is primarily monoprotonated, that at 0 °C the $^+$S-H proton exchanges slowly and the 2 proton resonance is an AB quartet, that at 70 °C the $^+$S-H proton exchanges rapidly and the 2 proton resonance is a singlet, and that the 4 and 6 protons and carbons are nonequivalent at all temperatures. The last observation is extraordinary, because it means that the rapidly exchanging $^+$S-H proton must always return to the same sulfur that it left. Such a selective exchange is unprecedented.

We have now made similar observations in FSO_3H for 1,3-dithiolane (2), 1,3,5-trithiane (3), and 1,3-diselenane. The acyclic disulfides dithiomethyl-methane ($CH_3SCH_2SCH_3$) and 1,3-dithiomethylpropane ($CH_3SCH_2CH_2CH_2SCH_3$), however, do not show this behavior but rather produce complete symmetrization at rapid $^+$S-H exchange. We have now also made definitive ^{1}H and ^{13}C assignments by synthesis of the 2,2-d$_2$, 5,5-d$_2$, 4,4,6,6-d$_4$, 2,2,5,5-d$_4$, and 2,2,4,4,6,6-d$_6$ derivatives of protonated 1,3-dithiane.

We have not yet been able to duplicate this behavior in acids other than FSO_3H. These weak sulfur bases require a very strong acid for protonation. We have tentatively attributed the phenomenon of selective kinetic averaging to the maintenance of hydrogen bonds during the exchange process.

Sincerely,

Joseph B. Lambert

Michał W. Majchrzak

Title: Selective Chemical Shift Averaging in Cyclic 1,3-Disulfides

ANORGANISCH-CHEMISCHES INSTITUT
DER
TECHNISCHEN UNIVERSITÄT MÜNCHEN

VORSTÄNDE: o. PROF. DR. DR. h. c. mult. D. Sc. h. c. E. O. FISCHER
o. PROF. DR. H. P. FRITZ
o. PROF. DR. H. SCHMIDBAUR

D-8046 GARCHING, den 23. 3. 1978
Lichtenbergstraße 4
Ruf-Nr. (089) 3209/3080 (Prof. Fischer)
Telex 05/22854   3110 (Prof. Fritz)
3130 (Prof. Schmidbaur)
/3109

Wiss. Rat Dr. Frank H. Köhler

Prof. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77 843

Title: Paramagnetic nmr
isotope shifts.

Dear Professor Shapiro!

A few months ago, our chemistry department moved into a new build-
ding somewhat outside Munich (note change in address please). We
certainly got more space as well as safer and better equipped
laboratories, but there are still lots of craftsmen finishing the
interior. Some of them are electricians. So you may not be sur-
prised that this led to a remarcable number of breakdowns of the
power supply. Our Bruker HX 90 which besides this suffers from
some kind of mid-life crisis was seriously affected. We are sorry
that this delayed our contribution (another one on the account of
Prof. Fritz) to the TAMUNMR Newsletter.

Recently we have examined the question of whether an isotope effect
on nmr shifts may be observed not only for diamagnetic but also
for paramagnetic molecules. Metallocene radicals seemed to be a
very attractive system since they would allow a study of a possible
effect as a function of unpaired electron spin and of different
metals in identical molecular surroundings. In a series of pre-
ceding papers we have shown that paramagnetic ^{13}C nmr measurements
are straight foreward. So we planned to observe this nucleus for
corresponding ^{1}H and ^{2}H compounds.

The syntheses of the perdeuterated metallocenes proved to be most
time consuming. We first checked Cp_2Fe-d_{10} which later served as
diamagnetic standard; it gave an isotope shift of $\Delta\delta(^{13}C) = -0.40$
and $^{1}J(^{13}C-^{2}H) = 26.8$ Hz. To our surprise, the study of $Cp_2Cr-d_{10}/$
h_{10} and Cp_2V-d_{10}/h_{10} yielded paramagnetic isotope shifts
$\Delta\delta(^{13}C)_{para}$ which are up to eighteen times greater than that for
Cp_2Fe-d_{10} and which are shifted in both field directions: Cp_2Cr-d_{10},
$\Delta\delta(^{13}C)_{para} = -4.3$ and Cp_2V-d_{10}, $\Delta\delta(^{13}C)_{para} = +7.3$ (negative shifts
to low field).

These paramagnetic isotope shifts must be attributed to different
Fermi contact interactions between the unpaired electrons and the
^{13}C nuclei for the d_{10}/h_{10} species. Clearly, a variety of similar
experiments is indicated. We hope to stimulate discussions about
isotope effects among your readers by communicating these findings
as part of a future publication.

Yours very sincerely

(W. Prößdorf)   (F.H. Köhler)

THE OHIO STATE UNIVERSITY

April 19, 1978

Dr. B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77840

Introducing ^{6}Li Nmr

Dear Barry:

And now for something completely different.

Some time ago we announced how the ^{13}C resonance, proton decoupled, of $CH_3CH_2{}^{13}CH_2{}^7Li$ in cyclopentane broadens with decreasing temperature, due to slower interaggregate C-Li bond exchange. At $-60°$ or so a new broad resonance appears to lower field. It increases at the expense of the original peak as the sample is further cooled. We were unable to observe splitting from $^{13}C,{}^7Li$ scalar coupling because ^7Li quadrupole relaxation becomes more efficient at lower temperature. However, a line shape analysis of the ^{13}C spectrum was made using quadrupole relaxation times of $CH_3CH_2{}^{12}CH_2{}^7Li$ and a local environment where each $(CH_2)_1$ is interacting equally with three ^7Li's (as should be in the octahedral RLi hexamer). Although this has been done in the dark the assumptions are all reasonable.

Now we have repeated the whole business using ^6Li (actually 95% ^6Li plus 5% ^7Li), whose quadrupole moment is 0.01 of that for ^7Li. Now we can see the $^6Li,{}^{13}C$ scalar coupling and $CH_3CH_2{}^{13}CH_2{}^6Li$ 1-^{13}C nmr shows <u>three</u> resonances, the two at lower field corresponding to the broad line seen for the sample containing mainly ^7Li. The seven line multiplet for the applied resonance clearly indicates a local environment where each 1-^{13}C is coupling equally with three ^6Li's. We think the two other peaks represent two other aggregates. Interestingly, the ^6Li resonance of $CH_3CH_2{}^{12}CH_2{}^6Li$ shows at least three lines but two are at best shoulders of the third. Actually an appropriate $90°-\tau-180°$ sequence disentangles this to two lines 3 Hz apart plus some other stuff we have yet to elucidate.

Clearly in studying carbon-lithium covalence ^6Li is the preferred isotope since it is not subject in a serious way to quadrupole relaxation effects. With our Brukarian we routinely carry out all these experiments with proton decoupling. There is even a NOE!

Next time look out for: ^6Li Nmr Line Shape Analysis.

With all good wishes to colleagues everywhere in their quest for the NSF NMR Facility.

Sincerely yours,

Gideon

Gideon Fraenkel
Professor of Chemistry

$$CH_3CH_2{}^{13}CH_2{}^6Li$$

$$^{13}C \text{ NMR}$$

-5.42	-7.63	-9.84	-12.05
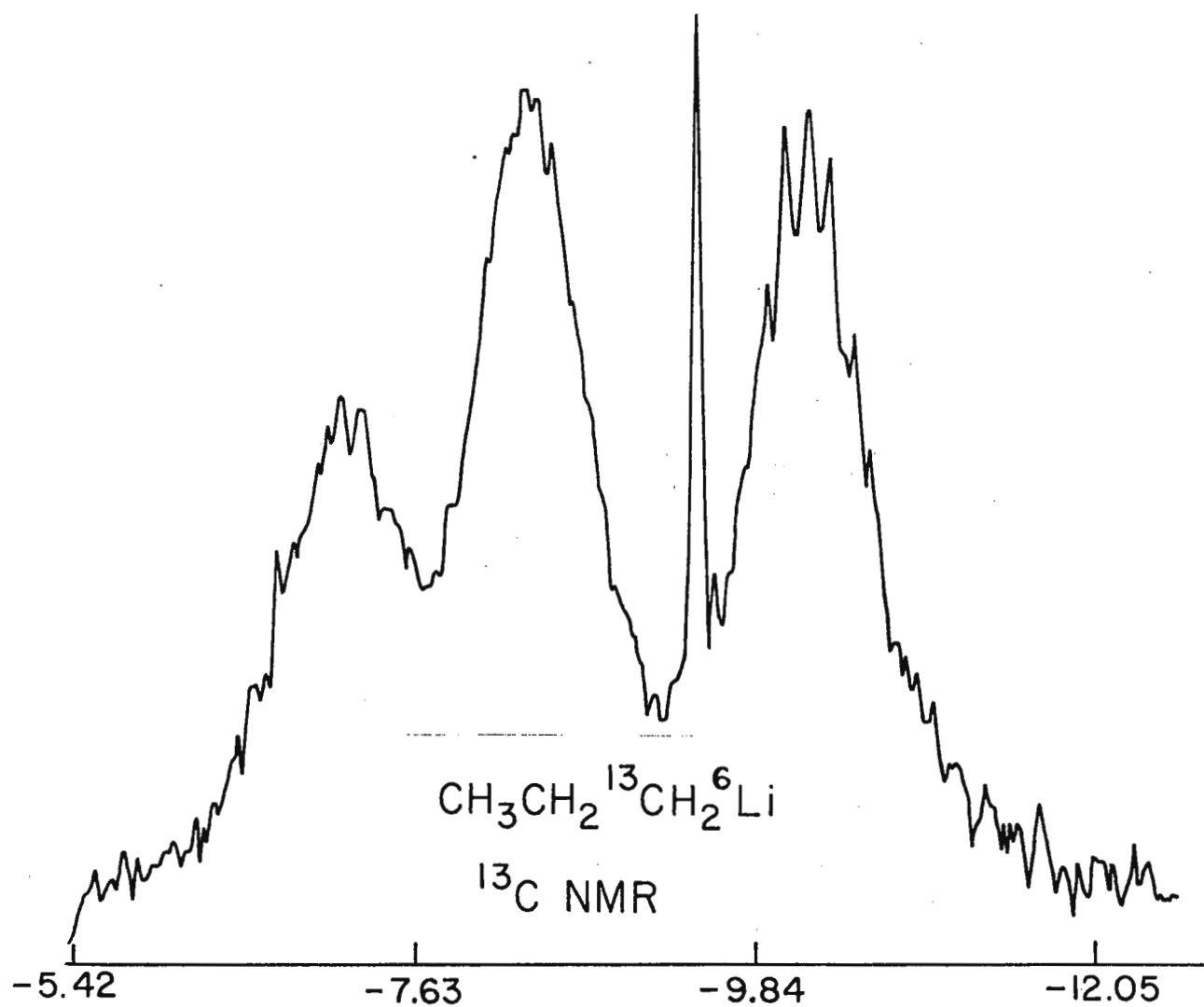
The University of Liverpool

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

21st April, 1978.

Dear Barry,

OH Chemical Shifts in Alcohols.

In reply to your Jacobean letters, I would like to mention some recent results which Jan Bakke and I obtained on OH proton chemical shifts during my summer visit to Trondheim.[1]

The use of OH chemical shifts in structural studies has been bedevilled by their large intrinsic concentration dependence and the errors involved in the extrapolation of data from moderately concentrated solutions are well-known.[2] However, measurements at low concentrations largely eliminate these errors, mainly because the slope of the OH/dilution curve <u>decreases</u> at low alcohol concentrations.[3]

Using the external lithium lock on the JEOL FX-100 and alcohol concentrations of $\approx 10^{-2}$ M in CCl_4 allowed simple interpolation to give OH ∞ dilution shifts to - 0.05 p.p.m. (Table, which also gives the corresponding shifts in more concentrated DMSO solutions).

The results allowed us to infer the conformation of benzyl alcohol in solution, and settle the controversy over the presence (or absence) of an intramolecular H-bond in benzyl alcohol. Our results are in good agreement with I.R. studies and indicate that the two I.R. OH bands are due to two different rotamers and not to intra-molecular H-bonding.

We can also see clearly S.C.S. on the OH proton from the para substituents and the effect of intra-molecular H-bonding to the ortho substituents, and we are currently studying these effects further.

With best wishes,

Yours sincerely,

Ray

Dr. R.J. Abraham.

Table.   OH   CHEMICAL   SHIFTS (δ)   FOR ALCOHOLS.

Compound	OH Chemical Shift	
	CCl_4 (∞ dil^n)	DMSO-d_6
MeOH	0.34	4.09
EtOH	0.65	4.35
iPrOH	0.75	4.34
benzyl alcohol	1.09	5.14
o-nitro benzyl alcohol	2.08	5.55
p-nitro benzyl alcohol	1.48	5.53
o-methoxy " "	1.63	4.96
p-methoxy " "	0.98	5.03
t-Bu OH	0.70 (ref. 3)	

1.   R.J. Abraham and J.M. Bakke   Tetrahedron (in press).
2.   J.C. Davis and K.K. Deb   Adv. in Mag. Res. 4, 201 (1970).
3.   E.E. Tucker and E.D. Becker   J. Phys. Chem. 77, 1783 (1973).

Department of Energy
Laramie Energy Research Center
P.O. Box 3395, University Station
Laramie, Wyoming 82071

April 10, 1978

20th Annual Rocky Mountain Conference
on Analytical Chemistry

Denver Convention Complex
Denver, Colorado
August 7-9, 1978

EPR Symposium
G. R. Eaton, Chairman
Tuesday, August 8, 1978

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

Dear Dr. Shapiro:

NMR AND EPR SYMPOSIA IN DENVER

Many of your readers may be interested in coming to
the Rocky Mountains this summer. Enclosed is a listing
of the NMR and EPR presentations to be given at the
20th Annual Rocky Mountain Conference on Analytical
Chemistry and Spectroscopy. This Conference will be
held at the Denver Convention Complex, August 7-9,
1978. The Conference also includes General Papers as
well as Symposia on GC/MS and Environmental Chemistry.
If anyone is interested, additional information on the
Conference can be obtained by writing to me.

Sincerely,

Daniel A. Netzel
Conference Chairman

Enclosures: As stated
             above

Time	
9:00	Introduction - Dr. Gareth R. Eaton
9:05	Detection of Free Radicals in Aqueous Solutions by Spin Trapping, E. G. Janzen, University of Guelph.
10:00	ESR Studies of Stable Spin Probes in Liquid Crystals, G. V. Bruno and M. P. Eastman, University of Texas at El Paso.
10:50	Thermal and Spin Label Studies of Scorpion Cuticle, T. R. White and W. S. Glaunsinger, Arizona State University.
11:30	The Internal Viscosity of Spinach Thylakoids, A Spin Label Study, S. P. Berg, D. M. Luxczakoski, and P. D. Morse, II, University of Denver and Wayne State University.
2:00	Metal-Nitroxyl Interactions, P. M. Boymel, G. A. Braden, J. R. Chang, D. L. DuBois, K. More, R. E. Smith, D. J. Greenslade, G. R. Eaton, and S. S. Eaton, University of Denver, University of Exxex and University of Colorado at Denver.
2:40	Analysis of EPR Spectra of Spin-Labeled Copper Complexes, D. L. DuBois, G. R. Eaton, and S. S. Eaton, University of Denver and University of Colorado at Denver.
3:10	EPR Studies of $[FeNO]^7$ Complexes, R. D. Feltham, H. Crain, and T. Malone, University of Arizona.
3:35	EPR Linewidths in Linear Chain Systems, B. Garrett, Florida State University and S. Holt, University of Wyoming.
4:15	Charge Compensation in the Impurity Centers of Doped Ionic Crystals. Determination by EPR Spectroscopy, G. L. McPherson, Tulane University.
Evening	Demonstration of the University of Denver computer-interfaced EPR facility.

20th Annual Rocky Mountain Conference
on Analytical Chemistry

Denver Convention Complex
Denver, Colorado
August 7-9, 1978

NMR OF MACROMOLECULES SYMPOSIUM

D. A. Netzel, Chairman

SESSION I - MACROMOLECULES IN THE SOLID STATE

Monday Morning - Dr. Gary E. Maciel, Presiding

8:30   Introduction - Dr. Daniel A. Netzel

8:35 ^{13}C and ^{31}P NMR of Macromolecules in the Solid State,
J. S. Waugh. Massachusetts Institute of Technology.

9:15 ^{13}C NMR in Cured Epoxies: The Role of Molecular Motion,
A. N. Garroway, W. B. Moniz, and H. A. Resing. Naval
Research Laboratory.

9:55   Solid State ^{13}C NMR in Polyethylene: A Quest for Molecular
Insights in a Strongly Coupled System,
D. L. VanderHart and A. N. Garroway. National Bureau
of Standards.

10:35   Carbon-13 $T_{1\rho}$ Experiments in Solid Polymers, J. Schaefer,
E. O. Stejskal, and T. R. Steger. Monsanto Company.

11:15 ^{13}C NMR Studies of Some Natural Macromolecules, V. J. Bartuska,
J. H. Ackerman, and G. E. Maciel. Colorado State University.

Monday Afternoon - Dr. Fran P. Miknis, Presiding

2:00   Carbon-13 NMR Studies of Solid Polymers: Polymers Based
on p-hydroxybenzoic Acid, J. Economy, C. A. Fyfe, J. R.
Lyerla, W. Volksen, and C. S. Yannoni. IBM Research
Laboratory.

2:30   Dipolar, Quadrupolar, and Magic Angle Spinning NMR in Biologi-
cal Systems. R. G. Griffin. Massachusetts Institute of
Technology.

3:00   Approaches to NMR Spectroscopy of "Big" Molecules in the
Solid State: Fossil Fuels and Polymer Network. J. L.
Ackerman. University of Cincinnati.

3:30 ^{13}C NMR Studies of Solid Fossil Fuels, G. E. Maciel,
V. J. Bartuska, and F. P. Miknis. Colorado State University.

4:00   Coal, Polymers, and the Time Dependent Schrodinger Equation,
B. C. Gerstein. Iowa State University.

4:30   Analysis of Proton Types in Solid Pitch Samples, R. M. Pearson,
Kaiser Aluminum Chemical Corporation.

SESSION I - Continue

Tuesday Morning - Dr. Vic Bartuska, Presiding

8:30   High-Resolution ^{13}C NMR in Solids Using Variable Temperature
Magic Angle Spinning, C. S. Yannoni, C. A. Fyfe and J. R.
Lyerla. IBM Research Laboratory.

9:00   Multiple Quantum NMR of Macromolecules, A. Pines. University
of California, Berkeley.

9:30   Pulse Programmer for High Resolution NMR in Solids, R. A. McKay,
Monsanto Company.

10:00   A New Technique for Selective High Resolution Proton NMR in
Solids, J. A. Reimer and R. W. Vaughan. California Institute
of Technology.

10:30   Application of High Resolution Solid State NMR Techniques to
Formic Acid Adsorbed on Y Zeolites, M. T. Duncan and R. W.
Vaughan. California Institute of Technology.

11:00   Studies of Low Frequency Polymer Motion by Multiple-Pulse
NMR, C. R. Dybowski and R. G. Pembleton. University of
Delaware.

11:30   Magic Angle Spinning without the Magic, K. Zilm and D. Grant.
University of Utah.

SESSION II - GENERAL NMR TECHNIQUES

Tuesday Afternoon - Dr. Roger Assink, Presiding

2:00 ^{13}C-^{1}H Cross-Polarization Studies of Organic Liquids,
R. D. Bertrand, A. N. Garroway, G. Chingas and W. B. Moniz.
Navel Research Laboratory.

2:25   High Temperature Studies of Coal Products, H. Dorn, T. Glass
and L. T. Taylor. Virginia Polytechnic Institute.

2:50   A Possible Proton NMR NOE Reference Material, E. P. Mazzola,
and S. W. Page. Food and Drug Administration.

3:15   Identification of Mono- and Di-substituted Acridine Isomers
by Micro ^{1}H and ^{13}C NMR Techniques Following Chromatographic
Separation. R. J. Warren, D. B. Staiger, L. B. Killmer and
J. E. Zarembo. Smith Kline & French Laboratories.

3:40   Carbon-13 FT NMR of Sub-milligram Amounts, T. H. Mareci and
K. N. Scott. University of Florida, Gainesville, FL 32601

4:05 ^{19}F and ^{13}C NMR Spectroscopy of Halocarbons, A. Foris.
E.I. DuPont de Nemours & Company.

4:30   The Study of Phase Separation in Block and Segmented
Copolymers by NMR, R. Assink. Sandia Laboratories.

SESSION III - BIOPOLYMERS

Tuesday Morning - Dr. Michael Burke, Presiding

9:00   High-field NMR of Membranes and Proteins, E. Oldfield. University of Illinois.

9:30   NMR Relaxation and Diffusion of Phospholipids in Model Membranes, A. Kuo and C. G. Wade. University of Texas.

10:00   NMR Studies of Transfer RNA, M. P. Schweizer. University of Utah.

10:30   Development of NMR Techniques for Delineating Conformation of Peptides and Proteins, J. D. Glickson, N. R. Krishna, R. E. Lenkinski and D. G. Agresti. University of Alabama in Birmingham.

11:00   NMR Studies of Bleomycin Interaction with Nucleic Acids and Metals, D. M. Chen, T. T. Sakai, R. E. Lenkinski, D. J. Patel, G. C. Levy and J. D. Glickson. University of Alabama in Birmingham.

11:30   Fluorine NMR Studies of Enzyme-Polymer Conjugates, J. T. Gerig and D. T. Leohr. Yale University.

Tuesday Afternoon -

2:00   Coordinated Carbon Monoxide as a Probe of the Heme Pocket, J. D. Satterlee and J. H. Richards. California Institute of Technology.

2:30   270 MHz NMR Study of Insulin, K. L. Williamson, R. J. P. Williams, and G. Bentley. Mount Holyoke College.

3:00   Structure of Xanthoviridicatin D, a Metabolite of Penicillium Viridicatum. Application of Proton and Carbon-13 Nuclear Magnetic Resonance, E. P. Mazzola and M. E. Stack. Food and Drug Administration, Washington, D.C.

3:30   Structural Studies of A. Variabilis Cytochrome c-553, E. L. Ulrich, J. L. Markley and D. W. Korgmann. Purdue University.

4:00   Application of Nuclear Magnetic Spectroscopy to the Chemical Structure of Humic Acid, R. L. Wershaw, D. J. Pinkey, and L. Cary. U.S. Geological Survey, Denver.

SESSION IV - POLYMERS

Wednesday Morning - Dr. Fran P. Miknis, Presiding

9:00   NMR of Macromolecules, D. Fiat. University of Illinois at the Medical Center.

9:30 ^{13}C NMR Studies of ^{13}C Enriched Macromolecules, N. Matwiyoff. Los Alamos Scientific Laboratory.

10:00 ^{13}C NMR Study of the Structure and Solution Dynamics of Polysulfones, F. A. Bovey. Bell Laboratories.

10:30   A ^{13}C Spin Relaxation Study of Chain Mobility in Some Terephthalic Acid Polyesters, R. A. Komoroski. Diamond Shamrock Corporation.

11:00   Evaluation of Complex Molecular Dynamics in Polymers from Variable Frequency ^{13}C Relaxation Measurements, G. C. Levy, D. Wright and D. E. Axelson. Florida State University.

Wednesday Afternoon - Dr. Gary E. Maciel, Presiding

2:00   Carbon-13 FT NMR Analysis of Phenol-Formaldehyde Resins: Structure and Reaction Mechanisms, S. A. Sojka and R. A. Wolfe. Hooker Research Center.

2:30   Sequence Distributions and Number Average Sequence Lengths in Propylene-Butene-1 and Ethylene-Propylene Copolymers, J. C. Randall. Phillips Petroleum Company.

3:00   Relaxation Studies in the System Poly(Ethyl Methacrylate)-Chloroform by Carbon-13 and Proton NMR, L. J. Hedlund, W. G. Miller and R. M. Riddle. University of Minnesota.

3:30   The Use of NMR Spectroscopy in the Analysis of Polyester Polymer Systems, M. J. Vaickus and D. Anderson. DeSoto, Inc.

4:00   NMR Studies of Charged Polymers and Copolymers, A. C. Watterson, Jr., J. C. Salamone, C. C. Tsai, M. Mahmud, A. Olson, and S. F. Krauser. University of Lowell, North Campus.

MONTEDISON

Professor Bernard Shapiro
Dpt. of Chemistry
Texas A & M University
College Station - TX 77843 - USA

DIPE/PM/CER
Stab. Petrolchimico
Via G. Motta
30175 - PORTO MARGHERA
(Venezia) ITALY

Dear Professor Shapiro,

Title: Interpretation of the NMR ^{13}C spectrum of a polyesther copolymer of adipic acid and of monoethylenglycole.

A copolymer of adipic acid (AAD) and monoethylenglycole (MEG) was prepared using an excess of MEG. A 13% solution w/v of the copolymer in $CDCl_3$ and $DMSO_{d6}$ (2 : 1 v/v) was examined by ^{13}C NMR with a Bruker WH-90 FT spectrometer.

The following experimental conditions were used:

Pulse: 45 degrees, Cycle Time: 3.5 sec., Memory: 8K Points, Sweep width: 6000 Hz, Number of Sweeps $\sim$ 1000, 10 mm o.d. tube.

The chemical shifts of the more intense lines relative to TMS, their intensities (in brackets) and the assignements are the follo wing:

$$\delta_1 = 23.98 \ (57) \quad \beta CH_2 \text{ of AAD}$$

$$\delta_2 = 33.34 \ (57) \quad \alpha CH_2 \text{ of AAD}$$

$$\delta_3 = 61.87 \ (52) \quad \overset{O}{\overset{\|}{-C}}-O-\underline{CH}_2-\underline{CH}_2-O-\overset{O}{\overset{\|}{C}}- \text{ of MEG}$$

$$\delta_4 = 172.61 \ (34) \quad CO \text{ of AAD}$$

These attributions were obtained in comparison with the usual literature data (1).

There are two other weaker resonances at

$$\delta_5 = 59.59 \ (5) \quad \text{and} \quad \delta_6 = 65.70 \ (5)$$

The aim of this letter is to demonstrate that δ_5 and δ_6 are the resonances of the $-\underline{CH}_2-OH$ and of the $-COO\underline{CH}_2$ terminal groups of MEG, respectively.

Two arguments, i.e. a spectroscopical and a stoichiometrical one, will be used. The two c.s. δ_5, δ_6 are not those of the unpolymerized MEG because the single c.s. of the unreacted MEG is

$$\delta_{\underline{C}H_2 - OH} = 63.27$$

With the label "i" are indicated the $-CH_2-$ of the internal units of MEG, with "α" and "β" labels the $-CH_2-$ of the terminal ones indicated in the structural formula:

$$O-\overset{i}{C}H_2 - \overset{i}{C}H_2 - OCO \ldots COO-\overset{\beta}{C}H_2 - \overset{\alpha}{C}H_2 - OH$$
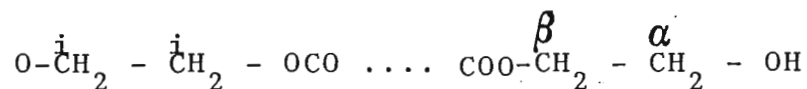
We can observe the differences between the chemical shifts of the aliphatic esters of the acetic acid and the corresponding aliphatic alcohols for the α carbons (1) as it is indicated in table 1:

TABLE 1

	Ethyl	Propyl	Butyl	Pentyl
C_α (alcohols)	57.3	63.9	61.7	62.1
Acetic esters	60.1	65.5	63.8	64.6
Δ_1	2.8	1.6	2.1	2.5

The average value is $\bar{\Delta}_1 = + 2.3$ ppm.
In table 2 are reported the differences between the chemical shifts of β carbons of the aliphatic esters of the acetic acid and the corresponding aliphatic alcohols.
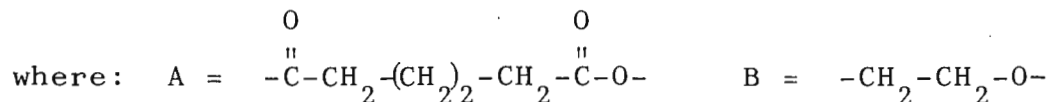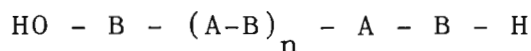
TABLE 2

	Ethyl	Propyl	Butyl	Pentyl
C_β (alcohols)	17.9	26.1	35.3	32.8
Acetic esters	14.3	22.5	31.2	29.3
Δ_2	-3.6	-3.6	-4.1	-3.5

The average value is $\bar{\Delta}_2 = -3.7$ ppm.
In our copolymer we observe that $\delta_3 - \delta_5 = 2.28$ ppm and $\delta_3 - \delta_6 = -3.83$ ppm and so we assign δ_5 to the α methylene and δ_6 to the β methylene of the terminal MEG.

The fit between the experimental and literature differencies is satisfactory and so we consider this a proof of the attribution.

The experimental number average molecular weight of the copolymer is about: 2000. The copolymer structure is:

$$HO - B - (A-B)_n - A - B - H$$

where: $A = -\overset{O}{\overset{\|}{C}}-CH_2-(CH_2)_2-CH_2-\overset{O}{\overset{\|}{C}}-O-$ $B = -CH_2-CH_2-O-$

It is possible to evaluate the $\overline{PM}_n$ of the polymer:

$$\overline{PM}_n = H_2O + n\,AB + 2B + A$$

$$n = \frac{\overline{PM}_n - 234}{172} = 10.3$$

The number of the moles of glycole is = n + 2, i.e. = 12.3; the number of the moles of AAD = n + 1 = 11.3 Therefore the calculated molar ratio is:

$$R = \frac{moles\ of\ MEG}{moles\ of\ AAD} = 1.09$$

If the before mentioned attribution is correct the molar ratio spectroscopically obtained is:

$$R_{exp} = \frac{I_3 + I_5 + I_6}{\frac{1}{2}\,(I_1 + I_2)} = 1.09$$

The fit between the experimental and the calculated data is very satisfactory and in this case it is a proof of the correctness of the assignement. Conversely, from the NMR data it is possible to calculate an approximate molecular weight of the copolymer.

Yours sincerely

GIORGIO GURATO   GIORGIO RIGATTI*

(*) Physical Chemistry Institute of the University
    Via Loredan, 2 - PADOVA

(1) Stothers - Carbon 13 NMR Spectroscopy, Academic Press,
     NEW YORK - 1972, pag. 140 and 150.

UNIVERSITÉ DE GENÈVE

SCHOLA GENEVENSIS MDLIX

Prof. G.-J. Béné
Section de Physique
24, quai Ernest Ansermet
CH - 1211 - Genève 4
Tél. 21'93'55

GJB/cc

Professeur B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College of Science
College Station Texas
77843 USA

Genève, le 24 avril 1978

Cher Professeur Shapiro,

Merci de votre lettre de rappel du 5 avril 1978.

1. Application du magnétisme nucléaire dans le champ terrestre au diagnostic médical

   a) Note au C.R. de l'Académie des Sciences de Paris, t.285 p.211 - 213 - Série B - 1977

   "Magnétisme nucléaire - Temps de relaxation des protons de liquides amniotiques humains en champ faible. Application à la magnétographie nucléaire"
   de Georges Béné, Bernard Borcard, Emile Hiltbrand, Patrick Magnin, Robert Séchehaye, Martial Dumont, Daniel Raudrant et Bernard Béné transmise par Monsieur Pierre Grivet.

   Measurement relaxation times of T_1 and T_2 of amniotic fluid protons in the low field range lead to a unique identification of some pathological states of women during the final period of pregnancy. A qualitative interpretation of relaxation times is proposed.

   b) "Relaxation magnétique nucléaire protonique de liquides pleuraux en champ faible - Application au diagnostic médical"
   de G.-J. Béné, B. Borcard, Mlle E. Ducommun, E. Hiltbrand, P. Magnin et R. Séchehaye.

   The measurements of relaxation times in the weak field of the protons in the water of pleural liquids, obtained by punctions

230-56

on patients under treatment, distinguishes clearly between
two kinds of liquids. In the first category "the transudates"
the relaxation rate increases linearly with the concentration
of proteins. Thus, knowing the proportionality factor, we can
evaluate the proportion and the correlation time of the
water molecules fixed to proteins.
In the second category "the exsudates", produced in particular
by cancers, this linear law is not obeyed. In this case, the
pleural liquid contains relatively high concentrations of
leucocytes and lipoproteins.
Because of the weak amplitude of the applied fields, this
technic could be applied in situ without danger for the
patients.

(A publier dans Helvetica Physica Acta - 1978)

c) "Détermination, in situ, de la relaxation transversale de
   fluides physiologiques humains"
   de B. Borcard, E. Hiltbrand, P. Magnin et G.-J. Béné.

   La précession libre des protons dans le champ magnétique terres-
   tre après prépolarisation a été utilisée pour déterminer, in si-
   tu, le temps de relaxation T_2 de deux fluides physiologiques
   humains : l'urine et le sang, par simple application de la bobi-
   ne de mesure sur la face antérieure du corps correspondante
   (bas abdomen et poitrine). On discute brièvement les résultats
   obtenus.
   (A publier dans Helvetica Physica Acta - 1978)

d) "Relaxation magnétique nucléaire protonique du sang en champ
   faible"
   de E. Hiltbrand, B. Borcard, P. Magnin et G.-J. Béné.

   A l'aide d'une technique décrite dans une précédente communication
   (1), on a déterminé, en champ faible, les temps de relaxation
   spin-réseau (T_1) et spin-spin (T_2) des protons de l'eau, d'échan-
   tillons de sang humain ou animal soit pur, soit après centrifu-
   gation pour faire varier l'hématocrite, soit mêlé à une
   solution isotonique (ClNa 9o/oo) en proportions calibrées. Les
   résultats obtenus sont interprétés à l'aide du modèle de
   O. DASZKIEWICZ et al. (2).
   On examine quelques applications possibles de ces résultats.

   (A publier dans Helvetica Physica Acta - 1978)

2. Prochains Meetings du Groupement Ampère

   a) XXth Congress Ampère
      Tallinn (R.S.S. d'Esthonie)
      21-26 August 1978.
      "Magnetic Resonance and Related Phenomena"

      Adresse pour information :

      Professor T.A. Saluvere - XXth Congress Ampère - Academy of
      Sciences of the Estonian SSR - Lenini Puiestee 10 -
      Tallinn 200001 - USSR
      Tél. : 441 - 304 ; 605 - 729

b) Vth Ampere International Summer School on
   "Nuclear Resonance in Solids" and Symposium
   Rhodes - Greece, 4 - 14 September, 1978

   Adresse pour information :

   Dr F. Milia - Nuclear Research Center - "Democritus" -
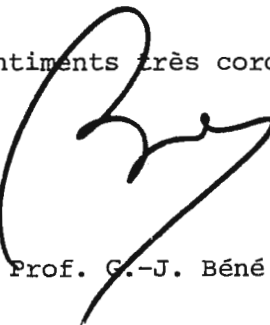   Aghia Paraskevi - Attikis - Greece.

c) IVth Specialized Colloque Ampere
   LEIPZIG - Germ. Dem. Rep.
   17 - 21 September 1979

   "Dynamic Processes in Molecular Systems as studied
    by RF-Spectroscopy"

   Adresse pour information :

   Prof. Dr. A. Lösche - Physikalisches Institut der Karl-
   Marx Universität - Linnéstrasse 5 - 701 - LEIPZIG Cl - DDR.

                    Avec mes sentiments très cordiaux.

                              Prof. G.-J. Béné

UNIVERSITY OF DELAWARE
NEWARK, DELAWARE
19711

DEPARTMENT OF CHEMISTRY

April 26, 1978

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

TITLE: Calculating Nuclear Overhauser Effects
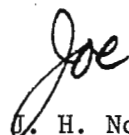
Dear Barry:

The Bloch equations for magnetic resonance show clearly that, in the presence of an rf field, the longitudinal magnetization M_z does not relax independently of the transverse magnetization M_x or M_y. The usual treatment of steady-state NOE's (1) seem to assume that M_z can be treated independently of M_x and M_y. The reason that this is legitimate is that the use of an on-resonance, strong, saturating rf field destroys the transverse magnetization.

The recent popularity of selective NOE's as a structural tool, especially in Biochemistry, has brought forth calculations in which one or more of these conditions is violated. Caution is advised when calculating NOE's off-resonance or with less than infinite power since transverse magnetizations may exist.

Another factor which is often neglected is the existence of J couplings. Again, infinite decoupling power can obviate this problem but one does not always have, or even want, such large powers. Since resolution deteriorates with power, the temptation to use low powers is great. The lesson of DMF(2) should not be forgotten; even small unresolved J couplings can cause trouble when you are attempting to calculate band <u>shapes</u>.

I have been working recently on a density matrix theory for the calculation of steady-state NOE's which avoids these assumptions. Interested parties may wish to request pre-prints which may be available in June.

Yours very truly,

J. H. Noggle
Professor of Chemistry

(1) Noggle and Schirmer, "The NOE," (Academic Press) esp. pp. 11-16.

(2) Allerhand, Gutowsky, Jonas and Meinzer, J. Am. Chem. Soc. <u>88</u>, 3185 (1966).

ISTITUTO CHIMICO

della

UNIVERSITÀ DI TORINO

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

Fe-57 Satellites in the C-13 n.m.r. spectrum of $Fe_3(CO)_{12}$.

Dear Professor Shapiro,

The solution structure and the dynamic behaviour of $Fe_3(CO)_{12}$ has not yet been solved. The detection of a sharp singlet in the C-13 spectrum down to -150°C, only suggests an extremely low activation energy barrier for the carbonyl scrambling in this molecule. In order to get more insight into this problem, we have done an experiment to observe the Fe-57 satellites in the C-13 n.m.r. spectrum of $Fe_3(CO)_{12}$. Since iron-57 ($I = \frac{1}{2}$) is 2,24% naturally abundant, there are 6,72% of the molecules of $Fe_3(CO)_{12}$ containing one n.m.r. active iron atom (the occurence of molecules containing two or three ^{57}Fe nuclei is, of course, very remote). In the figure it is reported the carbonyl region spectrum of an highly enriched sample ($\sim$ 40%) of $Fe_3(CO)_{12}$ obtained with a 90° pulse sequence, 5 sec. pulse delay and in absence of relaxation agents.

Among the molecules containing a ^{57}Fe nucleus, if the tri-iron framework were maintained in solution, there would be two

types of molecules, in the ratio 2:1, depending on the position
of the Fe-57 atom in the isoscele triangular cluster. The ob-
servation of the Fe-57 satellites as a single doublet strongly
suggests that, besides the carbonyl scrambling, an intermetal-
lic rearrangement is occuring in the cluster entity to give the
observed equivalence of the two different iron atoms on the
n.m.r. time scale. Attempts to observe the Fe-57 satellites,
at low temperature, have been, until now, unsuccessfull. The
detected separation of 8.3 ± 0.1 Hz gives an average value of
24.9 Hz for $^{1}J_{Fe-C}$ coupling constant (if $^{2}J_{Fe-Fe-C}$ is assumed
to be neglegible), which is in good agreement with the value
of 23.4 Hz reported for $Fe(CO)_5$.

Sincerely yours

S. Aime   D. Osella   L. Milone

$\Leftarrow 8.3 Hz \Rightarrow$
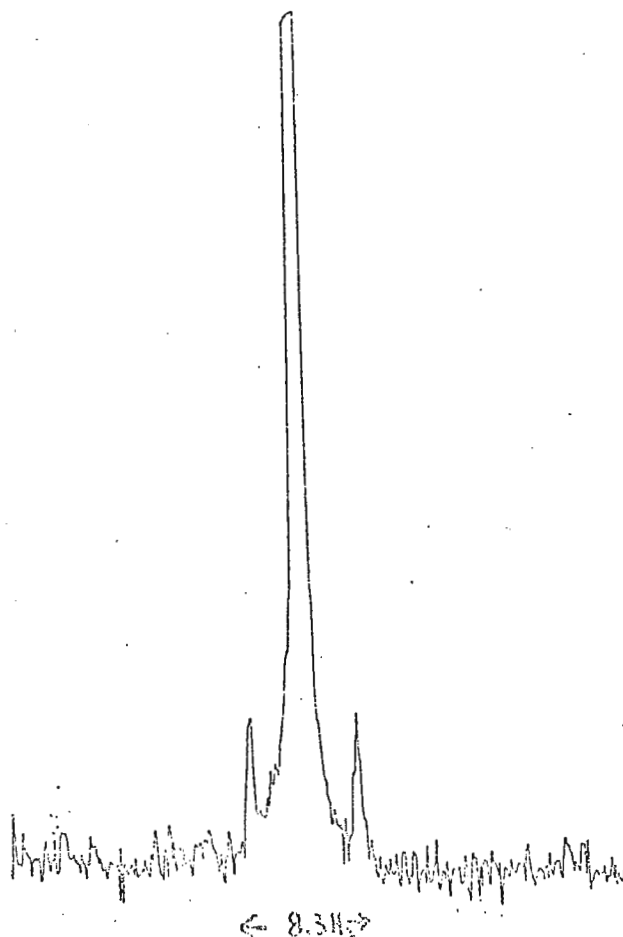
CALIFORNIA INSTITUTE OF TECHNOLOGY

April 28, 1978

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

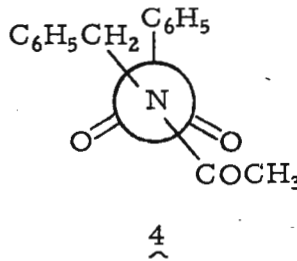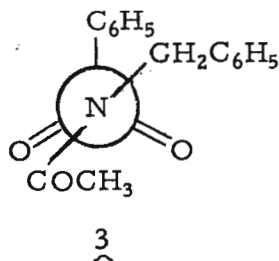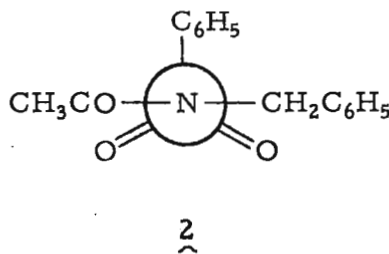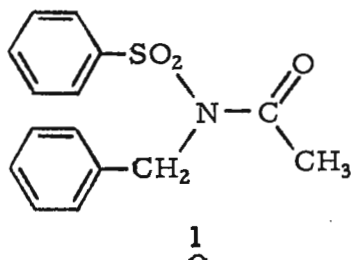JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

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

## Low-Temperature Proton NMR Study of a Mixed Amide

Dear Barry,

We have studied the low-temperature ^{1}H NMR spectrum of N-acetyl-N-benzylbenzenesulfonamide, 1, in sulfuryl chloride fluoride and in difluorochloromethane solution to determine the effect of the benzene-sulfonyl group on the rotational barrier about the N-acetyl carbon-nitrogen bond. The spectra shown are for a 0.5-M solution of 1 in sulfuryl chloride fluoride. Line-shape analysis gave free energies of activation of 9.2 and 9.4 kcal/mole for SO_2ClF and $CHCl_2F$ solutions, respectively, based on the methyl resonance.

These values are considerably lower than those for rotation about the C(O)-N bond of similar N,N-dibenzylacetamide (18.0 kcal/mole in CH_2Br_2) and seem most likely to be the result of the $-I$ effect of the benzenesulfonyl group. Perhaps surprisingly, the methylene resonance exhibits multiple splitting at low temperature. This may be the result of the slowing of the rotation about the sulfur-nitrogen bond which would lead to diastereotopic benzyl CH_2 protons for each of the conformations 2-7.
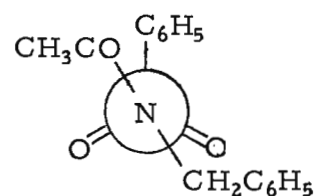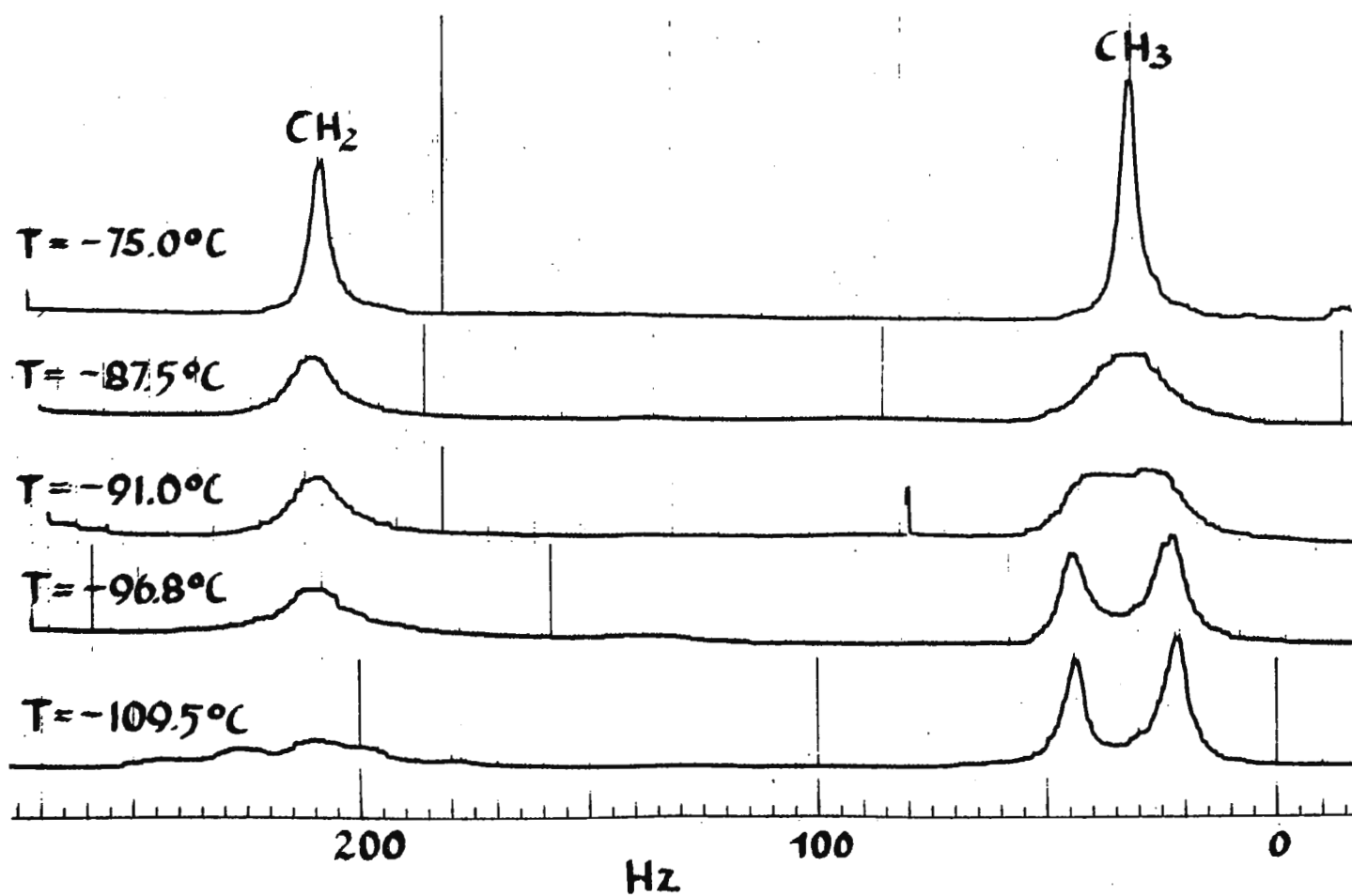

1

2

3

4

C_6H_5
$C_6H_5CH_2$ — N — $COCH_3$

5

C_6H_5 $COCH_3$
N
$CH_2C_6H_5$

6

CH_3CO C_6H_5
N
$CH_2C_6H_5$
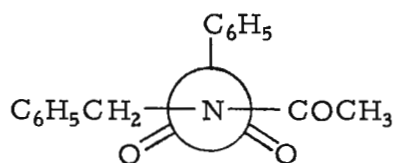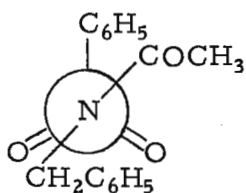
7

With all good wishes,

Very truly yours,

Ingeborg Schuster

Ingeborg I. Schuster

Jack

John D. Roberts

CH₂

CH₃

T = -75.0°C

T = -87.5°C

T = -91.0°C

T = -96.8°C

T = -109.5°C

200

100

0

Hz

SANDOZ, Inc.

May 2, 1978

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

Dear Barry:

A mundane but hopefully practical and useful contraption
for high-volume nmr users:

Unattended, Multiple NMR Tube Cleaner for Soluble Impurities

The extraction apparatus-arrangement described below
is based on the following phenomena:

1. If saturated vapors bathe a cavity, air with slowly, but
    completely diffuse out and be replaced by the vapors.

2. A soluble material will attract solvent from saturated
    vapor phase to form solution (Osmosis).

The apparatus (Fig.) consists of a conventional magnetic
stirrer (to provide even boiling), heating mantle with rheostat,
round flask for boiling, extraction chamber and reflux condenser.
The extraction chamber was constructed by sealing a smaller male
ground glass joint to the longer stem, narrowed down to match on
the lower end, of a wide female joint. A conventional adapter
tops this to accept the small joint of the condenser. The flask
is half-filled with solvent, preferably 2:1 methanol: chloroform
for most organic substances. A cylindrical stainless steel wire
mesh basket, open at the top, was constructed to fit into the ex-
traction chamber. A wire handle eases removal by lifting out.

NMR tubes (up to 50-100) are placed upside down into
the basket, which is then bathed in the gently refluxing vapors
for approximately two days. One can convince oneself of the
effectiveness of this procedure by seeing the disappearance of
some highly colored soluble deposits, if present at the bottom
of tubes. The apparatus is tilted approximately 15° from ver-
tical for easier drainage.

This extraction will clearly not remove insoluble residues. It must be stated that in our own high volume nmr operation we encountered too many resolution-degrading crocodiles, presumably some insoluble fraction of silicone grease and possibly silicagel redeposited from polar chromatography fractions. Change of solvent may circumvent this. Other (less sample diversified) high volume nmr users may have cleaner, or a more homogeneous set of samples.

If desired, the tubes may even be dried in the same apparatus without extra manipulation: A heating tape can be wound around the extraction chamber. When the extraction is complete, the heating mantle is switched off and the heat to the chamber applied (can be timed circuits). The basket with the tubes is then lifted out hot.

The apparatus' advantages outweigh disadvantages:

Large numbers of tubes can be cleaned;

Essentially no manual labor is involved;

Chemical exposure and fire hazard are minimized;

One filling of solvent cleans a large number of tubes; always "fresh" solvent in the vapor phase; no rentry of dirt or one tube dirtying another;

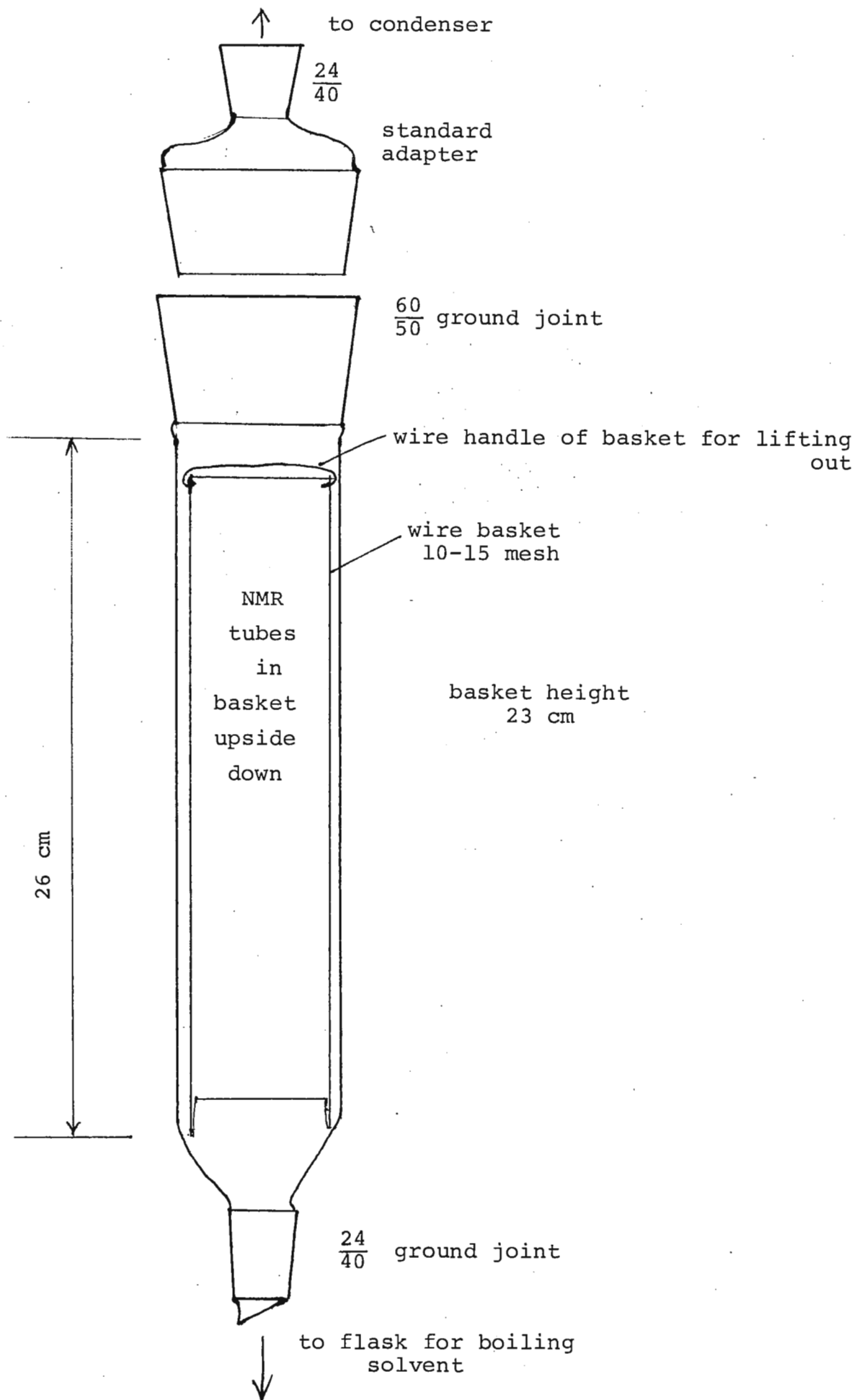Simple construction, mostly commercial components;

(It might be mentioned that a more complex version of this apparatus delivered refluxing liquid solvent via wide hypodermic needles, one into each tube, open end up.)

Sincerely,

Sandor Barcza

SB:rck
attach.

to condenser

$\frac{24}{40}$

standard
adapter

$\frac{60}{50}$ ground joint

wire handle of basket for lifting
out

wire basket
10-15 mesh

NMR
tubes
in
basket
upside
down

basket height
23 cm

26 cm

$\frac{24}{40}$ ground joint

to flask for boiling
solvent

EM-360L

The leading family of permanent-magnet NMR spectrometers has a new addition!

Varian's line-up of low-cost, high-performance permanent-magnet NMRs now includes the EM-360L—a 60-MHz instrument of extraordinary experimental flexibility. Like the EM-360A and EM-390, the EM-360L offers you ease of operation, low utility costs (it requires no cooling water and uses very little electric power), a convenient desk-type console with built-in 11x17″ flatbed recorder, pneumatic sample handling for reduced breakage, and optional variable-temperature capability utilizing Joule-Thomson cooling (no liquid nitrogen). And the EM-360L is, like its cousins, backed by the name of the world's largest manufacturer of high-resolution, permanent-magnet NMR systems.

Whether your lab is considering an analytical NMR for the first time or replacing an existing instrument, check out the leading family first:

EM-360A
Along with its predecessor model, the EM-360A is unquestionably the most popular low-cost 60-MHz NMR; almost 700 EM-360s and EM-360As are now

EM-360L
This new, highly versatile, deluxe version of the 14-kG EM-360A provides 30:1 sensitivity and 0.3 Hz resolution. As standard features, the EM-360L includes a built-in internal lock channel

EM-360L operating console—engineered for maximum functionality.

EM-360A

installed around the globe! Designed for routine proton analysis, the EM-360A delivers a guaranteed sensitivity of 25:1 (5-mm sample; 1% ethylbenzene) and 0.5 Hz (FWHM) resolution—but it can also tackle research problems with the addition of lock/decoupler, variable temperature, and signal averager accessories. In fact, the EM-360A is the only 60-MHz NMR in its class to offer VT operation ($-100°C$ to $+150°C$).

with AutoShim™ (automatic Y-gradient homogeneity adjustment), wide sweeps (0.2 to 100 ppm) and digitally selectable offsets (-200 to $+200$ ppm), 25-kHz modulation frequency with single side-band detection, and fast normalization of spectrum and integral amplitudes. The EM-360L can also readily be extended to double-resonance experiments (decoupling, spin tickling, and INDOR), VT ($-100°C$ to $+175°C$), ^{19}F,

EM-390

^{31}P, and sensitivity enhancement (signal averager or rapid-scan correlation NMR).

EM-390
This spectrometer has all the functional features and options of the EM-360L, but affords the high sensitivity (50:1) and chemical shift dispersion of 21-kG (90-MHz) operation. The latter are particularly attractive to investigators dealing with limited amounts of sample, sparingly soluble substances, or large, complex molecules. The EM-390 is rapidly becoming the high-performance standard of analytical NMR spectroscopy.

If you wish to discuss the leading family of permanent-magnet NMR spectrometers with a Varian representative, write: Varian Instrument Div., 611 Hansen Way, Palo Alto, CA 94303.

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