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No. 214

July, 1976

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DEADLINE DATES: No. 215:   2 August 1976

                   No. 216:   6 September 1976

All Newsletter Correspondence, Etc. Should Be Addressed To:

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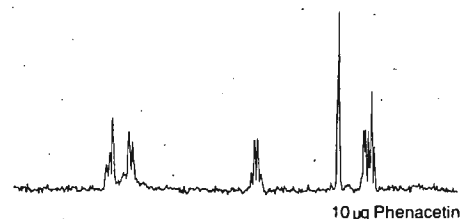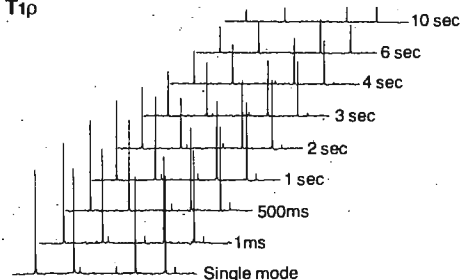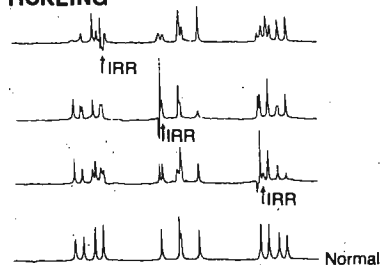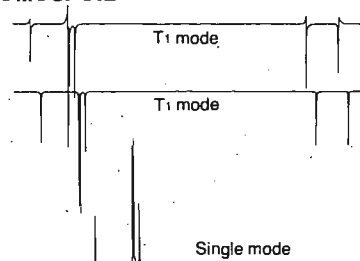   College Station, TX 77843 U.S.A.

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DEPARTMENT OF CHEMISTRY　　　　　　　　　　　　　BERKELEY, CALIFORNIA　94720

June 8, 1976

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

Dear Professor Shapiro:

Fourier Transform Double-Quantum NMR

We have shown recently[1] that our new technique Fourier Transform Double-Quantum (FTDQ) NMR can be used to eliminate the broadening from electric quadrupole couplings ($\sim$ 100 KHz) in ordered deuterium systems so that small effects, i.e., chemical shieldings ($\sim$ 100 Hz), can be observed. As an example of this technique we determined the carboxyl deuteron shielding anisotropy in a single crystal of partially deuterium labeled oxalic acid dihydrate.

The extension of high resolution FTDQ spectroscopy to powders would allow direct determination of shielding anisotropies for deuterium. The experiments are complicated by the fact that the intensity of double-quantum coherence observed is dependent upon the quadrupole splitting for a particular nucleus or orientation. However, application of an appropriate sequence of pulses[2] allows one to map out the double-quantum coherence for all orientations simultaneously. After Fourier Transformation this gives a powder pattern with a predictable lineshape. In such a spectrum all quadrupole splitting has been completely removed. As an example of this we measured the shielding anisotropy of deuterons for 10% benzene d-1 doped into normal protonated benzene. From the powder pattern we derived an anisotropy of $\Delta\sigma \sim$ -6.5 ppm. This measurement was performed on our home-built spectrometer operating at 28 MHz for deuterium, with high power proton decoupling. A complete description of this and other FTDQ work will be coming out soon.

Sincerely,

David Wemmer

Shimon Vega

Please credit to the account of Professor Alex Pines

1.　S. Vega, T. W. Shattuck, and A. Pines, Phys. Rev. Lett., in press; A. Pines, Materials and Molecular Research Division Annual Report 1975, Lawrence Berkeley Laboratory No. 4550.
2.　S. Vega, D. Wemmer and A. Pines, to be published.

benzene d-l

-40°C

σ (ppm from C_6D_6)
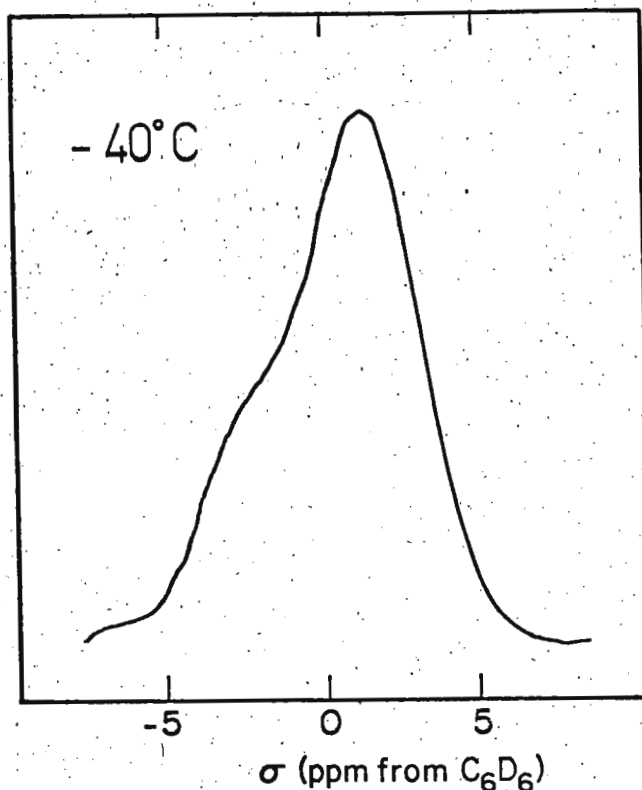
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June 1, 1976
AR/1187

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

Dear Barry:

SUBJECT: C-F Coupling in 2-Fluoro-Naphthalenes

Some time ago I had the opportunity to measure the ^{13}C nmr spectra of the three 2-fluoro-napthalenes in the Table attached. From the results obtained on II and III, I felt the necessity of remeasuring I. The spectrum obtained supported the assignments of II and III, but disagreed with the literature[1,2] available at that time. A 1974 paper[3] agreed with the others[1,2] but not my results. My results do, however, agree with those of Ernst[4,5] and I believe that considerable revision of the assignments of 2-fluoro-naphthalene derivatives[7] and their analogs are necessary. Characteristic coupling patterns in fully coupled spectra provide a useful method for assigning peaks in the naphthalene series[6] and selective [13]C-{H} double resonance should be used to remove any remaining ambiguties.

Sincerely,

Michael L. Maddox, Ph.D.

M. L. Maddox Contribution Continued from P. 2:

TABLE I[a]
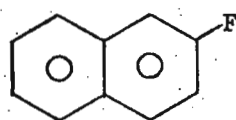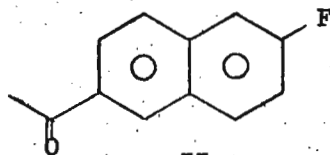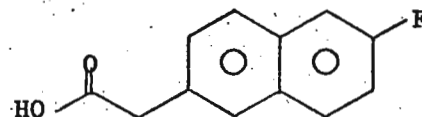
	I δ_c	I J_{cf}	II δ_c	II J_{cf}	III δ_c	III J_{cf}
1	110.98	20.3	111.21	21.0	110.85	20.5
2	160.79	245.8	162.32	250.4	160.87	246.0
3	116.34	24.4	117.38	25.5	116.76	25.3
4	130.41	9.0	132.00	9.2	130.18	9.2
5	128.00	1.2	129.80	1.5	128.29	1.2
6	125.19	2.7	133.85	2.6	130.16	2.7
7	126.97	0.7	124.79	0.7	128.49	0.6
8	127.39	5.6	127.50	5.5	127.81	5.2
9	134.31	9.3	136.41	9.9	133.42	9.2
10	130.61	0.7	129.31	0.9	130.53	1.2
			197.75 C=O		41.06 CH_2	
			26.56 Me		177.83 CO_2	

a)   Spectra measured on Bruker WH-90 in $C Cl_3$ using 6 KHz or 2 KHz sweep width and
       16 K data tables. δ_c reported in ppm to high frequency from internal TMS
       coupling constants in Hz $\pm$ 0.2 Hz.

[1]F. J. Weigert and J. D. Roberts, J. Am. Chem. Soc., 91, 4940 (1969), J. Am. Chem. Soc.,
93 2361 (1971)

[2]D. Doddrell, D. Jordan, and N. V. Riggs, J.C.S. Chem. Comm., (1972) 1158

[3]P. R. Wells, D. P. Arnold, and D. Doddrell, J.C.S. Perkin II, (1974) 1745

[4]L. Ernst, Z. Naturforsch, 30b, 800 (1975)

[5]L. Ernst, J. Magn. Resonance, 20, 544 (1975)

[6]L. Ernst, Chem. Ber., 108 2030 (1975), H. Günther, H. Schmickler, and G. Jikeli,
J. Magn. Resonance, 11, 344 (1973)

[7]F. D. Doddrell, M. Barfield, W. Adcock, M. Aurangzeb, and D. Jordan, J.C.S. Perkin II
(1976) 402

Prof.Dr.H.Kessler
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der Johann Wolfgang Goethe-Universität
Frankfurt am Main
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D— 6000 Frankfurt/Main 70
Theodor-Stern-Kai 7
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Telefon 63 01 — 6032/33

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

May 31, 1976

Title: Rate Processes in an Alkoxyboran Complex

Dear Professor Shapiro,

We have studied the dynamic behaviour of the alkoxyboran complex $\underline{1}$ with the aid of variable temperature NMR. The following processes A, B, and C have been observed simultaneously.

$\underline{1}$

A: proton exchange

B: nitrogen inversion

C: ligand exchange
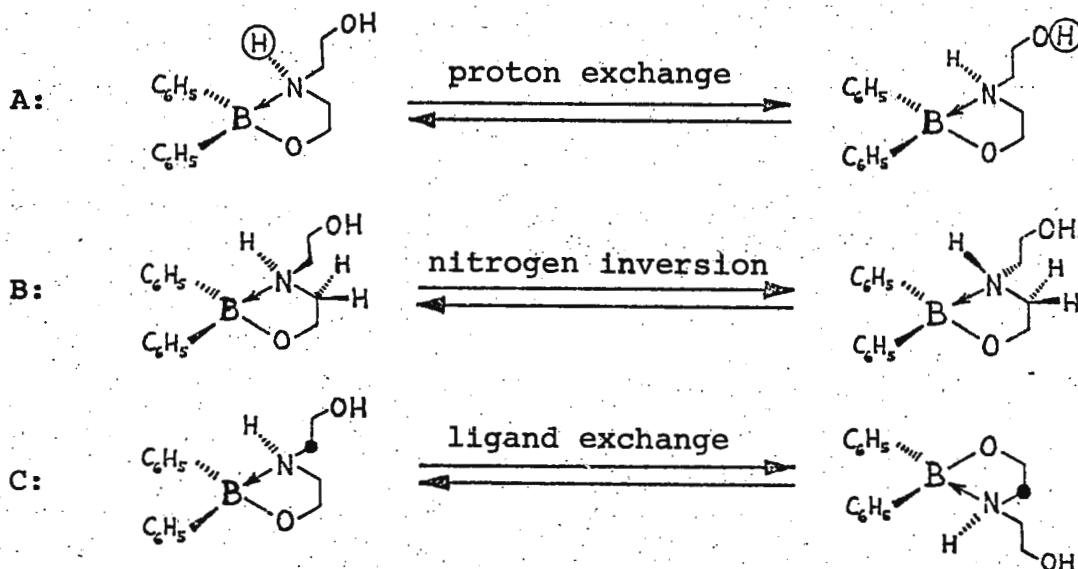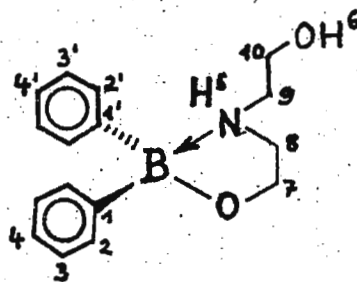
The OH-signal in the ^{1}H-NMR spectra is strongly shifted upfield on raising the temperature and is coalescing due to process A with the almost non-shifted NH-signal at 4.9 ppm (see figure).

Starting from low temperatures the very complex spectrum of the methylene protons first coalesces to a broadened 4 line spectrum

(disappearance of the gem. methylene proton nonequivalence by nitrogen inversion B) and finally at high temperature only two tripletts for the O-methylene and N-methylene protons are observed (fast ligand exchange C). The processes B and C can also be followed in the ^{13}C-NMR spectrum. B leads to coalescence of the two non-equivalent sets of aromatic carbon signals[1]. The coalescence phenomena of the signals between 50 and 63 ppm are caused by ligand exchange C.

The data are listed in the table and rough estimation of the free enthalpy of activation is added.

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1) The broadening of the C_1-signals at higher temperatures is due to the quadrupol relaxation and coupling of the boron nuclei.
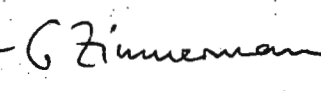
Table: Kinetic Data for the Rate Processes of $\underline{1}$ in CD_2Cl_2

Process	Nucleus	exchanging groups	$T_c [K]$ a)	$\Delta\nu_c [Hz]$	$\Delta G_c^{\ddagger} [kcal/mol]$ a)
A	^1H	OH, NH	290 ± 10	94	13.9 ± 0.5
B	^{13}C	C-2, C-2'	260 ± 5	56.6	12.6 ± 0.3
		C-3, C-3'	250 ± 10	16	12.8 ± 0.5
	^1H	H-8, H-8'	265 ± 5	44	13.0 ± 0.3
		H-9, H-9'			
		H-7, H-7'	260 ± 5	38	12.8 ± 0.3
C	^{13}C	C-8, C-9	308 ± 5 b)	85.5	14.8 ± 0.3
		C-7, C-10	313 ± 5 b)	122	14.8 ± 0.3
	^1H	H-8, H-9	292 ± 5	23.5	14.8 ± 0.3
		H-7, H-10	297 ± 5	43	14.7 ± 0.3

a) rough estimated values

b) observed in $C_2D_2Cl_4$

Sincerely yours,

(H.Kessler)   (G.Zimmermann)

¹³C DNMR

solvent: C₂D₂Cl₄

OCH₂ NCH₂

T[K]
320
308
294

C-1
C-2
C-3
C-4

solvent: CD₂Cl₂

310
260
253
225

160   δ [ppm]   120   80   40

¹H DNMR

solvent: C₂D₂Cl₄

T[K]

377

C₆H₅   OH/NH   OCH₂   NCH₂

323

solvent: CD₂Cl₂

OH/NH

305

NH

285

OH

265

245

225

8 δ[ppm]   6   4   2

214-6
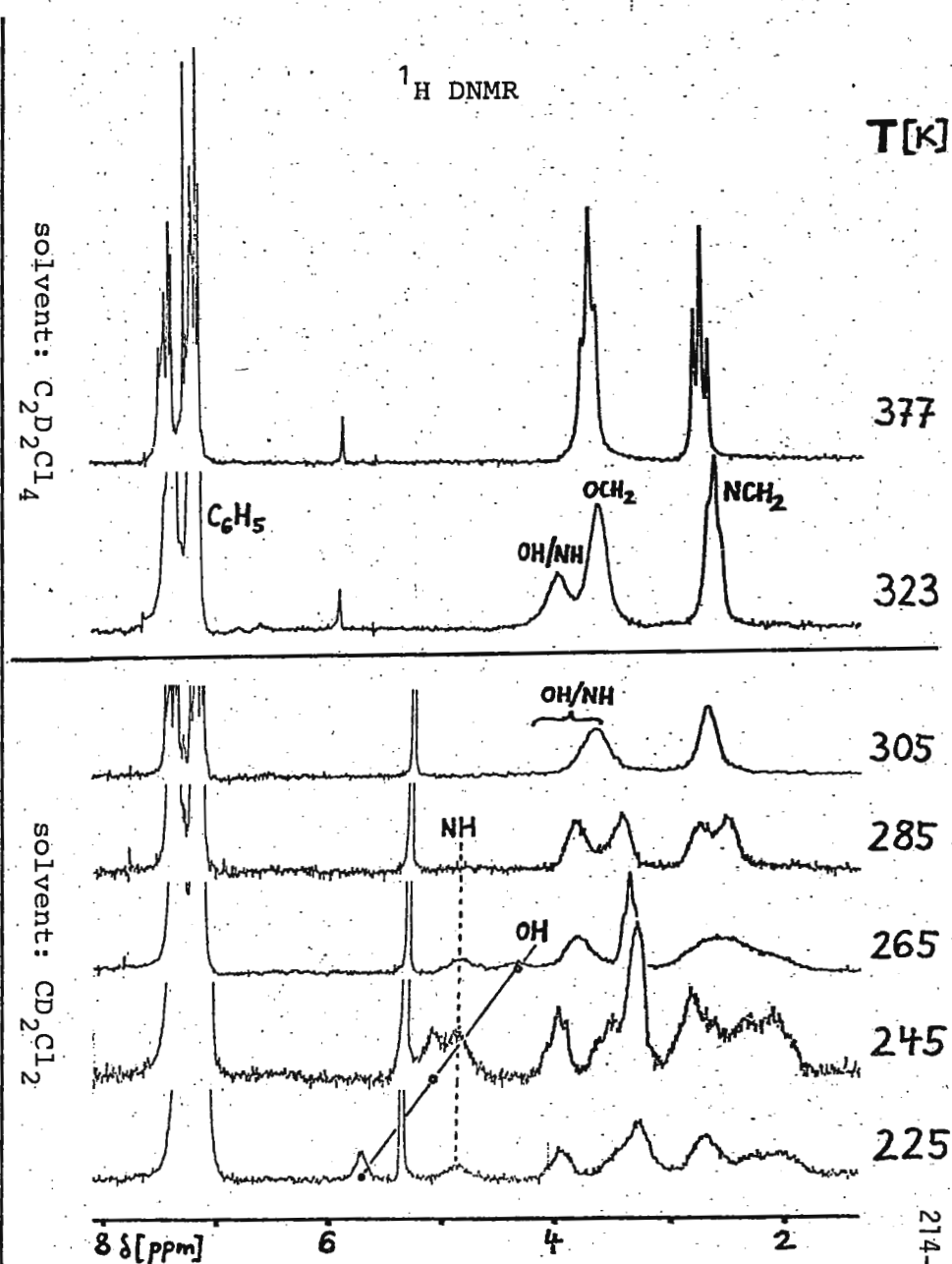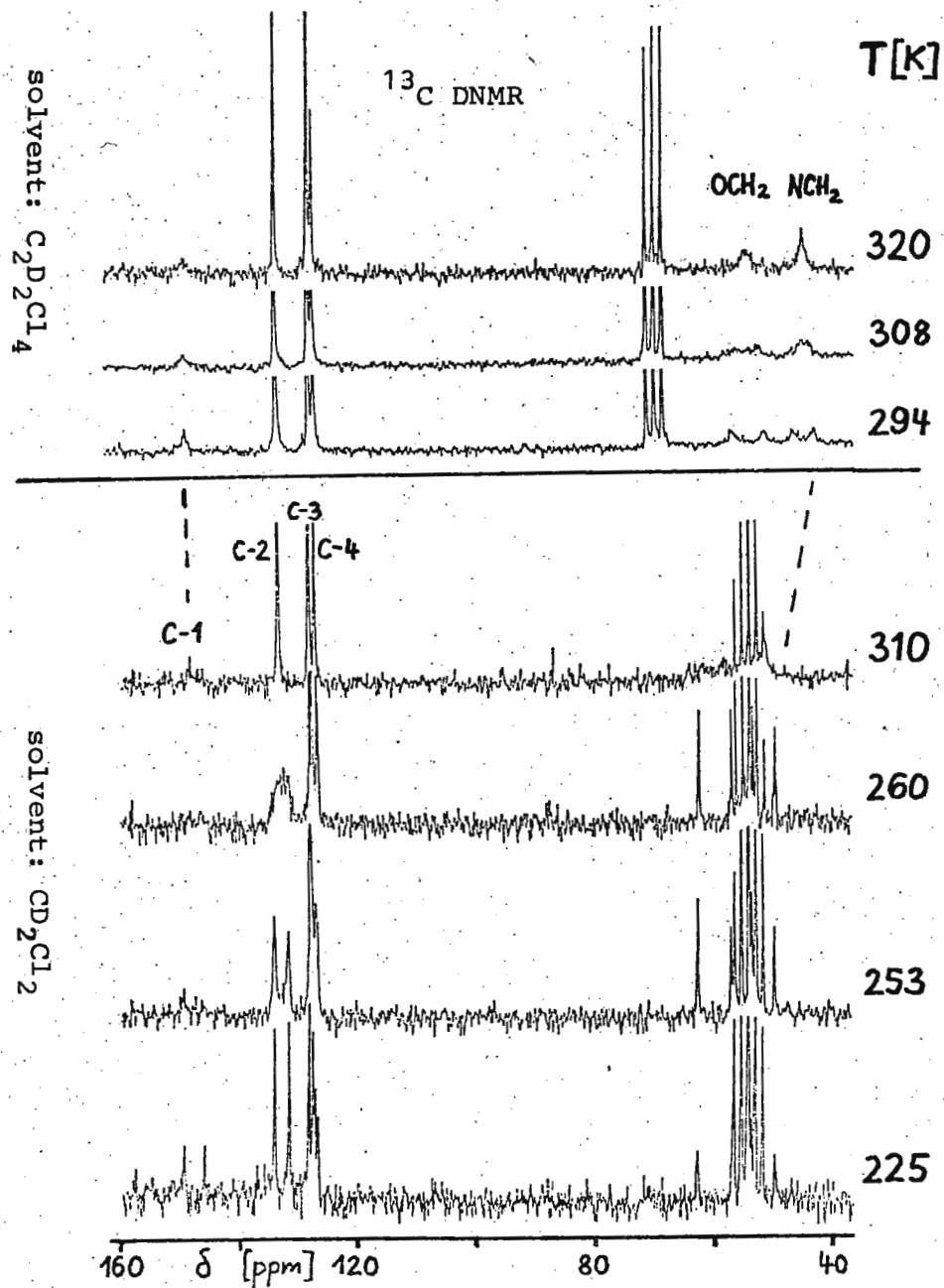
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DEPARTMENT OF CHEMISTRY   9 June, 1976

Prof. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843 U.S.A.
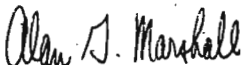
<u>Magnetic and Non-Magnetic Relaxation: A Comparison</u>

Dear Barry,

As you know, I have been collaborating with Prof. M. B. Comisarow here at
the University of B.C., in the development of Fourier transform ion cyclotron
resonance (FT-ICR) spectroscopy.[1] Part of that development has been inspired
(and occasionally nurtured) by analogies to prior FT-NMR theory, which is in
turn based on long-known linear response theory. Similarly, there have
recently appeared a number of line-narrowing experiments in optical spectroscopy[2]
which bear strong analogy to pulsed NMR "echo" techniques.

In trying to gain further physical insight into any phenomenon, one can often
progress more easily by analogy than by deduction. We have therefore been
led to examine a number of correspondences between relaxation in NMR and ICR
in work which will shortly be published, some of which are listed on the next
page.[3] While the various processes listed in the NMR (or ICR) column are
certainly known to those in NMR (or ICR), the close parallels between NMR and
ICR shown in the table should facilitate future cross-fertilization between
theory and experiment in the two types of spectroscopy.

Sincerely,

Alan G. Marshall
Associate Professor

1. M. B. Comisarow and A. G. Marshall, "Theory of Fourier transform ion
        cyclotron resonance mass spectroscopy. I. Fundamental equations
        and low-pressure line shape," J. Chem. Phys. <u>64</u>, 110 (1976).

2. J. Schmidt, P. R. Berman, and R. G. Brewer, "Coherent Transient Study
        of Velocity-Changing Collisions," Phys. Rev. Letters <u>31</u>, 1103 (1973).

3. M. B. Comisarow and A. G. Marshall, "Theory of Fourier transform ion
        cyclotron resonance mass spectroscopy. II. Relaxation and spectral
        line shape," to be published.

Comparison of NMR and ICR Resonance and Relaxation

Process	Manifestation in NMR	Manifestation in ICR
Circular motion due to magnetic field:	precession of nuclear magnetic moment	orbiting of electrically charged ion
Source of coherent radiation excitation:	linear or circularly polarized r.f. magnetic field (from r.f. current in one or more coils)	linear or circularly polarized r.f. electric field (from r.f. voltage to one or more plates)
Coupling between resonances detected by "double" irradiation:	Scalar or chemical coupling between two or more nuclei	kinetic (chemical reaction) coupling between 2 or more ions
Exchange between 2 different resonant frequencies:	Chemical exchange	Charge exchange (ion-molecule reaction; charge-transfer)
Signal amplitude proportional to:	Difference in population between two nuclear spin states	Number of ions of a given charge-to-mass ratio
Signal saturation due to:	depletion of spin state population difference due to stimulated (by applied r.f.) transitions	depletion of number of excited ions of a given (q/m)-ratio, due to ion removal on reaching the charged plates of the sample container
Inhomogeneous line-broadening:	Spatial inhomogeneity in H_o or H_1	Spatial inhomogeneity in H_o or E_1
Homogeneous line-broadening Secular relaxation:	T_1 phenomena: spin state transitions between states differing in energy by approximately the Larmor frequency, due to temporal magnetic field fluctuations near Larmor freq.	Ion-molecule reactions: loss of ICR signal due to loss of ion identity
Homogeneous line-broadening Non-secular relaxation:	T_2 phenomena: transitions at frequencies of about zero or about the Larmor frequency, due to field fluctuations at those frequencies	Non-reactive or reactive ion-molecule collisions: loss of ICR signal due either to loss of coherence in orbital ion motion or to loss of ion identity
Extreme narrowing limit:	$T_1 = T_2$: Time-dependent perturbations fluctuate rapidly compared to the Larmor frequency--NMR line width determined wholly by T_1 ("lifetime") broadening	All ion-molecule collisions are reactive--ICR line width determined wholly by reactive collision rate
Spinning the sample to reduce spatial inhomogeneity in H_o:	Sample is spun externally	Sample "spins itself" by inherent cyclotron orbital motion

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7 June 1976

COMMENTS ON J. SHOOLERY'S LETTER IN TAMU NO 211

Professor Shapiro,

I was interested in Jim Shoolery's letter entitled "Carbon-13 NMR for the Micro-Chemist". He remarks about the slow appreciation and utilisation of carbon-13 NMR, as it is currently practised, by many chemists. However, I should like to comment that the blame for this situation does not entirely lay with the chemist. One of the main reasons for this can be seen on the back page advertisement of the TAMU newsletter containing Jim Shoolery's letter. Many chemists still associate carbon-13 NMR with an entire room full of very expensive electronics which only a relatively few institutions or companies can afford. The point that ought to be now made is that it does not require a room full of electronics to produce high quality carbon-13 NMR spectra. It does not require a 15" (or 18") magnet to produce a highly uniform magnetic field of 2.3T over the kind of sample volume used to obtain the spectra shown by Jim Shoolery. In fact the magnet need only be a fraction of the size (and cost) of the XL100 magnet. The developments that have taken place in RF pulse amplifiers and in low noise RF signal amplifiers over the last two decades or so now make the manufacture of these units not a particularly difficult or expensive business. True one is left with the mini-computer (soon micro-computer) to control and order the various instrument and data collecting functions, but anyone who has looked behind the front panel of a typical modern mini-computer will know how much can be packed into such a small space and at such modest cost. Thus the point I should like to make is that the stage is now set for the production of literally a 'table top' carbon-13 NMR spectrometer with a very high performance. Such an instrument would be greatly welcomed by the majority of organic chemists and could augment the existing range of simple 60 MHz cw instruments now in such wide use. As pioneer in so many new NMR ventures perhaps Varian could lead the way in such an exciting development.

Yours sincerely,

S.A. Knight

varian/611 hansen way/palo alto/california 94303/u.s.a./415/493-4000

June 29, 1976

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

Title: We Aim to Please

Dear Barry:

Thank you for sharing the comments by Dr. Knight regarding the
possibility of using a smaller (and presumably less expensive)
spectrometer system than the XL-100 to obtain ^{13}C spectra from
small samples similar to those in my letter "Carbon-13 NMR for
the Micro-Chemist" (TAMU 211). Anticipating this point, we had
gone ahead with the development of 1.7 mm ^{1}H and ^{13}C microprobes
for the CFT-20 with very gratifying results. Many of your readers
may have seen some of these spectra at the last ENC meeting, but
for those who did not I offer Figures 1 and 2 which are the ^{1}H
spectrum of 1.0 µg of Cortisone Acetate and the ^{13}C spectrum of
500 µg of Ethyl Vanillin respectively, both obtained with an
overnight run. The prophecy is thus fulfilled, at least in some
degree, although I must admit that a very strong table is needed
to support a CFT-20. (Available as an optional accessory.)

Sincerely,

James N. Shoolery
Applications Chemist
NMR Applications Laboratory
Instrument Division

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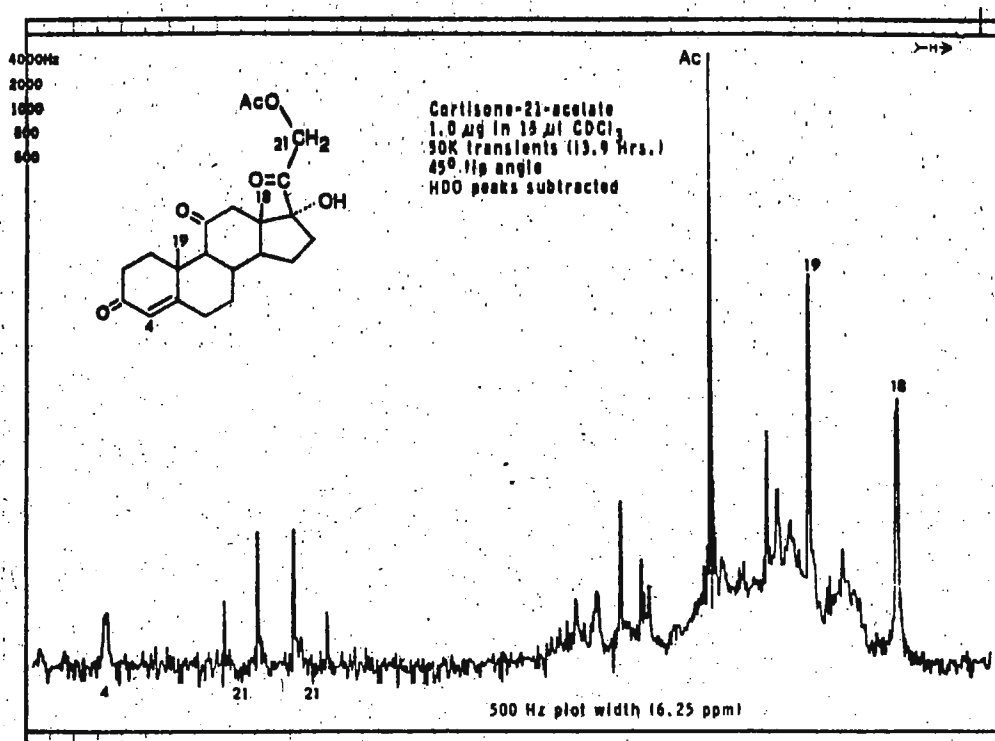
Figure 1

Figure 2
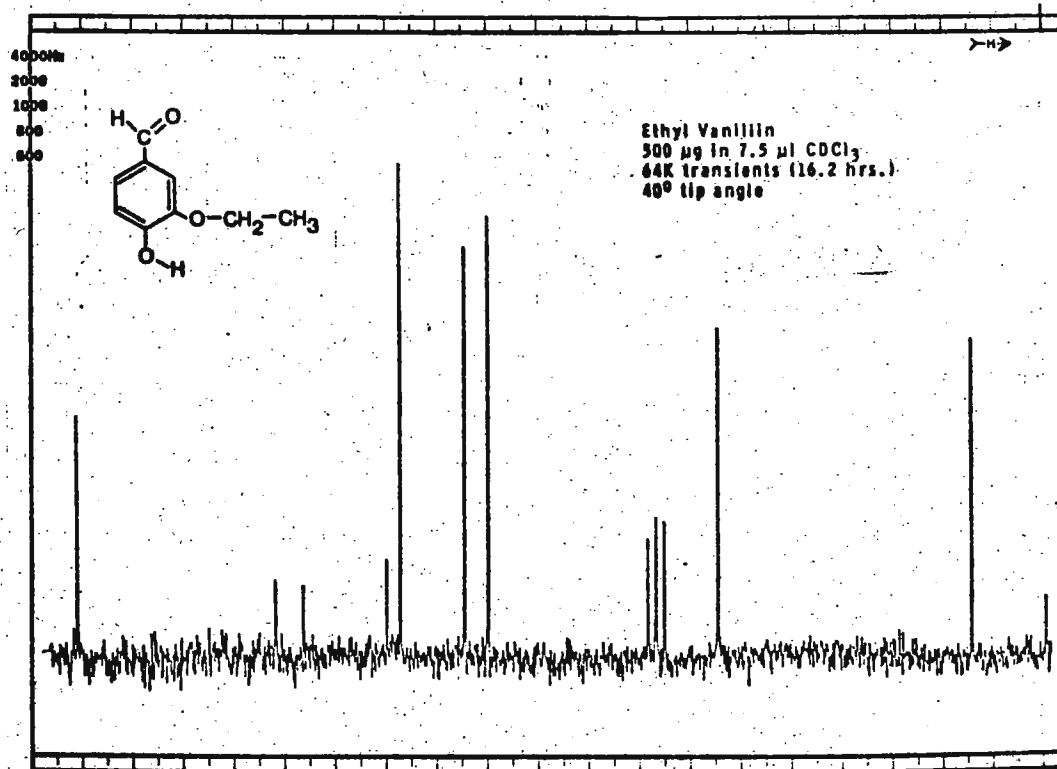
CHEMICAL CENTER
PHYSICAL CHEMISTRY 2

Lund, June 1, 1976

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

^{1}H NMR Bandshapes for Phospholipid Vesicles

Dear Barry:

For lecithin lamellar liquid crystalline phases the shape of the
proton resonance signal is determined by static dipolar couplings,
and is very broad with little structure. On sonicating lecithin-water
systems vesicles 25 - 30 nm in diameter are formed, which give
proton spectra with typical high resolution features. The way in
which the sonication leads to this narrowing has been argued in
the literature for some time. The mechanisms proposed are (i) rota-
tional Brownian motion of the vesicles, (ii) rapid lateral diffu-
sion and (iii) more structural disorder in the fluid state of the
lipids in vesicle bilayers than in lamellar systems. Recently we
have analyzed theoretically the PMR bandshape of vesicles using a
detailed density matrix description of the transverse relaxation
process. The analysis is based on the following:

1) The vesicle rotation is fast enough to give an effective zero
average value for the dipolar couplings, and these couplings give
only relaxation effects.

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2) The molecular motion can be divided into two independent parts, a fast local motion within the bilayer that is assumed to be the same in sonicated and unsonicated systems and a slow motion due to vesicle rotation and/or lateral diffusion in the bilayer.

The total bandshape is then a superposition of Lorentzians with different widths. Figure (a) shows an experimental spectrum and (b) the corresponding simulated spectrum. The fit between the two spectra is very good even far out in the wings of the spectrum. This shows that is is not possible to assign a single T_2 to any one of the peaks, It also follows that the width at half height $\Delta v_{1/2}$ is not at all sufficient to characterize a signal and should be used with care when analyzing spectral changes.

Sincerely yours,

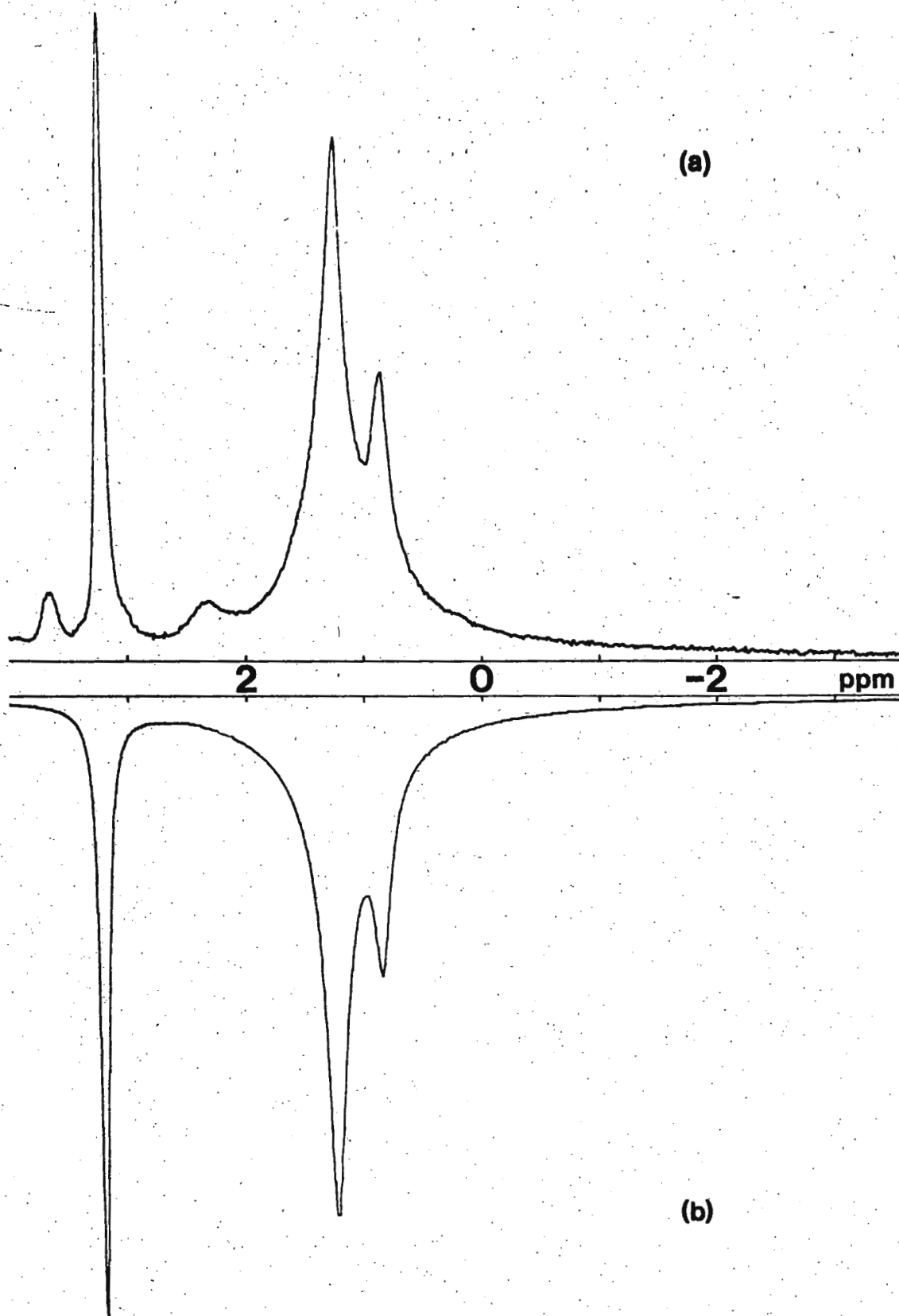Sture Forsén   Jan Ulmius   Håkan Wennerström

Fig a: A 100 Mhz ^{1}H NMR spectrum of dimyristoyl lecithin vesicles with a diameter of approximately 27 nm recorded at 30°C.

Fig b: A simulated spectrum. The small peaks at δ = 2.33 and 3.64 ppm in the experimental spectrum have not been included in the simulation.

University of East Anglia

From: Dr. R.K. Harris and Mr. R.H. Newman

School of Chemical Sciences
The University of East Anglia
Norwich NR4 7TJ , ENGLAND.

Telephone Norwich (0603) 56161
Telegraphic Address UEANOR NORWICH

10th June 1976

SILICON-29 N.M.R. OF TRIMETHYLSILYLATED MINERALS

Dear Barry,

When silicate anions are leached from acid-soluble minerals, the silicic acids rearrange too rapidly for isolation and identification. Lentz[1] overcame this problem by trimethylsilylating the silicic acids during leaching. The trimethylsilyl derivatives are stable, and the major product retains the structure of the original silicate in the mineral. Trimethylsilylation is a valuable technique for analysis of poorly-crystallised specimens that cannot be satisfactorily analysed by X-ray diffraction; e.g. it has been possible to follow polymerisation of silicates during curing of cement pastes[2]. The volatile trimethylsilyl derivatives are identified by g.l.c., the residue being classified as "unidentified polysilicates".

We have been investigating the possibility of using ^{29}Si to identify the trimethylsilyl derivatives. Silicon-29 chemical shifts for the trimethylsilyl groups are not sufficiently dispersed to be useful, but chemical shifts for the silicate ^{29}Si's are spread over about 5 p.p.m. We have run ^{29}Si spectra of four of the smaller structures. The solvent was benzene, and chemical shifts (for the silicate ^{29}Si only) are given below in p.p.m. from TMS (positive shifts are to high frequency)

$(Me_3Si)_4SiO_4$	(monomer)	-104.1	
$(Me_3Si)_6Si_2O_7$	(dimer)	-106.5	
$(Me_3Si)_8Si_3O_{10}$	(linear trimer)	(-109.2	(central)
		(-106.8	(ends)
$[(Me_3Si)_2SiO_3]_4$	(cyclic tetramer)	-107.8	

The monomer and dimer were obtained from I.C.I. Ltd. (Organics Division) and the Paint Research Association, and we are grateful for the help of these organisations. The linear trimer and cyclic tetramer were prepared by trimethylsilylation[1] of the appropriate minerals (natrolite and laumontite, respectively).

The trends of the ^{29}Si shifts are qualitatively similar to trends observed for silicate anions in aqueous solutions[3]; e.g. increasing condensation results in low frequency shifts by steps of about 2.6 p.p.m. (monomer → end units → chain units) compared with steps of about 7 p.p.m. for aqueous silicates. Cyclisation results in a high frequency shift

of 1.4 p.p.m. (linear chain → cyclic tetramer) compared with a
shift of about 2 p.p.m. for aqueous silicates.

We are now working on the possibility of identifying structural
units in the benzene-soluble non-volatile polymers.

We hope this letter keeps us on the TAMU N.M.R. mailing list.

With best wishes,

Yours sincerely,

R.K. Harris
R.H. Newman

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

RKH/RHN/DB

References

1. C.W. Lentz, Inorg.Chem. 3, 574 (1964).

2. C.W. Lentz, Ind.Chim.Belge 32, 487 (1967).

3. Von G. Engelhardt, D. Zeigan, H. Jancke, D. Hoebbel and W. Wieker,
    Z.anorg.allg.Chem. 418, 17 (1975).

Remember this ad?

We ran this ad in mid-1972 when six of us formed Transform Technology Incorporated with the help of Nicolet Instrument Corporation. Now, less than four years later we have over three dozen employees and are now a Nicolet operating division, known as Nicolet Technology Corporation.

What has happened since our first ad? Well, we don't mind tooting our horn by pointing out that NTC has become established as a leader in the development of FT NMR equipment. We have developed, produced and installed scores of FT accessories for use on instruments such as the XL-100, HR-220, T-60, R-12 and R-32. In fact, for over a year we have been the leader in U.S. sales of FT data systems. Now we're working on becoming the leader in overseas sales as well.

Why the success story? We feel it's because we're responsive to customers' needs. Being a relatively small group of dedicated souls we can move quickly in the development of equipment which utilizes the latest techniques.

Consider some of our "firsts" in commercial equipment:

FIRST to employ a single sideband crystal filter for improved signal-to-noise ratio,

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FIRST to develop a complete software package which includes provision for five methods of measuring T_1 values and three methods for T_2 values.

You can be sure that we are actively working on new "firsts." For example, we'll be demonstrating a complete Fourier Transform Mass Spectrometer very soon. To repeat the closing statement from our original ad—write or call collect to discuss your requirements. Maybe we can work together to add another "first."

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NICOLET TECHNOLOGY CORPORATION
145 East Dana Street
Mountain View, California 94041
Phone: 415/969-2076
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CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

June 8, 1976

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

JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

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

Gadolinium Salts for Reduction of Long ^{15}N Relaxation Times in Polar Solvents

Dear Barry,

We have been taking natural-abundance ^{15}N spectra of several nucleosides, using dimethyl sulfoxide (DMSO) as solvent. A major problem in this study has been the very long time (up to nine hours) required to obtain spectra of even 0.7 - 1.0 M solutions. For this reason, we have tried several different metals and metal complexes in the hope of reducing the observed T_1's of these and other, similar compounds. Because we wished a reagent soluble in both DMSO and water, the classical relaxation reagents such as $Cr(AcAc)_3$ were not suitable. The best results were obtained with the rather implausible combination of $Gd(NO_3)_3$ with an equal molar amount of inositol. The inositol was essential because of the prohibitive line broadening which resulted with $Gd(NO_3)_3$ alone. As an example of the use of this relaxation reagent, we ran 0.7 M solutions of adenosine in DMSO—with and without the relaxing reagent. Without the relaxation reagent, the S/N was 2.2, using a 90° pulse, 10-second delay, and proton decoupling during acquisition only.* The sample with the reagent (4×10^{-5} M, or 6×10^{-4} mole ratio of $Gd(NO_3)_3$ to adenosine) gave a S/N of 5.4 with the same instrumental parameters. The improvement in S/N corresponded to a six-fold saving in time. The spectra obtained with and without the relaxing reagent had the same line shapes and chemical shifts. Similar results have been obtained with formamide in both DMSO and in water as solvents.

Other ligands besides inositol may give still better results; but, at least, the $Gd(NO_3)_3$-inositol combination is very useful for DMSO and water.

With all good wishes,

Very truly yours,

William H. Bearden

Glenn R. Sullivan

Jack
John D. Roberts

*Gated decoupling was used, because the small negative NOE produced by full decoupling resulted in a reduction in the signal intensity.

June 8, 1976

**ROHM
IHAAS
COMPANY**

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

Dear Dr. Shapiro,

I would like to pass along some information which might be useful to those of your readers using capillary inserts with their NMR spectrometers. In my particular case, the one millimeter insert used with the Varian XL-100, the normal commercially available capillary tubes which are supplied are coagulation capillary tubes sealed at one end which are 75 mm long and vary from 0.5-0.9 mm I.D. These tubes are not of precision quality to begin with, and their length has proved to be a severe drawback. The 75 mm length is just long enough that the tube may be sealed by melting the end shut rather than by the more desirable "pull-seal" method, and we have had occasional problems with imperfect seals resulting in ultimate evaporation of the sample from the capillary tube. I have located a commerical source which will produce precision open-ended capillary tubes of 1.0 mm O.D. and 0.8 mm I.D. at a length of 100 mm. The tubes are made of SF glass and are custom order items available at a cost of about $3 per hundred from Drummond Scientific Company, 500 Parkway, Broomall, Pa. 19008; phone (215) 353-0200.

These tubes may be "pull-sealed" at both ends to produce excellent seals relative to the end melting technique. Perhaps the most useful application I have found for these tubes is in preparing samples of microgram quantities of materials in hygroscopic solvents such as DMSO, where the introduction of what would normally be considered negligible amounts of water can cause problems. The sample is made by preparing five microliters of solution under dry nitrogen in a glove bag, trans-ferring the solution into a one millimeter tube by capillary action, plugging the ends of the tube with corks, and removing the sample from the glove bag and "pull-sealing" both ends. This procedure prevents introduction of water into the sample from either the atmosphere or the sealing flame, and we have achieved good results in minimizing the water content of our samples. I hope this information will be of use and would be happy to discuss the details further if anyone wants to.

Very truly yours,

David G. Westmoreland

DGW:pt

University of Houston

HOUSTON, TEXAS 77004

Department of Chemistry
713/749-2612

June 9, 1976

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

<u>It works, it must be a Fluke</u>

Dear Barry:

We have recently begun a series of heteronuclear decoupling experiments on our new XL-100 using an unusual configuration. We use a Fluke 6160 synthesizer for our decoupling frequency and an ENI 320L linear amplifier to provide the power for broad band decoupling. We have used standard matching networks on the V-4415 probe. Proton noise decoupled ^{13}C spectra are as good as expected. The modulation is provided by NTC's adaptation of one of their decoupler networks.

We have been so anxious to observe ^1H decoupled from ^{31}P that we performed the following experiment: The Fluke synthesizer output was amplified by the ENI to about 5 W and applied to the decoupling coils by the standard match-box. The frequency of the synthesizer was set to the ^{31}P frequency (ca. 40.45 MHz), and the whole thing worked. In addition we found no birdies or other problems in the ^1H spectrum. The total time to set up the experiment was about ten minutes.

We are now building match-boxes for other frequencies to see if the spectral purity of the Fluke synthesizer will permit other easy decouplings. Details on request.

With best regards.

Sincerely yours,

M. R. Willcott
Professor of Chemistry

MRW:dar

June 11, 1976

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

Dear Barry:

Titration Behavior of Individual Tyrosine Residues of Myoglobins from Sperm Whale, Horse and Red Kangaroo.

My co-worker Dr. David J. Wilbur has studied the
titration behavior of individual tyrosine residues of
myoglobins by observing the pH dependence of the chemical
shifts of C^{ζ} and C^{γ} of these residues in natural
abundance ^{13}C Fourier transform NMR spectra (at 15.18 MHz,
in 20-mm sample tubes, at 37°) of cyanoferrimyoglobins
from sperm whale, horse, and red kangaroo (Figure 1).
These three species were chosen, because the myoglobin
from sperm whale contains three tyrosine residues (at
positions 103, 146, and 151), the protein from horse
has tyrosines only at positions 103 and 146, and the
kangaroo myoglobin has a single tyrosine at position
146 in the sequence.

A comparison of the pH dependence of the spectra of
the three proteins (Figures 2-4) yielded specific
assignments for the resonances of Tyr-151 (sperm whale)
and Tyr-103 (sperm whale and horse). Selective
proton-decoupling yielded specific assignments for C^{ζ}
of Tyr-146 of the cyanoferrimyoglobins from horse and
kangaroo, but not the corresponding assignment for sperm
whale. The pH dependence of the chemical shifts indicated
that only Tyr-151 and Tyr-103 are titratable tyrosine
residues. The titration behavior of C^{ζ} and C^{γ} of Tyr-151
of sperm whale cyanoferrimyoglobin yielded a single pK
value of 10.6. The pH dependence of the chemical shift
of each of the resonances of Tyr-103 of the cyanoferrimyoglobins
from horse and sperm whale could not be fitted with the use
of a single pK value, but was consistent with two pK values
(about 9.8 and 11.6). Furthermore, the resonances of C^{ζ}
and C^{γ} of Tyr-103 broadened at high pH.

The titration behavior of the tyrosines of sperm
whale carbon monoxide myoglobin and horse ferrimyoglobin
was also examined. A comparison of all the experimental
results indicated that Tyr-151 is exposed to solvent,
Tyr-146 is not exposed, and Tyr-103 exhibits intermediate

behavior. These results for myoglobins in solution are consistent with expectations based on the crystal structure.
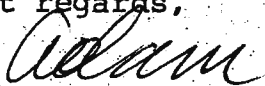
A preprint is available upon request.

Best regards,

Adam

Adam Allerhand
Professor of Chemistry

FIGURE CAPTIONS

Fig. 1. Region of aromatic carbons and C^ζ of arginine residues in convolution-difference natural abundance ^{13}C Fourier transform NMR spectra of cyanoferrimyoglobins in H_2O (0.1 M KCl) at pH 10.5 (complete aromatic region) and pH 7.9 (155-165 ppm only), recorded at 15.18 MHz, under conditions of noise modulated off-resonance proton decoupling [see Oldfield, Norton, and Allerhand, J. Biol. Chem. (1975) 250, 6368-6380 and 6381-6402]. (A) 10 mM sperm whale cyanoferrimyoglobin at 36°, after 32,768 accumulations with a recycle time of 0.555 s (pH 10.5) or 1.055 s (pH 7.9). (B) Horse cyanoferrimyoglobin at 38°, after 32,768 accumulations with a recycle time of 1.045 s (at both pH values). Protein concentration was 12 mM at pH 10.5 and 7 mM at pH 7.9. (C) About 12 mM red kangaroo cyanoferrimyoglobin at 36°, after 65,536 accumulations with a recycle time of 1.045 s at pH 10.5, and after 32,768 accumulations with a recycle time of 0.555 s at pH 7.9.

Fig. 2. Effect of pH on the chemical shifts of some nonprotonated aromatic carbons and C^ζ of arginine residues of sperm whale cyanoferrimyoglobin at 36°. Observed nonprotonated aromatic carbon resonances which are not shown (105-115 ppm and 130-145 ppm) have chemical shifts which are practically pH independent above pH 8. Peak numbers are those of Fig. 1A. Open circles, closed circles, triangles and squares indicate peaks that arise from 1, 2, 3, and 4 carbons, respectively. Figure 1A gives typical sample and spectral conditions. The solid lines are best-fit theoretical titration curves, with one pK for Tyr-151 and two pK values for Tyr-103. Dashed lines are best-fit single pK titration curves for Tyr-103. Below pH 10.5, the dashed curves for C^ζ of Tyr-103 coincides with the solid curve for C^ζ of Tyr-151.

Fig. 3. Effect of pH on the chemical shifts of some
nonprotonated aromatic carbons and C$^\zeta$ of arginine residues
of horse cyanoferrimyoglobin at 38°. Peak numbers and
typical sample and spectral conditions are given in Fig.
1B. The behavior of omitted resonances and the meaning of
symbols and curves are given in the caption of Fig. 2.

Fig. 4. Effect of pH on the chemical shifts of some
nonprotonated aromatic carbons and C$^\zeta$ of arginine residues
of red kangaroo cyanoferrimyoglobin at 36°. Peak numbers
and typical sample and spectral conditions are given in
Fig. 1C. The behavior of omitted resonances and the
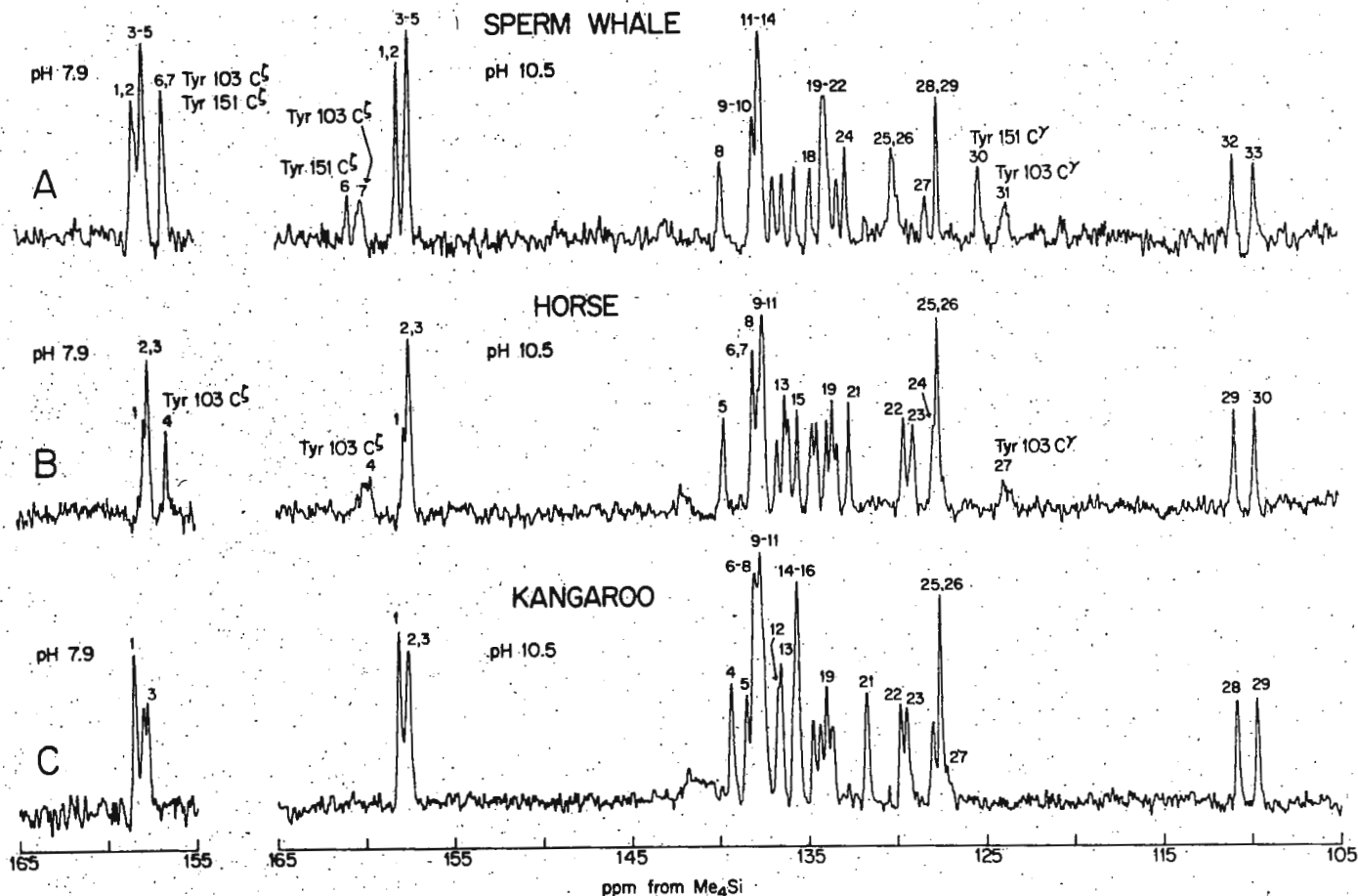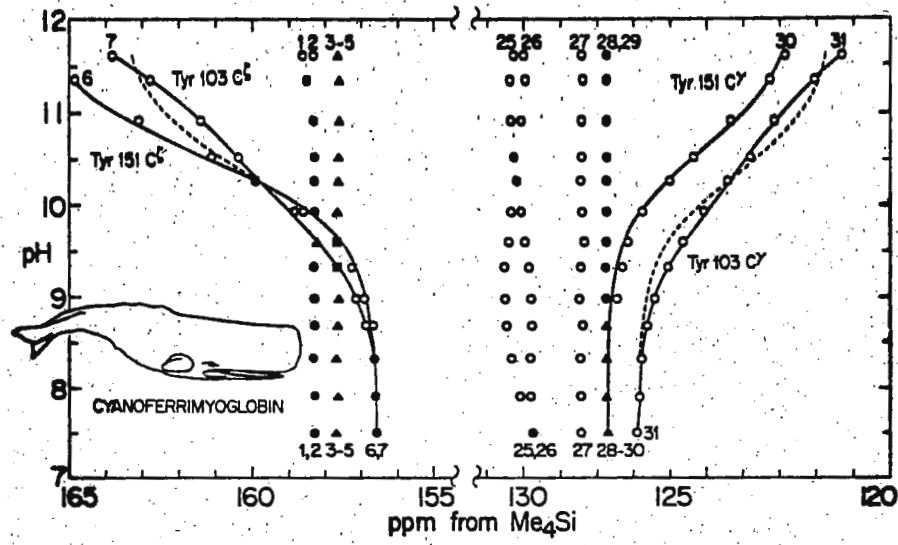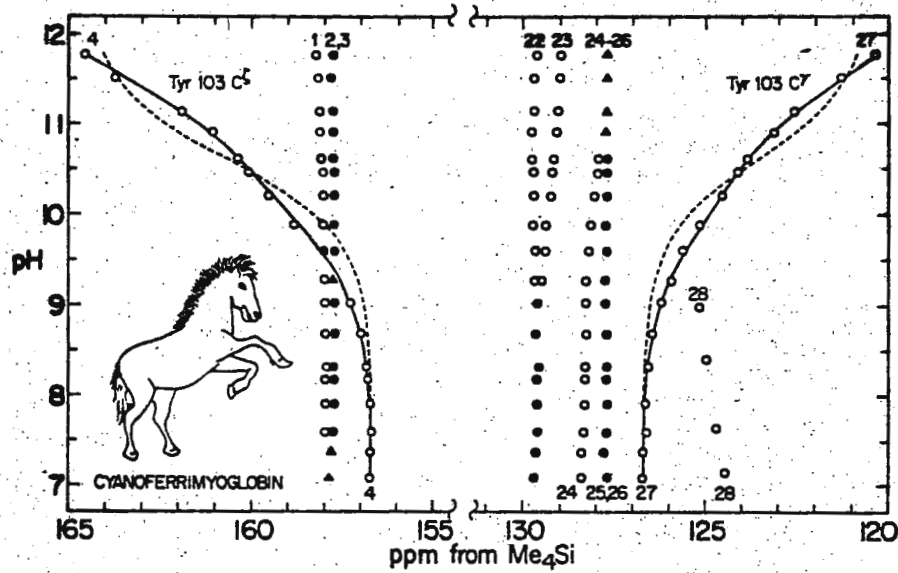meaning of symbols are given in the caption of Fig. 2.
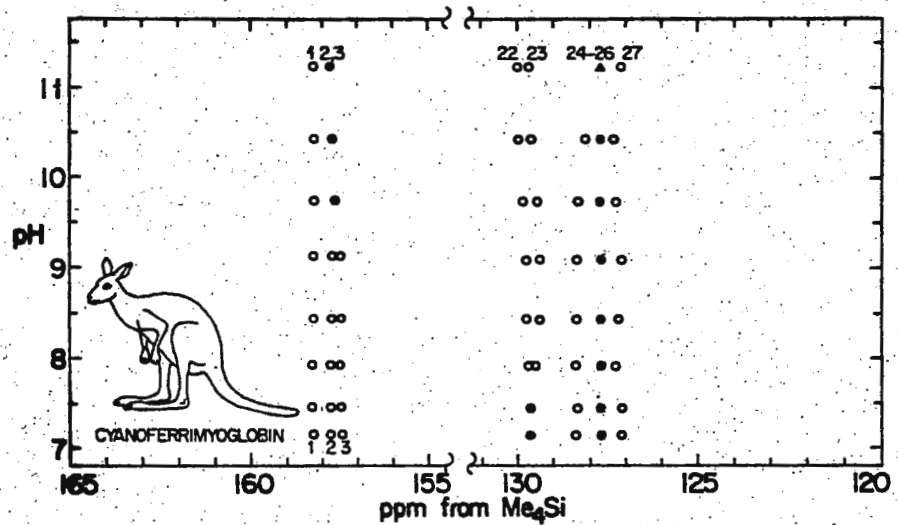

Figure 1

Fig. 2

Fig. 3

Fig. 4

CHEMICAL INSTITUTE

UNIVERSITY OF AARHUS

DEPARTMENT OF ORGANIC CHEMISTRY
HANS JØRGEN JAKOBSEN

8000 Århus C, Denmark   June 11, 1976
Telephone (06) 12 46 33   HJJ/ATL

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

Indirect Observation of Bloch-Siegert Shifts (or Where are
the Protons) in ^{13}C-{^{1}H} Multiple Resonance Experiments;
3rd EENC

Dear Barry,

In connection with our work on determination of rela-
tive signs of ^{13}C-X coupling constants using various selec-
tive ^{13}C-{^{1}H} double resonance methods (1) we came across
some examples which required selective irradiation at two or
more positions in the ^{1}H spectrum in order to remove simul-
taneously the multiplet structure caused by one-bond $(^1J_{C-H})$
and long-range ^{13}C-^{1}H couplings in the observed ^{13}C spectrum.
These experiments are complicated by the fact that the power
of the coherent rf field needed to collapse a one-bond ^{13}C-^{1}H
splitting completely (using on-resonance conditions) causes
extraordinarily large Bloch-Siegert shifts for other protons
in the ^{1}H spectrum. An indirect observation of these Bloch-
Siegert shifts is illustrated in the ^{13}C-{^{1}H,^{1}H} triple reso-
nance experiment on toluene in Fig. 1b. The ^{13}C-{^{1}H} double
resonance spectrum of the aromatic carbon atoms obtained with
strong $\underline{H_2}$ irradiation ($\gamma\underline{H_2}/2\pi = 486$ Hz) at the exact decou-
pling frequency for the ortho (H2) and para (H4) protons ($\nu_{H2}=$
484.5 Hz, $\nu_{H3} = 493.4$ Hz and $\nu_{H4} = 484.8$ Hz relative to the
methyl protons, ν_{CH_3}, in the ^{1}H spectrum at 100.1 MHz) is
shown in Fig. 1a. Under these conditions the C1 and C2 carbon
signals display residual quartet splittings of approximately
3-5 Hz (2a), whereas much smaller quartet splittings may be
observed for the C4 carbon. C3 shows mainly a residual one-
bond splitting, $^1J_{C3-H3}^{res}$. These observations are in agreement
with the magnitudes determined for the long-range ^{13}C-^{1}H cou-
plings between the ring carbons and methyl protons in toluene
(2b). In order to remove the residual quartet splittings from
the spectrum observed in Fig. 1a a second coherent rf field $\underline{H_3}$
of weaker amplitude ($\gamma\underline{H_3}/2\pi = 58$ Hz) was applied to the methyl
proton resonance. However, from the ν_3 decoupling frequency it
was empirically observed that these protons experienced a Bloch-
Siegert shift of 195 Hz to lower frequency due to the strong
$\underline{H_2}$ field. The experiment was performed using various $\underline{H_2}$ decou-
pling amplitudes and the results in Table 1 show that even mo-
derate decoupling amplitudes in coherent ^{13}C-{^{1}H} off-resonance
decoupling experiments may easily shift the proton resonances
completely outside the frequency range of the normal ^{1}H spec-
trum.

The Bloch-Siegert shifts observed in the experiments described above $(\nu_A - \nu_2 \neq 0)$ may be accounted for (Table 1) using the formula

$$\text{B.-S. shift} = (\nu_A - \nu_2)\left[\sqrt{\left(\frac{\gamma H_2}{2\pi}\right)^2 \Big/ (\nu_A - \nu_2)^2 + 1} - 1\right]$$

which includes the sign of the frequency shift. The high-frequency Bloch-Siegert shift of a methyl proton resonance line of weaker intensity is not considered here. A full account on these results, some experimental applications, and experimental details has been submitted for publication.

(1) S.Aa.Linde and H.J.Jakobsen, J.Amer.Chem.Soc. 98, 1041 (1976) and references therein.

(2) a) S.Sørensen, M.Hansen, and H.J.Jakobsen, J.Magn.Resonance 12, 340 (1973). b) M.Hansen and H.J.Jakobsen, J.Magn. Resonance 20, 520 (1975).

Table 1. Experimentally Observed and Calculated Bloch-Siegert Shifts of the Methyl Protons in Toluene from the Experiments Described in the Text.

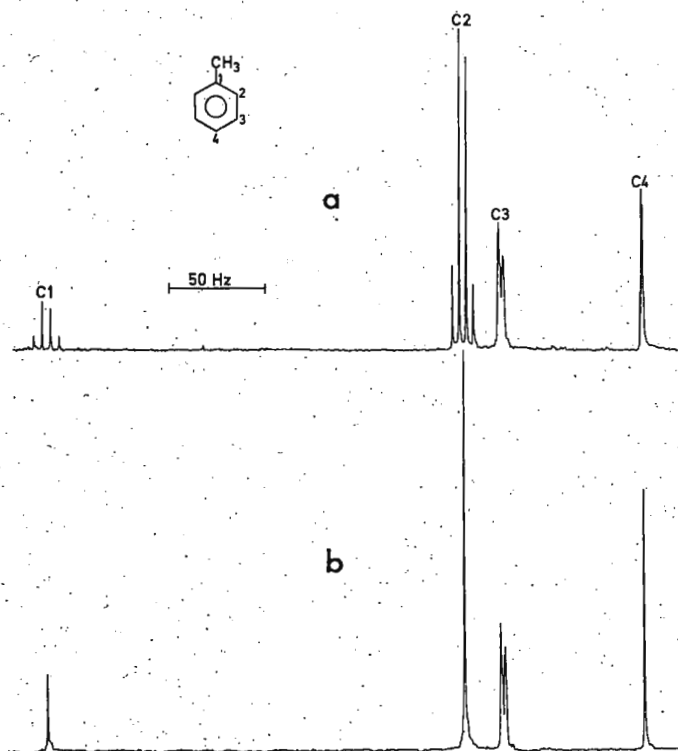|	$\gamma H_2/2\pi$ (Hz)	Calc. B.-S. Shift (Hz)	Exp. B.-S. Shift (Hz)
Exp. 1	486 ± 12	200 ± 9	195 ± 3
Exp. 2	930 ± 15	559 ± 13	562 ± 3
Exp. 3	1330 ± 20	922 ± 19	939 ± 3

Figure 1.

a) ^{13}C-$\{^1H\}$ double resonance spectrum of the aromatic carbons in toluene with coherent irradiation of H2 and H4, $\gamma H_2/2\pi$ = 486 Hz (Exp. 1).

b) Same as in 1a but with coherent irradiation, $\gamma H_3/2\pi$ = 58 Hz, of the B.-S. shifted strong methyl proton resonance line (see text).

3rd EENC

The 3rd EENC (European Experimental NMR Conference) will be held in Elsinore, Denmark

April 27-29, 1977.

Elsinore, the city of Shakespeare's Hamlet, is located on the cost 25 miles from Copenhagen.

Based on the experience from the previous conferences an _incomplete_ list of tentative subjects would be:

- Magnet developments;
- $T_{1\rho}$ and T_2 measurements;
- Elimination of dipole broadening in solids and liquid crystals;
- NMR detection of quadrupole transitions;
- Spatial resolution of NMR signals;
- Development of pulse techniques for weak signals and less common nuclei;
- On-line and off-line data handling;
- "Unexpected results and unexplainable phenomena"

All correspondence concerning the conference should be addressed to

Dr. Kjeld Schaumburg
3rd EENC
University of Copenhagen
The H. C. Ørsted Institute
Kemisk Laboratorium 5
Universitetsparken 5
DK-2100 KØBENHAVN Ø
Denmark

Sincerely yours,

Hans Jørgen Jakobsen

Pfizer

CENTRAL RESEARCH

PFIZER INC., EASTERN POINT ROAD, GROTON, CONNECTICUT 06340
203-445-5611   June 10, 1976

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

                SUBJECT: Whatever turns you on.

Dear Barry:

When one encounters a variety of chemical structure problems simultaneously,
it becomes attractive to consider systems for coping with the more routine
aspects of interpretation on a more organized basis, which involves some
thought about the strategy by which one derives a chemical structure from
NMR evidence alone. This is not only remarkably consistent from problem
to problem (differing mainly in the shortcuts provided by evidence from
other sources), but lends itself to a natural heirarchy of experiments
that increase in difficulty as they become more specific in purpose. We
are presently restricting our standard formats to molecules containing
only carbon, hydrogen, oxygen, and nitrogen atoms for which the empirical
formula is known. These are conveniently divided into peripheral (surface)
and framework types, based on the number of atoms to which they are attached
by arbitrary bond multiplicities. This division is natural for NMR spectro-
scopy, since PMR and CMR (excepting isocyanides) each deal exclusively with
atoms of a single type. One begins by attempting to define the set of <u>basic
structure units</u>, consisting of each framework atom plus its attached peri-
pherals, using such observables as the chemical shift ranges of the frame-
work atom, the number of protons on the unit, and dynamic and isotopic
exchange characteristics. This may or may not require the direct observation
of additional nuclei, depending on the number of types encountered. The
structure units are topographically classified into terminals (T), links (L),
branches (B) and intersections (I), which are related by the rule

$$T = B + 2 (I + 1 - R)$$

from which the number of rings, R, in the structure can be determined.

Our standard format for summarizing the essential data and listing the
basic structure units is illustrated in Figure 1, using a simple molecule
with empirical formula $C_{21}H_{30}O_2$. In this instance there are no nitrogen
atoms or peripheral (carbonyl) oxygen, the latter fact being apparent from
the CMR shifts; one hydroxyl unit is evident from its exchangeable proton,
and one other unit is assignable by elimination. The structure is therefore
deduced to contain three rings and four double bonds, all between carbon.

A general solution to the structure problem now consists of defining all
binary sequences of basic structure units. The second stage of a problem
therefore involves the systematic linking of basic structure units into
extended sequences. Spin coupling information is most naturally suited
to this purpose, and can be augmented by chemical shift correlations of

all observable nuclei in a unit with model systems. As an example, our previous structure can be systematically shown to have the extended structure units tabulated in standard form in Figure 2. Units A, C, and D were in this instance established on the basis of straightforward para- meter correlations, and unit B by homonuclear proton decoupling. The details are available for the asking.

The final stage of a problem occurs if and when the set of extended structure units becomes small enough to permit the delineation of a manageable set of alternative structures, and its accomplishment depends on one's ability to devise a critical series of experiments to differentiate among them. Relaxation times, Overhauser effects, and shift-reagent studies are examples of experiments best suited to this level of attack.

In our present example, only two structural arrangements of the extended units are possible, and one can show that II with $m = 1$, $n = 0$ is correct on the basis of CMR relaxation rates related to the length of the alkyl chain:

I (m, $n \geq 1$, $p_{max} = 1$)   II ($m \geq 1$, $p_{max} = 2$)
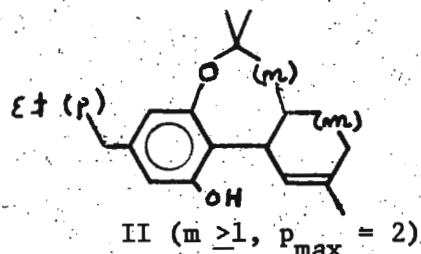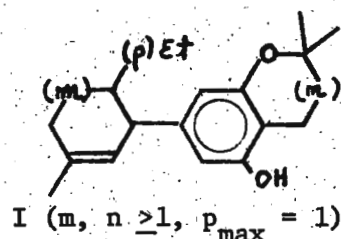
We thereby arrive at structure III, with its <u>trans</u> ring juncture also evident from PMR coupling data.
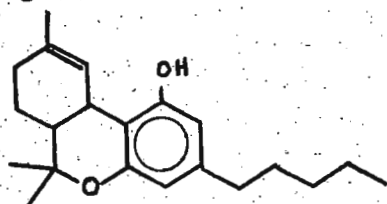
While none of this is really new, we find it useful, and at the least propose that our old preoccupation with ethyl alcohol be replaced with an example more suited to the times. I wonder if the hospitality suites will go along?

Sincerely yours,

E. B. Whipple

NMR SUMMARY AND BASIC STRUCTURE UNITS

COMPOUND __Mary Jane__

LINES	RANGE	TYPE	#	0	1	2	3	TOTAL CH	BAND	RANGE	#CH₂	#CH	TOTAL
1-8	105-155	C=C	8	5	3	0	0	3	I	5.0-6.4	1	3	4
9	50-100	C-O	1	1	0	0	0	0	II	1.8-3.3	0	6	6
10-21	10-50	alkyl	12	0	2	6	4	26	III	0.8-1.7	0	20	20
TOTALS			21	6	5	6	4	29			1	29	30

FORMULA __$C_{21}H_{30}O_2$__   D+R = __7__   D = __4__   R = __3__

UNIT	TYPE	#	C	H	O	N	UNIT	TYPE	#	C	H	O	N
-OH	T	1	0	1	1	0							
-CH₃		4	4	12	0	-							
-CH₂	L	6	6	12	0	-							
=CH-		3	3	3	0	-							
-CH-	B	2	2	2	0	-							
>=		5	5	0	0	-							
-C-	I	1	1	0	0	-							
			21	30	1	-							
-O-	L	1	0	0	1	-							
							ATOM TOTALS			21	30	2	
										T	L	B	I
							UNIT TOTALS		23	5	10	7	1

STRUCTURE UNITS

COMPOUND __Mary Jane__   FORMULA __$C_{21}H_{30}O_2$__   D __4__   R __3__

UNIT	TYPE	#	C	H	O	N	A	B	C	D	R=
											Basic
-OH	T	1	0	1	1	-	1	0	0	0	
-CH₃		4	4	12	0	-	2	1	1	0	
-CH₂	L	6	6	12	0	-	0	1	1	1	3
-CH=		3	3	3	0	-	2	1	0	0	
-O-		1	0	0	1	-	1	0	0	0	
-CH	B	2	2	2	0	-	0	2	0	0	
>=		5	5	0	0	-	4	1	0	0	
-C-	I	1	1	0	0	-	1	0	0	0	
TOTALS		23	21	30	2	-	11	6	2	1	3

KEY:

(A)

(B)

$CH_3 - CH_2 \text{---} (R)$

(C)

$(R) \text{---} CH_2 \text{---} (A)$

(D)
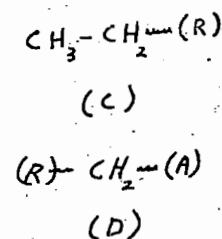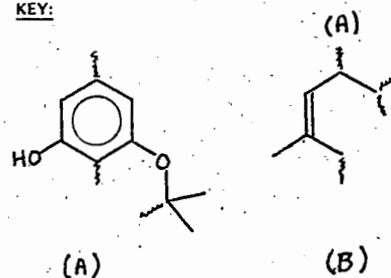
UNIVERSITE DE TUNIS

FACULTE DES SCIENCES

DEPARTEMENT DE CHIMIE

CAMPUS - UNIVERSITAIRE

T U N I S

Tél. : 264.577

الجامعة التونسية

كليـــة العلــــوم

قســم الكيميــا

المركب الجامعى

تـونس

الهاتف : 264.577

TUNIS, LE   12   Juin   1976   تونس في

V / Réf.
N / Réf.

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

College Station, Texas 77843
U.S.A.

Cher Professeur Shapiro,

Merci de votre lettre de rappel du 3 Juin.

Une méthode d'analyse quantitative de mélange d'hydrocarbures aromatiques monocycliques utilisant la résonance magnétique nucléaire du carbone-13 (R.M.N^{13} C) est proposée. Cette méthode permet de déterminer le pourcentage en moles des constituants du mélange par mesure de l'intensité des signaux RMN des carbones aromatiques seulement ; ainsi le pourcentage d'un composé A, du mélange d'aromatiques mononucléaires est donné par la relation :

$$\% A = \frac{x/y \cdot 100}{100/6} = \frac{6 \cdot x}{y}$$

où, n représente l'intensité relative l'un des carbones du cycle du composé A par rapport aux raies de tous les carbones cycliques (x étant donné en pourcentage) et y représente le nombre de carbones aromatiques identiques de la molécule A.

L'application de cette technique a permis la détermination des pourcentages en moles des constituants de mélanges d'aromatiques, issus des fractions (50 $\longrightarrow$ 180°C) de 4 bruts de pétrole tunisiens, monocycliques : preuve obtenue par chromatographie de partage en phase vapeur (C.P.P.V.) et par couplage C.P.P.V.-spectrométrie de masse. Dans ce but, nous avons enregistré les spectres R.M.N.^{13}C des différents échantillons à l'aide d'un appareil Bruker HX90 (22,63 MHz) équipé d'un accessoire pour transformée de Fourier en adoptant la technique du découplage avec annulation de l'effet Overhauser nucléaire et en choisissant un temps "trigger" de 300 s (temps d'attente entre 2 interférogrammes) tel qu'il soit égal au moins à 5 fois le temps de relaxation le plus élevé.

Ainsi nous avons pu mettre en évidence sans ambiguité approximative-
ment les 3/4 des constituants des différents mélanges. Ce travail nous
a révélé que le pseudocumène et le m-xylène représentent les pourcenta-
ges les plus élevés dans le mélange I, alors que dans l'échantillon II
le m-xylène constitue le 1/5 du total. De même, cette technique a montré
l'importance quantitative du toluène et du m-xylène dans le mélange III
et a révélé que le quart de l'échantillon IV est constitué de toluène.

La méthode, mise au point dans ce travail, est à notre avis susceptible
d'être étendue à l'étude d'autres mélanges de composés aromatiques subs-
titués par n'importe quels substituants, ce qui permettrait par exemple,
d'analyser et qualitativement et quantitativement des mélanges d'isomè-
res.

Nous tenons à signaler que ce travail a été réalisé
grâce à l'aimable concours de M. le Prof. J. J. Delpuech (Nancy) et
l'assistance de M. P. Rubini.

Croyez cher M. Shapire à nos sentiments cordiaux.

Titre : Etude par RMN du Carbone-13 des fractions aromatiques des coupes
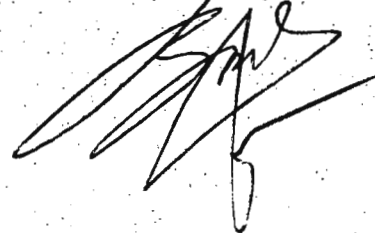légères des bruts de pétrole tunisiens.

Mohamed KERKENI
Assistant

Mohamed Larbi BOUGUERRA.
Professeur.

The University of Liverpool

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

18th June, 1976.

Dear Barry,

A cautionary tale, or when did you last check your CDCl₃ ?

TAMUNMR readers may be interested in a little problem which fooled us for some time recently. We[1] were investigating the complex formed in $CDCl_3$ solution between benzyl alcohol and $ClCH_2 CH_2 CH_2 NHMe_2 Cl$ (I), in which we propose that the interaction is due to a) the attraction of the benzene ring with the N part and b) a hydrogen bond between the OH and the Cl part of the ion-pair.

To test this hypothesis, we made the tetraphenyl borate salt of (I). However, on dissolving this in $CDCl_3$, we failed to get reproducible spectra; eventually we obtained the dilution curve shown which at first we thought was due to dissociation of the ion-pair. However, the shape of the curve is incorrect for a dissociation curve, and the correct answer was quite revealing.
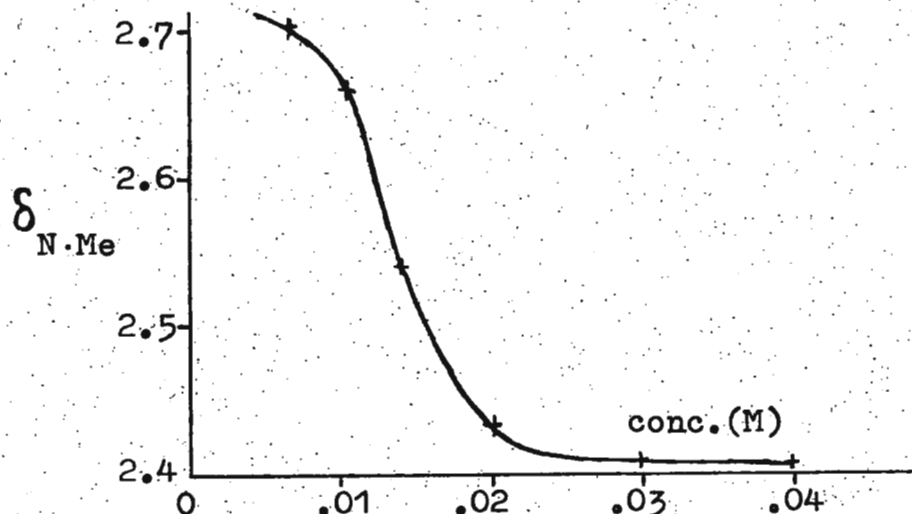
The curve shown is a <u>titration</u> curve in which we are titrating the DCl in the $CDCl_3$ against the solute, following the equation shown.

$$R \overset{+}{N}HMe_2 \, \overset{-}{B}Ph_4 \; + \; HCl \; \longrightarrow \; R \overset{+}{N}HMe_2 \, \overset{-}{C}l \; + \; BPh_3 \; + \; C_6H_6$$
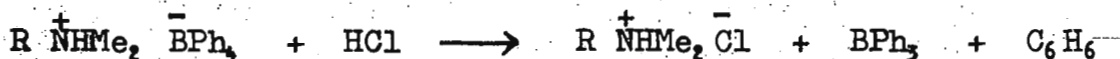
The infinite dilution shift is that of the hydrochloride but as the acid in the chloroform is used up the shift changes to that of the tetraphenyl borate.

Addition of HCl to the concentrated solution produced the ∞ diln. shifts, thus confirming this hypothesis.

This effect was seen despite considerable attempts to remove all acid by passing the $CDCl_3$ through alumina and storage over molecular sieves and silver foil. The problem was that the tetraphenyl borate was not very soluble in $CDCl_3$, and to achieve the required solution the mixture was usually warmed and shaken; precisely the right conditions for the formation of HCl!

With best wishes,

Yours sincerely,

Ray

Dr. R.J. Abraham.

[1] R.J. Abraham, K. Lewtas and W.A. Thomas, manuscript in preparation.

Stefan Berger
FACHBEREICH CHEMIE
DER PHILIPPS-UNIVERSITÄT
Marburg/Lahn

355 Marburg/Lahn, den 12.6.76
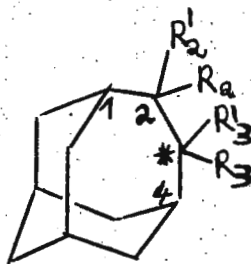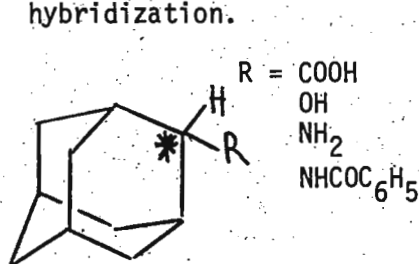Lahnberge
Fernruf (06421

Fachbereich Chemie 3550 Marburg/Lahn, Lahnberge

Professor B.L. Shapiro
Department of Chemistry
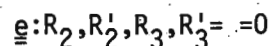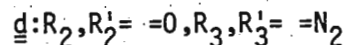Texas A & M University

College Station, Texas 77843

L   ⅃

The Absence of Long Range $^{13}C^{13}C$ Coupling Constants in

Homoadamantane Derivatives.

Dear Dr. Shapiro,

We have recently measured the long range $^{13}C^{13}C$ coupling constants in
2-substituted adamantanes $\underline{1}$ labelled at the α-carbon atom. (J.C.S. Chem.
Comm., in press). The conformational and substituent dependence of $^2J_{CC}$
and $^3J_{CC}$ in these compounds caused us to investigate a similar system
with slightly different bond angles. However, we were not able to detect
any three bond coupling constants in a series of homoadamantanes $\underline{2}$ label-
led at carbon atom 3. Two bond coupling constants could only be detected
in $\underline{2}$ $\underline{c}$, $\underline{d}$ and $\underline{e}$ between carbon atoms 1 and 3 where carbon atom 2 has sp^2-
hybridization.

R = COOH
OH
NH_2
$NHCOC_6H_5$

$\underline{\underline{2a}}$:$R_2=R_2'=R_3=R_3'=H$

$\underline{b}$:$R_3=R_3'=R_2=H,R_2'=OH$

$\underline{c}$:$R_2,R_2'=$ =O,$R_3=R_3'=H$

$\underline{d}$:$R_2,R_2'=$ =O,$R_3,R_3'=$ =N_2

$\underline{e}$:$R_2,R_2',R_3,R_3'=$ =O

* 8o at% ^{13}C
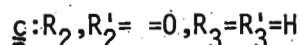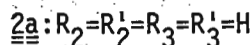
At present, we have no satisfactory explanation for the different behaviour
of adamantanes $\underline{1}$ and homoadamantanes $\underline{2}$. To obtain more experimental results
we are currently trying to synthesize some labelled noradamantane systems.

Sincerely yours

Stefan Berger

Klaus Peter Zeller
(Institut für Organische Chemie
der Universität Tübingen)

the University of Alabama in Birmingham / UNIVERSITY STATION/BIRMINGHAM, ALABAMA 35294

the Medical Center / SCHOOL OF MEDICINE / COMPREHENSIVE CANCER CENTER

JOHN R. DURANT, M.D., DIRECTOR

(205) 934-5077

June 22, 1976

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

SLIGHTLY OFF-COURSE FROM THE 'TOPIC OF CANCER'
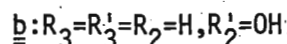
Dear Barry:

NMR studies in our group here at the Cancer Center include investigations
of tumor scanning agents, carcinogens, and cancer drugs. It is perhaps
also interesting to look at something structurally more simple and hopefully,
non-carcinogenic --the ammonium ion.

Employing a Bruker HX-90 modified to accomodate a wide band Traficante
insert, we have recently obtained ^{14}N spectra of NH_4^+ and ND_4^+ in the
lyotropic mesophase composed of decylammonium chloride, ammonium chloride
and H_2O or D_2O (1). The ensuing spectra show partially resolved coupling
between nitrogen and protons (sum of the scalar and the dipole-dipole
coupling $|J+<D_{zz}>|$) as well as very small ^{14}N quadrupole splittings
($\Delta\nu_N$). The ND_4^+ samples were also used to study the deuterium quadrupole
splittings of the same ion (under condition of identical probe temperature
and almost identical history of sample orientation in the magnetic
field). From the ratio of the ^{14}N and the ^{2}H splittings, the distortion
model for tetrahedral species of Bailey et al. (2) yields a ^{14}N quadrupole
coupling constant of 3.1 MHz (assuming e2qQ/h = 175 KHz and η = 0 for
deuterium). This seems to be a reasonable value, and in general sup-
ports the simple distortion model. This is in contrast to a recent
report (3) in which the same model apparently yielded results which
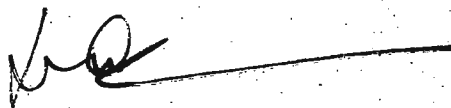
Professor B.L. Shapiro
June 22, 1976

COMPREHENSIVE CANCER CENTER
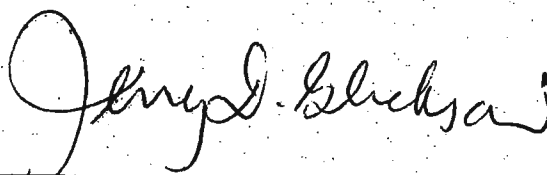
differ by one to two orders of magnitude from those obtained experimentally. A more detailed description of this study is being communicated to J. Amer. Chem. Soc.

Please credit this contribution to Dr. Robert Lenkinski's subscription.

Sincerely yours,

Douglas M. Chen, Ph.D.

Jerry D. Glickson, Ph.D.

REFERENCE.

1. L.W. Reeves, A. Tracey, J. Amer. Chem. Soc., 95 3799 (1973).
2. D. Bailey et al., J. Mag. Res., 18 344 (1975).
3. P. Diehl, presented at the 17th Experimental NMR Conference, Pittsburgh, April (1976).

DMC:JDG:swg

Enclosure

ISOTROPIC NH₄Cl SOLUTION

NH_4^+

$\Delta \nu_N$

500 Hz

$|J + \langle D_{zz} \rangle|$

100 Hz

ISOTROPIC ND₄Cl SOLUTION

ND_4^+

300 Hz

40 Hz

TITLE: HOMOALLYLIC COUPLING CONSTANTS AND DIHYDROAROMATICS --

CARBON-PROTON COUPLING CONSTANTS

Dr. B. L. Shapiro
Department of Chemistry   June 20, 1976
Texas A&M University
College Station, Texas 77843

North Texas
State
University

Denton, Texas
76203

Department
of
Chemistry

Dear Barry:

Some of your readers have been concerned with the utilization of homoallylic coupling constants in the conformational analysis of 1,4-cyclohexadienes. There has been some disagreement (too expansive to reference here) whether homoallylic coupling constants reflect the extent of puckering in dihydroaromatic compounds. A further complication is the possibility of rapidly interconverting conformers (e.g., boat ⇄ boat), giving rise to averaged nmr parameters.

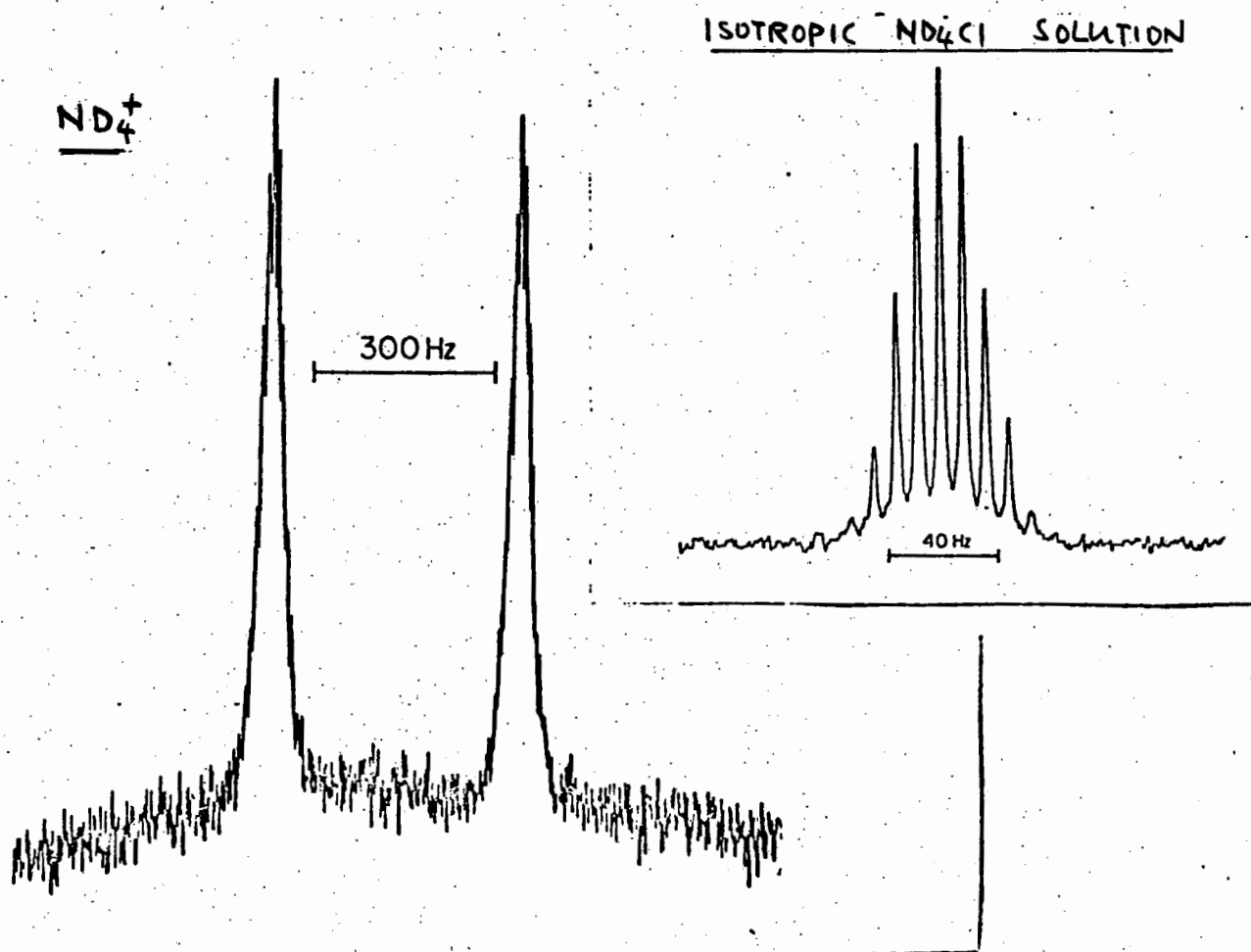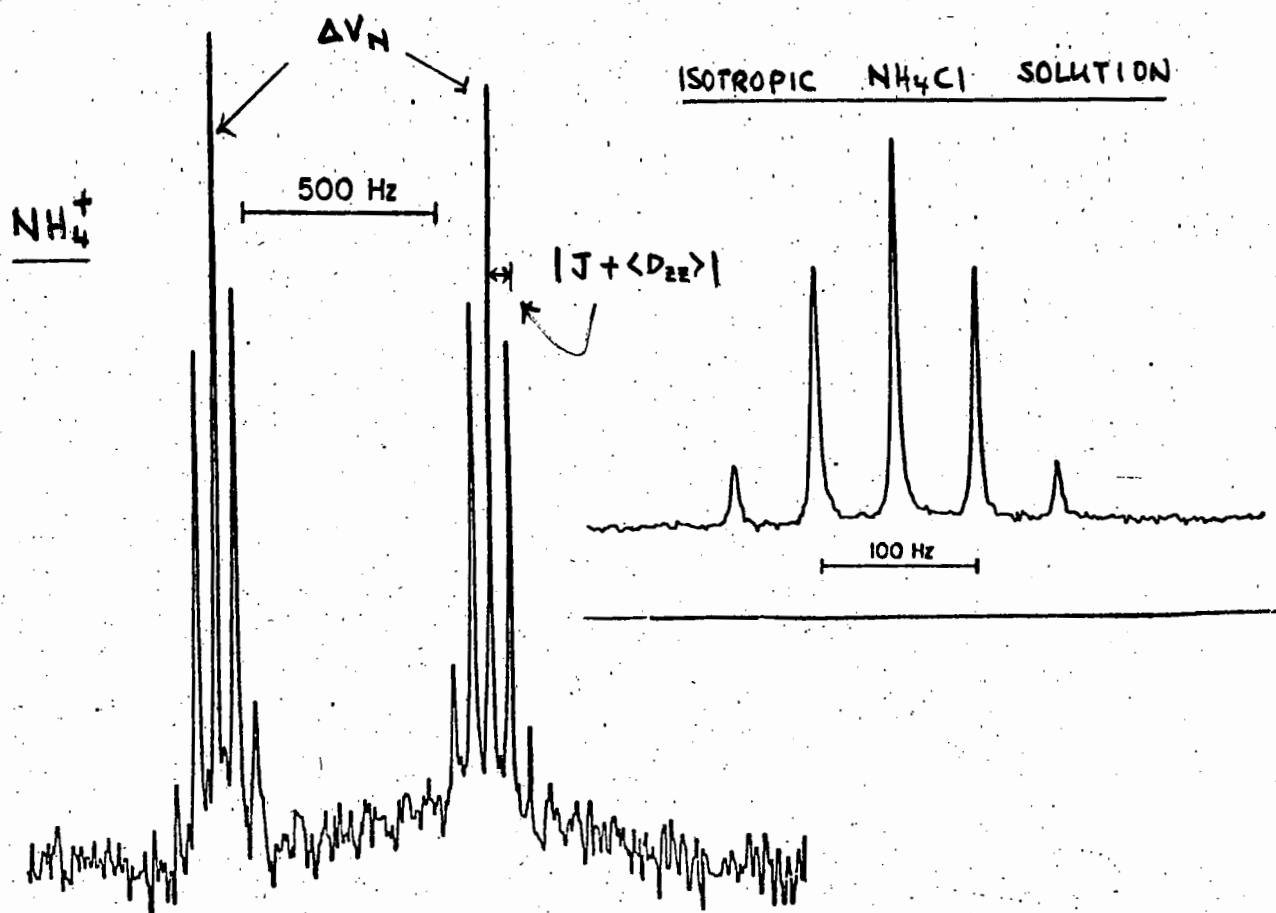The fact that carbon-proton coupling constants can be related to proton-proton coupling constants in a wide variety of systems (slope = 0.62, correlation coefficient = 0.98, in 2-, 3-, 4-, and 5-bonded olefinic, aromatic, acetylenic, and aliphatic systems for ^{13}C-labeled carboxylic acids; Organic Magnetic Resonance, in press) suggested to us that carbon-proton coupling constants could be used in the conformational analysis of dihydroaromatic compounds. Accordingly, we have synthesized the appropriate ^{13}C-labeled, deuterium labeled compounds to get the parameters listed below for 1,4-dihydrobenzoic acid (1), 1,4-dihydro-1-naphthoic acid (2), and 9,10-dihydro-9-anthroic acid (3). Several interesting observations can be made from this data.

First, for flat 1, the CH coupling constants seem to correlate with the HH coupling constants: the ratio of J(CH-cis)/J(CH-trans) is the same as the ratio J(HH-cis)/J(HH-trans) -- 1.23 ± 0.01. Further, the ratio of J(CH-cis)/J(HH-cis) and of J(CH-trans)/J(HH-trans) is the same as noted above -- 0.62 ± 0.01.

Second, if 2 were rapidly interconverting between two boat conformations, the two ratios J(CH-cis)/J(CH-trans) and J(HH-cis)/J(HH-trans) would be the same -- but they are not. Clearly, 2 is not a rapidly interconverting pair of conformers (we also tried to "freeze out" conformers at low temperature but were unsuccessful).

Third, there is a monotonic trend in J(CH-cis)/J(CH-trans) and in J(HH-cis)/J(HH-trans) through the series 1-3 (increase and decrease, respectively). We believe that these two ratios can fairly accurately reflect the extent of puckering in these, and in other, compounds. Sufficient space does not exist here to allow this comparison with literature cases.

Fourth, we have done SCF-INDO-FPT calculations on 1,4-cyclohexadiene itself at various conformations, and the ratios of J(cis)/J(trans) obtained from these calculations match up with the empirical values (e.g., for flat cyclohexadiene the calculated value of 1.29 compares with the empirical values of 1.22 (HH) and 1.24 (CH)).

Fifth, these studies point out the clear need to distinguish between the ratios J(eq-eq)/J(ax-eq) and J(ax-ax)/J(ax-eq) when applying the J(cis)/J(trans) ratio to the conformational analysis of cyclohexadienes. The data shown below illustrate what to expect for J(eq-eq)/J(ax-eq) ratios (viz., J(HH-cis)/J(HH-trans)) and for

J(ax-ax)/J(ax-eq) ratios (viz., J(CH-cis)/J(CH-trans)). We feel that "anomalies" in the literature can be explained once this distinction is recognized.

Sixth, and sufficient space does not exist here to tabulate this data, the calculated values in 1,4-cyclohexadiene show clearly that the expected values in this system are not just "doubled" values of the mono-path 2-butene. Instead, several changes can be noted. For example, the diaxial cis coupling does not simply increase throughout all possible conformers from a flat system to a highly puckered one (where the axial nuclei are parallel to the atomic p orbitals); instead, about half-way through these two extremes, the diaxial coupling starts to drift as the system continues to pucker further. Thus, claims to the "maximum degree of puckering" based on the "largest observed homoallylic coupling constant" can be misleading.

The main conclusion we have drawn from all this is that individual homoallylic coupling constants may be misleading in the conformational analysis of dihydro aromatics, but cis/trans ratios are more reliable. We further feel that ax-ax/ax-eq ratios are more reliable than eq-eq/ax-eq ratios.
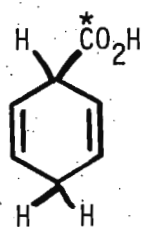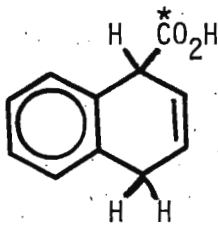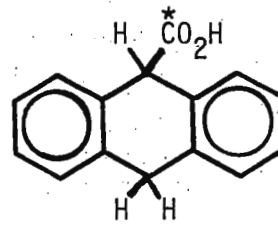
Compound	cis-$^5J_{HH}$	trans-$^5J_{HH}$	cis-$^5J_{CH}$	trans-$^5J_{CH}$
1	9.19	7.56	5.75	4.65
2	3.84	4.36	5.44	2.86
3	<0.5	0.9	3.2	0.7

Sincerely,

James L. Marshall
Professor of Chemistry

The University of Western Ontario, London, Canada

Faculty of Science
Department of Chemistry

June 22, 1976.

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

Dear Barry:

Antiperiplanar deshielding effects in ^{13}C spectra

can mislead the unwary

The receipt of your pink note has prompted me to bring my "subscription" up-to-date and I hope that the following finding will be of interest to some of the TAMU newletter readers.
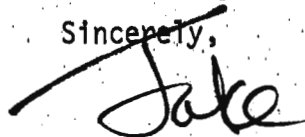
In collaboration with Bill Ayer (University of Alberta) I have been involved in the stereochemical assignment for a fungal metabolite, cybullol, isolated from one of the birds' nest fungi, Cyathus bulleri. This material was fairly readily shown to be a dimethyldecalindiol and, at the outset of my involvement in the project, the prime problem was its stereochemistry. Since eight of the nine possible 10-methyl-trans-decalols, as well as a few cis-decalols, had been examined in an earlier study, it seemed to be a straightforward project, simply the distinction between A and B below:
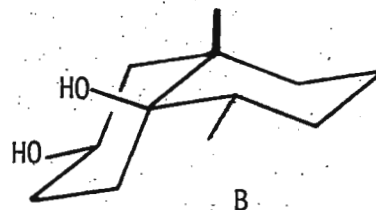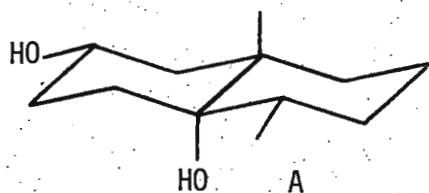
Since 10-methyldecalin itself has a methyl signal at 15.7 ppm and the effects of the equatorial secondary hydroxyl and methyl were not expected to be large, perhaps 1 ppm each. One need only estimate the effect of the tertiary hydroxyl group to arrive at a prediction for the methyl carbon shielding for A and it was originally thought that this effect would be small and possibly slightly shielding. Thus, δ_C for the angular methyl was estimated to be <18 ppm. For B, on the basis of available models, it was estimated that the effects of the secondary hydroxyl and methyl groups would approximately cancel and the tertiary hydroxyl group would shield the C-10 methyl by ca. -6 ppm. This led to a prediction of ~22 ppm. Cybullol exhibited methyl signals at 15.2 and 21.1 ppm and the latter was shown to be the angular methyl absorption by selective decoupling. This result indicated a cis ring junction but degradation of cybullol → geosmin (i.e. reduction of the secondary hydroxyl to -CH$_2$), whose structure had been established by synthesis as a trans-decalin derivative, pointed to the trans stereochemistry for cybullol. Subsequently a number of model compounds was prepared and examined to look at the effect of the 5α hydroxyl group in more detail for trans-fused 10-methyl-decalins and related systems. From these results it is apparent that the antiperiplanar arrangement of the hydroxyl and methyl groups at the ring junction leads to pronounced deshielding of the methyl carbon. Several examples are listed in the

accompanying Table. This effect has also been found for other substituents in steroids and some examples are included in the Table. Apparently the degree of substitution of the carbons bearing the substituents has a marked effect on the direction of the anti-periplanar γ shift since it has been known for some time that in less highly substituted systems the antiperiplanar hydroxyl, for example, <u>shields</u> the γ carbon by a few ppm. At the present time, there seems to be no simple interpretation of these observations but it is an interesting challenge for theoreticians. For stereochemical assignments from ^{13}C spectra, however, it reemphasizes the need for caution and the use of good model compounds before leaping to conclusions drawn from data for new systems.

Sincerely,

J.B. Stothers.

Angular methyl shieldings in some 10-methyl-decalins

Substitution	trans[a]		cis[a]	
	δ_c^{C-10}	$\Delta\delta$	δ_c^{C-10}	$\Delta\delta$
nil	15.7		28.2[b]	
5-OH	20.4	+4.7	22.4	-5.8
4α-Me-5-OH	20.3	+4.6	22.3[c]	-5.9
2α-OH	16.6			
2α, 5-(OH)$_2$	21.0	+4.4		
3-oxo	14.9			
3-oxo-4α-Me-5-OH	20.8	+5.9		
3-oxo-5-OH			21.5	-6.7

C-19 shieldings in some steroids

Cholestanes	Substitution	δ_c^{C-19}	$\Delta\delta$	Ref.
	nil	12.2		
	5α-OH	16.1	+3.9	d
	5α-N$_3$	18.2	+6.0	e
	5α-NH$_2$	17.6	+5.4	e
Cholestan-3-ones	nil	11.5		
	5α-Me	14.2	+2.7	f
	5α-OH	15.8	+4.3	f
	5α-F	15.9	+4.4	f
	5α-CN	19.5	+8.0	f

<u>a</u> Ring junction stereochemistry.

<u>b</u> D.K. Dalling, D.M. Grant and E.G. Paul. JACS, <u>95</u>, 3718 (1973).

<u>c</u> This compound was kindly provided by Prof. J.A. Marshall.

<u>d</u> H. Eggert, C.L. Van Antwerp, N.S. Bhacca and C. Djerassi, JOC, <u>41</u>, 71 (1976).

<u>e</u> Q. Khuong-Huu, G. Lukacs, A. Pancrazi and R. Goutarel , Tet. Letters, 3579 (1972).

<u>f</u> These compounds were kindly supplied by Prof. J. Levisalles.

Monsanto

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

June 22, 1976

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

MAGIC-ANGLE C-13 NMR ANALYSIS OF COAL

Dear Barry,

In collaboration with Vic Bartuska and Gary Maciel (MHPL,
Colorado State University at Fort Collins), we have estab-
lished the practicality of performing cross-polarization
C-13 nmr experiments on coal powders, with 3-kHz mechanical
spinning at the magic angle. Typical spectra of a lignite
and an anthracite are shown in the figure. Magic-angle
spinning removes from the determination of the relative
concentrations of aromatic and aliphatic carbons, any
ambiguity in the spectra arising from the overlap of
chemical shift anisotropies.

These experiments were performed using hollow rotors,
specifications for which have appeared earlier (JCP, 61,
2351 (1974)). The sample volume available in these rotors
is about one-fourth of the effective sample volume that
is realized by filling a 10-mm thin-wall nmr tube to a
height equal to that of the C-13 coil, and is about
one-half that of the total volume of the rotor. Naturally,
when we perform magic-angle spinning experiments on solids
which are not powders, but can be machined, we prefer to
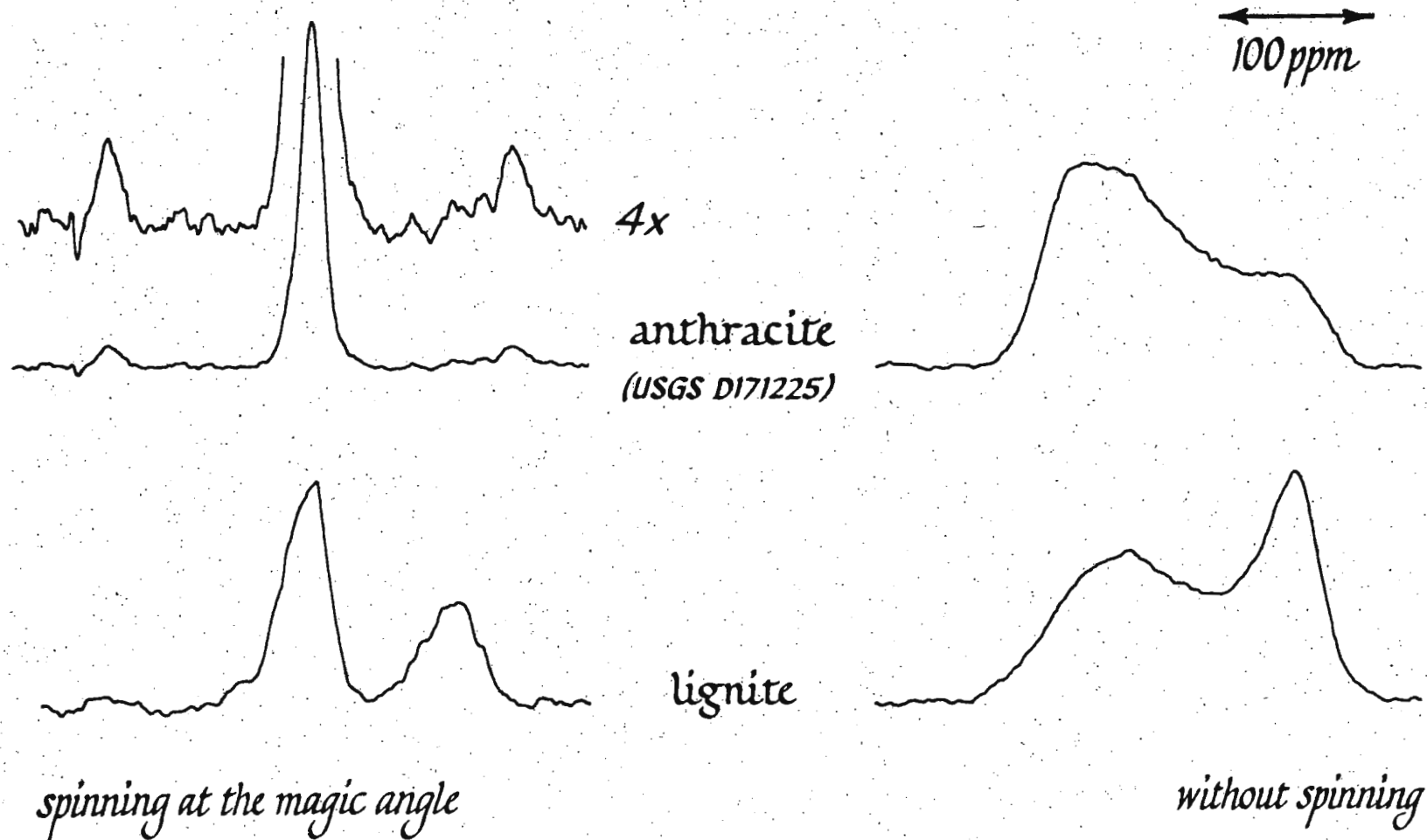use a solid rotor and take advantage of the gain in
sensitivity.

Sincerely,

Jacob Schaefer   E. O. Stejskal

rl

CP C-13 NMR spectra of coals

100 ppm

4x

anthracite
(USGS D171225)

lignite

spinning at the magic angle

without spinning

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

June 29, 1976

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

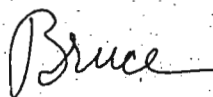Dear Barry:

Ion Pairing with TMS and TMAC Salts

In the May 1976 issue of the TAMU NMR Newsletter, 212-48,
W. A. Thomas illustrates some unusual shifts found for TMS
salts compared to t-BuOH, acetone, or dioxane internal
references with a series of aryl ethanolamine hydrochlorides
in aqueous solutions.

Of the reference compounds employed, only the TMS salts
are negatively charged and may hence undergo ion pairing with
the positively charged aryl ethanolamine hydrochlorides.
Similar ion pairing of negatively charged TMS salts with
cations probably occurs more frequently than recognized. The
ion pairing becomes especially evident when a properly posi-
tioned aryl group provides the anisotropy to produce an evident
chemical shift in the internal TMS reference.

Another ion pairing example was reported by H. Donato,
Jr. and R. B. Martin in J. Am. Chem. Soc., 94, 4129 (1972)
where the positively charged internal reference $(CH_3)_4N^+$
(TMAC) interacted with the trinegatively charged complexes
of tris 2,6-dipicolinate and several lanthanides. No shifts
were observed with bis nitrilotriacetate complexes, also with
three negative charges on the complex, attesting again to
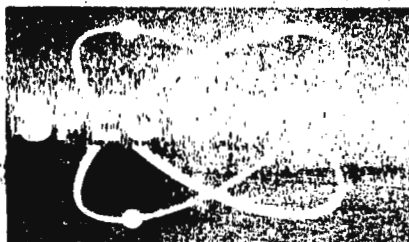the importance of an aryl group to produce an evident shift.

Other examples of ion pairing with charged internal
reference compounds must exist in the literature. Analysis
of the chemical shifts provides an opportunity to determine
equilibrium constants for ion pair formation in such systems.

Sincerely yours,

R. Bruce Martin
Professor of Chemistry

RBM/dhw

ANALYTISCHE MESSTECHNIK

Kern- und Elektronenresonanz • Elektronische Messgeräte

SPECTROSPIN AG, CH-8117 ZÜRICH-FÄLLANDEN
Industriestrasse 26, Telefon (01) 825 48 55, Telex 54850

Ihr Zeichen:
Unser Zeichen:

Reference: Improvement of the signal to noise ratio on a
              270 MHz Spectrometer.
              Reported by H. D. Kipnich, R. Esche, W. Maurer
              in Journal of Magnetic Resonance 22, 161-164 (1976)

Dear Barry,

This paper created quiete some confusion and I would like to comment
on a few points:

1)   We used some years ago the 3N200 Dual-Gate Fet as input stage
      because of its excellent overall performance and the measured
      noise figure of the complete Amplifier turned to be about 3.5 dB.

2)   Since for the past two years we have been using a very low noise
      silicon transistor with a noise figure of typ. 1dB and the mea-
      sured NF of the complete amplifier (including input match and
      second stage) is less than 2dB. This gave a signal to noise im-
      provement of about 20 % which corresponds to the NF-difference
      of about 2dB.

3)   We tried to replace all old version amplifiers in the field and
      if anyone still own's an old one or a defective one we would like
      him to call the nearest Bruker Office and not to write a new paper.

                          With best regards
                          SPECTROSPIN AG

   W. Schittenhelm

Discrete Frequency Artifacts in FT NMR Spectra of High Dynamic Range Samples

There are in the literature excellent discussions of random noise introduced into FT NMR spectra by digitization of either the incoming free induction decay or truncation of the data at intermediate stages of the fourier transformation process (see J.W. Cooper in "Topics in ^{13}C NMR Spectroscopy, Vol. 2," G. Levy ed.). We wish to point out that for high dynamic range samples, dilute H_2O samples of proteins for example, there are also discrete frequency artifacts. These discrete frequency artifacts can be illustrated by simply transforming a mathematically generated decaying sine wave and observing the resulting spectrum at high amplification. The artifacts are indicated with arrows in figure 1a.

The artifacts originate from imperfect representation of the FID by the digitization process. The frequencies at which they occur for a slowly decaying signal can be predicted by a simple qualitative analysis. If there are an integral number of data points per cycle of the incoming signal it is clear that the only errors in representation will be such that they recur with a frequency which is an integral multiple of the FID frequency, i.e., artifacts will appear at higher harmonics. If there are a non integral number of points per cycle of the FID one will have additional errors which will recycle after a sufficient time to have accumulated deviations from a perfect period which is an integral multiple of the dwell time. Artifacts can then appear at $N\Delta F$ where ΔF is the deviation of the true FID frequency from the spectrum's nearest integral frequency and will look like modulation sidebands.

The qualitative analysis of the artifacts suggests a simple means for their elimination, that is, adjusting the transmitter frequency so the most intense peak in the spectrum, the water resonance for example, is exactly in the center. With 4 data points per cycle for single phase detection harmonics will appear only at the edges of the spectrum and ΔF for sidebands will be zero. The elimination of artifacts is illustrated in figure 1b.

J.H. Prestegard, W. Krol and P. Demou
Southern New England High Field NMR Facility
Yale University, Department of Chemistry
New Haven, Connecticut 06520
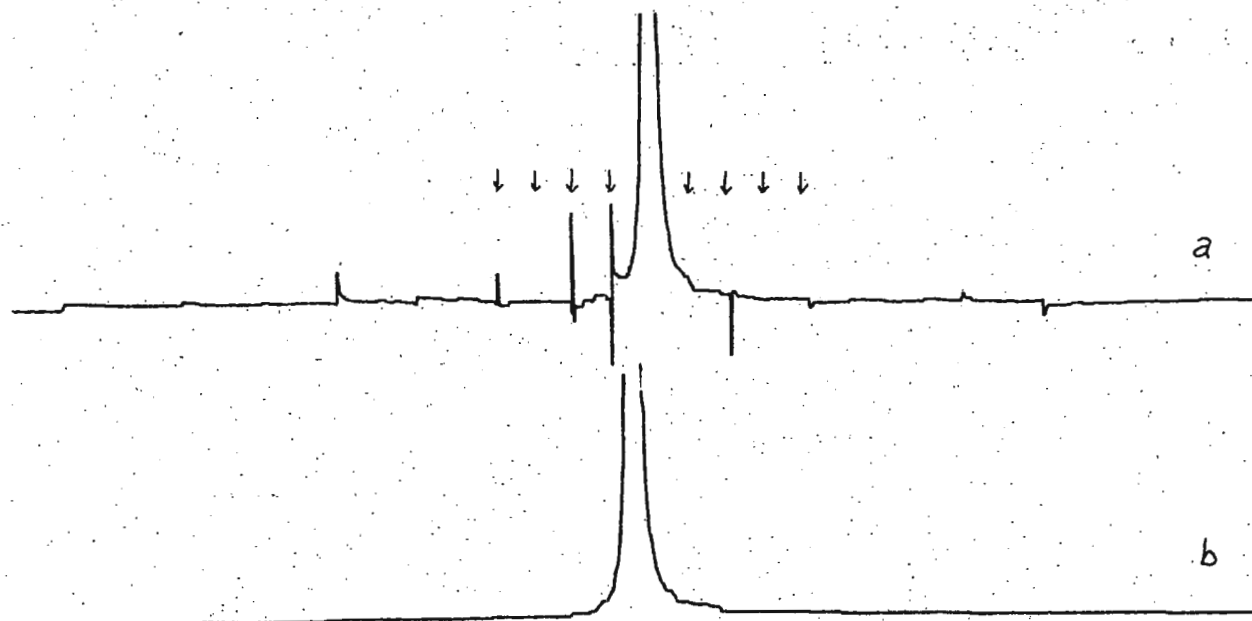
STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94035

STANFORD MAGNETIC RESONANCE LABORATORY

(415) 497-4062
(415) 497-6153

July 2, 1976

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

Dear Dr. Shapiro:

The Stanford Magnetic Resonance Laboratory wishes to announce:

The Second Annual

STANFORD CONFERENCE ON MOLECULAR STRUCTURAL
METHODS IN BIOLOGICAL RESEARCH

October 3 thru 6, 1976

At Stanford University

The Conference will be devoted to recent advances in the solution of biological structural problems by spectroscopic and crystallographic techniques, with a special emphasis on problems of protein and membrane structure and function.

A Partial List of Speakers
Includes:
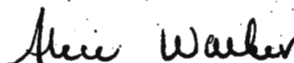
Y. Arata (Tokyo)
R. L. Baldwin (Stanford)
E. Blout (Harvard)
M. Bloom (British Columbia)
F. W. Dahlquist (Oregon)
W. Hubbell (Berkeley)
O. Jardetzky (Stanford)
M. P. Klein (Berkeley)

J. Markley (Purdue)
H. M. McConnell (Stanford)
D. Patel (Bell Labs)
M. Raftery (Cal Tech)
A. Redfield (Brandeis)
E. Reich (Rockefeller)
R. G. Shulman (Bell Labs)
J. S. Waugh (MIT)

The Conference is sponsored by the Biotechnology Resources Branch of the National Institutes of Health. Participation in the conference is limited to 120. A registration fee of $30 is required which covers luncheons on October 4, 5 and 6 and a banquet dinner in the evening of October 6. For further information and registration forms, contact me at the letterhead address (Phone: 415/497-6270).

Sincerely,

Alice Walker

Alice Walker
Conference Coordinator

Hunter College

OF THE CITY UNIVERSITY OF NEW YORK | 695 PARK AVENUE, NEW YORK, N.Y. 10021 | DEPARTMENT OF CHEMISTRY

(212) 360-2351

25 June 1976

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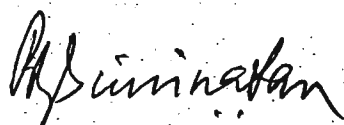Texas A&M University
College Station, Texas 77843

Dear Barry:

Your pink slips are only slightly more ominous than those expected by some of our people during the recent closing (lockout?) here. The latter event is a partial explanation for our tardiness in maintaining our subscription obligation, and with this contribution we request reinstatement.

In the course of our ^{13}C studies of some alkaloids (Org. Magn. Reson., 8, 198 (1976)) we noted changes in the resonance positions of carbon nuclei in the vicinity of amide functions on addition of one equivalent of trifluoroacetic acid (TFA). Since there appeared to be no systematic study of this effect to determine its diagnostic value, we decided to examine some simple amides under these conditions. We have included for comparison the changes in ^{15}N resonance positions. The results for some representative types of amides are given in the attached figure.

As is generally known, the carbonyl resonance moves downfield, reflecting partial protonation or extensive hydrogen bonding. Consistent with this change is the substantial downfield shift of the nitrogen resonance position. In the acyclic compounds N-alkyl carbons also move downfield, those cis to the carbonyl displaying larger changes than those trans. This contrasts with the upfield shifts experienced by the α carbons of amines on protonation. Alkyl groups attached to the carbonyl consistently move upfield. The same trends do not hold in the lactams, and at the moment we are playing with conformational influences as a working hypothesis. In all cases the changes in the resonance positions appear to level off at about four equivalents of TFA.

More detailed results and discussion will be submitted for publication shortly.

P.R. Srinivasan

Sincerely yours,

Robert L. Lichter
Associate Professor
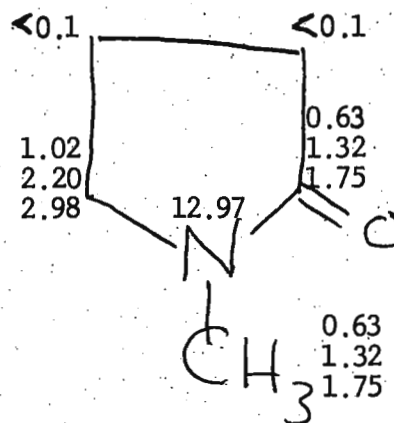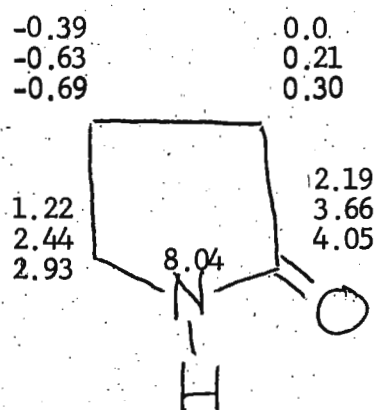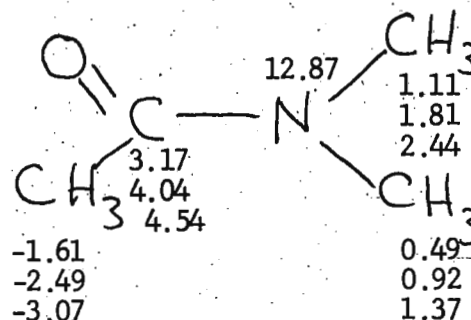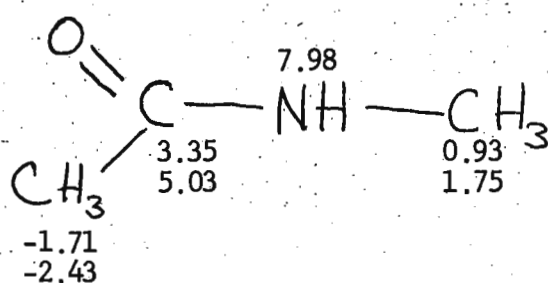
Figure. Chemical shift changes of amides in trifluoroacetic acid. Values are in ppm relative to the resonance positions in the absence of acid. Positive values denote shifts to lower applied field. Carbon spectra were run in CDCl$_3$ containing the amides in ca. 2M concentration, with TMS as internal reference and with successive addition of one, two, and three equivalents of trifluoroacetic acid. Nitrogen spectra were determined on ca. 4M solutions of the amides in CDCl$_3$, with subsequent addition of one equivalent of TFA. Chemical shifts were determined with respect to external [15]NH$_4$Cl in 1M HCl.

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

June 28, 1976

Prof. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77840

Dear Professor Shapiro:

Recently, we have prepared ^{15}N-labeled meso-tetraphenylporphyrin free base as part of a series of NMR studies of ^{15}N-labeled metallo-porphyrins. We have found that variation of temperature has an intriguing effect on the imino proton spectrum of the ^{15}N-labeled compound (Figure 1). At -49°, the resonance of N-H proton (δ -2.82) appears as a doublet with peak seperation of 97 Hz attributing to a typical one bond ^{15}N-H coupling in pyrrole, suggesting that the residence time of the imino proton on a given ^{15}N atom is relatively long in comparison to the nmr time scale. As the temperature is raised, the spectrum changes and finally shows a quintet with a observed coupling constant of 24.2 Hz, resulting from an <u>intramolecular</u> rapid exchange of the imino protons among four ^{15}N atoms. The quintet arises from the random spin orientations of four ^{15}N and the observed average coupling constant of 24.2 Hz ($\sim$ 97 Hz/4) arises from the fact that a jumping proton spends only ¼ of its time spin coupled to a given ^{15}N. We think that the result is a good example of four site exchange process which may be used as a homework problem in the first year NMR course.

Sincerely yours,

Herman J. Yeh, Mitsuo Sato

Isao Morishima

SUBJECT: <u>Example of intramolecular four site exchange</u>

Please give credit to HJY.

20°

9°

-8°

-18°

-29°

-39°

97 Hz

-49°

-2.0   -2.5   -3.0   -3.5

δ, ppm
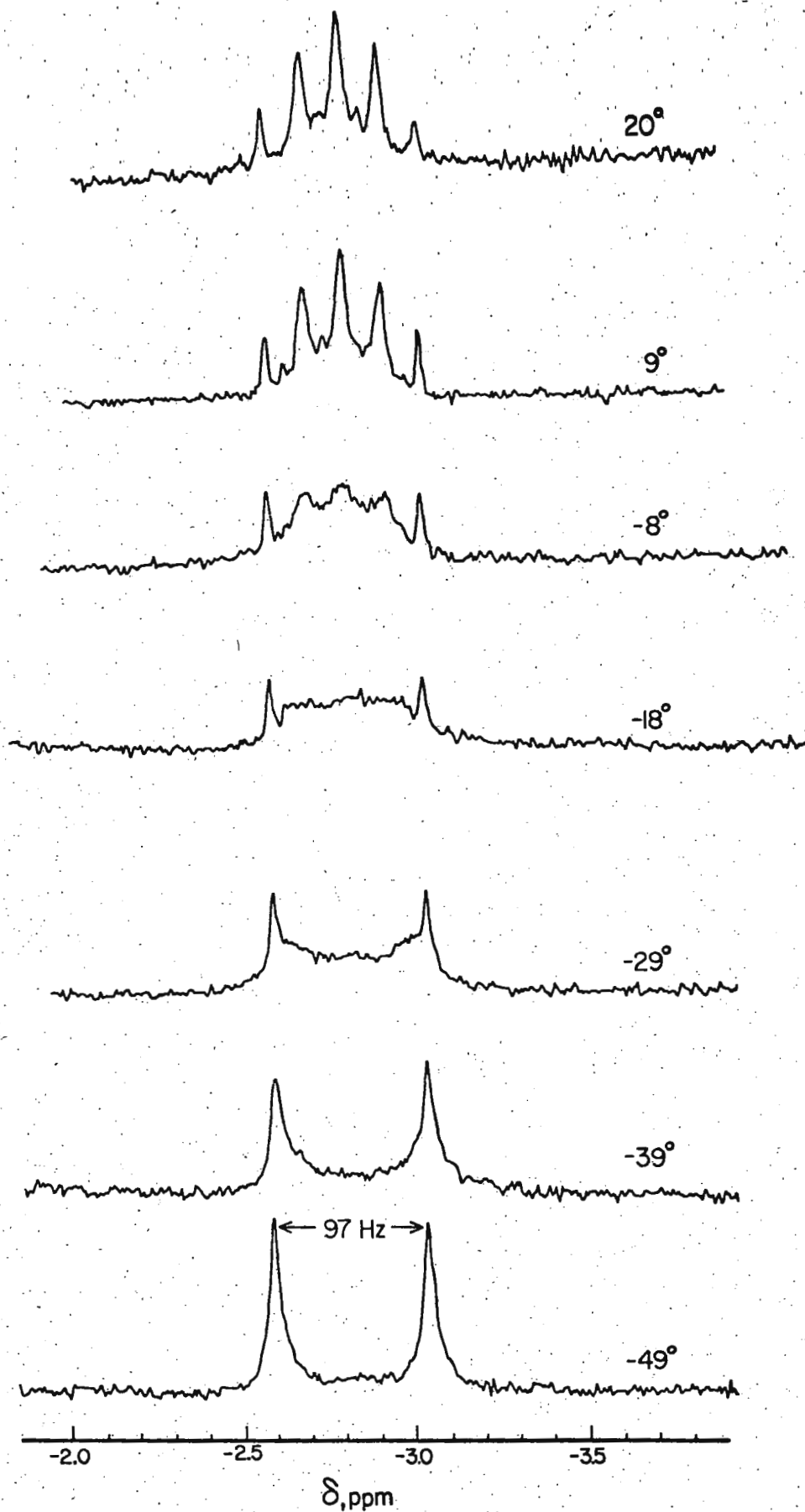
DEPARTMENT OF CHEMISTRY
OTTO MAASS CHEMISTRY BUILDING (514) 392-4467

McGILL UNIVERSITY

June 29, 1976

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

Dear Dr. Shapiro:

Natural Abundance ^{13}C SPT Experiment on a Basic WH-90

We made sign determinations of some two-bond ^{13}C-H coupling constants using the "selective population transfer (SPT)" technique[1] with our Bruker WH-90 equipped with a B-SV broad band proton decoupler.

The decoupler frequency was read to 1 Hz using a Heath-Kit frequency counter (model 113-1103). One minor modification to the decoupler was that the one-turn potentiometer (500 Ω) to vary the power was replaced by a ten-turn pot so that low power levels could be reproduced precisely.

The accompanying figure shows a typical set of SPT ^{13}C spectra obtained, using a 1,2:5,6-di-O-isopropylidene-D-glucose-3rd in CDCl$_3$ (~1 M). The procedure was as follows:

1. The H-2 resonant frequency was determined by observing the maximum collapse of the ^{13}C-2 signal with the lowest possible decoupler power (0.2 W on meter).

2. From the proton NMR spectrum and this frequency, all four H-2 transition frequencies were located.

3. Each of these lines was irradiated, in turn, with much weaker power (no meter deflection) for a short period (0.2 sec.) just prior to every ^{13}C pulse, 500 signals were accumulated for each spectrum.

In this example the sign was seen to be positive (+ 5.6 Hz).

Using the same technique, the signs of other two-bond coupling constants have also been determined:

$$^2J_{C(1)-H(2)} \text{ (in } \beta\text{-D-glucopyranose)} = - 5.7 \text{ Hz}$$

$$^2J_{C(2)-H(3)} \text{ (in methyl } \alpha\text{-D-glucopyranoside)} = - 4.7 \text{ Hz}.$$

These and related stereochemical aspects of two-bond coupling constants will be discussed elsewhere[2,3].

References:

1. e.g. S. Sorensen, R.H. Hansed and H.J. Jakobsen, J. Magn. Reson., <u>14</u>, 243, (1974).
2. J.A. Schwarcz, N. Cyr and A.S. Perlin, Can. J. Chem., <u>53</u>, 1872 (1975).
3. N. Cyr, G.K. Hamer and A.S. Perlin, to be published.

Yours sincerely,

N. Cyr

N. Cyr

NC/ntn

Enclosure

C2

H2

J_{C2-H1}

$J_{1,2} = 3.6\ Hz$

$J_{C2-H2} = 160\ Hz$
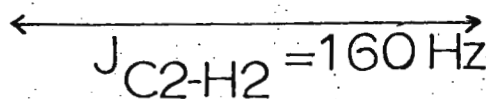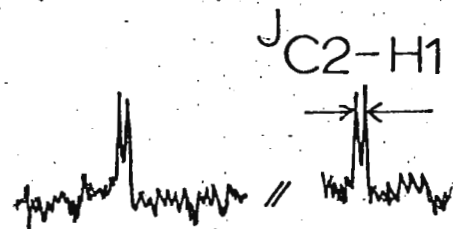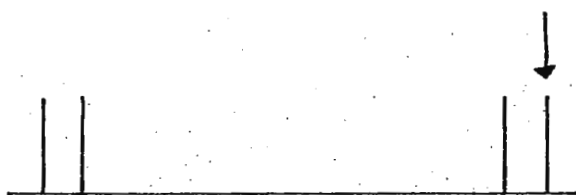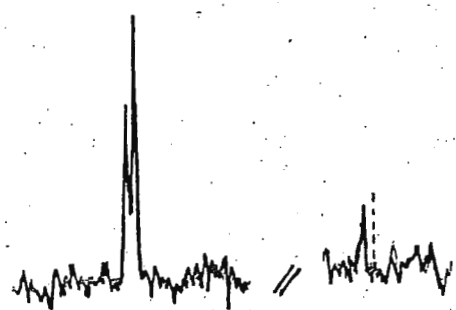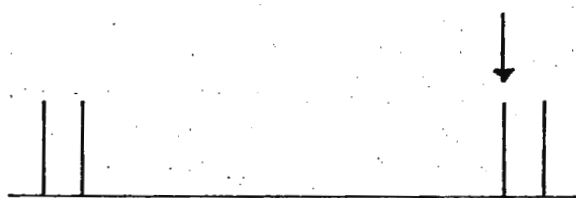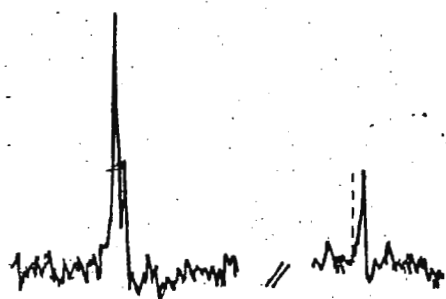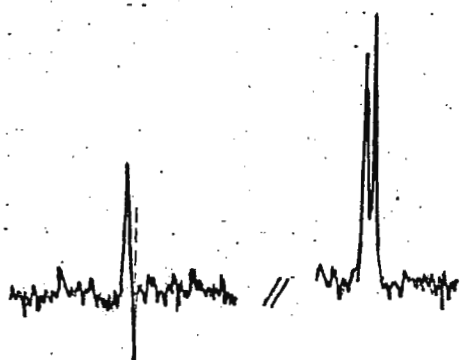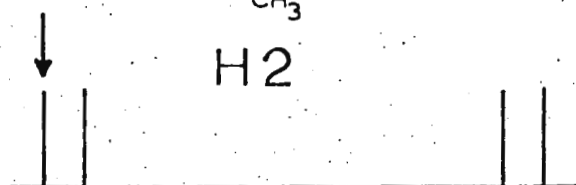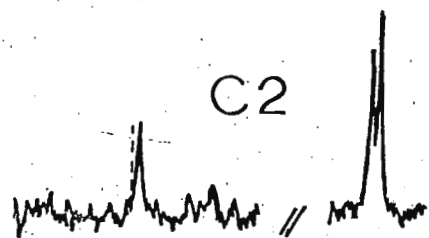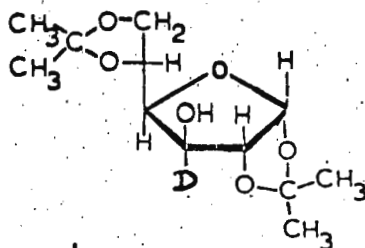
THE UNIVERSITY OF WINNIPEG

WINNIPEG, CANADA   R3B 2E9   5 July, 1976

^{1}H and ^{13}C nmr spectra of nitrobenzene-^{15}N

Dear Barry:

Recently Kelvin Chum and I completed an analysis of the ^{1}H and ^{13}C nmr spectra of nitrobenzene-^{15}N. The observed and simulated ^{1}H spectra are shown in Figures A and B respectively. The RMS deviation between observed and calculated ^{1}H transitions was 0.015 Hz; 119 transitions were assigned. The spectra shown in Figures C and D are observed and simulated double resonance spectra which help confirm the relative signs of the ^{15}N,H coupling constants. The observed ^{15}N,H and ^{15}N,^{13}C coupling constants are given below and compared with those observed for aniline-^{15}N.

	nitrobenzene-^{15}N	aniline-^{15}N (1-3)
$^3J(^{15}N,H)$	−1.921 ± 0.005 Hz	−1.94 Hz
$^4J(^{15}N,H)$	−0.837 ± 0.005 Hz	−0.48 Hz
$^5J(^{15}N,H)$	−0.303 ± 0.008 Hz	0.0 Hz
$^1J(^{15}N,^{13}C)$	−14.6 ± 0.1 Hz	−11.47 Hz
$^2J(^{15}N,^{13}C)$	±1.7 ± 0.1 Hz	−2.68 Hz
$^3J(^{15}N,^{13}C)$	±2.5 ± 0.1 Hz	−1.29 Hz
$^4J(^{15}N,^{13}C)$	±0.7 ± 0.1 Hz	0.27 Hz

The observed coupling constants (Fermi contact contribution) have been compared with those calculated using FPT and semi-empirical MO theory at the INDO level of approximation. INDO predicts $^1J(^{15}N,^{13}C)$ in nitrobenzene and aniline to be −29.8 Hz and −16.3 Hz respectively.

I am presently writing a review for "Annual Reports on NMR Spectroscopy" on ^{13}C-X nuclear spin-spin coupling constants where X is a first row element. I would appreciate any preprints of papers on this topic. Thank you.


References

1) R. E. Wasylishen. Can. J. Chem. 54, 833 (1976).
2) M. Hansen and H. J. Jakobsen. Acta Chem. Scand. 26, 2151 (1972).
3) R. E. Wasylishen, J. B. Rowbothan, L. Ernst, and T. Schaefer. Can. J. Chem. 50, 2575 (1975).

Yours sincerely,

Rod

Rod Wasylishen

$^{15}NO_2$

H_o H_m

H H

H_p

$H_m \rightarrow$

$H_p \rightarrow$

$H_o \rightarrow$

5 Hz

(A)

(B)

(C)

(D)
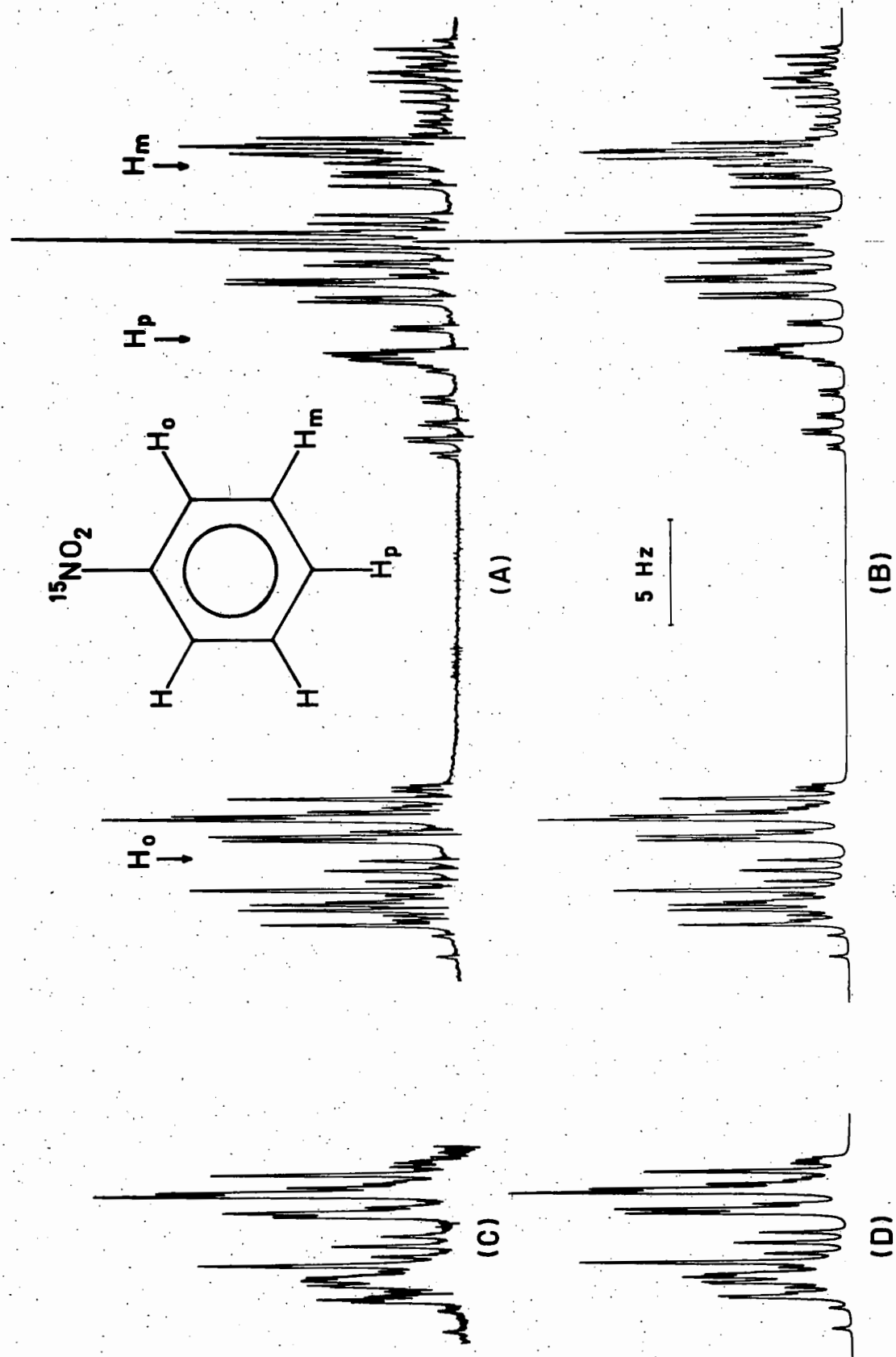
PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING
WEST LAFAYETTE, INDIANA 47907

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

July 6, 1976

Dear Barry: Select - A - Spin

The word is out - the periodic table has spins;[1] and they are accessible to most multinuclei spectrometers. In our search for things bright and beautiful we have often needed a nuclear table arranged according to frequency. Using a series of controlled scissor pulses, Kathy has transformed the Lee and Anderson table[2] into this new dimension. Fear prompted us to restrict ourselves to the non-radioactive nuclei. Frequencies for 23.5 Kg field should act as an appropriate page filler.

1. R. K. Harris, Chem. Soc. Revs., 5, 1 (1976). 2. E. D. Becker, "High Resolution NMR", Academic Press, New York, 1972, Appendix A.

Yours sincerely,

Kathy Ley   John Grutzner

El	A	Freq	El	A	Freq	El	A	Freq
H	3	106.663	Cd	111	21.204	Mo	95	6.515
H	1	100.000	Pb	207	20.922	Zn	67	6.255
F	19	94.077	Ho	165	20.505	Mg	25	6.119
He	3	76.177	I	127	20.007	Cr	53	5.652
Tl	205	57.708	Si	29	19.865	Ti	49	5.638
Tl	203	57.150	Se	77	19.067	Ti	47	5.637
P	31	40.481	Hg	199	17.827	Nd	143	5.437
Li	7	38.862	Yb	171	17.613	Se	79	5.214
Sn	119	37.272	As	75	17.127	Ru	101	4.932
Sn	117	35.626	H	2	15.351	Y	89	4.899
Rb	87	32.720	Li	6	14.716	Yb	173	4.852
Sn	115	32.699	La	139	14.126	Dy	163	4.697
B	11	32.084	Be	9	14.053	Gd	157	4.697
Te	125	31.591	O	17	13.557	K	39	4.666
Ga	71	30.496	Cs	133	13.117	Ag	109	4.652
Pr	141	29.359	Sb	123	12.959	Pd	105	4.580
Cu	65	28.394	Ta	181	11.969	Sr	87	4.334
Xe	129	27.661	Lu	175	11.415	W	183	4.161
Br	81	27.006	Ba	137	11.113	Sm	147	4.134
Cu	63	26.506	Eu	153	10.952	Ag	107	4.047
Na	23	26.452	B	10	10.746	Kr	83	3.847
V	51	26.282	N	15	10.133	Gd	155	3.758
Te	123	26.212	V	50	9.970	Ge	73	3.488
Al	27	26.057	Ba	135	9.934	Ru	99	3.382
C	13	25.144	Cl	35	9.798	Nd	145	3.335
Br	79	25.054	Rb	85	9.655	Dy	161	3.288
Eu	151	24.800	Zr	91	9.330	Sm	149	3.288
Mn	55	24.664	Ni	61	8.936	Fe	57	3.231
Nb	93	24.443	Tm	169	8.268	Rh	103	3.148
Sc	45	24.293	Xe	131	8.200	Hf	177	3.053
Ga	69	24.004	Cl	37	8.155	Er	167	2.889
Sb	121	23.931	Ne	21	7.894	K	41	2.561
Co	59	23.614	Os	189	7.759	Os	187	2.303
Tb	159	22.689	S	33	7.670	Hf	179	1.879
Re	185	22.514	N	14	7.224	Ir	193	1.871
Cd	113	22.184	Ca	43	6.728	Ir	191	1.719
In	113	21.867	Mo	97	6.652	Au	197	1.713
Pt	195	21.498	Hg	201	6.560			

Isotope				NMR frequency (MHz for a 10-kG field)	Natural abundance (%)	Relative sensitivity at constant field	Magnetic moment μ (multiples of the nuclear magneton $eh/4\pi Mc$)	Electric quadrupole moment Q (multiples of barns (10^{-24} cm²))
Z	Element	A	Spin I					
79	Au	197	3/2	0.729188	100	2.51×10^{-5}	0.143489	0.59
77	Ir	191	3/2	0.7318	37.3	2.53×10^{-5}	0.1440	1.5
77	Ir	193	3/2	0.7968	62.7	3.27×10^{-5}	0.1568	1.5
72	Hf	179	9/2	0.80	13.75	2.16×10^{-4}	−0.47	3
76	Os	187	1/2	0.98059	1.64	1.22×10^{-5}	0.06432	—
19	K	41	3/2	1.0905	6.88	8.40×10^{-5}	0.21459	
68	Er	167	7/2	1.23	22.94	5.07×10^{-4}	−0.565	2.83
72	Hf	177	7/2	1.3	18.50	6.38×10^{-4}	0.61	−3
45	Rh	103	1/2	1.3401	100	3.11×10^{-5}	−0.08790	—
26	Fe	57	1/2	1.3758	2.19	3.37×10^{-5}	0.09024	—
62	Sm	149	7/2	1.40	13.83	7.47×10^{-4}	−0.643	6.0×10^{-1}
66	Dy	161	5/2	1.4	18.88	4.17×10^{-4}	−0.46	1.4
60	Nd	145	7/2	1.42	8.30	7.86×10^{-4}	−0.654	−0.25
44	Ru	99	5/2	1.44	12.72	1.95×10^{-4}	−0.284	
32	Ge	73	9/2	1.4852	7.76	1.40×10^{-3}	−0.87679	−0.2
64	Gd	155	3/2	1.6	14.73	2.79×10^{-4}	−0.32	1.6
36	Kr	83	9/2	1.638	11.55	1.88×10^{-3}	−0.9671	0.15
47	Ag	107	1/2	1.7229	51.82	6.62×10^{-5}	−0.11301	—
62	Sm	147	7/2	1.76	14.97	1.48×10^{-3}	−0.807	−0.208
74	W	183	1/2	1.7716	14.40	7.20×10^{-5}	0.116205	—
38	Sr	87	9/2	1.8452	7.02	2.69×10^{-3}	−1.0893	0.2
46	Pd	105	5/2	1.95	22.23	1.12×10^{-3}	−0.639	
47	Ag	109	1/2	1.9807	48.18	1.01×10^{-4}	−0.12992	—
19	K	39	3/2	1.9868	93.10	5.08×10^{-4}	0.39097	0.11
64	Gd	157	3/2	2.0	15.68	5.44×10^{-4}	−0.40	2
66	Dy	163	5/2	2.0	24.97	1.12×10^{-3}	0.64	1.6
70	Yb	173	5/2	2.0659	16.13	1.33×10^{-3}	−0.67755	2.8
39	Y	89	1/2	2.0859	100	1.18×10^{-4}	−0.13682	
44	Ru	101	5/2	2.1	17.07	1.41×10^{-3}	−0.69	
34	Se	79	7/2	2.22	—	2.98×10^{-3}	−1.02	0.9
60	Nd	143	7/2	2.315	12.17	3.38×10^{-3}	−1.063	−0.48
22	Ti	47	5/2	2.4000	7.28	2.09×10^{-3}	−0.78710	
22	Ti	49	7/2	2.4005	5.51	3.76×10^{-3}	−1.1022	
24	Cr	53	3/2	2.4065	9.55	9.03×10^{-4}	−0.47354	
12	Mg	25	5/2	2.6054	10.13	2.67×10^{-3}	−0.85449	
30	Zn	67	5/2	2.663	4.11	2.85×10^{-3}	0.8733	0.15
42	Mo	95	5/2	2.774	15.72	3.23×10^{-3}	−0.9097	0.12
80	Hg	201	3/2	2.8099	13.22	1.44×10^{-3}	−0.55293	0.50
42	Mo	97	5/2	2.832	9.46	3.43×10^{-3}	−0.9289	1.1
20	Ca	43	7/2	2.8646	0.145	6.40×10^{-3}	−1.3153	
7	N	14	1	3.0756	99.63	1.01×10^{-3}	0.40347	7.1×10^{-2}
16	S	33	3/2	3.2654	0.76	2.26×10^{-3}	0.64257	-6.4×10^{-2}
76	Os	189	3/2	3.3034	16.1	2.34×10^{-3}	0.65004	0.8
10	Ne	21	3/2	3.3611	0.257	2.50×10^{-3}	−0.66140	
17	Cl	37	3/2	3.472	24.47	2.71×10^{-3}	0.6833	-6.21×10^{-2}
54	Xe	131	3/2	3.4911	21.18	2.76×10^{-3}	0.68697	−0.12
69	Tm	169	1/2	3.52	100	5.66×10^{-4}	−0.231	—
28	Ni	61	3/2	3.8047	1.19	3.57×10^{-3}	−0.74868	
40	Zr	91	5/2	3.97249	11.23	9.48×10^{-3}	−1.30284	
37	Rb	85	5/2	4.1108	72.15	1.05×10^{-2}	1.3482	0.27
17	Cl	35	3/2	4.1717	75.53	4.70×10^{-3}	0.82091	-7.89×10^{-2}
56	Ba	135	3/2	4.2296	6.59	4.90×10^{-3}	0.83229	0.25
23	V	50	6	4.2450	0.24	5.55×10^{-2}	3.3413	
7	N	15	1/2	4.3142	0.37	1.04×10^{-3}	−0.28298	—
5	B	10	3	4.5754	19.58	1.99×10^{-2}	1.8007	7.4×10^{-2}
63	Eu	153	5/2	4.6627	52.18	1.53×10^{-2}	1.5292	2.9
56	Ba	137	3/2	4.7315	11.32	6.86×10^{-3}	0.93107	0.2
71	Lu	175	7/2	4.86	97.41	3.12×10^{-2}	2.23	5.68

|	Isotope		Spin I	NMR frequency (MHz for a 10-kG field)	Natural abundance (%)	Relative sensitivity at constant field	Magnetic moment μ (multiples of the nuclear magneton $eh/4\pi Mc$)	Electric quadrupole moment Q (multiples of barns (10^{-24} cm²))
Z	Element	A						
73	Ta	181	7/2	5.096	99.988	3.60×10^{-2}	2.340	3
51	Sb	123	7/2	5.5176	42.75	4.57×10^{-2}	2.5334	−0.7
55	Cs	133	7/2	5.58469	100	4.74×10^{-2}	2.56422	-3×10^{-3}
8	O	17	5/2	5.772	3.7×10^{-2}	2.91×10^{-2}	−1.8930	-2.6×10^{-2}
4	Be	9	3/2	5.9834	100	1.39×10^{-2}	−1.1774	5.2×10^{-2}
57	La	139	7/2	6.0144	99.911	5.92×10^{-2}	2.7615	0.21
3	Li	6	1	6.2653	7.42	8.50×10^{-3}	0.82192	6.9×10^{-4}
1	H	2	1	6.53566	1.5×10^{-2}	9.65×10^{-3}	0.857387	2.73×10^{-3}
33	As	75	3/2	7.2919	100	2.51×10^{-2}	1.4349	0.3
70	Yb	171	1/2	7.4990	14.31	5.46×10^{-3}	0.49188	—
80	Hg	199	1/2	7.59012	16.84	5.67×10^{-3}	0.497859	—
34	Se	77	1/2	8.118	7.58	6.93×10^{-3}	0.5325	—
14	Si	29	1/2	8.4578	4.70	7.84×10^{-3}	−0.55477	—
53	I	127	5/2	8.5183	100	9.34×10^{-2}	2.7937	−0.69
67	Ho	165	7/2	8.73	100	0.181	4.01	2.82
82	Pb	207	1/2	8.90771	22.6	9.16×10^{-3}	0.584284	
48	Cd	111	1/2	9.028	12.75	9.54×10^{-3}	−0.5922	
78	Pt	195	1/2	9.153	33.8	9.94×10^{-3}	0.6004	—
49	In	113	9/2	9.3099	4.28	0.345	5.4960	1.14
48	Cd	113	1/2	9.445	12.26	1.09×10^{-2}	−0.6195	—
75	Re	185	5/2	9.5855	37.07	0.133	3.1437	2.8
65	Tb	159	3/2	9.66	100	5.83×10^{-2}	1.90	1.3
27	Co	59	7/2	10.054	100	0.277	4.6163	0.40
51	Sb	121	5/2	10.189	57.25	0.160	3.3415	−0.5
31	Ga	69	3/2	10.22	60.4	6.91×10^{-2}	2.011	0.178
21	Sc	45	7/2	10.343	100	0.301	4.7492	−0.22
41	Nb	93	9/2	10.407	100	0.482	6.1435	−0.2
25	Mn	55	5/2	10.501	100	0.175	3.444	0.55
63	Eu	151	5/2	10.559	47.82	0.178	3.4630	1.16
35	Br	79	3/2	10.667	50.54	7.86×10^{-2}	2.0990	0.33
6	C	13	1/2	10.7054	1.108	1.59×10^{-2}	0.702199	—
13	Al	27	5/2	11.094	100	0.206	3.6385	0.149
52	Te	123	1/2	11.16	0.87	1.8×10^{-2}	−0.7319	—
23	V	51	7/2	11.19	99.76	0.382	5.139	-4×10^{-7}
11	Na	23	3/2	11.262	100	9.25×10^{-2}	2.2161	0.14–0.15
29	Cu	63	3/2	11.285	69.09	9.31×10^{-2}	2.2206	−0.16
35	Br	81	3/2	11.498	49.46	9.85×10^{-2}	2.2626	0.28
54	Xe	129	1/2	11.777	26.44	2.12×10^{-2}	−0.77247	—
29	Cu	65	3/2	12.089	30.91	0.114	2.3789	−0.15
59	Pr	141	5/2	12.5	100	0.293	4.09	-5.9×10^{-2}
31	Ga	71	3/2	12.984	39.6	0.142	2.5549	0.112
52	Te	125	1/2	13.45	6.99	3.15×10^{-2}	−0.8824	—
5	B	11	3/2	13.660	80.42	0.165	2.6880	3.55×10^{-2}
50	Sn	115	1/2	13.922	0.35	3.50×10^{-2}	−0.91320	—
37	Rb	87	3/2	13.931	27.85	0.175	2.7414	0.13
50	Sn	117	1/2	15.168	7.61	4.52×10^{-2}	−0.99490	—
50	Sn	119	1/2	15.869	8.58	5.18×10^{-2}	−1.0409	—
3	Li	7	3/2	16.546	92.58	0.293	3.2560	-3×10^{-2}
15	P	31	1/2	17.235	100	6.63×10^{-2}	1.1305	—
81	Tl	203	1/2	24.332	29.50	0.187	1.5960	—
81	Tl	205	1/2	24.570	70.50	0.192	1.6116	—
2	He	3	1/2	32.433	1.3×10^{-4}	0.442	−2.1274	—
9	F	19	1/2	40.0541	100	0.833	2.62727	—
1	H	1	1/2	42.5759	99.985	1.00	2.79268	—
1	H	3*	1/2	45.4129	—	1.21	2.97877	—
Free electron with			1/2	2.80246×10^{4}	—	2.84×10^{8}	−1836.09	

New 18-mm Probe for the XL-100
^{13}C Spectra 10 Times Faster

Now Varian XL-100 users can run natural abundance ^{13}C spectra at millimolar concentrations. Varian's new V-4418 Variable-Temperature Probe accommodates 18-millimeter sample tubes and boosts sensitivity to over three times that of the standard 12-mm probe. Compare the two spectra of 10 mM sucrose — clearly this new probe could extend the application of ^{13}C NMR to entirely new areas of chemical research.

The V-4418 is Varian's latest offering to the scientist who needs ^{13}C spectra of samples of limited solubility or limited molarity; or who studies certain equilibria and requires low concentration; or who works with relaxation properties that are best studied at low concentration. The V-4418 lets him use samples less concentrated by a factor of 3, or reduces the time required for an experiment by a factor of 10 — with results second to none.

Not only is the **absolute sensitivity** of the V-4418 Probe outstanding, it also offers excellent **sensitivity per milliliter** of solution, an important asset if you study scarce or expensive (most often both) macromolecules. The Probe develops its full sensitivity potential with 6 milliliters, a volume only three times that required with the standard 12-mm probe!

And that's not all. When the V-4418 Probe is used together with the recently introduced single-sideband filter, overall sensitivity of the XL-100 increases by a factor of 5. Or, in terms of time savings, these combined capabilities reduce a formerly 24-hour experiment to a routine 1-hour run.
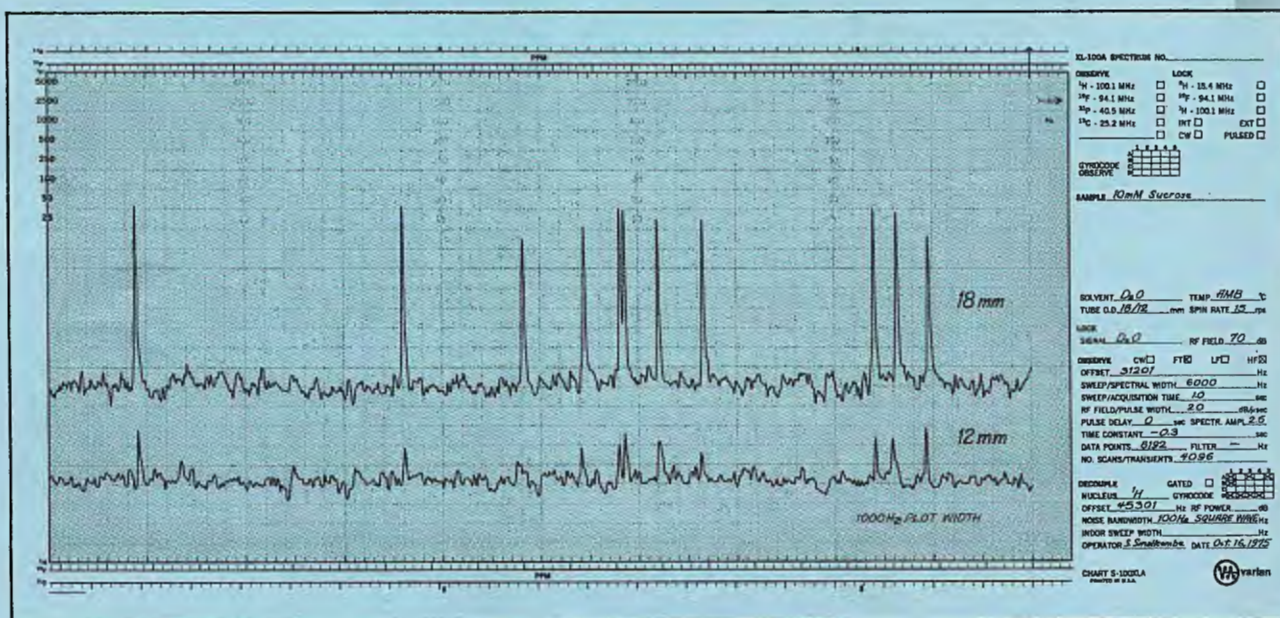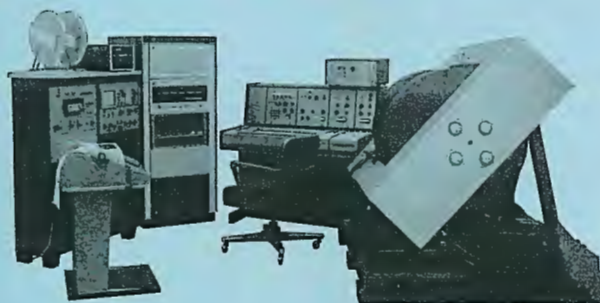
Compare these two broadband proton-decoupled carbon spectra of 10 mM sucrose in D_2O, one using an 18-mm sample, the other the standard 12-mm sample! Data were accumulated for 4096 transients, with a one-second 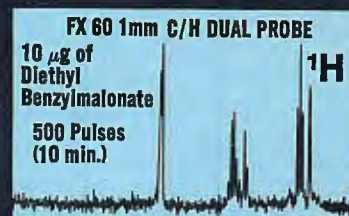acquisition time and a 90° pulse.