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NMR NEWSLETTER

BRIAN SYKES

NO. 323

AUGUST 1985

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FORTHCOMING NMR MEETINGS (Additional listings are solicited)

Second International Symposium on the Synthesis and Applications of Isotopically Labeled Compounds - September 3-6, 1985; Kansas City, Missouri; Dr. Donald Wilk, Symposium Coordinator, University of Missouri-Kansas City, School of Pharmacy, 5100 Rockhill Road, Kansas City, MO 64110-2499.

FACSS (Federation of Analytical Chemistry and Spectroscopy Societies) - September 29 - October 4, 1985; 12th Annual Meeting; Philadelphia, PA; Included are eight sessions on NMR. Contact A.H. Ullman, Procter & Gamble Co., 6250 Center Hill Rd., Cincinnati, OH 45242, 513-659-6445.

J.H. Goldstein Retirement Symposium - October 25, 1985; Emory University, Atlanta, Georgia; see page 23.

1985 Eastern Analytical Symposium - November 19-22, 1985; Penta Hotel, New York; see Newsletter No. 321, pages 17-18.

British Radiofrequency Spectroscopy Group Meeting - April 9-11, 1986; Oxford University, Oxford OX1 3QR, England; see page 23.

27th ENC - April 13-17, 1986; Baltimore Hilton; Chairman: R.G. Bryant, Department of Radiology, University of Rochester Medical Center, 601 Elmwood Avenue, Rochester, NY 14642, 716-275-5541; see page 31.

U.S.-Latin American Workshop on Recent Developments in Organic and Bioorganic NMR - July 7-11, 1986; Campinas, Brazil; see page 59.

Suggestions for other types of articles, news items, etc., to appear in the Newsletter would be welcomed - please make your wishes known.

Have you received and processed your 1985-86 subscription invoice? Your cooperation is appreciated.

All Newsletter Correspondence Should be Addressed to:

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

DEADLINE DATES

No. 325 (October) --- 27 September 1985

No. 326 (November) ---- 25 October 1985

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Dear Professor Shapiro,

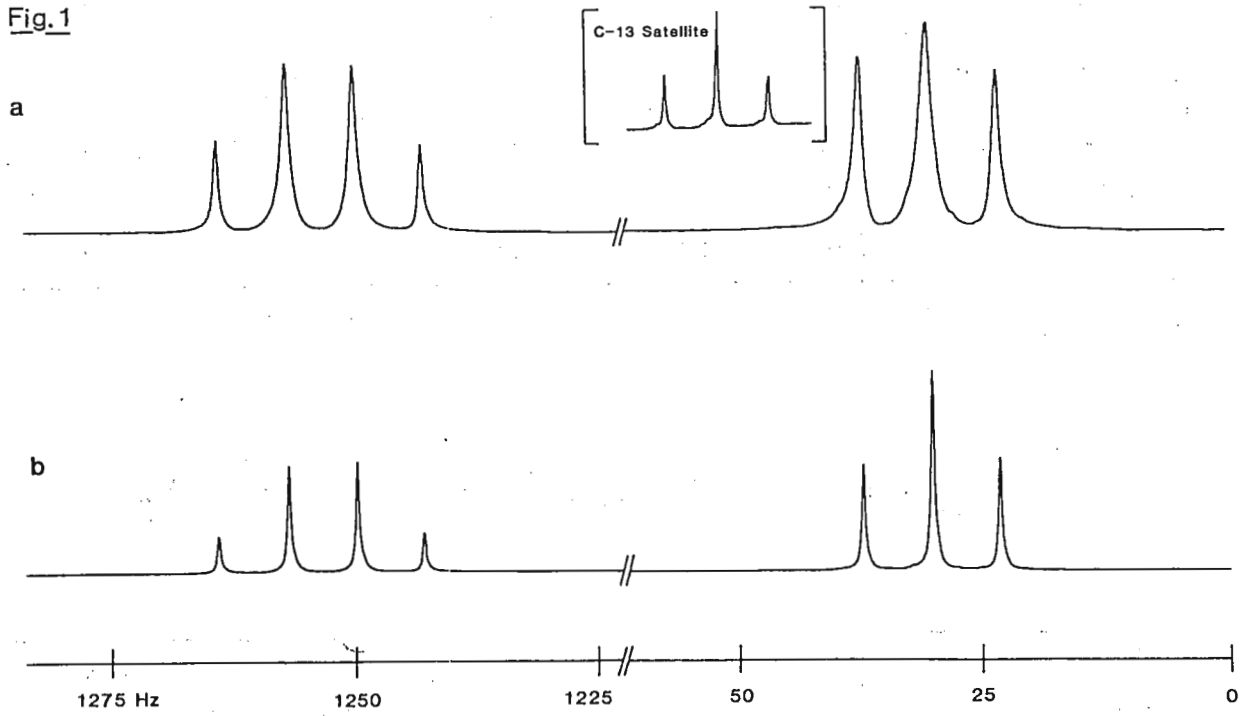
RADIATION DAMPING EFFECTS IN HIGH-FIELD NMR

Although the phenomenon of radiation damping has been known since the earliest days of NMR it can still cause the occasional surprise. Damping effects increase with the intensity of the signal involved and are therefore more prevalent with high-field spectrometers; they can also have different effects on the various components of a multi-line spectrum. A text-book example was observed at 500 MHz here when a 35 mol% ethanol/D_2O sample was prepared with the intention of testing some two-dimensional experiments. Instead of the expected well-resolved multiplets with binomial peak heights the spectrum shown in figure 1a was obtained. Clearly, the relative peak-heights within each multiplet and those between the two multiplets are far from binomial. A closer inspection shows that the line-shapes are also distorted with, for example, the outer lines of the triplet having a noticeably asymmetric shape and a somewhate smaller line-width than the central component. Radiation damping was conclusively identified as the culprit by the following observations:

(i) The carbon-13 satellite signals in the spectrum of figure 1a do have the anticipated binomial peak-heights and have lines which are narrower, more symmetric, and of nearly identical shape: one satellite is shown inset in figure 1.

(ii) If a spectrum is obtained with the probe grossly detuned the main ethanol signals also have narrow lines and the "correct" relative intensities, as shown in figure 1b.

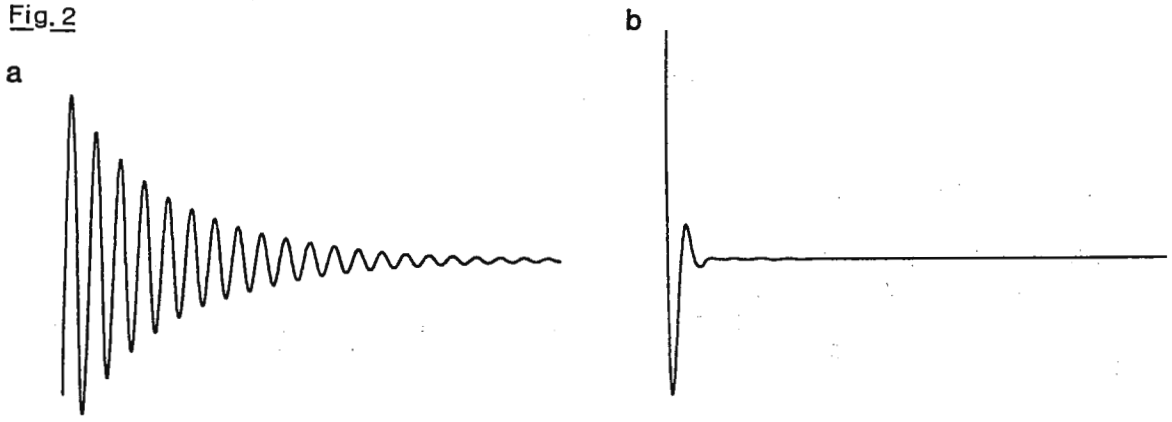
Fig.1



Classically, for a single resonance radiation damping can be attributed to an oscillating magnetic field which tends to rotate the magnetization vector towards the equilibrium position. The source of this field is the circulating current induced in the probe's tuned circuit by the transverse component of the magnetization vector itself. De-tuning the probe reduces the magnitude of the current and so also reduces the damping (hand-in-hand with the signal-to-noise ratio): this is the traditional test for radiation damping. Even when the probe is properly tuned the carbon-13 satellite signals are not materially affected by radiation damping as these signals are too weak to operate significant reaction fields themselves and the fields due to the parent peaks, although much more intense, are off-resonance by an amount which is large relative to their magnitude.

The reduction in damping which is obtained by detuning the probe can be put to good use for shimming samples which have an intense solvent peak, a situation that arises whenever substances are to be studied in aqueous solution. Optimizing the field homogeneity by observing a free induction decay is easier and quicker than looking at a deuterium lock level but is only practicable if the observed decay is dominated by magnetic field inhomogeneity. For many samples which have a strong solvent resonance this can be ensured simply by detuning the probe to the point where radiation damping is insignificant. The solvent signal can then be used for shimming and once the required homogeneity has been obtained the probe can be returned for maximum sensitivity. An extreme but not uncommon example of the effects of probe-tuning on a 90% H_2O signal is shown in figure 2: the FID shown is part a of the figure was obtained after shimming with the probe greatly detuned and corresponds to a line-width of 0.9Hz, whereas once the probe is returned the signal decays much faster (figure 2b) and the line-width increases to nearly 15Hz.

Fig. 2



Regards,

Tom Frenkiel.

T. Frenkiel

ABBOTT

Abbott Laboratories
North Chicago, Illinois 60064

June 4, 1985

Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843-3255

Dear Professor Shapiro:

COSYER

Occasionally, excessive t_1 noise, due for example to a solvent peak, obliterates the crosspeaks at (Ω_A, Ω_B) in a pure phase 2D-COSY experiment. In this case better digital resolution is needed in Ω_1 in order to measure coupling constants on resonance B accurately from the (Ω_B, Ω_A) crosspeak. There is a simple way to do this without having to accumulate any more t_1 slices. It involves a modified COSY experiment, which we have dubbed COSYER (COSY with Expanded Ω_1 scalar coupling Resolution). The pulse sequence is:

$$90\text{-}t_1\text{-}(\frac{t_1}{2}\text{-}180\text{-}\frac{t_1}{2})\ 90\text{-}t_2$$

An additional period, $(\frac{t_1}{2}\text{-}180\text{-}\frac{t_1}{2})$, is included which varies with t_1. This period refocusses the chemical shift but not the scalar coupling. Hence when processed, the experiment has an apparent doubling of all coupling constants in Ω_1 without affecting the chemical shift dispersion. Systematic errors in coupling constant measurement in the Ω_1 dimension are thus decreased by a factor of two.

In the Figure a normal COSY experiment (A) is compared to a COSYER experiment (B). Five hundred twelve t_1 values were accumulated. The final data matrix after processing was 1K by 1K. The doubling of the apparent scalar coupling constant in Ω_1 is quite obvious in the COSYER spectra.

The major shortcoming of the experiment is a decrease in signal-to-noise due to the increased length of the modified t_1 period. This tends to negate any signal-to-noise improvement one might expect from reduced cancellation of antiphase components for crosspeaks with small coupling constants.

Sincerely yours,

S. Fesik

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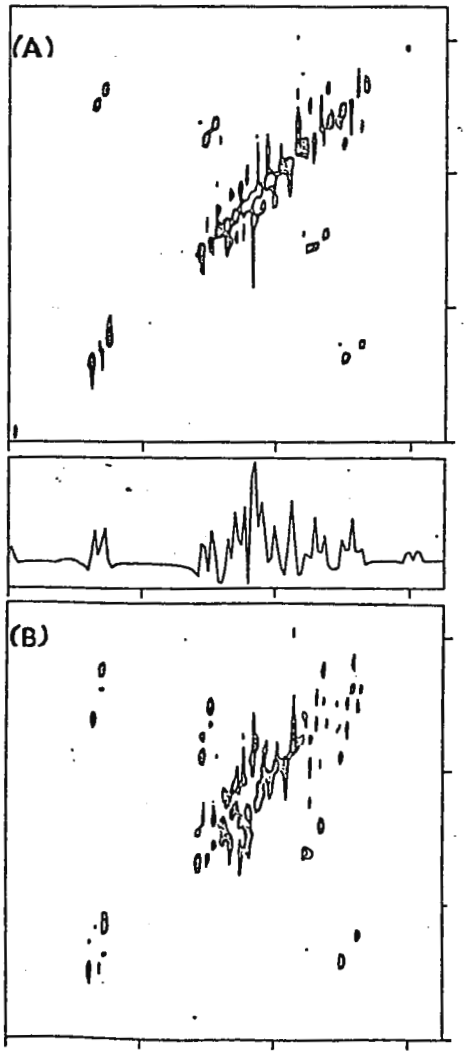

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DEPARTMENT OF CHEMISTRY

10 July 1985

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

Sensitivity of Two-Dimensional NMR as a Function of Field Strength

Dear Barry:

While working on a budget justification for a grant proposal I decided to include a description of the sensitivity of two-dimensional NMR as a function of field strength. Since I did not remember ever seeing such a calculation I decided doing it was easier than going to the library. If we consider the case of going from 200 to 400 MHz with a two-fold gain in intrinsic sensitivity (in a one-pulse experiment) then the total time for a 400 experiment will consist of one-fourth as many transients for each increment of t_1 but twice as many increments of t_1 for equal resolution. Thus, the sensitivity is given by:

sensitivity= ((ratio of intrinsic sensitivity)^2/ratio of B fields)$^{\frac{1}{2}}$

Since the intrinsic sensitivity is known to increase with the 3/2 power of the field the theoretical limit for increase in sensitivity of two-dimensional NMR with field strength is merely linear. Since the increases in intrinsic sensitivity are never quite up to the theoretical limit the actual gains in two-dimensional NMR sensitivity tend to be about $B^{\frac{1}{2}}$. Nevertheless, the dispersion of the two-dimensional data does go as B^2.

Sincerely,

Philip Bolton

Philip Bolton

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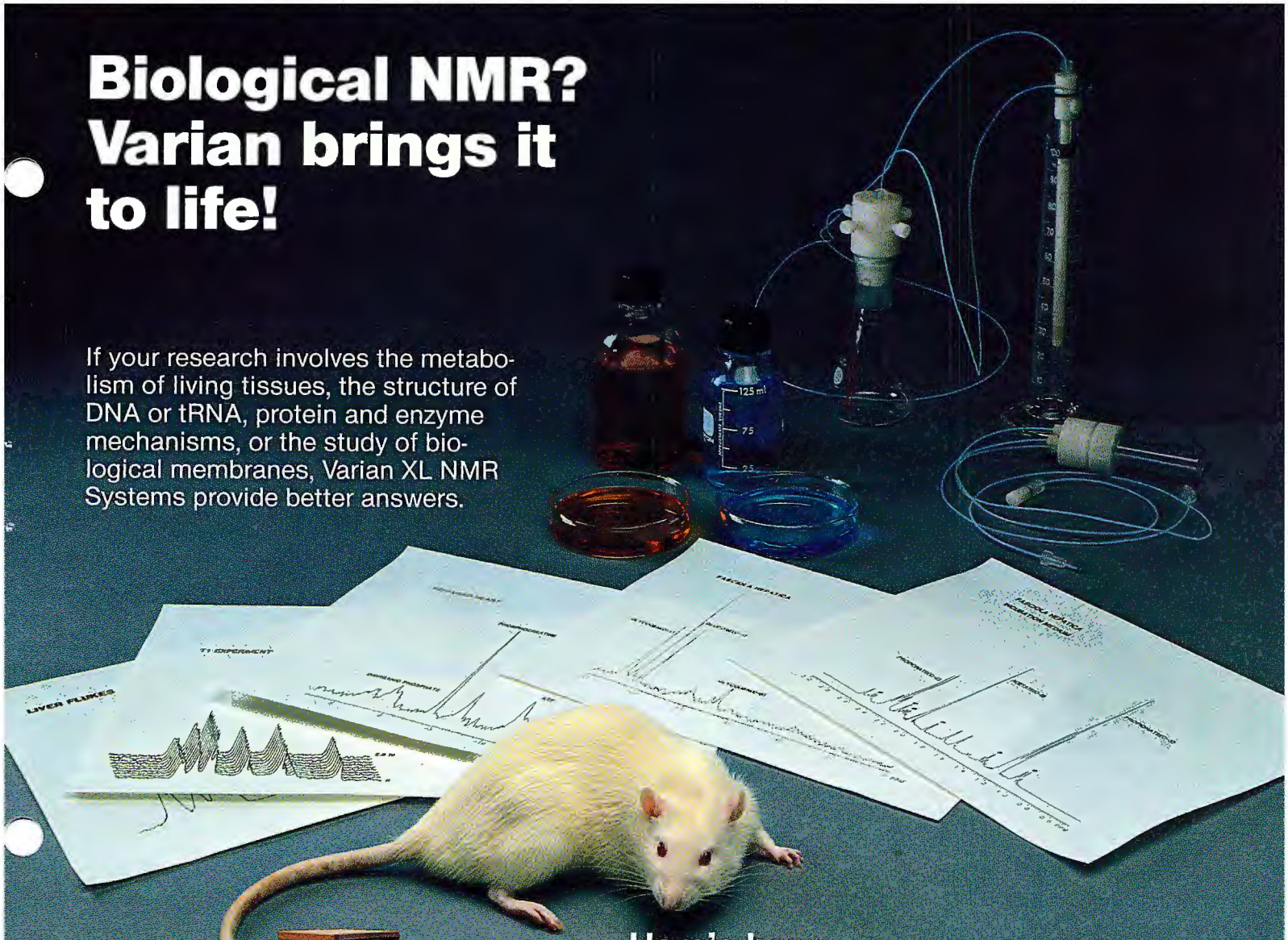

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CANADA

July 21, 1985

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

pK's in THF

Dear Barry:

In response to your request* I'm providing a summary of our recent results on measurement of pK's in THF using ^{13}C nmr spectra from an FT-80. Though this may be considered a mundane application of nmr, I think the numbers obtained will be of interest to the organic chemists amongst us.

Yours sincerely,

Bob

R.R. Fraser

RRF:cmg

* What 'request', Bob?
Barry

Département de chimie
Faculté des sciences et de génie

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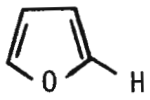

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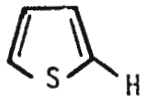

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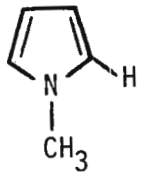

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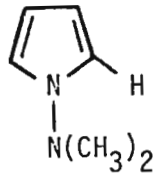

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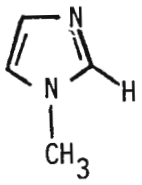

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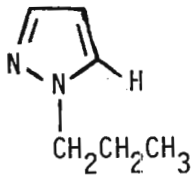

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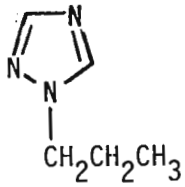

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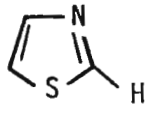

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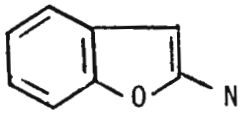

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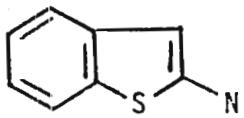
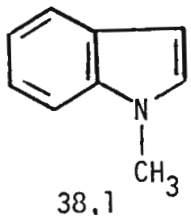
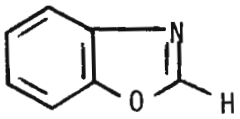


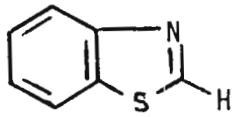
32.4(33.5)



38.1



< 15.7[a]



~ 28

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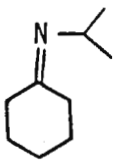
[a] represents pK of rearranged isomer, o-cyanophenol

pK's in T.H.F.

$ACID_1$	REFERENCE $ACID_2$ (pK_2)	K_{eq}	-log K	pK_1	LIT. DATA
2-picoline	DA(35.7)	50	-1.7	34	34(1)
3-picoline	TMP(37.3)	0.4	0.4	37.7	
4-picoline	$(CH_3)_3CNHSi(CH_3)_3$(33.6)	25	-1.4	32.2	
Xanthene	$(CH_3)_2CHNHSi(CH_3)_3$(31.4)	.9	-.03	31.4	
$\phi_2CHS\phi$	3 BP(30.2)	32	-1.5	28.7	26.7(13)
2-BP (Benzylpyridine)	$\phi_2CHS\phi$(28.7)	2.8	-0.4	28.3	28.2(8)
2-BP	3 BP(30.2)	59	-1.8	28.4	
3-BP	$(CH_3)_2CHNHSi(CH_3)_3$(31.4)	18	-1.3	30.1	30.1(8)
3-BP	Xanthene (31.4)	17	-1.2	30.2	
4-BP	$[(CH_3)_3Si]_2NH$(25.8)	6.4	-0.8	25.0	26.7(8)
4-BP	2 BP	1400	-3.1	25.3	
4-Lepidine	$[(CH_3)_3Si]NH$(25.8)	0.02	+1.7	27.5	
$[(CH_3)_3Si]_2NH$	2 BP(28.4)	406	-2.6	25.8	
Fluorene	$[(CH_3)_3Si]_2NH$(25.8)	27	-1.4	24.4	22.6(10)
Fluorene	4 BP(25.0)	4.5	-0.7	24.3	
	$(CH_3)_2CHNHSi(CH_3)_3$(31.4)	1.2	-0.1	31.3	

323-12

TH Delft

Technische Hogeschool Delft

Afdeling der Technische Natuurkunde

Postbus 5046
2600 GA Delft

Lorentzweg 1
2628 CJ Delft
Telefoon (015) 78 91 11
Telex bhthd 38151

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

Uw kenmerk en datum	Ons kenmerk	Doorkiesnummer	Datum
–	–	(015) 78	12 June 1985

Onderwerp	Onderdeel
–	–

Dear Barry,

In vivo ^{31}P NMR study of dose dependent tumor response to X-irradiation.

Localised ^{31}P NMR spectroscopy gives information about tissue metabolism and might therefore be used to study tumor-response to therapy in animals and humans. In collaboration with the department of Radiotherapy, University Hospital Utrecht (Paul Sijens) we investigated this possibility by studying the response of subcutaneously implanted murine mammacarcinomas NU 82 to 10 and 20 Gy gamma radiation. 48 mice were studied during 2 days by in vivo ^{31}P NMR at 7 T.
Tumors with an average mass of 1.5 gr in the flank of the animals were measured using solenoidal coils, in a way analogous to the one described by Evanochko e.a. Magn.Reson.Med.1, 508 (1984).
Results are shown in the figure. During the time of observation no change in intracellular PH (as derived from the chemical shift of the P_i peak) and tumor size was observed. Untreated tumors increased 30% in volume during that time.

As appears from the figure, treatment with a dose of 20 Gy induced metabolic changes to the murine tumor NU 82 which differed significantly from the 10 Gy dose treatment. Studies are now in progress to explain the observed spectral changes.

Dr. W.M.M.J. Bovee

Dr.P.Sijens

Please credit this contribution to professor J.Smidt

840440

Vermeld bij beantwoording kenmerk en datum. Behandel niet meer dan één onderwerp per brief.

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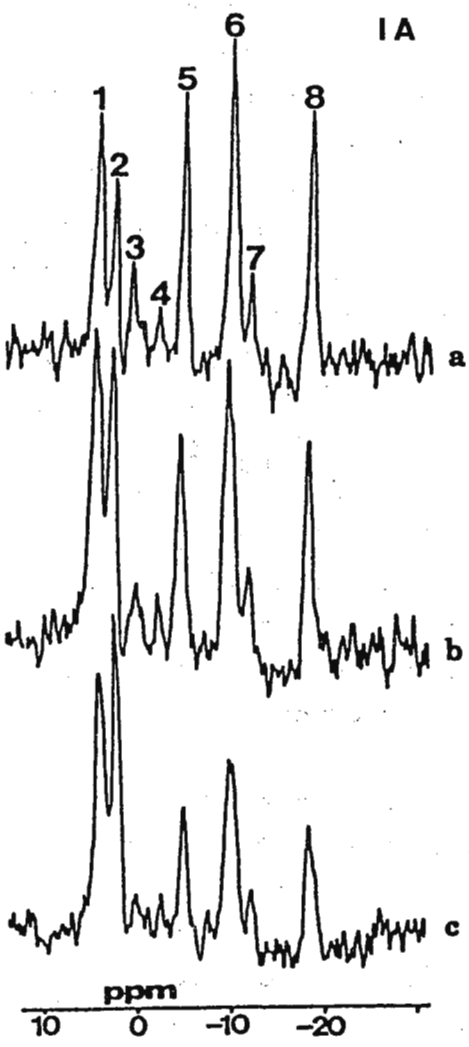
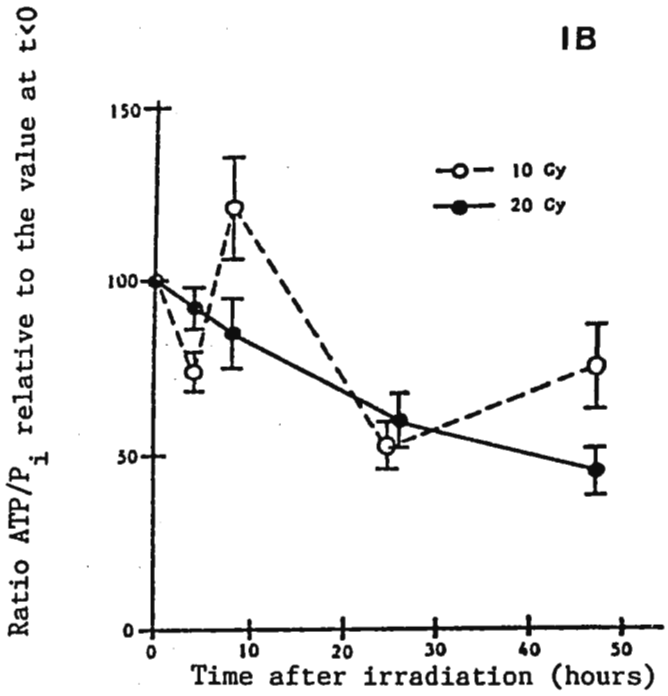
Afdeling der Technische Natuurkunde

Figure 1A: In vivo ^{31}P NMR spectra of tumors NU-82 of different size: each spectrum took 7 minutes. Peak assignment; 1: phosphomonoesters, 2: inorganic phosphate, 3: phosphodiesters, 4: phosphocreatine, 5: γ- ATP, 6: α -ATP, 7: diphosphodiesters, 8: β - ATP.

Figure 1B: The ratio ATP/P_i after radiotherapy with a dose of 10 and 20 Gy as a percentage of the value before treatment, plotted versus time. Bars indicate the standard error of the mean.





323-14

Prof. V.F. Bystrov
USSR Academy of Sciences
Shemyakin Institute
of Bioorganic Chemistry

Ul. Miklukho-Maklaya, I6/IO
117871 GSP-7 Moscow V-437
USSR

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

June, I3, I985

Title: Gramicidin A Helix in Micelles

Dear Barry,

The linear pentadecapeptide gramicidin A (GA) forms ion permeable channels in biological and artificial membranes. The problem of the channel conformation is dramatically complicated by diversity of energetically allowed conformations of GA. Although the dimeric nature of the GA channel is established, still numerous forms of both single- and double-stranded helices have to be considered.

We made use of 500 MHz 2D NMR (COSY, NOESY, RELSY, NOERELSY, 2QT) for conformational analysis of [Val^1]GA and its metal complexes in different milieus. In dioxane solution GA forms four basic conformational species (1). The species 3 was isolated and demonstrated to be a left-handed antiparallel double helix $\uparrow\downarrow\pi\pi^{5.6}_{LD}$ with 5.6 residues per turn (2). The species 4 was represented by synthetic analog des-3,4,5,6 [Val^1]GA, which forms a right-handed parallel double helix $\uparrow\uparrow\pi\pi^{5.6}_{LD}$ in dioxane (3). The conformation of the caesium-GA complex 1:1 in mixed methanol-chloroform solvent is a right-handed antiparallel double helix $\uparrow\downarrow\pi\pi^{7.2}_{LD}$ (4) which has proper luminal diameter (~0.4 nm) of the central axial cavity to incorporate Cs^+ cations. Although these double helical structures of GA meet general requirenments of the transmembrane channel, the direct NMR study of GA in detergent micelles demonstrates crucially different structure.

GA was incorporated into sodium dodecyl sulphate (SDS) micelles by dropwise addition of the 2,2,2-trifluoroethanol-D_3 (TFA) solution of GA into SDS-D_{25} dispersion in H_2O or D_2O. The final condition (5 mM GA and 0.25 M SDS-D_{25} in 16:1 water/TFA, molar ratio) corresponds to incorporation of not more than two GA molecules into one micelle. CD spectrum of GA in SDS micelles is identical to those of GA in dipalmitoyl phosphatidilcholine liposomes and lysolecithin micelles. The ^1H-, ^7Li-, ^{13}C- and ^{23}Na-NMR spectra prove that GA in SDS micelles interacts with alkali metal cations

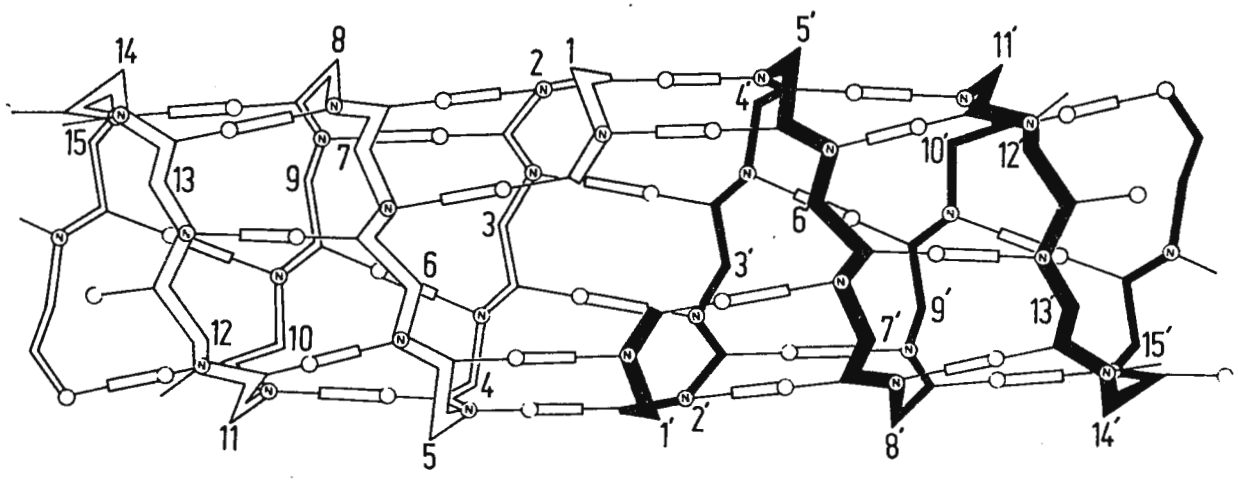
(Li^+ or Na^+). Results of the proton 2D NMR spectroscopy, model building and further refinements by means of conformational energy minimization demonstrate that the molecular structure of the Na^+-GA complex in micelles is a head-to-head $\overrightarrow{\pi}^{6.3}_{LD}\overleftarrow{\pi}^{6.3}_{LD}$ dimer (See Figure), formed by two right-handed single-stranded $\beta^{6.3}$ helices with 6.3 residues per turn. The dimer of ~2.6 nm length has C_2 symmetry axis perpendicular to the channel axis. The conformation of GA transmembrane channel differs from the structure proposed by Urry et al. (5) in handedness of the helices.

With kind regards,

Sincerely yours,

Vladimir Bystrov and Alexander Arseniev

1. W.R. Veatch, E.T. Fossel, E.R. Blout, Biochemistry 13,5349(1974).
2. A.S. Arseniev, et al. FEBS Lett.165,51(1984); Biol. Membr.(USSR) 1,5(1984).
3. A.S. Arseniev, et al. Bioorg. Khim.(USSR) 11,5(1985).
4. A.S. Arseniev, et al. FEBS Lett.180,33(1985).
5. D.W. Urry, T.L. Trapane, K.U. Prasad, Science 221,1064(1983).



Na^+-gramicidin A in SDS: $\overrightarrow{\pi}^{6.3}_{LD}\overleftarrow{\pi}^{6.3}_{LD}$

323-16

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June 27, 1985

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

"Broadline NMR Probe Construction at IUPUI"

Dear Professor Shapiro:

We intend to enter the realms of broadline NMR at IUPUI. Although construction of a homebuilt broadline machine is underway, initially we shall attempt to use Durgu Rao's Nicolet NT-300 high resolution spectrometer.

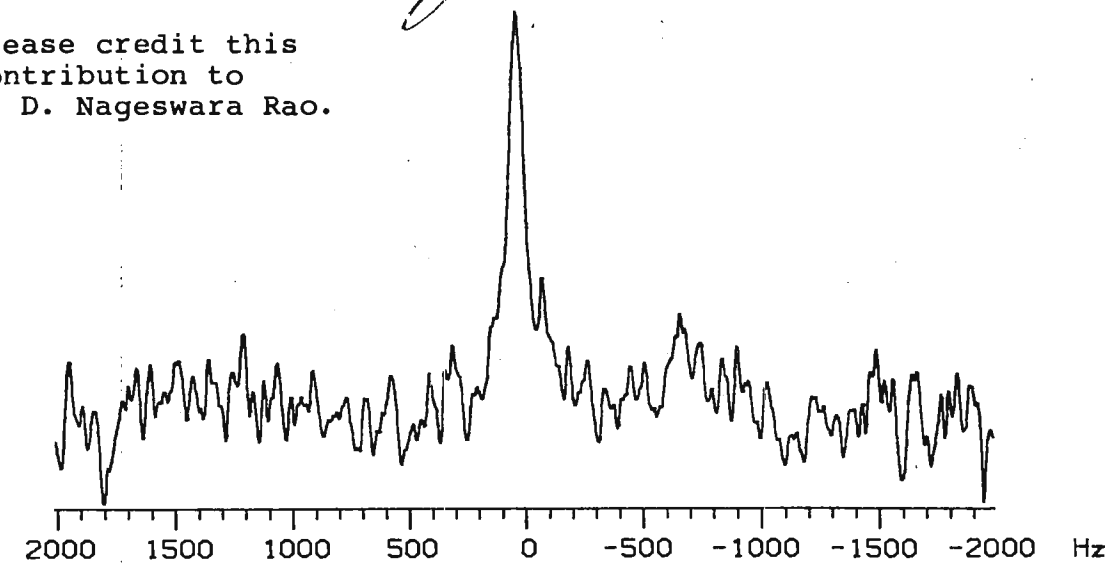
The ^{2}H NMR spectrum shown below represents the first test of a homebuilt probe. The probe is a horizontal mounted coil (9 turns 18 AWG wire, 1 cm length and diameter) with two Polyflon 0.8-10 pf variable capacitors for tuning and matching. The S/N is 10 for 32 scans on natural abundance ^{2}H in water which, given the poor homogeneity of the spectrum, is not too bad. The $\pi/2$ pulse width of $\sim$9 μs (200 w rf power) needs improving. Bigger (wider) and better things (spectra) will hopefully follow .

Yours sincerely,

Bruce D. Ray

Stephen R. Wassall

Please credit this
contribution to
B. D. Nageswara Rao.



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307 East McCarty Street
Indianapolis, Indiana 46285
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July 11, 1985

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

Dear Professor Shapiro:

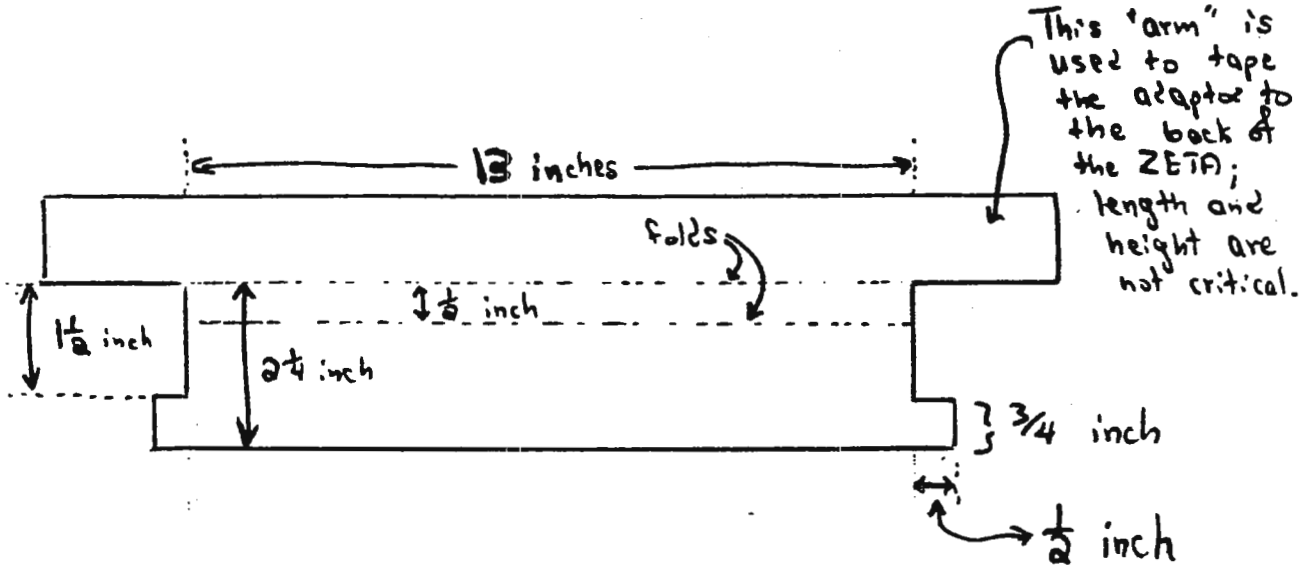
Plotter Modification on the QE-300

We have finally caught up with our NMR backlog by turning all of our routine proton and carbon requests over to a GE QE-300 with an automated sample-changer. We have had some struggles getting the thing to go, but we are now fairly pleased with the results--one instrument has replaced three (^{1}H on an automated T-60, ^{1}H on a WM270, and ^{13}C on an FT-80), and one person handles the samples which formerly took two persons plus a lot of overtime hours. The sample-changer will hold up to 99 samples, and we have run queues of 60 or more tubes on several occasions.

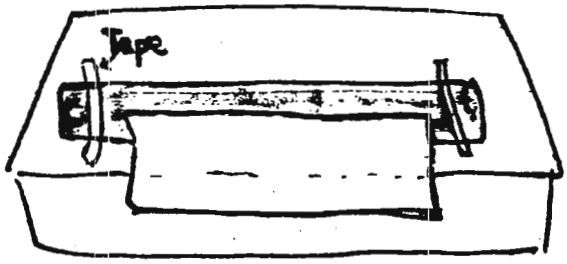
One problem that has occurred from time to time is that we arrive in the morning to discover that the queue has been completed, but unfortunately the paper on the plotter jumped off track during the run, leading to useless plots for all subsequent samples. The cause for this disaster seems to be that the paper is being pulled back and forth so rapidly that it sometimes flips off of the sprockets of the ZETA-8. We have been able to recall the stored FIDs and to spend the day retransforming and replotting, but I have finally cured the problem by the following modification (well, it hasn't happened again since I installed the adaptor on May 20, anyway).

The prototype device is made of cardboard, but we plan to cut a new one out of something prettier.

This device forces the Z-fold paper to stay down near the sprockets at all times, but it does not get in the way when several folds of paper are suddenly sent out the back by an RZ command, for example. We have never actually been present when the paper has gone off track, so we can't describe exactly how it happens. We have seen the results several times however, and this device seems to eliminate them effectively. If anybody else with a ZETA has the same problem, I recommend that you find a cardboard box and a sharp knife and go to work!



Back view of ZETA-8 with adaptor installed



Side View

Taped to outside of ZETA-8

Folded inside the ZETA, on top of the wire or spring paper guide

Sincerely,

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Ann H. Hunt

Ann H. Hunt, Ph.D.
Research Scientist
Physical Chemistry Research

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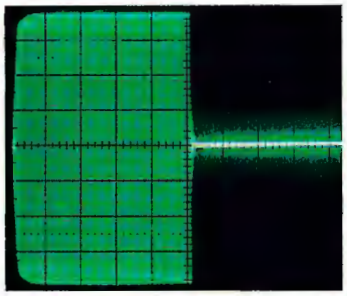
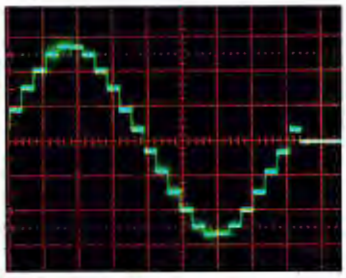
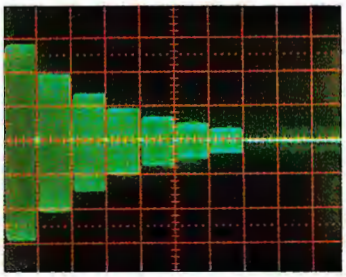




15° phase shift through 360°. ►



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July 24, 1985

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

Dear Barry:

Postdoc Position; Ionic Strength Affects Cytochrome c Proton NMR Spectra

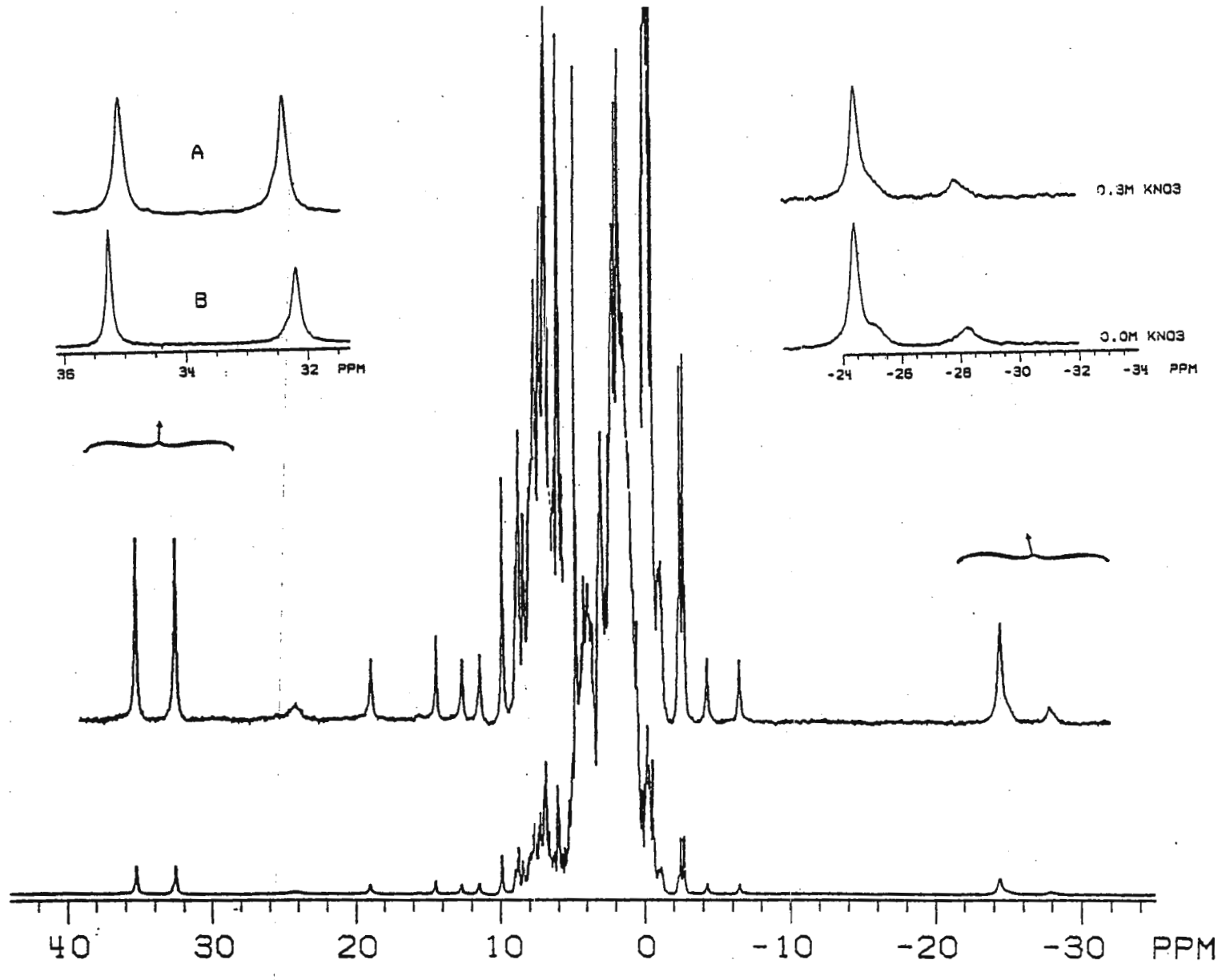
In the course of recent studies involving the molecular redox/docking complex between cytochrome c's and cytochrome c peroxidase we noticed that proton NMR spectra of cytochrome c exhibited a dependence upon the salt concentration of the protein solution. The accompanying spectra indicate that quite severe shifts are encountered, ranging up to 0.7 ppm for several hyperfine shifts. We have also observed significant linewidth variations in the hyperfine shifts as a result of different salt concentrations. I bring this to readers' attention for several reasons. Cytochrome c is, perhaps, the heme protein that has been most commonly studied, however cytochrome c peroxidase also exhibits this effect and it may be general. Studies that include pH dependence must be acknowledged to involve alteration in the ionic strength of the protein solution so that observed shifts may be due, in part, to changes in ion concentrations.

On a different topic, beginning September 1, 1985, I shall have a postdoctoral position available for one to five years. The person I am seeking should be capable of performing modern NMR experiments and will do work on NIH funded research involving small heme proteins. My lab currently consists of two graduate students working on the same project as this postdoc will, and a second postdoc working on an NSF supported project. Our lab is very well equipped for modern biochemistry and my group has access to a newly installed GE 360MHz spectrometer for 25 days per month, on the average. The spectrometer has a wide bore magnet, is completely broadband, has an X-nucleus decoupler, an array processor and a 96 Mbyte CMD disc drive. UNM is an equal opportunity, affirmative action employer and interested people should write to me or call me collect at (505-277-3621).

Sincerely,

James D. Satterlee

361 MHz proton NMR spectrum of 2.5 mM cytochrome c (horse), pH=7.3. The full spectrum is of a solution in 0.300 M KNO_3. The inserts show the differences in selected regions between (A) 0.300 M KNO_3 and (B) 0.00 M KNO_3 solutions of this protein. In each case the temperature was 23 C.



PROFESSOR J. H. GOLDSTEIN'S RETIREMENT SYMPOSIUM

Prof. J. H. Goldstein is retiring at the end of 1985 after a long and distinguished NMR career at Emory University, Atlanta, GA. His former students are organising a one-day symposium to mark the occassion. It will be held in the Chemistry Building, Emory University, Atlanta, GA, on Friday, October 25, 1985. The program will include.

1. Roast and Boast Session
2. Several NMR presentations by his former students
3. After-dinner Symposium

All of Jake's colleagues, students and other NMR spectroscopists are invited to take part and make the event a memorable one. If anyone would like to make a presentation, scientific or otherwise, they are welcome to do so and they will be included in the final program.

Further information and details can be obtained by contacting.

Gade S. Reddy
CR&D - E328/129
Du Pont Experimental Station
Wilmington, DE 19898
Tel: (302) 772-3116 or 772-3738

British Radiofrequency Spectroscopy Group

Spring Meeting 1986

High Resolution NMR in Solids

Oxford, April 9-11, 1986

This meeting is designed to discuss recent developments in solid state NMR and to illustrate their applications in areas of research from biology and chemistry to materials science and technology.

Speakers include: E.R. Andrew (Florida), G. Bodenhausen (Zurich), C.A. Fyfe (Guelph), R.G. Griffin (MIT), R.K. Harris (Durham), G.E. Maciel (Colorado), K. Packer (BP), A. Pines, Berkeley), J.M. Thomas (Cambridge), W.S. Veeman (Nijmegen).

For further details, please contact **Dr. C.M. Dobson,** Inorganic Chemistry Laboratory, South Parks Road, Oxford, U.K. OX1 3QR, Tel. (0865) 53424.

Weyerhaeuser Company

Tacoma, Washington 98477
(206) 924-2345

June 19, 1985

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

Dear Professor Shapiro:

Re: Structure-Strength Relationships in PF Adhesives

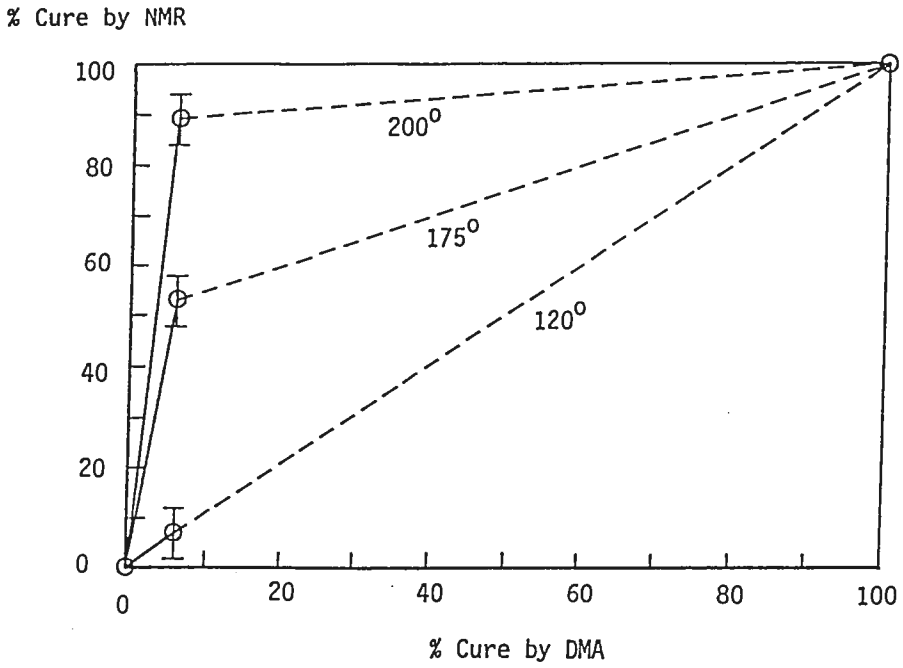
The advent of color copying and the increasing use of pink papers to grab the reader's attention make me more exasperated - these materials are not recyclable and their use entails the waste of a valuable resource.

Dr. Robert H. Young and I have been pursuing PF resin cure chemistry in moderate detail since a CP/MAS study appeared last year (1). Bob's interest is dynamic mechanical analysis (DMA), which measures a strength modulus as a resin cures under carefully controlled conditions; my interest is in following cure structurally by CP/MAS NMR on our S-100; our mutual interest is whether the structure and strength measurements agree. The DMA modulus-time data resemble a titration curve, going from liquid resin (0% cure) up to a modulus plateau (100% cure). NMR samples can be taken at any DMA cure state; the integrated spectrum yields the amounts of strengthening structures (methylene bridges and dimethylene ether linkages), weakening structures (methyls, methylols and aldehydes) and total aromatic substitution. These also are convertible into % cure numbers, zero being the gelled liquid resin and 100 the terminal polymer.

Ideally, a plot of % cure (NMR) against % cure (DMA) will be linear. However (see figure), this occurs only at low curing temperatures; at higher temperatures, NMR cure leads, which confirms Bob's suspicion that the DMA modulus is partly canceled by thermal softening of the resin matrix, especially in the early stages, and that softening effects increase with temperature. Even though curing chemistry is going on, the DMA doesn't see it for awhile. Now we can calibrate the DMA (after we get some more data points in the figure) to compensate for softening effects in this resin system - others might need separate calibrations. We also will report later the reaction rates for formation of various linkages and groups.

Incidentally, I hear that Don Sawyer is joining up as Department Chairman; please relay my best regards.

(1) G. E. Maciel, I-S. Chuang and L. Gollob, Macromol., 17(5), 1081 (1984).



Respectfully,

Larry

Larry W. Amos

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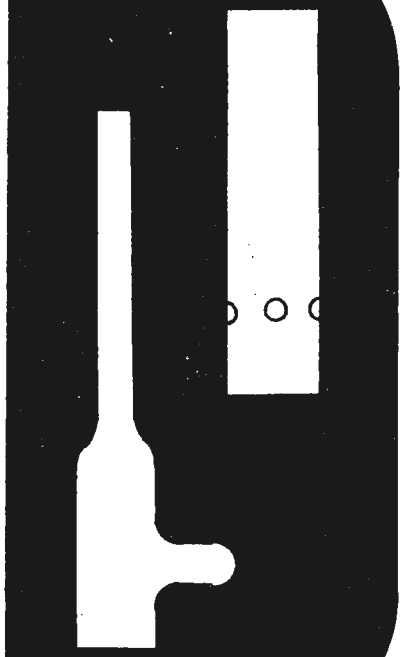

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1985 May 09

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

Dear Barry:

PHASE STRUCTURE DETERMINATIONS OF POLYETHYLENE USING ^2H SPIN LATTICE RELAXATION STUDIES

As an initial contribution for my TAMU subscription, I thought that I would present some recent solid state ^2H NMR spin lattice relaxation data. Polyethylenes are known from laser Raman work to exist in three distinct phases; crystalline (orthorhombic packing), interfacial (pseudohexagonal packaging) and amorphous (1). Since the chains in each phase experience different motions, the recovery of the ^2H magnetization after saturation can be used to determine the phase structure of polyethylene.

A sample of linear, perdeuterated polyethylene was pressed as a thin film and then rapidly cooled. The sample magnetization was saturated with seven 90° pulses separated by 1 msec delays. After a variable delay, the spectrum was acquired with a solid echo, using 45° pulses, and phase cycling of the pulses.

Figure 1 shows the decay of the total magnetization with time as well as the mass fractions and ^2H T_1 values for each component. These values were extracted graphically and the solid line in Figure 1 is the calculated decay using these values.

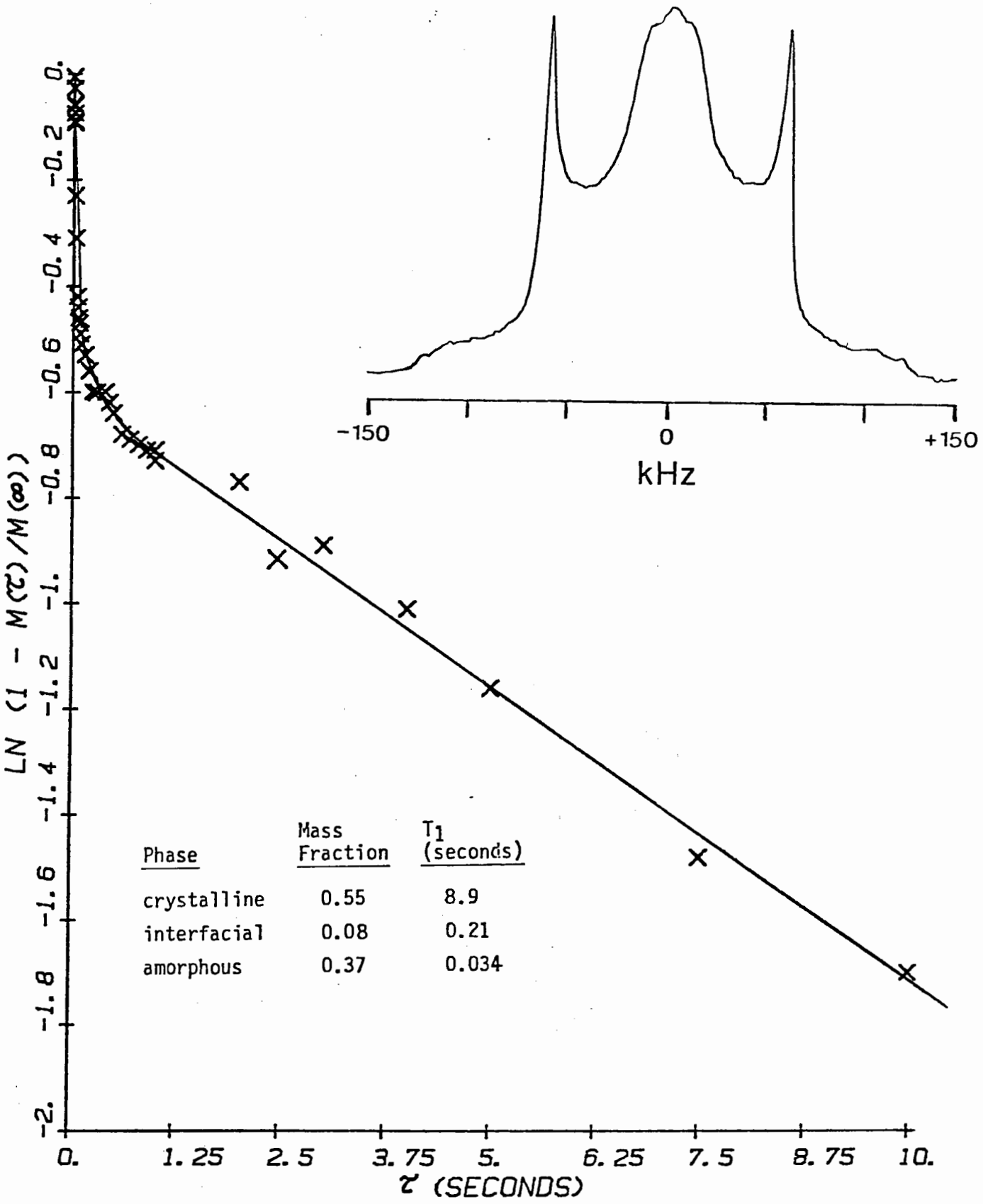

FIGURE 1 - Decay of the ^2H magnetization with time for a linear, perdeuterated polyethylene. The table contains the T_1 and mass fraction data. The insert is the fully relaxed spectrum.

The advantage of ^{2}H NMR over ^{13}C or ^{1}H NMR, in studies of this type is twofold. First, spin diffusion is largely quenched in ^{2}H NMR and second, ^{2}H NMR gives well defined lineshapes (see insert to Figure 1). These lineshapes can give insight into the type and symmetry of the motions which are occurring in not only the amorphous and crystalline phases (2), but also the interfacial phase of polyethylene.

Yours truly,

DU PONT CANADA INC.

Eric Kelusky

E.C. Kelusky
Research Scientist

(1) G.R. Strobl and W. Hagedorn, J. Polym. Sci., Polym. Phys. Ed. 16, 1181-1193 (1978).

(2) D. Hentschel, H. Sillescu and H.W. Spiess, Polymers 25, 1078-1086 (1984).

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DEPARTMENT OF CHEMISTRY

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July 15, 1985

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

XL-200 Spectrometer for Sale

Dear Dr. Shapiro:

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Sincerely,

Albert J. Fry
Chairman and Professor
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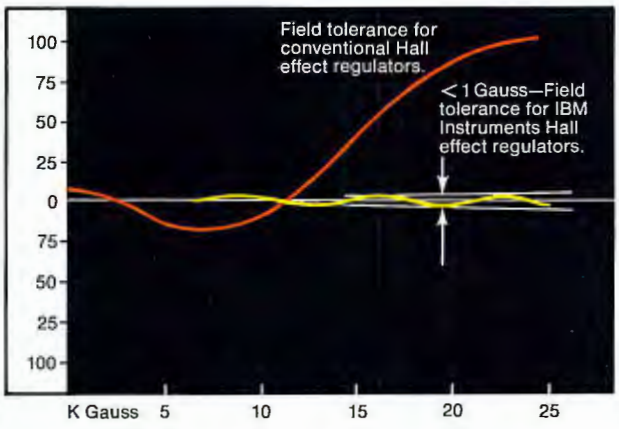

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Asilomar, California, April 21-25, 1985

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July 1, 1985

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

Dear Barry:

Re: 27th Experimental NMR Conference

The 27th Experimental NMR Conference will be held at Baltimore, Maryland on April 13th through the 17th 1986 and will focus, as usual, on experimental aspects of nuclear magnetic resonance. The meeting will include both oral and poster presentations. The only mailing will be made in November of 1985 and will contain the registration information. Applications must be returned by January 15, 1986. This registration packette will include instructions for the submission of poster presentations. Any changes of address should be brought to the attention of P. Mark Henrichs, Eastman Kodak Company, Research Laboratories, Rochester, New York 14650, telephone 716-477-6229.

Very truly yours,

Robert G. Bryant
Dean's Professor

University of Illinois
at Urbana-Champaign

School of Chemical Sciences
505 South Mathews

Urbana
Illinois 61801

Wanted: Used 360/52 470 or 500/41 Magnets

I would be interested to hear if anyone has a used 360, 470 or 500/41 magnet for sale. Please contact me at the above address.

Eric Oldfield
Professor of Chemistry

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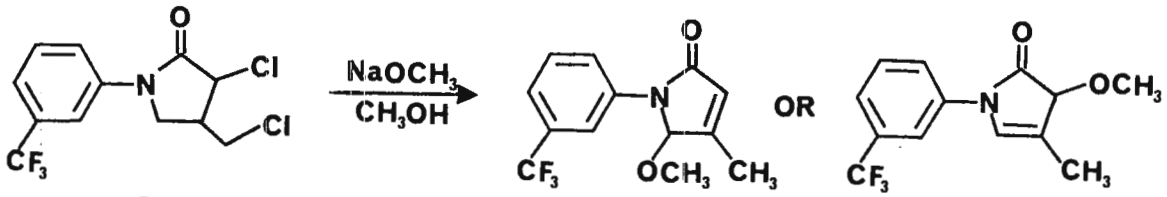
June 21, 1985

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

"INADEQUATE Spectrum of A Novel
Rearrangement Product from A
Substituted Pyrrolidinone"

Dear Barry:

Fluorochloridone (I) is an active ingredient of RACER®, a registered selective herbicide from Stauffer Chemical Company. When (I) was reacted with sodium methoxide in methanol, a very unusual rearrangement product was isolated. Based on proton, carbon-NMR and mass spectra, the structure of this product was assigned as either II or III.



I II III

Only through the use of INADEQUATE technique, we were able to establish the actual connectivity of the pyrrolidinone ring and assign the structure of this product as (II) without ambiguity. The carbon chemical shifts and C-13 coupling constants of the pyrrolidinone ring are listed in Table I. The mechanism of this reaction and other spectroscopic data will be reported elsewhere.

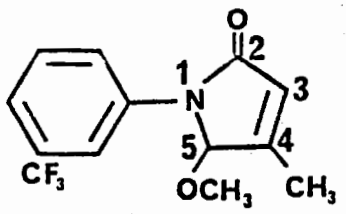
Sincerely,

Lydia L. Chang

C. K. Tseng

mn:2:35
attachment

Table I*



C#	δ(ppm)	J_{C-C} (Hz)	
2	168.9	2 - 3 = 63.4	2 - 5 = 9.8
3	125.3	2 - 3 = 63.5	3 - 4 = 66.7
4	155.1	3 - 4 = 66.8	4 - 5 = 42.1
5	89.5	4 - 5 = 42.1	2 - 5 = 9.8
CONNECTIVITY		$C_2 - C_3 - C_4 - C_5 - N - C_2$	

*The spectra were obtained on a Varian XL-200 NMR spectrometer. The INADEQUATE spectrum was obtained using C13SAT pulse sequence provided by Varian. The spectral width is 5KHz with 32K data points, pulse width (90°)=14 µsec, N=0 and JCC=54 Hz.

Kodak

June 21, 1985

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

Dear Professor Shapiro:

Subject: CMR of Trifluoroacetanilide Derivatives

CMR chemical shifts and values for J_{CF} and J_{CCF} for several trifluoroacetanilide derivatives are reported here. All samples were dissolved in DMSO-d_6 and data were collected at ambient probe temperature. CMR data for trifluoroacetanilide are reported elsewhere (S. Bradamante and G. A. Pagani, J. Org. Chem., **45**, 114 (1980)). A compilation of CMR substituent effects for monosubstituted benzenes (D. F. Ewing, Org. Mag. Res., **12**, 499 (1979)) and the data for trifluoroacetanilide were used to test the reliability of calculated CMR chemical shifts for the aromatic ring carbons of the trifluoroacetanilide derivatives (Table I). Additivity parameters provided reliable CMR chemical shifts for the disubstituted compounds. The CMR chemical shifts calculated from the additivity parameters for the trisubstituted compound were not as useful because the experimental chemical shifts for the ring carbons of the trisubstituted compound are similar.

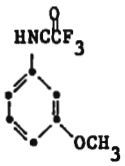
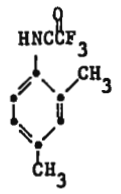
Yours very truly,

Doug

Douglas W. Lowman
Senior Research Chemist
Research Laboratories
P. O. Box 1972

bgm/TR0191f

Table I

	$\delta^a(^{13}C)$									J_{CF}[b]	J_{CCF}[b]
	C_1	C_2	C_3	C_4	C_5	C_6	CH_3	C=O	CF_3		
	129.4 (0.6)[c]	122.8 (−0.3)	114.2 (−0.6)	157.0 (0.4)			55.3	154.4	116.1	288.2	36.5
	137.8 (0.1)	107.1 (−0.5)	159.8 (−0.7)	111.2 (0.3)	129.9 (−0.4)	113.4 (−0.8)	55.2	154.8	116.0	287.7	36.9
	137.8 (−2.1)	108.2 (−2.3)	157.8 (0.6)	111.7 (−2.1)	129.7 (−2.4)	112.8 (−2.4)		154.2	115.9	288.8	37.0
	138.0 (−0.5)	115.4 (−2.4)	148.1 (−1.8)	120.1 (−1.0)	130.4 (−0.7)	126.9 (−2.2)		155.3	115.8	288.4	37.8
	137.0 (0.0)	131.0 (−2.8)	131.3 (−2.0)	133.9 (−3.2)	127.5 (−2.1)	127.0 (2.5)	2: 17.3 4: 20.5	155.4	116.4	288.6	36.3

[a]PPM relative to TMS
[b]In Hertz
[c]Number in parenthesis represents the difference in chemical shifts, i.e., δ(experimental)−δ(calculated)

323-36

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Directeur : Professeur J. REISSE

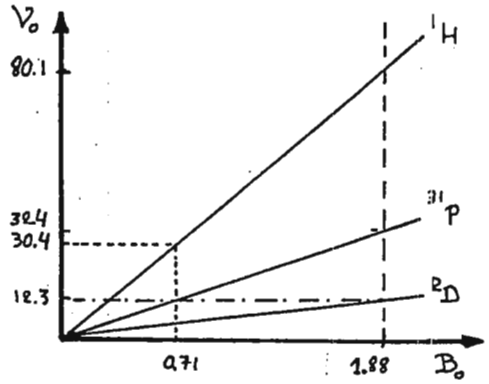
B-1050 Bruxelles, le 9th July 1985.

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

Re : Proton NMR measurements at different frequencies.

Dear Professor Shapiro,

The growing interest for biological applications of NMR is at the origin of the need for T1 and T2 measurements at different frequencies.
We describe here the modification of a WP80SY wide bore Bruker spectrometer, modification which does not loose the advantage of the field-frequency lock.



As an example, the graph shows three Larmor lines for proton, phosphorus 31 and deuterium.
The nominal value at 1.88 T are ν_H = 80.1MHz and ν_{lock} = 12.28 MHz for deuterium. After reducing the field to about 0.71 T; the proton signal can be observed at 30.4 MHz with a broad band probe, whereas the electronic of the lock channel remains at 12.28 MHz.
As it is shown on the graph, the lock can be achieved with a coaxial cell containing a phosphorus derivative.
The same principle can be extented to other nuclei.
The table shows a series of lock nuclei with the corresponding proton frequency.

lock	^1H freq.
^{19}F	13,1 MHz
^{205}Tl	21,3
^{31}P	30,4
^{13}C	48,9
^2H	80,1

Yours sincerely,

O. FABRE

D. ZIMMERMANN.

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1983: Entrance into NMR Imaging (MRI) and in-vivo spectroscopy.

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nology. Today we offer an unequalled line of NMR spectrometer systems up to 500 MHz including such recent advances as in-vivo spectroscopy, mini and whole body NMR imaging and real time processing, such as the first fiberoptics data link for high-speed data transfer, and high speed array processors that perform Fourier transformations of 32 kiloword data tables in a few hundred milliseconds.

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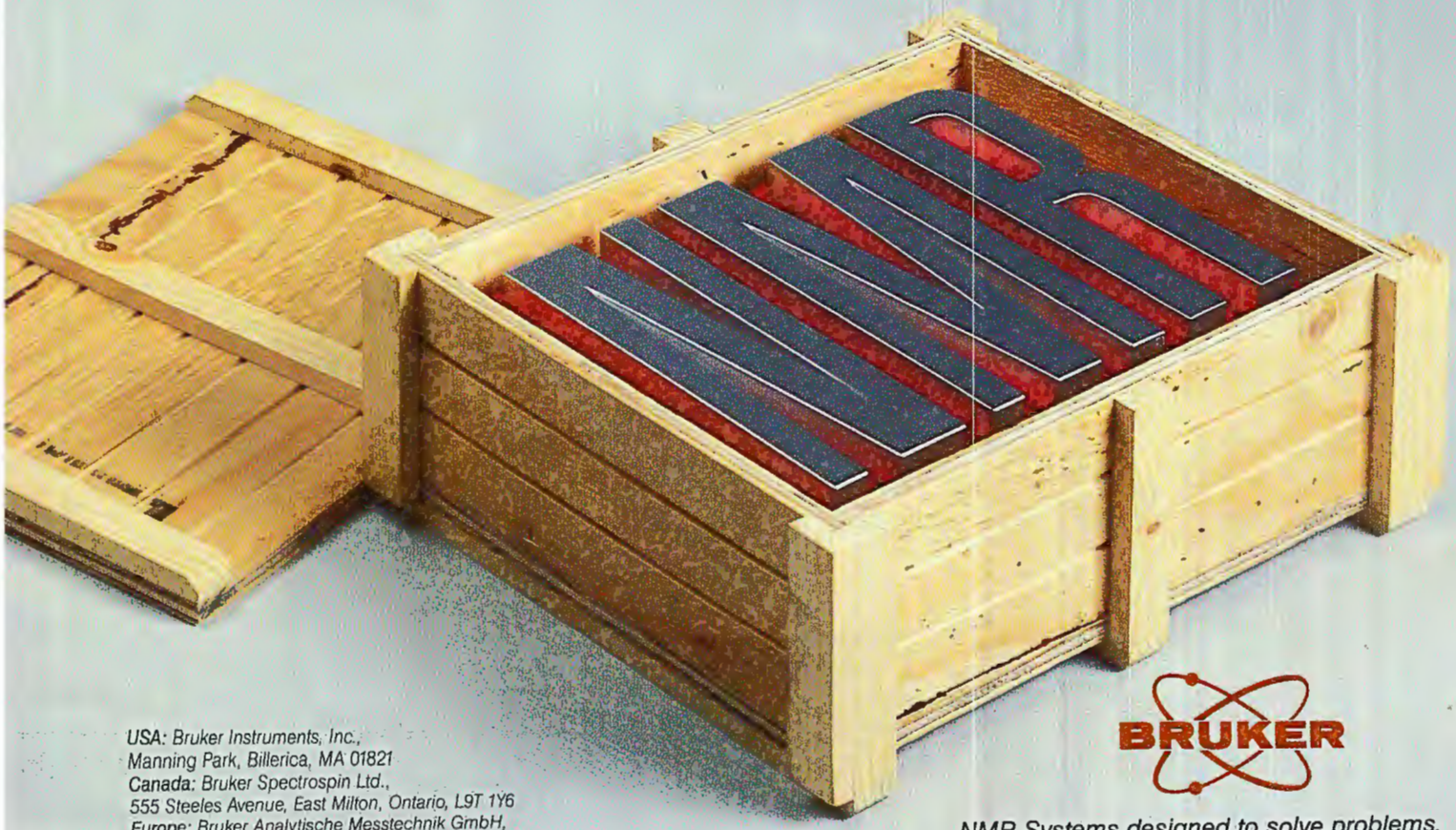

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MFAD/JS

5 July 1985

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

Dear Professor Shapiro

^{53}Cr and ^{17}O Chemical Shift for Cr(VI) Species

As yet very little NMR data is available for the only magnetic isotope of chromium, ^{53}Cr. One of the main reasons is the low sensitivity of the ^{53}Cr nucleus which has a receptivity of 8.62×10^{-5} relative to the proton (1). The natural abundance of ^{53}Cr is only 9.55% and spin-spin coupling constants are expected to be small on account of the low magnetogyric ratio of chromium; a consequence of this is that it should be more advantageous to look for such couplings in the ^{53}Cr spectra rather than in those of ligand nuclei. Another problem is that the nucleus is quadrupolar (I = 3/2). The reported values of the quadrupole moment, Q, range from 0.022 to 0.04 barn (2) and a more recent determination has measured Q as -0.15 barn (3). Therefore quadrupolar broadening gives rise to a further decrease in signal-to-noise ratios. The only two ^{53}Cr resonances so far reported for Cr in solution are for CrO_4^{2-} and $Cr(CO)_6$ (4-6). The Cr nucleus is in a cubic environment in both of these species. The chemical shift of $Cr(CO)_6$ in THF is -1795 ppm relative to aqueous CrO_4^{2-}, which is taken as the standard.

Using a high field Bruker NMR spectrometer (WH 400) it has been possible to record ^{53}Cr and ^{17}O spectra for chromate, dichromate, halochromate and chromyl halide species. Tetraethylammonium salts of CrO_4^{2-}, $Cr_2O_7^{2-}$ and CrO_3X^- were prepared and spectra recorded for 1 molar solutions of acetonitrile. CrO_2X_2 species were recorded as melts; it was possible to reduce the linewidth of CrO_2F_2, which is known to be associated in the solid state, by using $CClF_2CClF_2$ as solvent. CrO_2ClF was generated by halogen redistribution of CrO_2F_2 and CrO_2Cl_2.

The observed ^{53}Cr and ^{17}O chemical shifts and the approximate ^{53}Cr linewidths are given in the Table.

The ^{53}Cr chemical shifts recorded show that ^{53}Cr exhibits inverse halogen dependence. When bonded to chlorine, chromium gives rise to a larger paramagnetic contribution than when fluorine is the ligand. This causes a deshielding effect, as can be seen in the series CrO_2F_2, CrO_2ClF and CrO_2Cl_2. Thus, the chemical shift of CrO_2Cl_2 occurs to low field of CrO_2F_2; CrO_2ClF has a chemical shift which is almost exactly the average of CrO_2Cl_2 and CrO_2F_2. Similar results have been obtained for the vanadyl species $VO_2Cl_2^-$, VO_2ClF^- and $VO_2F_2^-$ (7).

In CrO_3F^- a two bond oxygen-fluorine coupling constant, $^2J(^{17}O - ^{19}F) = 33$ Hz, was obtained from the ^{17}O spectrum. However, no coupling was observed in CrO_2F_2 even when the ^{17}O linewidth was reduced to 10 Hz by using $CClF_2CClF_2$ as solvent. We attribute this to the halogen scrambling process which is responsible for the facile production of CrO_2ClF when CrO_2Cl_2 is added to CrO_2F_2. Incidentally, the integrals for the ^{53}Cr spectra of such mixtures of CrO_2F_2, CrO_2ClF and CrO_2Cl_2 indicates the equilibrium constant $K = [CrO_2ClF]^2/[CrO_2F_2][CrO_2Cl_2]$ to be 1.11. This value is slightly smaller than the value of 2, estimated by mass spectrometry (8) and significantly less than the value predicted for statistical halogen redistribution.

Yours sincerely

E. Lloyd Jones Michael F.A. Dove O. Howarth

Eleanor Lloyd Jones M F A Dove Oliver Howarth

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TABLE ^{53}Cr and ^{17}O Chemical Shifts in Chromium(VI) Compounds

		CHEMICAL SHIFT (ppm)		
		^{53}Cr	Approximate line width Hz	^{17}O
Chromate				
Na_2CrO_4/D_2O	(298K)	0	(9)	-
$(NEt_4)_2CrO_4/MeCN$	(298K)	16.3	(15)	834.8
$(NEt_4)_2CrO_4/MeCN$	(343K)	25.5	(9)	834.0
Dichromate				
$(NEt_4)_2Cr_2O_7/MeCN$	(343K)	50.6	(827)	
$(NBu_4)_2Cr_2O_7/MeCN$	(298K)			[347.8 (bridging) 1119.7 (terminal)
Halochromates				
$NEt_4CrO_3F/MeCN$	(343K)	64.8	(235)	1211.0
$NEr_4CrO_3Cl/MeCN$	(343K)	112.0	(537)	1237.4
Chromyl Halides				
CrO_2F_2	(313K)	-79.1	(443)	1517.2
CrO_2F_2/in $C_2Cl_2F_4$	(298K)	-87.4	(262)	1503.9
CrO_2ClF	(313K)	85.5	(715)	1481.4
CrO_2Cl_2	(298K)	260.6	(675)	1456.8
CrO_2Cl_2	(313K)	262.8	(738)	1458.0

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Vibration Isolation System
for Superconducting Magnet

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

Dear Dr. Shapiro:

To initiate our subscription to the TAMU NMR newsletter, we describe how the 9.4 T magnet of our Bruker WM-400 NMR spectrometer is isolated from floor vibrations.

Since our research center was built directly over an underground train tunnel, detectors (our feet!) had forwarned us of severe floor vibrations. Prior to installation of the spectrometer, a survey of our building showed the presence of severe vibrations of 2.5 μm at 8-10 Hz, 2.18 μm at 6 Hz, and lesser ones at other frequencies. The Bruker specification for a 9.4 T magnet is that vibrations should not exceed 1 μm at any frequency. Due to the high sensitivity of the instrument, failure to eliminate the severe vibrations would result in symmetrical spikes/modulations at the base of strong resonances.

To isolate the magnet from the building vibrations we have mounted it on a Vibration Isolation Table (Figure 1) purchased from Optikon Corporation Ltd. They designed it based on the magnet's weight and center of mass, as well as the frequency and amplitude of the floor vibrations. From Figure 1, one sees that the magnet is inside the well of a cradle that floats ~ 2" above the floor. Vibration isolation of this cradle assembly is maintained by four automatic pneumatic isolator units (black bellows in Figure 1) mounted between the structural frame and the cradle assembly. The construction is

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entirely aluminum and needs only a ~ 20 psi air supply. The isolator units keep the base plate level and can quickly respond to, and compensate for any changes in the position of the cradle. The design is very effective at isolating the magnet from floor vibrations, even down to the low frequency vibrations which are usually difficult to remove. For example, the maximum displacements at 2 Hz and 4 Hz are 0.42 μm and 0.17 μm, respectively. The RMS amplitudes of the vibrations throughout the range of frequencies from 1 to 1000 Hz are all within the tolerances specified by Bruker.

We have found that this vibration isolation table does not pose any problems during probe and sample changes, probe tuning, or magnet shimming and maintenance. Another bonus of the vibration isolation table is that it restricts large objects (e.g. helium transfer dewars) from approaching within 1-2 feet of the magnet. The entire unit has been maintenance free for the 2 1/2 years that it has been in operation.

We recommend this or similar vibration isolation tables to anyone who does not have the luxury of a vibration-free floor for their superconducting magnet.

Yours very truly,

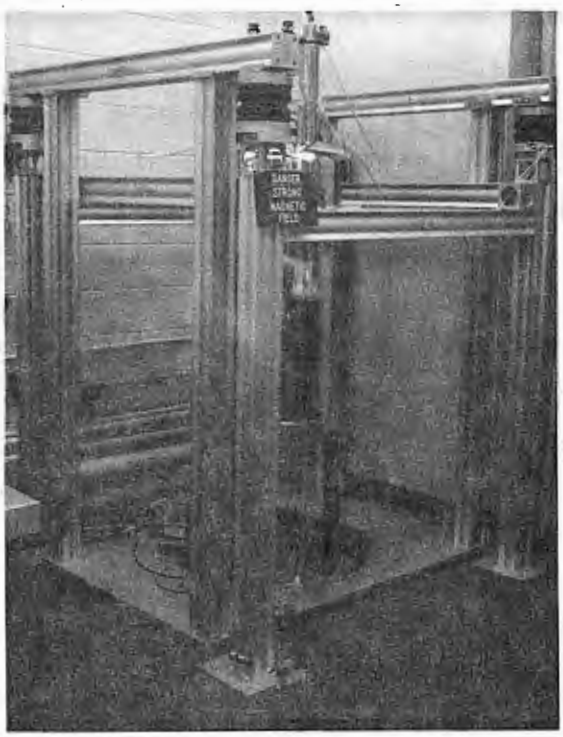
Gordon J. Kennedy
G.J. Kennedy
Research Chemist

Richard Ozubko
R.S. Ozubko
Sr. Research Chemist

Cathy Michael
C.A. Michael
Technician

GJK/tlf
1472V

c.c. R. VanderLinden



Prof. Dr. F.H. Köhler
ANORGANISCH-CHEMISCHES INSTITUT
DER
TECHNISCHEN UNIVERSITÄT MÜNCHEN

D-8046 GARCHING 21.06.85
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Professor B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77 843

USA

Title: NMR study of electron spin crossover

Dear Professor Shapiro,

this letter hopefully saves us from your ultimatum. - For quite some time we have been active in the NMR spectroscopy of paramagnetic transitionmetal π-complexes. In the classical series of metallocenes there was a strange gap between chromium and iron. For instance, we were unable to obtain easily interpretable ^1H spectra at ambient temperature for several manganocenes with the general formula $(Rcp)_2Mn$. This was strange since McConnell and Holm [1] saw a signal for Cp_2Mn and Switzer, Wang, Rettig and Maki [2] published data on $(Mecp)_2Mn$. We then found out [3] that at high temperature the full set of expected ^1H and even ^{13}C signals appears. This led us to perform a more thorough investigation which showed that at low and high temperature the spectra are completely different. As shown in the figure no problems seem to arise at 390 K whereas two sets of ^1H signals are present at 200 K. One belongs to a species which has a low concentration (cf. insert A with the vertical scale blown up) and which can be related approximately to the signals at 390 K by the Curie law. The other set of signals is new; note that now the shifts are surprisingly small. The two sets of signals belong to two different spin isomers of the manganocene: $^2E_{2g}$ and $^6A_{1g}$. More precisely, the signals at 390 K have averaged shifts of about 85 % high-spin and 15 % low-spin species. Coales-

cence occurs near room temperature, and this is why serious problems arise when detailed information is extracted under these conditions as has been done in Ref. 2.

The low-spin/high-spin equilibrium can be nicely studied, e.g. $\Delta H^\circ \approx 12$ kJmol^{-1}, $\Delta S^\circ \approx 45$ Jmol^{-1}K^{-1}, and $\Delta G^{\ddagger}(^6A_{1g} \rightarrow {}^2E_{2g}) \approx 47$ kJmol^{-1} in the case of $(Mecp)_2Mn$. It turns out that these parameters depend strongly on the substitution of the cyclopentadienyl ligand. Together with some other influences on the manganocene spin state a whole story results; it will be published soon.

Yours sincerely

(F.H. Köhler) (N. Hebendanz)

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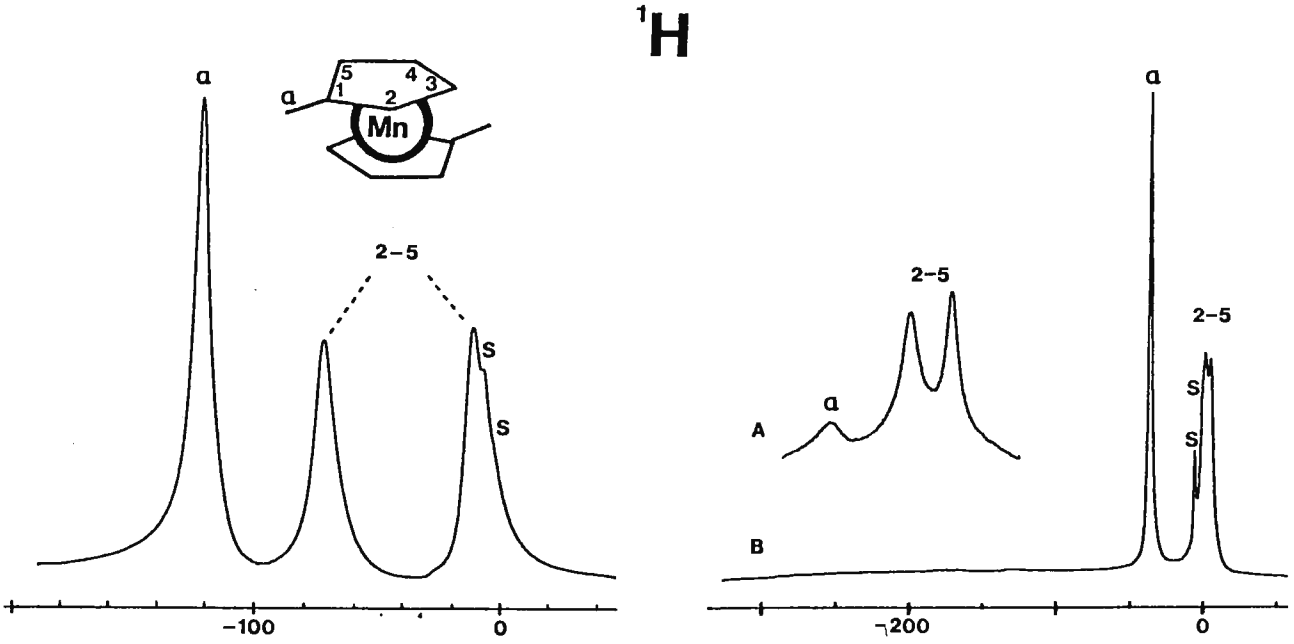

NMR spectra of $(Mecp)_2Mn$ dissolved in toluene-d_8 (S) at 390 K (left) and 200 K (right).

323-46

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SADIS BRUKER SPECTROSPIN, Boîte Postale N 67160 WISSEMBOURG

Professor B.L. SHAPIRO
Dpt of Chemistry
Texas A & M University

COLLEGE STATION
TX 77843-3255
USA

N./Réf.

V./Réf.

Wissembourg, le June 27, 1985

Polarize ! ^{13}C to ^{103}Rh and reverse polarisation transfer.

Dear Barry,

In a cooperative work with Prof. JM LEHN and Dr JP KINTZINGER in Strasbourg, we had a look at the 50 % enriched * $(CO)_4Rh_2Cl_2$ compound.

The ^{13}C spectrum shows the expected doublet (J_{C-Rh} = 76 Hz) and we used a $\{^{13}C\} \rightarrow ^{103}Rh$ INEPT sequence to detect the ^{103}Rh resonance (expected gain in sensitivity 7,9 / 1).

Much to our surprise, the ^{103}Rh spectrum consists of two resonances ($\Delta\delta$ = 10,4 Hz with respectively 76 Hz and 152 Hz splittings).

This represents a nice determination of the enrichment procedure, and tells us that the Rhodium complex was enriched ca, 57 % on both CO's and 43 % on only one CO. As a check, we run the $\{^{13}C\} \rightarrow ^{103}Rh$ DEPT experiment which provides the Rh - 2(CO) resonance down (triplet) and Rh - 1(CO) resonance up (doublet) (fig 2). The $\Delta\delta$ of - 1, 096 ppm corresponds then to a $^{12}C/^{13}C$ primary isotope shift on the Rhodium resonance.

Finally, figure 3 is the reverse $\{^{103}Rh\} \rightarrow ^{13}C$ 2D retro-INEPT (1) alternative for RH103 detection (measuring time : 1 hour).

With my best regards,

christian

C. BREVARD

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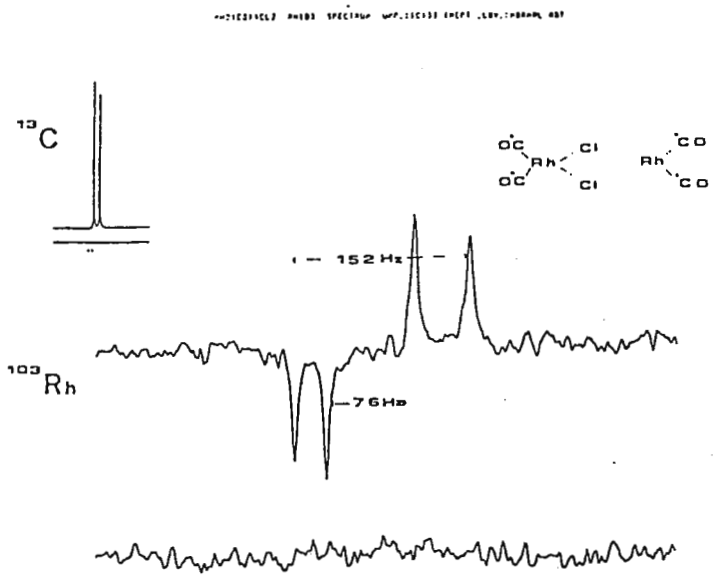

Fig 1 : {C13}-Rh103 INEPT (lower : normal AQT)
upper : INEPT AQT)

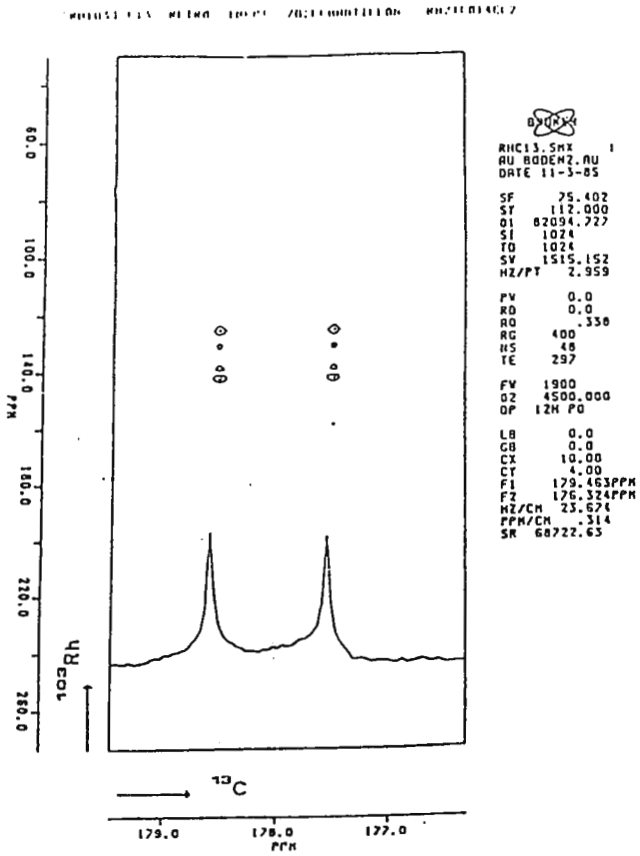

Fig 3 : 2D retro-INEPT {Rh103}-C13 contour plot. Note the clean distinction between RH-1CO and Rh-2CO species

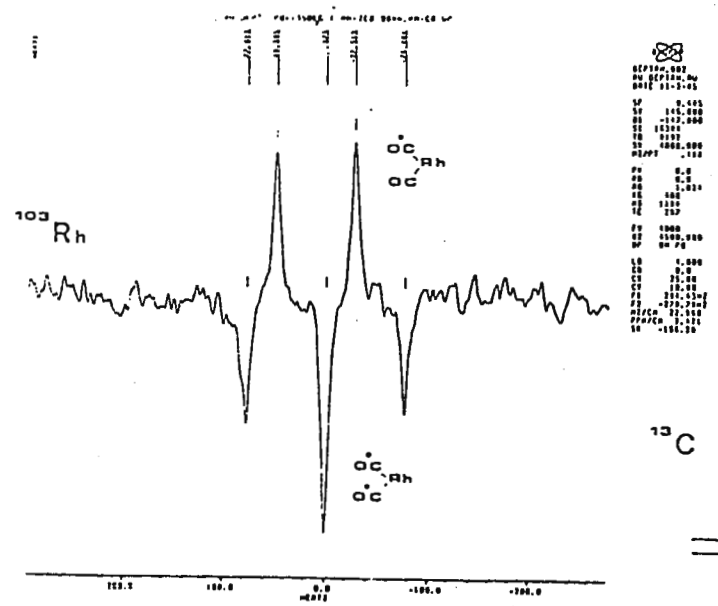

Fig 2 : DEPT 135° {C13}-Rh103 INEPT Spectrum

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C. Brevard, B. Mann, P. Maitlis, J.C.S. Chem. Commun. 1985 p. 65

DUKE UNIVERSITY MEDICAL CENTER

Department of Radiology

13 June 1985

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

Re: Paramagnetic Radicals and Peptide Structure

Dear Professor Shapiro:

Kopple and Schamper suggested several years ago that the ^1H NMR resonance line broadening produced by association with a nitroxide radical could be used to probe the amide protons in studies of peptide structure.(1) Recently we applied their method to study a monodisperse glutamate heptamer, Boc-(Glu-OMe)$_7$-OPOE in $CDCl_3$, at conditions where we believe the molecule is free of intermolecular hydrogen bonding and molecularly disperse in solution. As Fig. 1 shows, addition of the radical preferentially broadens the Glu^1-Glu^3 NH protons in the N-terminus as opposed to the other NH groups in the C-terminal portion. By other criteria (coupling constant, temperature dependence, solvent denaturation), the N-terminal NH groups were implicated in intramolecular hydrogen bonding while NH groups in the C-terminal portion were solvent exposed. This gave a paradoxical situation wherein the NH groups most affected by the dipolar broadening (and presumably accessible to solvent as in the cyclic gramicidin S peptide(1)) were also the groups involved in hydrogen bonds.

A possible explanation was obtained through model building. Models show that in certain intramolecularly hydrogen-bonded forms, such as C_7 ring structures, the NH groups could be more accessible than NH groups in the extended conformation. The C_7 ring forced glutamate side chains to be equatorial, thereby permitting access of bulky free radical molecules to the hydrogen bonded NH. In addition, the C_7 rings are relatively planar and the radical has nearly equal access from either side of the plane. Seen in this light, the free radical results do not conflict with the other NMR data, and leads us to caution that criteria developed for cyclic peptides is not simply extrapolated to linear peptide systems.

Incidentally, monodisperse homo-oligopeptides show a surprisingly large fraction of intramolecular hydrogen bonding at dilute conditions in weakly interacting environments. For example, recent infra-red studies suggest

that four NH groups are intramolecularly hydrogen bonded in a glutamate hexamer[2] and several years ago, we suggested that four NH groups are intramolecularly hydrogen bonded in a methionine heptamer in $CDCl_3$[3].

Sincerely yours,

Anthony A. Ribeiro

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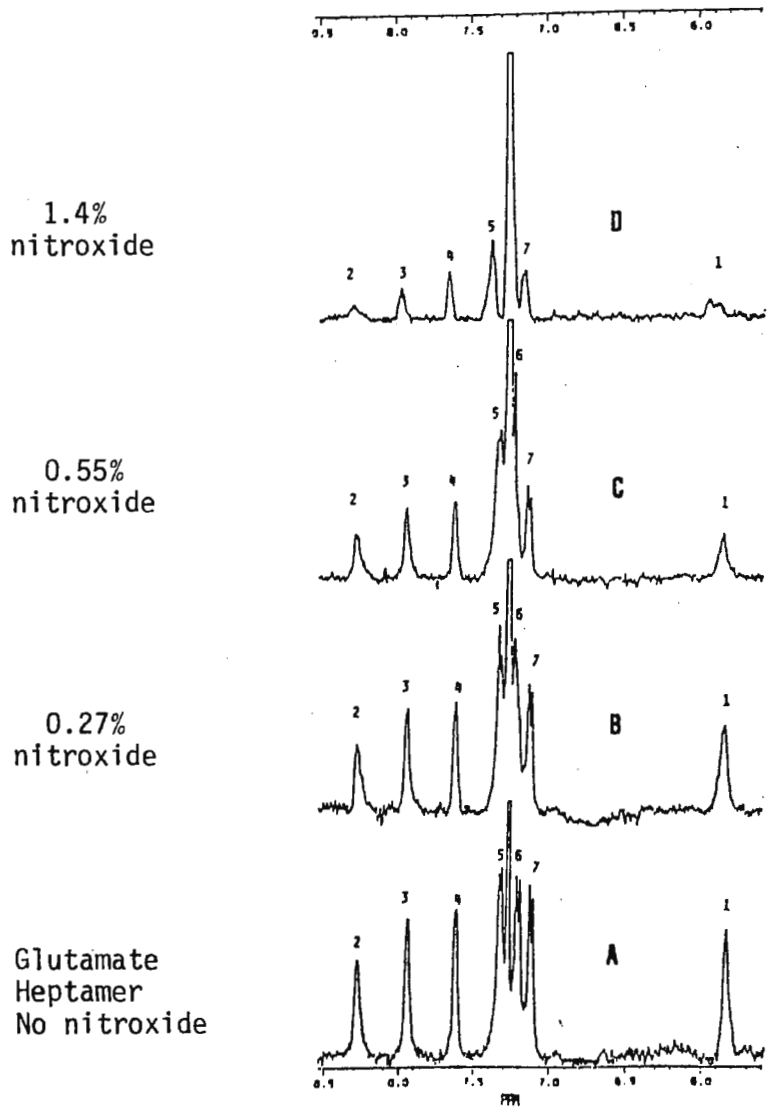

Fig. 1.

323-50

DEPARTMENT OF ORGANIC CHEMISTRY
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1983
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TECHNOLOGICAL ACHIEVEMENT

The University of Liverpool

18th June, 1985

RJA/AS

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

Dear Professor Shapiro,

PROTON SHIFTS AND S.C.S. IN SIMPLE MOLECULES

We have commenced an investigation in our laboratory into proton substituent chemical shifts (S.C.S.), in the pious hope that we may perhaps be able to quantitatively explain these shifts, in terms of the various mechanisms proposed previously.[1]

We have, to date, been gathering data on molecules of precisely known geometry, and we selected the cyclic systems of norbornane, norbornene, adamantane and cyclohexane as suitable substrates. In the hope that our refined data may be of use to TAMU NMR readers I enclose a table of proton chemical shifts of the parent molecules and the S.C.S. of the bromo substituents in norbornane, adamantane, and cyclohexane.[2,3]

Two comments may be pertinent. Every investigation we discovered in the literature of the low-temperature proton shifts of cyclohexane had used CS_2 as solvent. This well-known anisotropic solvent produces large differential solute shifts, as can be seen by comparison with the date for $CFCl_3$ solvent which we obtained.

Finally, no combination of the usual effects attributed to the bromo substituent can even begin to explain quantitatively the data in the Table.

With best wishes,

Yours sincerely,

Ray

DR. R.J. ABRAHAM

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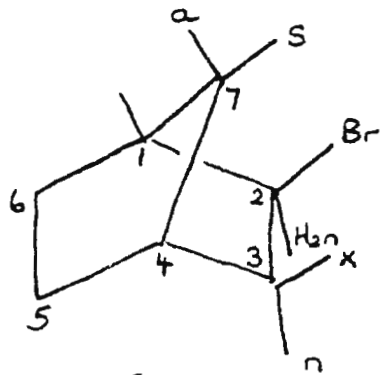
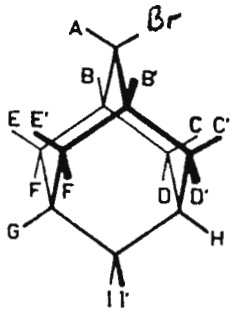
2,3. R.J.Abraham and J.Fisher, *Org.Mag.Res.*, (in press).

Substituent chemical shift for bromo compounds

2-exo-bromo-norbornane (1)		2-bromo-adamantane (2)		1-bromo-adamantane (3)		1ax-bromo cyclohexane (4)		1eq-bromo-cyclohexane (4)	
H		H		H		H		H	
1	0.324	A	2.924	α	0.615	1eq	3.097	1ax	2.839
2n	2.827	B	0.276	β	0.231	6eq	0.353	6eq	0.606
3x	0.599	C	0.587	γ	-0.022	6ax	0.576	6ax	0.523
3n	0.868	D	-0.130						
4	0.122	F	0.220						
5x	0.009	E	0.113						
5n	-0.079	G	0.009						
6x	0.174	H	0.009						
6n	0.017								
7s	0.675								
7a	0.107								



[1]



[2]

		This work	Previous Data
Adamantane	CH	1.874	1.88, 1.85
	CH_2	1.753	1.78, 1.75
Norbornane	bridgehead	2.192	2.20, -
	bridge	1.181	1.21, ∿1.13
	exo	1.471	1.49, 1.43
	endo	1.162	1.18, ∿1.13
Norbornene	1,4	2.841	2.80 - 2.83
	7 syn	1.313	1.32 - 1.33
	7 anti	1.073	1.03 - 1.06
	exo	1.603	1.53 - 1.59
	endo	0.951	0.93 - 0.96
	olefinic	5.985	5.92 - 5.96
Cyclohexane	equatorial	1.679	1.607
	axial	1.188	1.136

323-52

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF HELSINKI
E. HESPERIANKATU 4
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FINLAND

Helsinki July 4, 1985

New values for Q(^{6}Li), Q(^{7}Li) and Q(^{14}N) from quantum chemistry

Dear Professor Shapiro,

We have recently developed an improved method for calculating electric field gradients, q, in diatomic molecules by combining a two-dimensional ("2D"), fully numerical Hartree-Fock value with correlation and rovibrational contributions obtained from Complete Active Space (CAS SCF) LCAO calculations using large basis sets. The 2D method provides for the first time an unequivocal Hartree-Fock limit for q while the CAS SCF method accounts for most of the correlation[1,2]. The final values are given in the Table.

Concerning ^{7}Li, the old LiH value of Green[3] suffers from basis-set problems. His q_{HF} (R = 3.015 a.u.) is -0.044 a.u. while our benchmark is -0.0398 a.u. The two atomic measurements[4,5] have large experimental error bars. Of the nuclear, Coulomb scattering values, that of ref. 7 agrees with our value while that of ref. 6 does not.

In the case of ^{14}N, the old small-basis values from polyatomic molecules without correlation (Q(^{14}N) ≃ 0.016 b)[9] are inadequate. Our solid-state N_2 and gas-phase NO^+ values are in an adequate agreement with each other and with the atomic, N^+ 2p3p $^1P_1$ value of Winter and Andrä[8].

Please credit this letter to the account of Professor Kalevi Pihlaja at the University of Turku.

Sincerely yours,

Pekka Pyykkö

Pekka Pyykkö
Professor of Chemistry

References

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9 C.M. Lederer and V.S. Shirley (Eds.), Table of Isotopes, 7th ed. (Wiley, New York, 1978).

Table 1. Values of nuclear quadrupole moments Q (in barn = 10^{-28} m^2)

Nucleus	System	Q/b	Reference
^{7}Li	LiH	-0.0406	Present work [1]
	LiH	-0.0366(3)	[3]
	$Li(2^2P)$	-0.041(5)	[4]
	$Li(3^2P)$	-0.059(6)	[5]
	nuclear scattering	-0.0370(8)	[6]
	nuclear scattering	-0.040(11)	[7]
^{6}Li	$Q(^6Li)/Q(^7Li)$ from LiF or LiBr	-0.00083	Present work [1]
^{14}N	NO^+ (g)	0.0205	Present work [2]
	N_2 (s)	0.0204	Present work [2]
	$N^+(2p3p\ ^1P_1)$	0.0193(8)	[8]
	polyatomic molecules	0.016	[9]

323-54

Brock University

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Telephone (416) 688-5550 Extension 3406

July 10, 1985.

Prof. B. L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, Texas 77843-3255, U.S.A.

Selenium-77 MAS NMR of Inorganic Compounds

Dear Barry:

In collaboration with Gary Schrobilgen and Már Bjorgvinsson of McMaster University I have been exploring possible uses of solid-state high-resolution selenium-77 nmr in inorganic chemistry and report some preliminary results. Selenium-77 is an easy nucleus for MAS nmr in that it is spin-1/2 and 7.6% abundant, but long relaxation times can be a problem. Relaxation delays of 5 minutes between 30° pulses seem optimal for some samples. A further problem is large chemical shift anisotropy that can lead to multiple spinning sidebands when the symmetry about selenium is low. This effect is illustrated in the attached spectra of selenium dioxide.

Na_2SeO_4 has tetrahedral symmetry about selenium and K_2Se has the antifluorite structure with eight potassium atoms about selenium at the vertices of a cube. Each of these compounds gives a single peak with negligible spinning sidebands, at +1037 and -442 ppm from Me_2Se, respectively. SeO_2, in contrast, has a low-symmetry structure involving infinite chains in which selenium is bonded to three oxygens in a flat pyramid; two of the oxygens are bridging and one is terminal. At both 4.7 tesla (spectrum A) and 9.4 tesla (spectrum B) a multiple-sideband pattern is obtained. Variable spin rate experiments identify the centre band at +1462 ppm from Me_2Se.

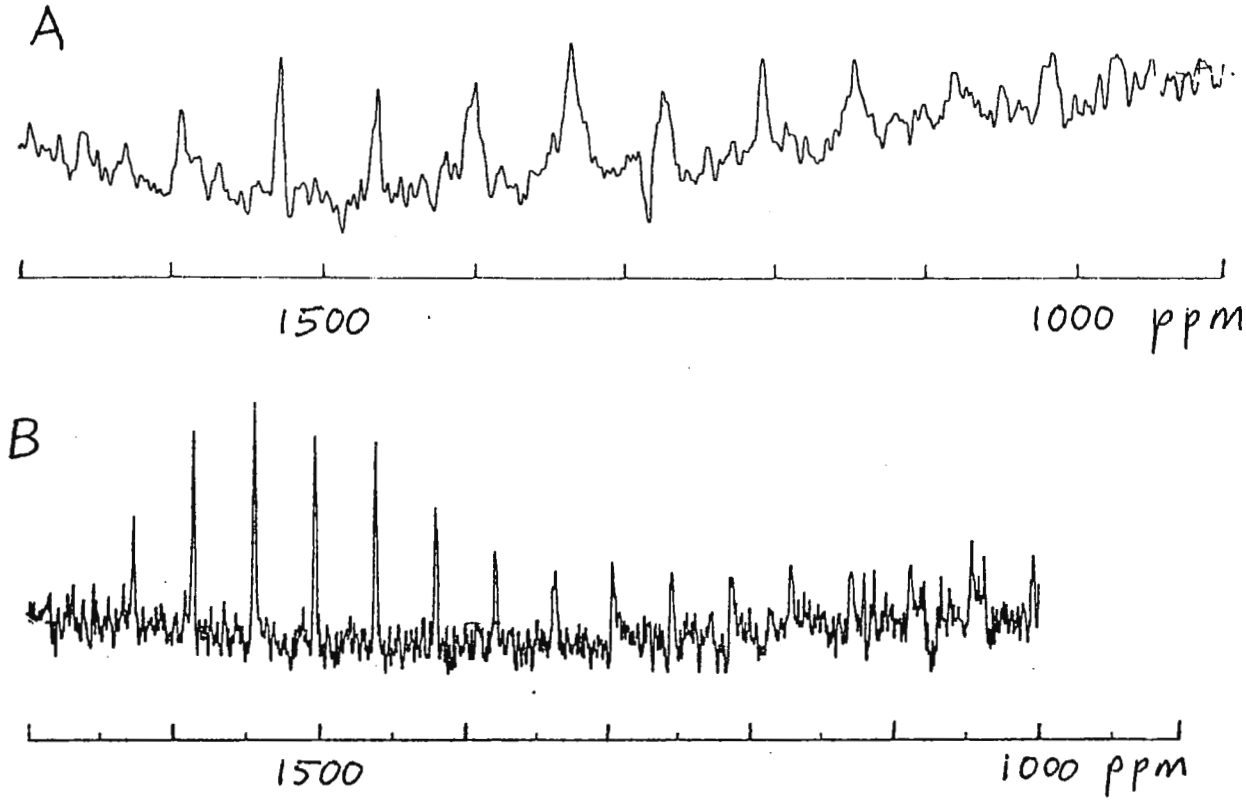
Thus selenium-77 MAS nmr seems easy until the more interesting (i.e., less symmetrical) compounds are tried. Recently-developed sideband suppression methods should however get around this problem. The spectra shown were obtained on the Bruker CXP-200 and WH-400 instruments of the South Western Ontario High Field Nmr Centre, with the assistance of Bob Lenkinski and Bill Klimstra.

I hope this contribution suffices to reinstate the Brock University subscription.

Yours sincerely,

Steve Hartman

J. S. Hartman,
Professor of Chemistry.



^{77}Se MAS Nmr Spectra of SeO_2.

A. 38.2 MHz, 43 scans, 5 min relaxation delay between 30° pulses, 100 Hz line broadening.

B. 76.3 MHz, 14 scans, 5 min relaxation delay between 30° pulses, 50 Hz line broadening. Some sidebands are folded.

NMR Spectroscopist

As a specialist in NMR spectroscopy, contribute to the solution of structural, mechanistic, and process problems arising out of on-going research programs within the Chemical Research Division of American Cyanamid. Work on polymers, composites, specialty chemicals, and intermediates in close collaboration with project scientists and other instrumental specialists. Carry out self-initiated research in NMR spectroscopy. Proficiency in the operation of a variety of instruments and the application of modern data acquisition and handling techniques required. Both solution and solid-state applications are to be carried out for ^{1}H, ^{13}C, and other nuclei. Familiarity with FT pulse sequences and quantitative analysis by NMR is essential. Acquisition of a high-field instrument is planned and the successful candidate will be expect to play a major role in evaluating and specifying the new equipment. Preferred applicants will have attained the Ph.D. degree in physical, organic, polymer, or analytical chemistry, or a related discipline, and have a demonstrated record of achievement in NMR spectroscopy. Of particular interest are those with experience in new solid-state NMR techniques.

This position is being offered by the Scientific Services Department of the Chemical Research Division of American Cyanamid located in Stamford, Connecticut. As a member of this department, the candidate will join more than 90 other scientists who utilize a complete range of modern analytical tools to promote the growth of Cyanamid's chemical businesses. As a corporate resource for analytical excellence in a number of key areas, including analytical microscopy, inorganic analysis, polymer chemistry, physical chemistry and testing, and industrial hygiene, we actively participate in research, production, and customer service projects in Cyanamid's other business areas: medical, agricultural, and consumer products.

We offer a competitive salary and benefits package. Cyanamid is an equal opportunity employer. Those interested in further consideration should forward a resume to Dr. Teresa L. Muchnick, Group Leader, Chromatography and Spectroscopy, American Cyanamid, 1937 West Main Street, P.O. Box 60, Stamford, Connecticut.

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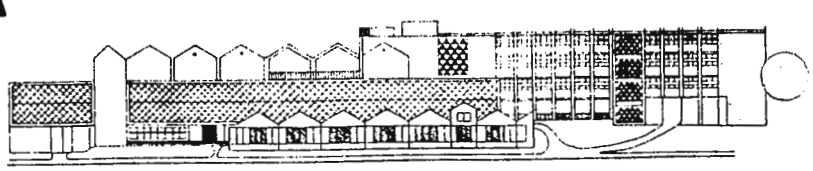
Kuala Lumpur.
Malaysia.



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17 June 1985

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

Dear Professor Shapiro,

Intramolecular Interactions of the Methyl Group

As part of our continuing effort to study the above interaction we have measured the spin–lattice relaxation parameters of 3-heptyne (ethyl-n-propylacetylene) in the neat liquid at 28 C and 25.05 MHz:

	C — C — C ≡ C — C — C — C					
T_1/s	8.7	15.5		12.6	10.4	10.7
η	1.9	1.8		2.0	1.9	1.7

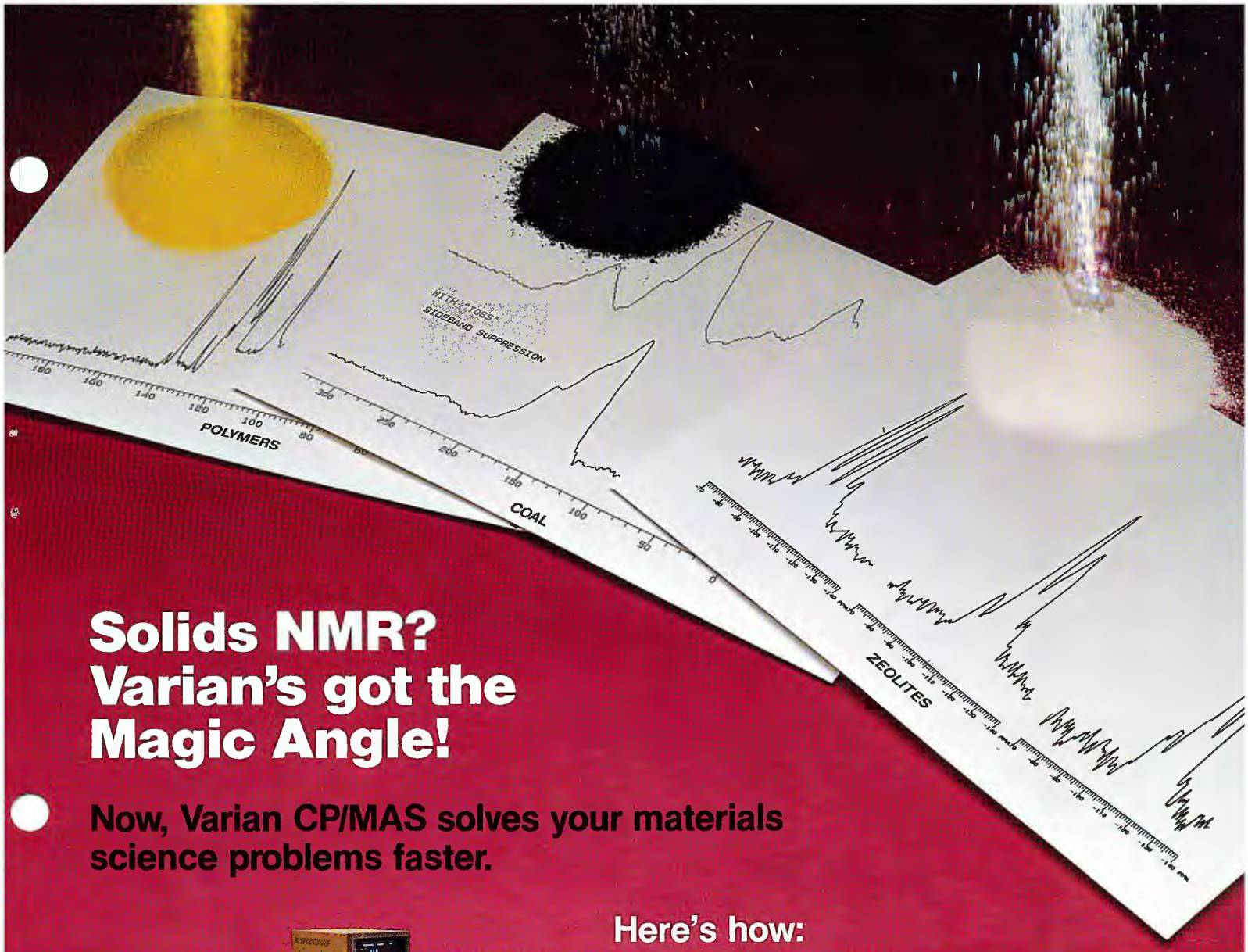
The methyl carbon of the ethyl group has substantially reduced T_1 value and this may indicate that the internal rotation of this methyl group is hindered so that the contribution to nuclear relaxation from the dipole–dipole mechanism is increased. The unusually high NOE factor (η) for this methyl carbon is consistent with this explanation. The methyl group is oriented at a favorable angle with respect to the triple bonds, so that an electrostatic (attractive) interaction between the polarizable methyl hydrogens and the π electron system can take place, thereby reducing the rate of rotation of the methyl group. The methyl carbon of the ethyl group in 3-heptyne is part of a three-carbon chain attached to a π system and the observation of a reduced T_1 value is similar to that of the methyl carbon of the n-propyl group attached to an electronegative atom, oxygen or nitrogen (1).

The methyl carbon of the n-propyl group in 3-heptyne does not show a significantly reduced T_1 value, no doubt because it is part of a four-carbon chain in which the freedom of rotation about an extra C–C bond does not favor the weak attraction between the methyl hydrogens and the π electron system.

Yours sincerely,

Soon Ng

(1) S. Ng, Org. Magn. Reson. 21, 50 (1983)



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Department of Chemistry

Evanston, Illinois 60201

July 18, 1985

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

Dear Barry:

Your readers may be interested in the following meeting.

U.S.-Latin American Workshop on Recent Developments in Organic and Bioorganic NMR, with emphasis on research in developing countries, will be held July 7-11, 1986, in Campinas, Brazil. This Workshop follows immediately the ISMAR conference in Rio de Janeiro. The Workshop will cover current developments and will explore how scientists in developing countries can gain access to new NMR methods for use in their research. The tentative list of speakers includes M. Barfield, A. A. Bothner-By, E. L. Eliel, J. B. Grutzner, J. B. Lambert, E. P. Mazzola, D. E. Wemmer, C. S. Yannoni (U.S.A.), F. Y. Fujiwara, A. J. Marsaioli, M. A. P. Martins, R. Rittner, P. R. Seidl, J. A. Vanin, N. Zanatta (Brazil), R. H. Contreras, D. G. de Kowalewski, V. J. Kowalewski (Argentina), and P. Laszlo (Belgium). For further information please contact one of the Directors.

Professor Joseph B. Lambert
Northwestern University
Department of Chemistry
2145 Sheridan Road
Evanston, IL 60201
U.S.A.

Professor Roberto Rittner
Instituto de Química
Unicamp
Caixa Postal 6154
13083 Campinas--SP
Brazil

Sincerely,

Joseph B. Lambert

JBL:cs

323-60

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June 20, 1985

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

POSITION AVAILABLE - NMR SPECTROSCOPIST

Dear Professor Shapiro:

Procter & Gamble Company has an immediate entry-level staff opening in NMR spectroscopy at the Miami Valley Laboratories in Cincinnati, Ohio. Applicants should have a Ph.D. in chemistry, biochemistry or a related field, preferably with postdoctoral experience. A strong background in high-field multinuclear FT-NMR and experience with two-dimensional NMR techniques are essential. Applicants should have the ability to solve chemical and structural problems using NMR spectroscopy, have a demonstrated interest in biochemical problems, and be knowledgeable with computer interfacing. Our primary interest is the study of the structure and dynamics of biomolecules in solution. The NMR laboratory is currently equipped with a Bruker CXP-300, JEOL FX-270 and several low-field spectrometers. We will be taking delivery of a General Electric GN-500 by August.

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July 16, 1985

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

Dear Dr. Shapiro:

Union Carbide has an immediate opening for an NMR spectroscopist at our Bound Brook Technical Center located in central New Jersey. The position is in the NMR laboratory of the R&D Analytical Section. This laboratory currently is equipped with an IBM WP-200/SY with a C-13 CPMAS accessory, an IBM WP-270/SY, and a Varian CFT-20. An IBM/Bruker AM-360 is expected to be delivered in October of this year.

The successful applicant should have a Ph.D. degree in chemistry with experience in high resolution, high field multinuclear NMR. Experience in polymer analysis and 2-D, multipulse, and solid state NMR would also be helpful. The assignment involves co-responsibility for operation of the NMR laboratory and requires extensive interaction with other members of the technical staff. The focus of the NMR laboratory is on the structure elucidation of polymers and polymer-related materials.

Interested applicants should send their resume to DR. K. POLLAK - UNION CARBIDE CORPORATION, P.O. BOX 670, BOUND BROOK, NJ 08805. Salary and benefits are competitive and commensurate with qualifications and experience. Union Carbide Corporation is an equal opportunity employer.

Sincerely,

K. Pollak

K. Pollak

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323-62

The University of Alabama in Birmingham
Comprehensive Cancer Center
NMR Core Facility / CHSB B-31
205/934-5696

August 1, 1985

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

Re Postdoctoral Position

Dear Barry:

I would like to announce a postdoctoral opening in my laboratory at the Cancer Center. The work will involve the structural studies of DNA oligomers and small proteins using various NMR techniques including 2D-NMR methods. Prior experience in this area and/or computer programming (Fortran and Basic) would be a definite advantage. An additional postdoctoral position involving in vivo applications of NMR may become available in the near future. The facilities at the Cancer Center include two high-field superconducting NMR spectrometers (Bruker WH-400 and CXP-300/200) and an iron magnet system (HX-90). Interested candidates should send a resume and arrange for three letters of recommendation to reach me at the Cancer Center.

Yours sincerely,

Ramu

N.R. Krishna, Ph.D.
Associate Professor of Biochemistry
Director, NMR Core Facility

UNIVERSITY OF
STOCKHOLM
Physical Chemistry

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

Stockholm, June 26, 1985

INTERACTION BETWEEN QUINUCLIDINE AND BENZENE

Dear Dr Shapiro,

We have recently studied quinuclidine, 1, in various hydrogen bond donors [1]. We found, by carbon-13 relaxation measurements, that the hydrogen bond formation led to substantial anisotropy in the rotational diffusion of quinuclidine. As the inert "reference" solvent, we have in that work used benzene. It bothered us, however, that even in this solvent the anisotropy was by no means negligible, the ratio of the diffusion constants R(parallel)/R(perpendicular) being about 2.5. Recently, we took another look at the problem by studying the motion of 1 in mixtures of benzene and cyclohexane. The results are shown in Figure 1. In pure cyclohexane, quinuclidine reorients almost isotropicly and the anisotropy increases quickly upon adding benzene. Obviously, the data indicate that the presence of benzene hinders the reorientation of the symmetry axis of quinuclidine due to some kind of attractive potential. An interesting question to ask is which geometrical arrangement of the two molecules gives such a potential minimum. We are going to try to look into this problem in the near future.

Yours sincerely

Jozef Kowalewski Arnold Maliniak

1. A. Maliniak, J. Kowalewski and I. Panas, J. Phys. Chem., 88, 5628 (1984).

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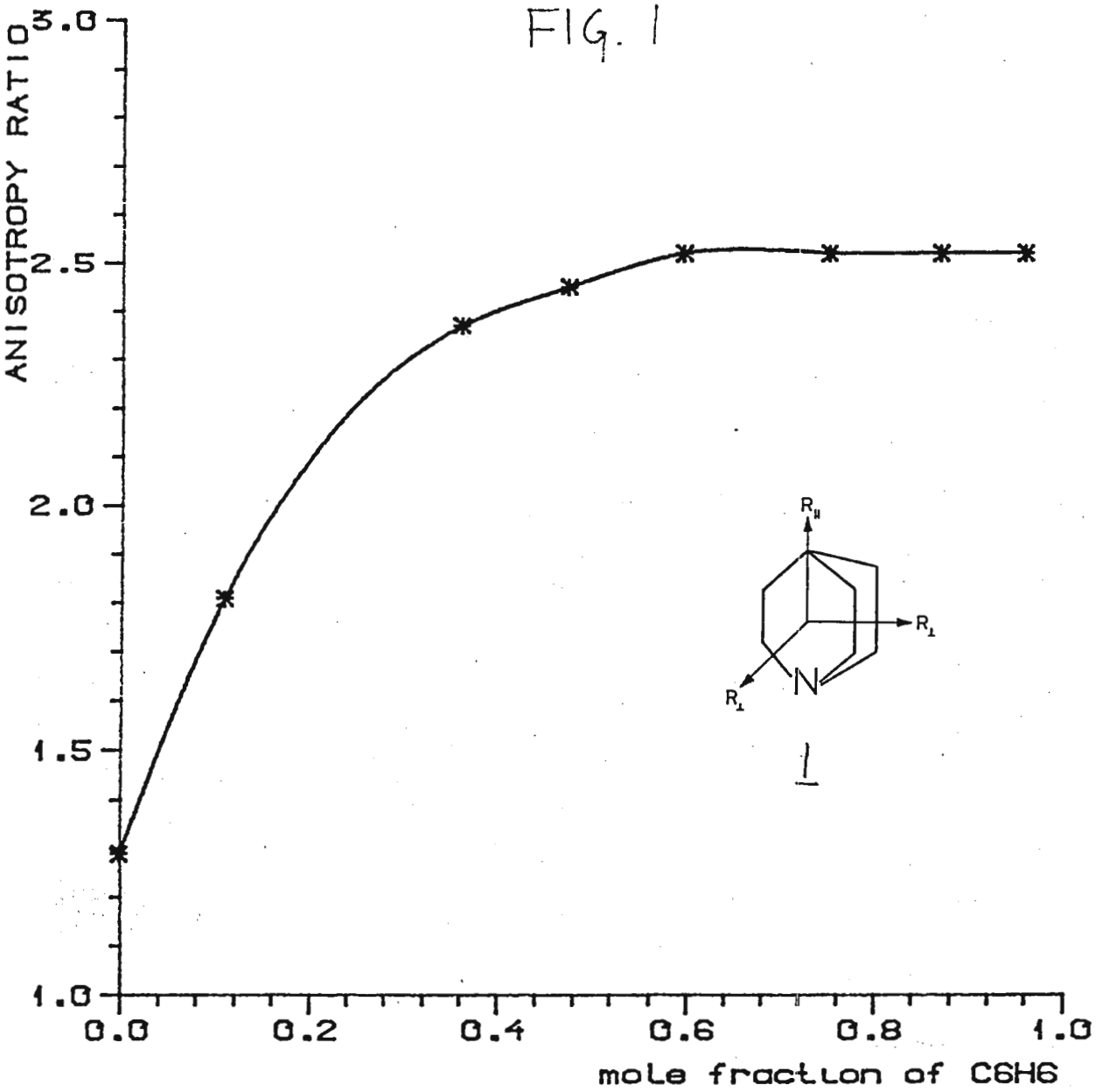
FIG. 1



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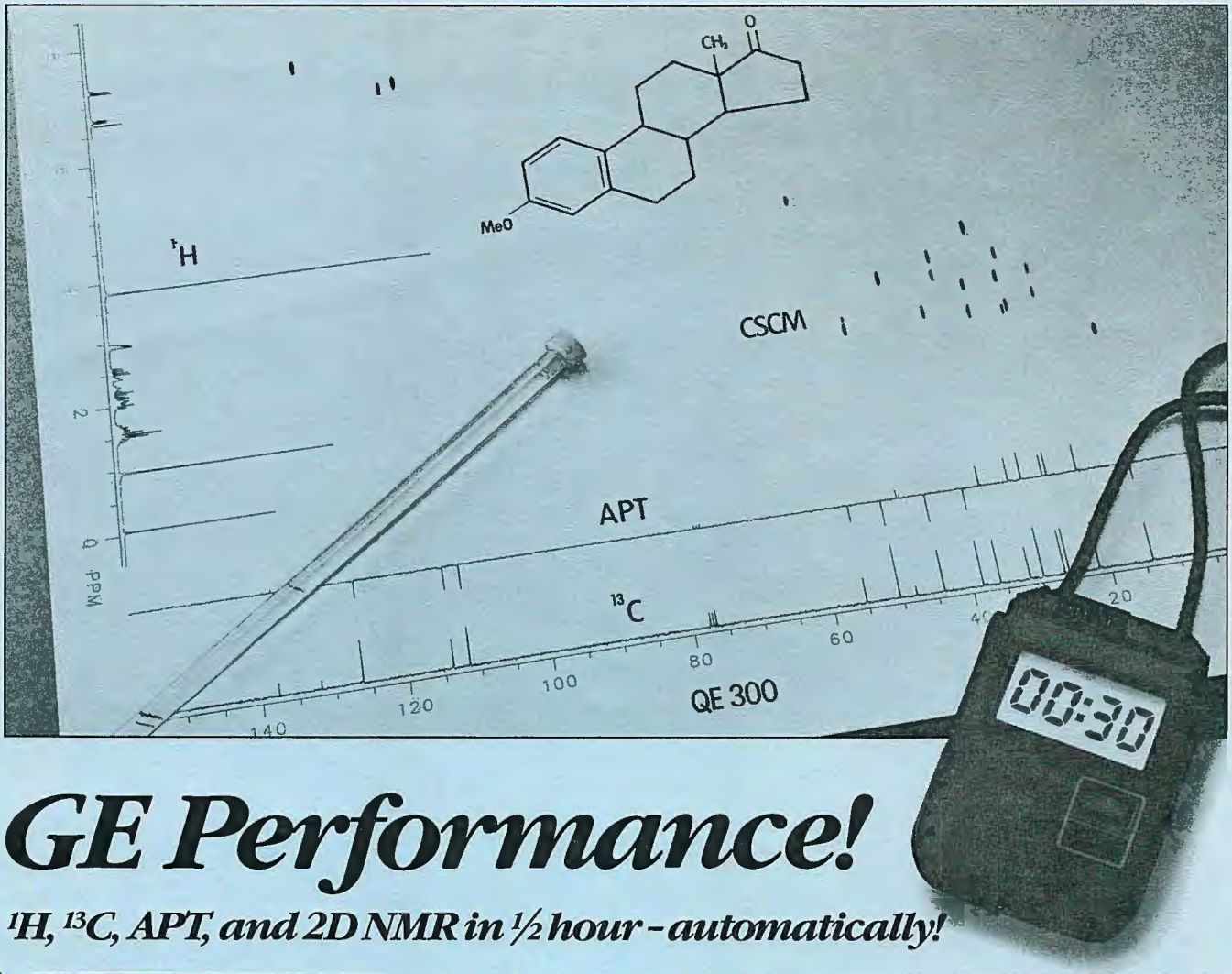

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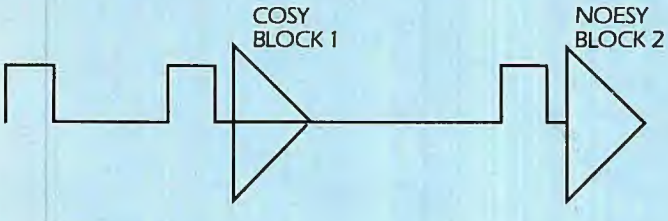

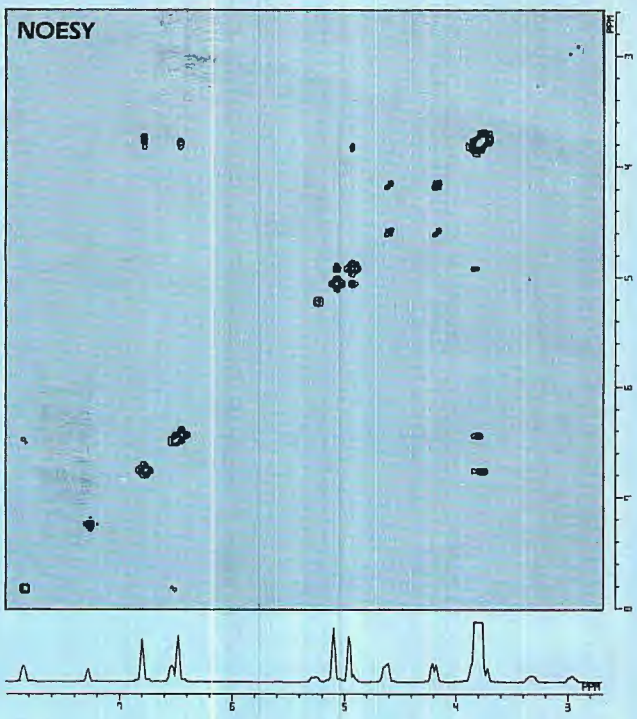

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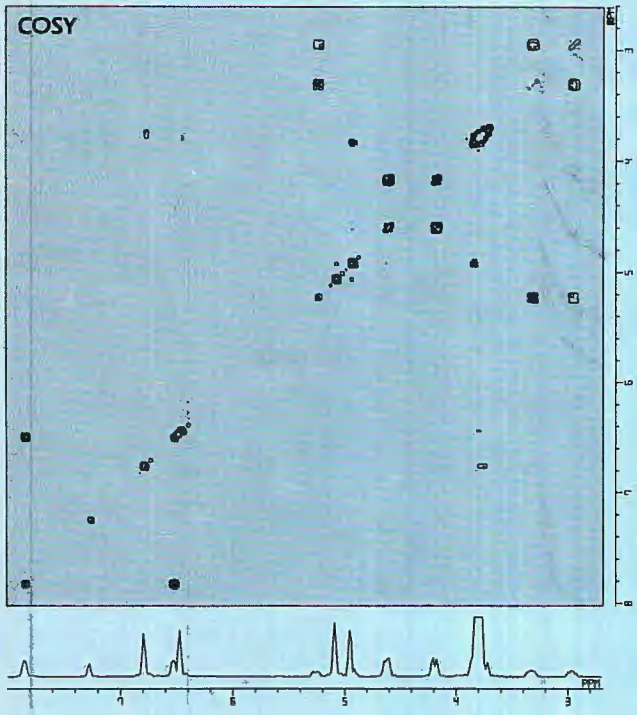

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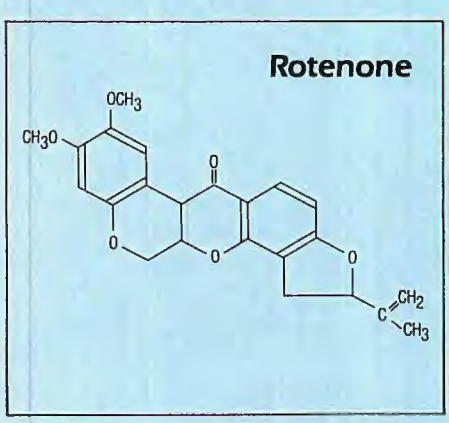

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