TEXAS A&M UNIVERSITY

NMR NEWSLETTER

NO. 316

JANUARY 1985

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NMR NEWSLETTER

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CONTRIBUTORS

Chemagnetics, Inc.
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AUTHOR INDEX ---- TAMU NMR NEWSLETTER, NO. 316, JANUARY 1984

Forthcoming NMR Meetings (Additional listings are solicited)

New Directions in Chemical Analysis, the 3rd Annual Symposium of the Industry-University Cooperative Chemistry Program, Texas A&M University, College Station, Texas, April 1-3, 1985. Papers to be presented by T.B. Hirschfeld, R.D. Macfarlane, C.A. Fyfe, R.L. Swofford, G. Guiochon, A.G. Marshall, A.T. Hubbard, A.C. Parr, J. Ruzicka, J. Callis, N. Winograd, D.H. Williams, M.V. Novotny, W.P. Rothwell, J. Schaefer. For further information, write Prof. E. A. Schweikert, Department of Chemistry, Texas A&M University, College Station, Texas 77843 U.S.A.; (409) 845-2341.

26th ENC - April 21-25, 1985, Asilomar, Pacific Grove, California; Chairman: P. Mark Henrichs, Research Laboratories, Eastman Kodak Company, Rochester, New York 14650.

Seventh International Meeting on NMR Spectroscopy - July 8-12, 1985, University of Cambridge - see p. 47.

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

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. 318 ---------- 4 March 1985

No. 319 ---------- 1 April 1985

Chemistry

UNIVERSITY OF STIRLING STIRLING FK9 4LA SCOTLAND | TELEPHONE: STIRLING (0786) 31

Professor B Shapiro
Chemistry Department
Texas A & M University
College Station
Tx 77843
U S A

7 November 1984

Dear Barry,

USE OF INDOR TO SOLVE AN INTERESTING EPOXIDE STRUCTURE

Some years ago we completed an INDOR ^1H study on a tris-epoxide of humulene that has never been reported but nonetheless is an interesting little piece of work (at least we think so!).

One of the four possible tris-epoxides of humulene was obtained by peroxyacid treatment of humulene and given to the nmr and X-ray labs to find out the relative stereochemistry. The relative stereochemistry of humulene-1,2,8,9-bisepoxide was already known from X-ray studies. Two or three hours of classical INDOR spectroscopy and about 5 minutes thought gave us the answer in the form of structure (1). About two weeks later the crystallographers caught up with us and we are happy to say that they got it right!

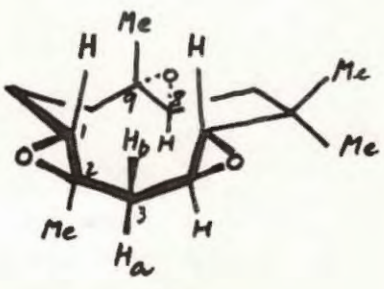
Perhaps the most interesting feature of the spectrum is the high field chemical shift (δ0.7) of one of the C-3 protons. From the coupling patterns observed and from the INDOR experiments, this can only be due to 3-H_b which is positioned within the shielding zone of both epoxide rings as indicated in (1). As can be seen from the spectra, the 3-H_a proton resonates at much lower field (δ2·8). The spectra were obtained at 90 MHz on a Perkin Elmer R32 instrument and the compound was supplied by Jim Roberts' group.

With best wishes,

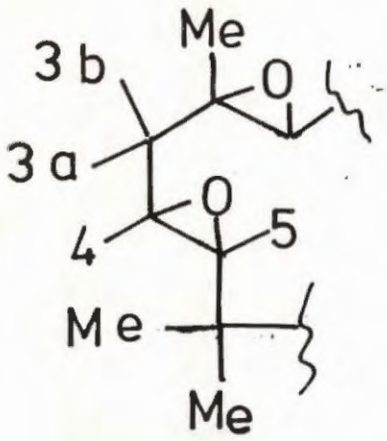
James S. Roberts

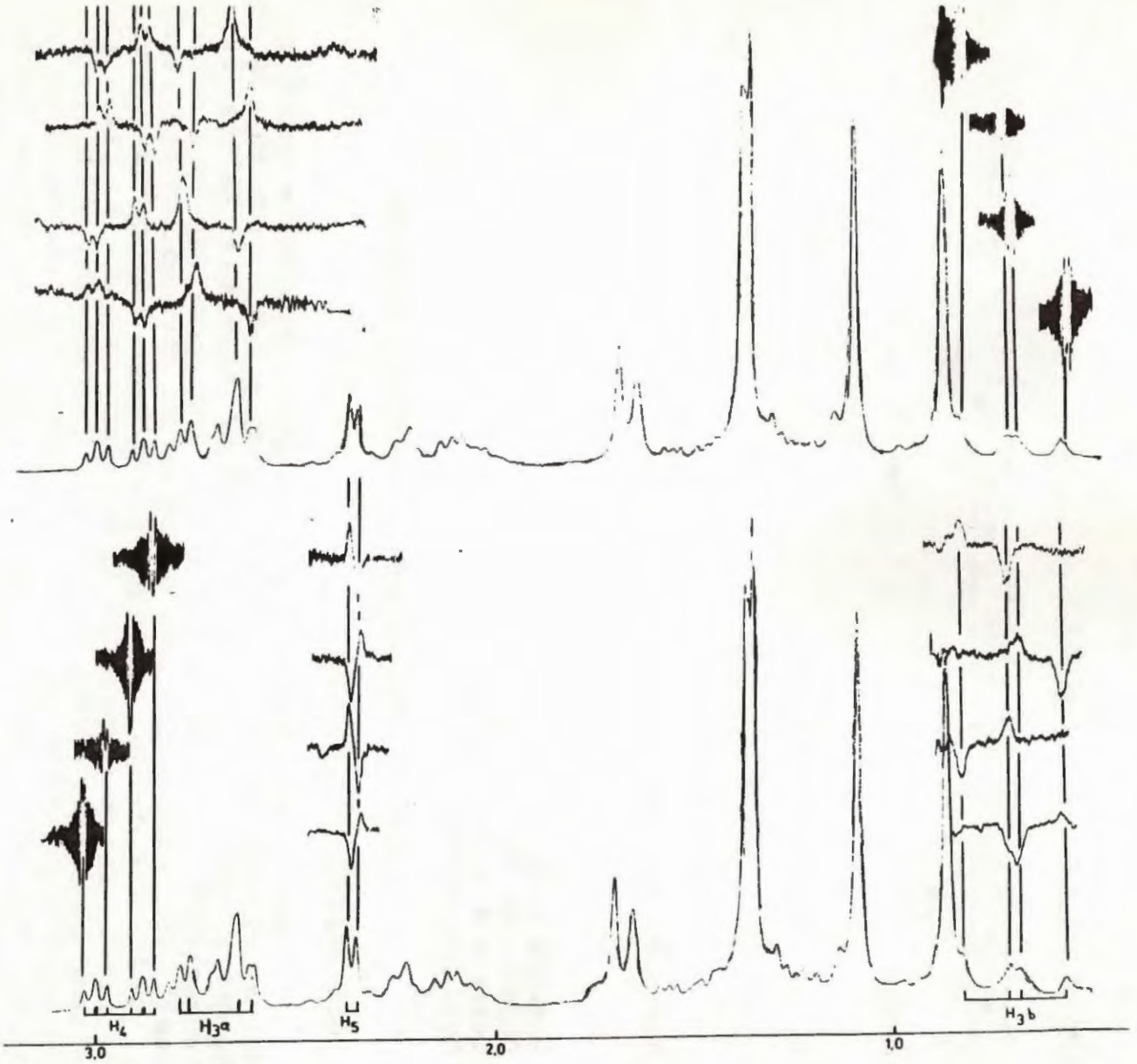
Dr J S Roberts

Dr F G Riddell



(1)


Me
3b
O
3a
O
4
5
Me
Me


H4
H3a
H5
H3b
3.0
2.0
1.0

316-3

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December 18, 1984

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

Shift vs. Temperature Calculator Program

Dear Barry,

While calibrating the variable temperature units on our spectrometers we felt that a simple BASIC program would be more useful than the charts of chemical shifts vs. temperature. Rich Mazzarisi in our lab wrote one in Nicolet Basic, the program provides selection of methanol or ethylene glycol, the range of temperature and increments to be printed. Shift is printed in both Hz and ppm. No limit is placed on spectrometer frequency, the program will not be rendered obsolete by future magnet technology for sometime to come. The questions are based on the paper by Amman, Meier and Merbach, Journal of Magnetic Resouance 46, 319 (1982).

Best Regards

Rudi Nunlist

```
LIST
   100 REM <<<<<<PROGRAM TMPCAL>>>>>>
   110 REM ***AMMANN ET AL., J. MAG. RES. 46:319-321 (1982)
   120 REM
   130 PRINT
   140 PRINT "TEMPERATURE CALIBRATION TABLE GENERATOR"
   150 PRINT
   160 PRINT "WHAT IS THE PROTON FREQUENCY (MHZ)";
   170 INPUT F
   180 PRINT
   190 PRINT " IS THE STANDARD ETHYLENE GLYCOL";
   200 INPUT R$
   210 IF R$="N" GOTO    250
   220 IF R$<>"Y" GOTO    190
   230 LET F1=1
   240 GOTO    330
   250 PRINT "  METHANOL";
   260 INPUT R$
   270 IF R$="N" GOTO    310
   280 IF R$<>"Y" GOTO    250
   290 LET F1=2
   300 GOTO    330
   310 PRINT "SORRY THOSE ARE THE ONLY CHOICES!"
   320 GOTO    750
   330 PRINT
   340 PRINT "ENTER LOWEST TEMPERATURE (C)";
   350 INPUT L
   360 ON F1 GOTO    370,   400
   370 IF L>=0 GOTO    430
   380 PRINT "LOWEST VALID TEMP FOR ETHYLENE GLYCOL IS 0C"
   390 GOTO    340
   400 IF L>=-95 GOTO    430
   410 PRINT "LOWEST VALID TEMP FOR METHANOL IS -95C"
   420 GOTO    340
   430 PRINT
   440 PRINT "ENTER HIGHEST TEMPERATURE (C)";
   450 INPUT H
   460 ON F1 GOTO    470,   500
   470 IF H<=143 GOTO    530
   480 PRINT "HIGHEST VALID TEMP FOR ETHYLENE GLYCOL IS 143C"
   490 GOTO    440
   500 IF H<=57 GOTO    530
   510 PRINT "HIGHEST VALID TEMP FOR METHANOL IS 57C"
   520 GOTO    440
   530 PRINT
   540 PRINT "WHAT TEMPERATURE INCREMENT WOULD YOU LIKE";
   550 INPUT I
   554 REM CURE FOR LOOP BUG
   555 IF (I-INT(I))=0 GOTO 560
   556 LET H=H+I
   560 PRINT
   570 ON F1 GOTO    580,   600
   580 PRINT "  ETHYLENE GLYCOL";
   590 GOTO    610
   600 PRINT "  METHANOL";
   610 PRINT " SHIFT DIFFERENCES VS. TEMPERATURE"
   620 PRINT "   FOR ";F;"MHZ"
   630 PRINT
   640 PRINT "TEMP,C","   PPM","    HZ"
   650 FOR X=L TO H STEP I
   660 ON F1 GOTO    680,   710
   670 REM *** EQN FOR ETHYLENE GLYCOL
   680 LET D=-(X-193.34)/102
   690 GOTO    720
   700 REM ***EQN FOR METHANOL
   710 LET D=-(36.54-SQR(1335.1716+87.4*(135.84-X)))/43.7
   720 PRINT X,D,D*F
   730 NEXT X
   740 PRINT
   750 END
```

Fachbereich 6
Biologie · Chemie · Geographie

Physikalische Chemie

Prof. Dr. R. Kosfeld

Universität · Gesamthochschule · Duisburg

D- 4100 Duisburg, den 20.12.84
Bismarckstr. 90

Dr. Bernard L. Shapiro

Department of Chemistry
Texas A & M University
College Station

TX 77843 U.S.A.

Structural Analysis of Oligomers

Dear Barry,

^{13}C nmr is one of the most efficient tools in characterizing constitution and configuration of polymers. Initiation, propagation and termination are basic steps in polyreactions. Especially, end groups are formed by termination and initiation. However, as we normally considered only on high polymers, end groups due to their low concentrations cannot be detected under normal conditions.

We prepared and characterized a serie of oligomers from styrene and vinylchloride by joint HPLC and ^{13}C nmr. We succeeded in structural determination and complete spectral assignment of oligomers with degree of polymerisation (DP) up to 5, e.g.

DP = 1	1-Phenylhexane
DP = 2	1,3-Diphenyloctane
DP = 3	threo-1,3,5-Triphenyldecane
	erythro-1,3,5-Triphenyldecane
DP = 4	xylo-1,3,5,7-Tetraphenyldodecane
	arabino-1,3,5,7-Tetraphenyldodecane
	lyxo-1,3,5,7-Tetraphenyldodecane
	ribo-1,3,5,7-Tetraphenyldodecane

At present the limiting factor is the resolution of the HPLC with respect to the configuration of oligomers. We expect this method to be extended up to DP = 8.

Best regards
Your sincerely

(Prof. Dr. R. Kosfeld)

(Dr. K.-F. Elgert)

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

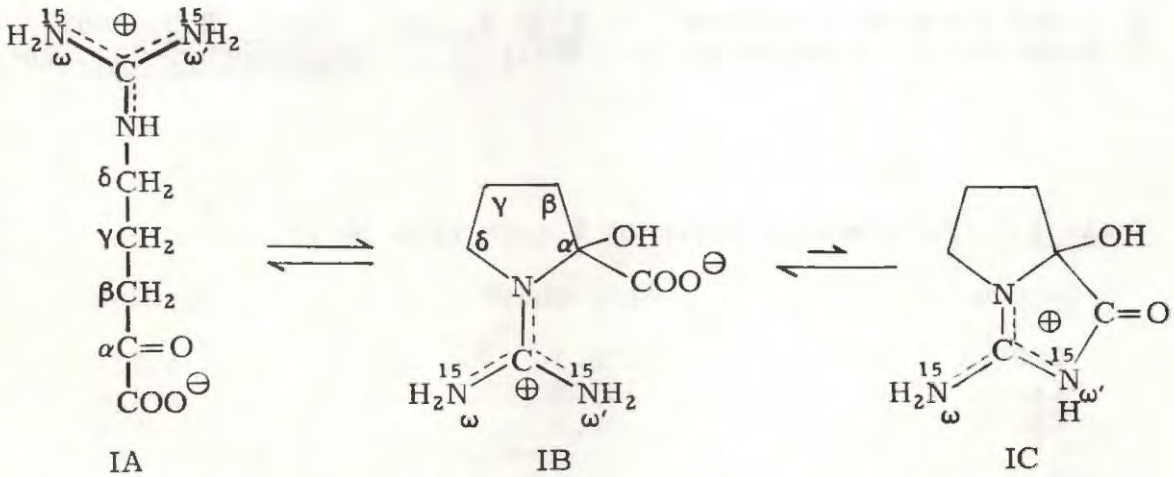
JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

December 10, 1984

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

Dear Barry,

α-Keto-δ-guanidinovaleric acid (α-keto acid analogue of arginine) (I) is a catabolic intermediate of arginine in human patients with hyperargininaemia and in microorganisms such as Pseudomonas putida and Arthrobacter simplex. Its open-chain form (IA) has been shown to exist in equilibrium with the cyclic form (IB) (1).



IA IB IC

However, the relative proportions of IA and IB at various pH values have not been studied. Our ^{13}C NMR studies of I, prepared by oxidative deamination of arginine with L-amino acid oxidase, showed that the open-chain and the cyclic forms occur in approximately equal proportions at pH 4, but the cyclic form becomes predominant at acidic pH. Table 1 shows the ^{13}C chemical shifts obtained at 125 MHz on a Bruker WM-500 spectrometer while Table 2 shows the relative proportions of IA and IB estimated from the peak intensities.

Furthermore, ^{15}N NMR spectra of I (enriched in ^{15}N at $N_{\omega,\omega'}$), obtained at 18.25 MHz on a Bruker WH-180, showed that, at pH 1.5, a small proportion of IB undergoes further cyclization to form IC, as shown by the appearance of new peaks at 284.5 ppm (N_{ω} of IC) and 234.8 ppm ($N_{\omega'}$ of IC) in addition to the peaks at 298.1 ppm ($N_{\omega,\omega'}$ of IB) and

303.1 ppm ($N_{\omega,\omega'}$ of IA) (Fig. 1a). The rate of interconversion of 1A and 1B is slow on the NMR time scale at pH <7, as indicated by the observation of separate $^{15}N_{\omega,\omega'}$ peaks for IA and 1B, but the two peaks coalesce around pH 9 (Fig. 1b). At pH >10.2, a sharp, averaged peak at 301.4 ppm is observed as a result of rapid base-catalyzed interconversion of IA and IB (Fig. 1c).

The interconversion of I between the open-chain and the cyclic forms probably accounts for the observed excessive broadening of the peak of this compound, compared to other guanidino compounds, on ion-exchange chromatograms (2), because IA and IB are expected to have different affinities to ion-exchange resins.

With all good wishes,

Very truly yours,

Keiko Kanamori

Keiko Kanamori

Jack

John D. Roberts

References

1. Cooper, A.J.L. & Meister, A. 1978 J. Biol. Chem., 253, 5407.
2. Marescau, B. & Lowenthal A. (1981) J. Chromatography, 224, 185.

Table 1. ^{13}C chemical shift of I (ppm from TMS)[a]

Carbon	Open-chain	Cyclic
$COO^{\ominus}$	176.3	170.2
$C\alpha$	205.9	92.6
$C\beta$	36.9	49.5
$C\gamma$	22.4, 22.7[b]	
$C\delta$	40.6, 41.3[b]	
$C_{guanidino}$	157.7	156.2

[a]Obtained at pH 2.8. [b]Assignment to open-chain and cyclic forms were not attempted.

Table 2. Percentages of open-chain and cyclic forms at various pH values.

pH	Open-chain	Cyclic
1.5	27%	73%
2.8	38%	62%
4.0	44%	56%

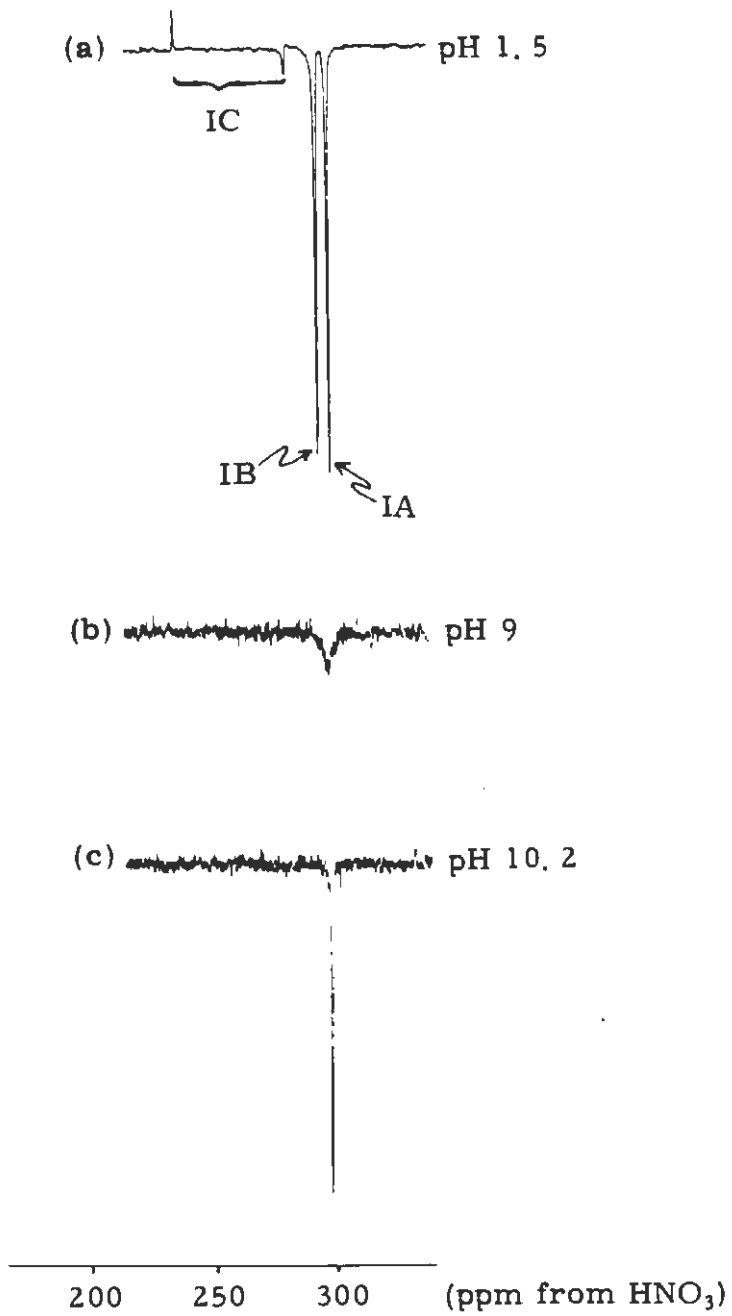


Figure 1. ^{15}N spectrum of I.

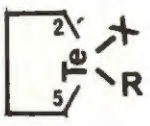
Professor B.L.Shapiro,
Department of Chemistry,
Texas A and M University,
College Station,
Texas 77843.

Basrah University
Chemistry Department
Basrah - IRAQ.

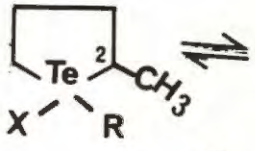
Dear Professor Shapiro,

Title : Cis/ Trans Configurational observation of New Cyclic Telluronium Salts. By Mean of ^{1}H n.m.r. Spectroscopy.

Recently[1], we reported on series of cyclic telluronium salts (I). In an extention work of structuarlly related compounds, derived from 2-Methyl-1-telluracyclopentane (II), a mixture of cis/trans isomer was observed, the mixture ratio been daduced from their assigned peak integral Table (1).

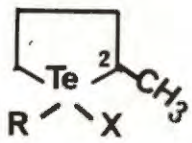


I



II

Cis



Trans

R	X
II_a : I	I
II_b : CH_3	I
II_c : CH_2CH_3	I
II_d : CH_2Ph	Br

Table (1)

Comp.	Cis/Trans ratio
II_b	(39 : 61) %
II_c	(27 : 73) %
II_d	(100) % trans.

The minority of the cis configuration was found to be greatly affected by the size of Te --- R alkyl group. The peaks assignment, fig. (1), were made from their intensity, multiplicity, as well as the adaptation of the antigauch downfield chemical shfft[2].

Yours Sincerely

Dr. A.Z. AL-RUBAIE

Dr. H. AL-SHRAYDA

REFERENCES :

1. A.Z. Al-Rubaie, M.Al-Shrayda and Prof. P.Granger (to be published in the J. Organometallic) Chem.)
2. J.P.Stother, C.T.Tan and K.C.Teo, J.Mag. Resonance 20 (1975) 570.

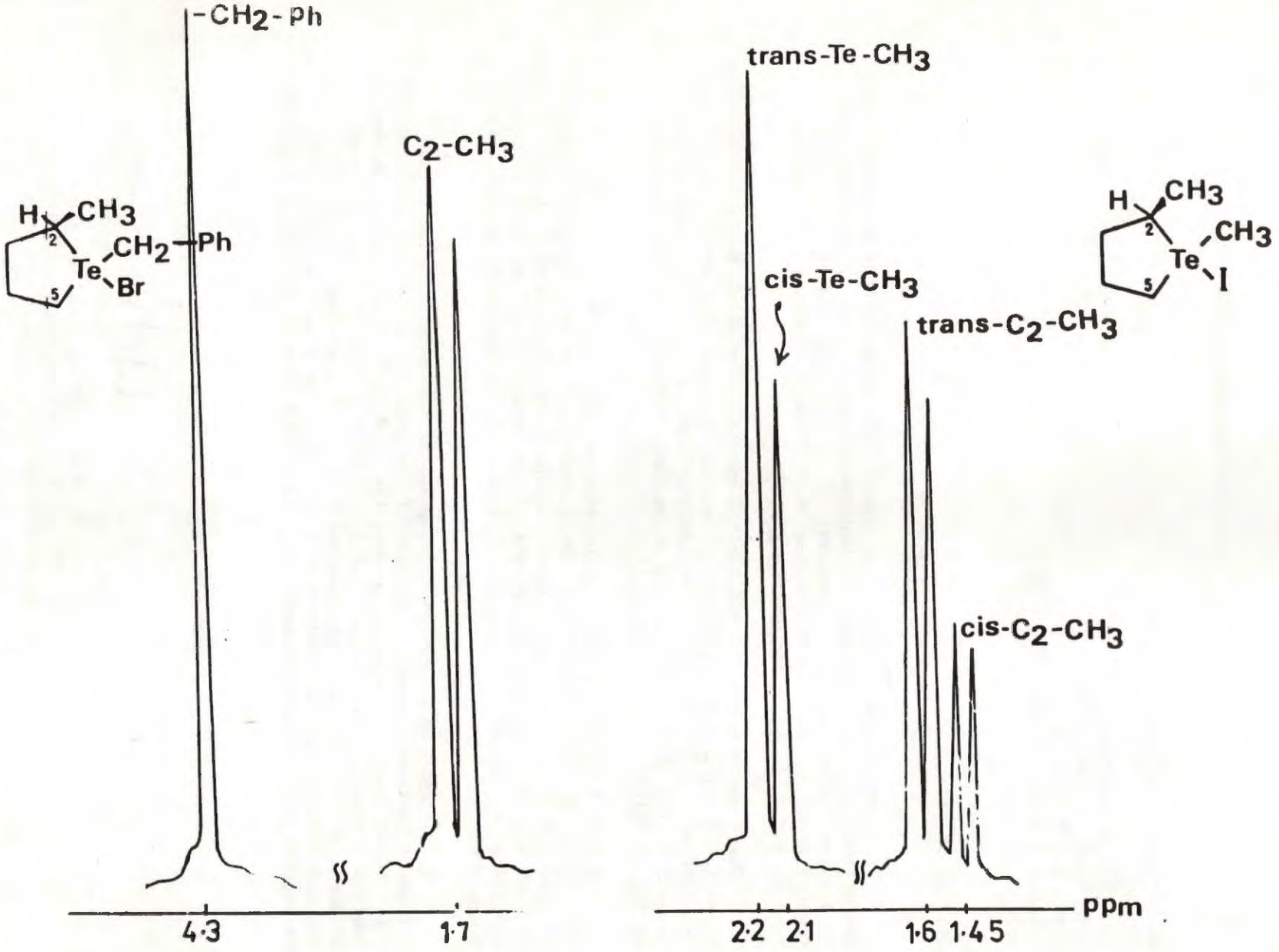


Figure 1. ^{1}H NMR spectra for compound IIb and IId in DMSO.

316-13

CSIRO

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MAW.jcm

19th December, 1984

Dr Bernard L. Shapiro
Editor
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
COLLEGE STATION TEXAS 77843-3255
USA

Dear Dr Shapiro,

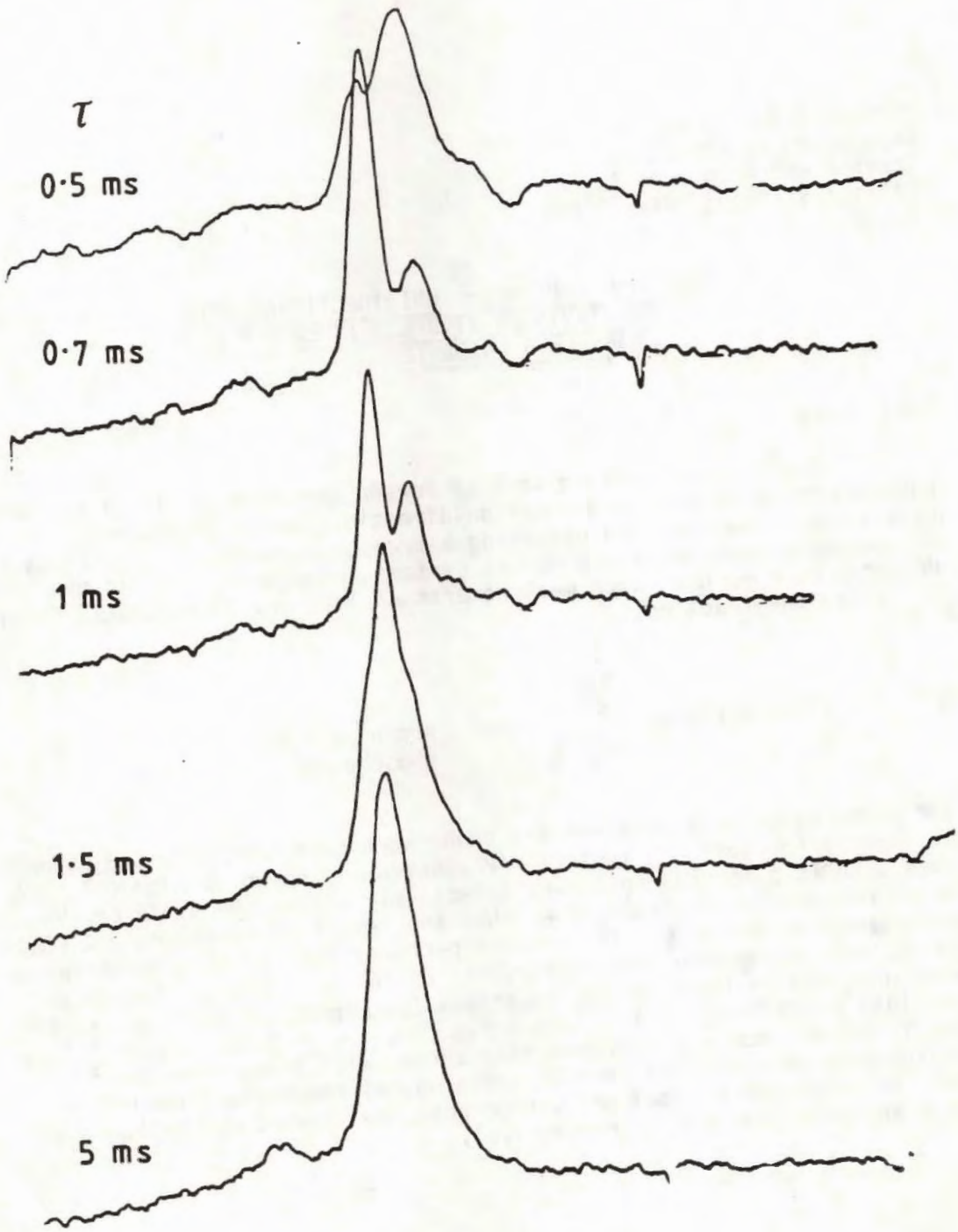
In recent years ^{29}Si and ^{27}Al n.m.r. have greatly contributed to the understanding of the structure of ordered materials such as zeolites, and to a lesser extent minerals. However, it is unlikely that n.m.r. will replace X-ray diffraction techniques in structural analysis. The major role of n.m.r. is as a complementary tool.

There are a number of geochemical materials in which X-ray diffraction gives little structural information such as the fine clay fractions of volcanic ash soils and their synthetic equivalents. N.M.R. has obvious potential with these samples, and so we have undertaken extensive studies on the structure of these materials.

Figure 1 shows typical results of some 180^{o}-tau-90^{o} pulse ^{27}Al experiments on these materials. The substances have considerable quantities of tetrahedrally co-ordinated aluminium which is observed as a single resonance. We have observed that the linewidths of the tetrahedral resonance is greatly reduced at or around a tau period of 1 ms, and the resonance is split into two peaks.

It is tempting to assign these peaks to two materials which have different isotropic chemical shifts. If this is so, then, the 180^{o}-tau-90^{o} pulse sequence may in someway, reduce the quadrapole interaction. However isotropic chemical shifts for ^{27}Al are usually higher than the observed chemical shift. We have not observed a shift of resonance downfield in our experiments. An alternative explanation is that we are selectively saturating some of the isotropic resonances and thereby enhancing resolution.

M.A. Wilson, A.M. Vassallo
P.J. Collin and S. McCarthy.


τ
0·5 ms
0·7 ms
1 ms
1·5 ms
5 ms

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December 19, 1984

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

CRAYFISH KINETICS: UNIDIRECTIONAL RATE CONSTANTS IN VIVO VIA INVERSION SPIN TRANSFER A LA DANTE

Dear Barry:

Since the pioneering work of Forsén and Hoffman (1) it has been possible in principle to measure unidirectional rate constants by saturating a reactant and observing a product resonance. Such studies are becoming popular in biological systems, especially via ^{31}P NMR (2). Recently we have done such measurements on live crayfish abdomen ("tail") to follow the reaction,

$$\text{ATP} + \text{Arginine} \underset{K_B}{\overset{K_A}{\rightleftharpoons}} \text{ADP} + \text{Arginine phosphate} + H^+$$

The geometry of both crayfish and probe were such that only the abdomen is seen by the coil. A typical ^{31}P spectrum is shown in Figure 1. We used a DANTE pulse (3) to invert selectively either the γ-ATP or the Arg P resonance. In Figure 2 we show the result of inverting γ-ATP(Δ) and observing Arg P(□). The initial parts of the curves are dominated by the rate constants, the latter parts by the T_1 values. The data were analyzed in terms of the equations for magnetization transfer (3), to yield at 25°C $K_A = 0.8\ s^{-1}$ $K_B = 1.8\ s^{-1}$, $T_{1A} = 2.0$ s, $T_{1B} = 1.0$ s. The T_1 values measured independently agreed with those from the fit. Measurement of the rates over a physiological temperature range for this poikilotherm yielded activation energies forward and backward of 11.2 and 10.0 kcal mol^{-1}, respectively.

Canada

We are happy to report that the crayfish are still crawling contentedly around in their tanks several months after the measurement. This is a neat, accurate, and harmless way to measure rate constants *in vivo*.

Yours sincerely,

Ian C.P. Smith, Yves Geoffrion, Roxanne Deslauriers

Keith Butler, Ray Somorjai, Jan and Ken Storey

1. S. Forsén and R.A. Hoffman, J. Chem. Phys. 39, 2892 (1963).

2. J.R. Alger and R.G. Shulman, Quart. Rev. Biophys. 17, 83 (1984).

3. G.A. Morris and R. Freeman, J. Mag. Res. 29, 433 (1978).

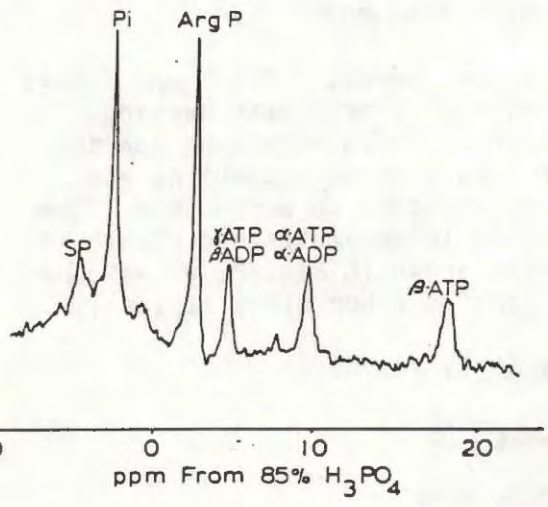

Figure 1

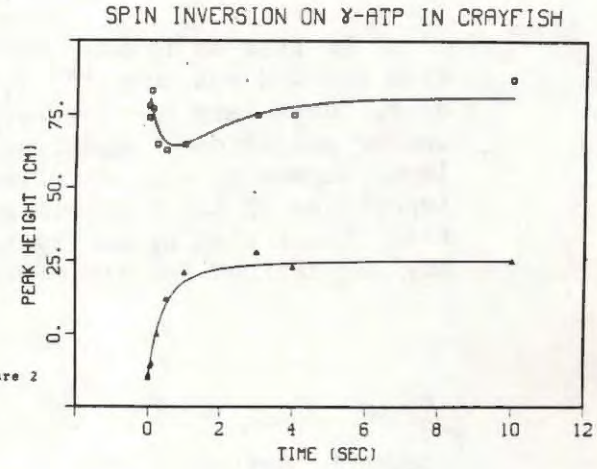

Figure 2

316-17

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Department of Chemistry
Telephone 413-542-2342

December 19, 1984

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

Dear Barry:

Your reminders find us at the hectic end of a semester in the wilds of western Mass., where we're continuing to develop a molecular rationale for the activity of lipolytic enzymes. Typically we conduct parallel kinetic and spectroscopic studies of micellar mixtures that serve, for example, as model systems for fat digestion in the small intestine. One modification of the aggregate surface involves the synthetic lipid diphenylvaleroyl phosphatidylcholine (diPVPC, Fig. 1), which is itself enzymatically accessible and also serves as a detergent matrix for triglyceride substrates.

Although we dubbed it "kinky" to suggest a possible splaying of the two bulky acyl chains, its efficient hydrolysis by phospholipase-A_2 suggested that key conformational features of the lipid glycerol backbone were retained. In CD_3OD diPVPC is present as monomers, and J-couplings derived from its high-field ^1H NMR spectrum (Fig. 1a) are in accord with values for other short-chain lipids. The diPVPC aggregates that the enzyme recognizes tend to predominate in D_2O, though these spectral data are more difficult to interpret (Fig. 1b). We found it reasonably straightforward to implement a 2D-J experiment on the XL-300 at Univ. of Mass....but we await the arrival of a Zeta plotter before any further progress can be made.

Be that as it may, Mary Roberts (Chem. Dept., M.I.T.) and I have also checked out some ^{13}C T_1's on a series of kinkys with varying alkyl chain lengths--the values are strongly field-dependent for the longer analogues, suggesting that both slow aggregate tumbling and local segmental motion influence the spin relaxation parameters. The importance of the phospholipid acyl chains in enzymatic hydrolysis is also illustrated by the synthetic species shown in Fig. 2; we welcome any suggestions for the missing name (or for other nifty lipids).

Very truly yours,

Stuart E. Levine

Ruth

Ruth E. Stark

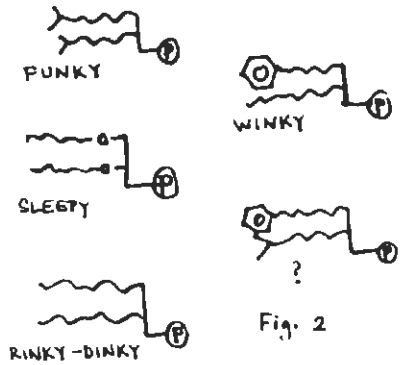
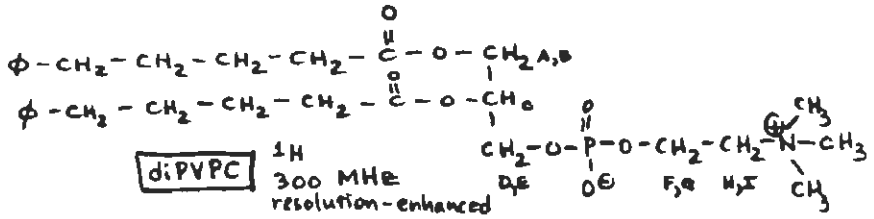


Fig. 2



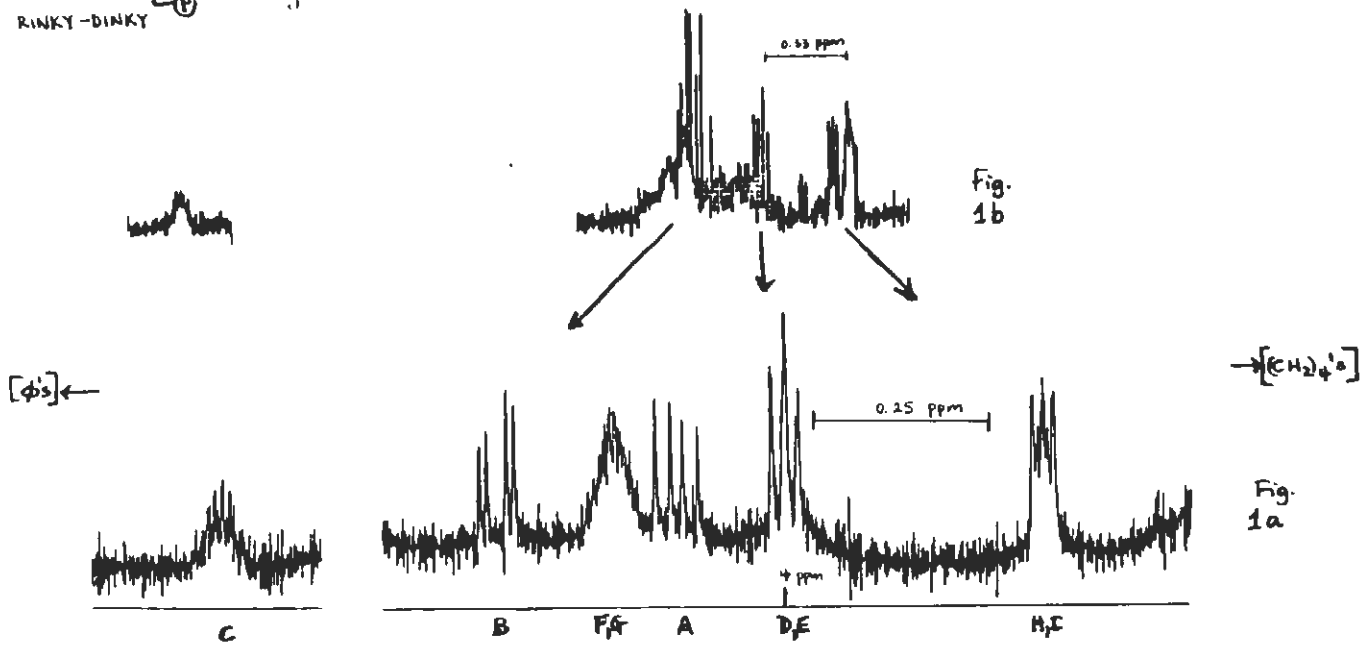


Fig. 1b

Fig. 1a

316-19

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

National Institutes of Health
National Institute on Aging
Gerontology Research Center
Baltimore City Hospitals
Baltimore, Maryland 21224

January 3, 1985

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

In Vivo NMR Probe for Varian XL-200

Dear Barry:

We recently took delivery of a 1.9T/310 mm bore Biospec NMR system from Bruker; we expect to add imaging capability later this month. The instrument will be used, among other things, to study the aging of rats.

Before receiving the wide-bore spectrometer designed for animal studies, we decided to use our older Varian XL-200 spectrometer, which operates at 4.7T, for some in vivo studies. The largest animal that will fit comfortably inside the XL-200 magnet, which has a clear bore of 45 mm, is a mouse. We built a probe consisting of a 2-turn, 1.0 cm diameter surface coil which tunes to the ^{31}P frequency of 81 MHz. The ^{31}P NMR spectrum from the brain of an anesthetized mouse obtained using this probe is given below. The field homogeneity was optimized by observing the ^{1}H FID from the brain, with the same ^{31}P coil, using the method of Ackerman et al. (1). With modest shimming, proton linewidths better than 30 Hz were routinely obtained for mouse brain and good ^{31}P spectra were obtained in 10-15 minutes.

With this probe the XL-200 can be used to monitor both ^{31}P and ^{1}H (with water suppresion) in intact mice. We shall gladly make the details of the probe available to anyone who is interested.

Sincerely,

Rajasekharan P. Pillai

Daniel Waysbort

Gunther L. Eichhorn

GLE:pab

1. J.J.H. Ackerman, D.G. Gadian, G.K. Radda & G.G. Wong: J. Mag. Res. 42, 498 (1981).

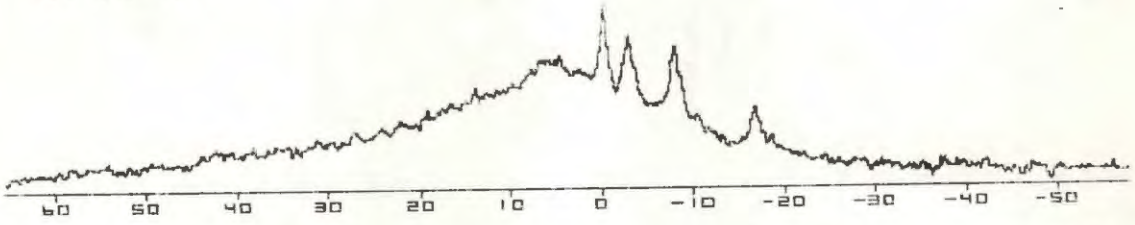


Figure 1. 81 MHz ^{31}P NMR spectrum from the brain of a 19-month old C57BL6 mouse under pentobarbital anesthesia: the spectrum was collected in approximately 15 minutes (2000 scans).

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DEPARTMENT OF PHYSICAL CHEMISTRY
UNIVERSITY OF CAMBRIDGE

LENSFIELD ROAD
CAMBRIDGE
CB2 1EP

Position Available

As from October 1st, 1985, a tenure-track position will be established in this Department for a Senior Technical Officer with proven postdoctoral skills in solid-state NMR. The person appointed will be involved in a wide-ranging programme of research, will be expected to train graduate students, to maintain and extend equipment and to be responsible for the day-to-day running of a Bruker MSL 400 MHz spectrometer.

The closing date for applications is March 22nd. Interested applicants should write to me, and send copies of their curriculum vitae.

John

J.M. Thomas
(Head of Department)

STANFORD MAGNETIC RESONANCE LABORATORY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

Director: Oleg Jardetzky, M.D., Ph.D.
Professor of Pharmacology

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

A position at the Research Associate level will become available at Stanford Magnetic Resonance Laboratory in January 1985. The responsibilities of the position will include maintenance and upgrading of the existing spectrometer systems (JEOL GX-500, Bruker/Stanford HXS-360, modified Varian XL-100), implementation and development of new techniques and supervising the use of the instruments. Proficiency in NMR electronics, hardware and software and familiarity with probe design and construction are essential. Candidates should have an advanced degree in engineering, physics or physical chemistry.

For more information write to: Dr. Oleg Jardetzky, Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, CA 94305. Stanford is an Equal Opportunity/Affirmative Action employer.

Yours sincerely,

Oleg

Oleg Jardetzky

316-23

19 December 1984

ROCHE

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

Roche Products Limited · PO Box 8 · Welwyn Garden City · Hertfordshire AL7 3AY
Telephone Welwyn Garden 28128 *Telex 262098 ROCHEW*

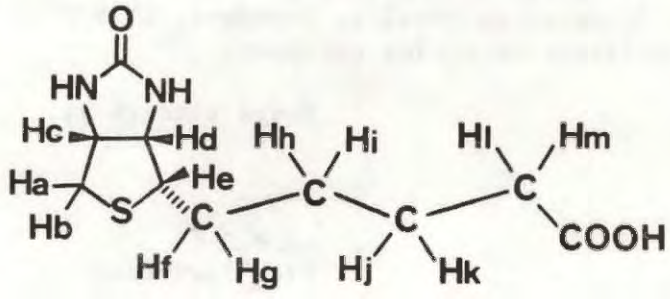
Dear Barry

Quick 2-D (Sebastian COeSY?)

In a busy nmr lab in the pharmaceutical industry, time, rather than experimental difficulty, is the main factor which restricts the use of most 2-D nmr programs. Since the long accumulation times are usually caused by the large data matrices employed, we investigated ways of reducing the latter. For the COSY experiment a resolution of 6 - 8 Hz is usually sufficient to provide the required correlations. With sufficient sample dissolved, using a phase alternating pulse sequence, the number of scans can be reduced to 4. Optimising the relaxation delay at 1.6 seconds and using a matrix size of 1024 X 64 points (zero filled to 1024 X 512 to allow for symmetrisation) gives an overall experiment time of 17 minutes. Using the spectrum of biotin (I) as a convenient example, the Figure shows a comparison of COSY spectra obtained on our Bruker WM-300 using the standard parameters (top spectrum) and using our adapted version of COSY-LR (lower spectrum), which improves the experimental time by a factor of 10, without much loss of coupling information. This is usually sufficient to solve most assignment problems, without causing large log-jams in the service.

Yours sincerely

W A Thomas I W A Whitcombe P J Gilbert



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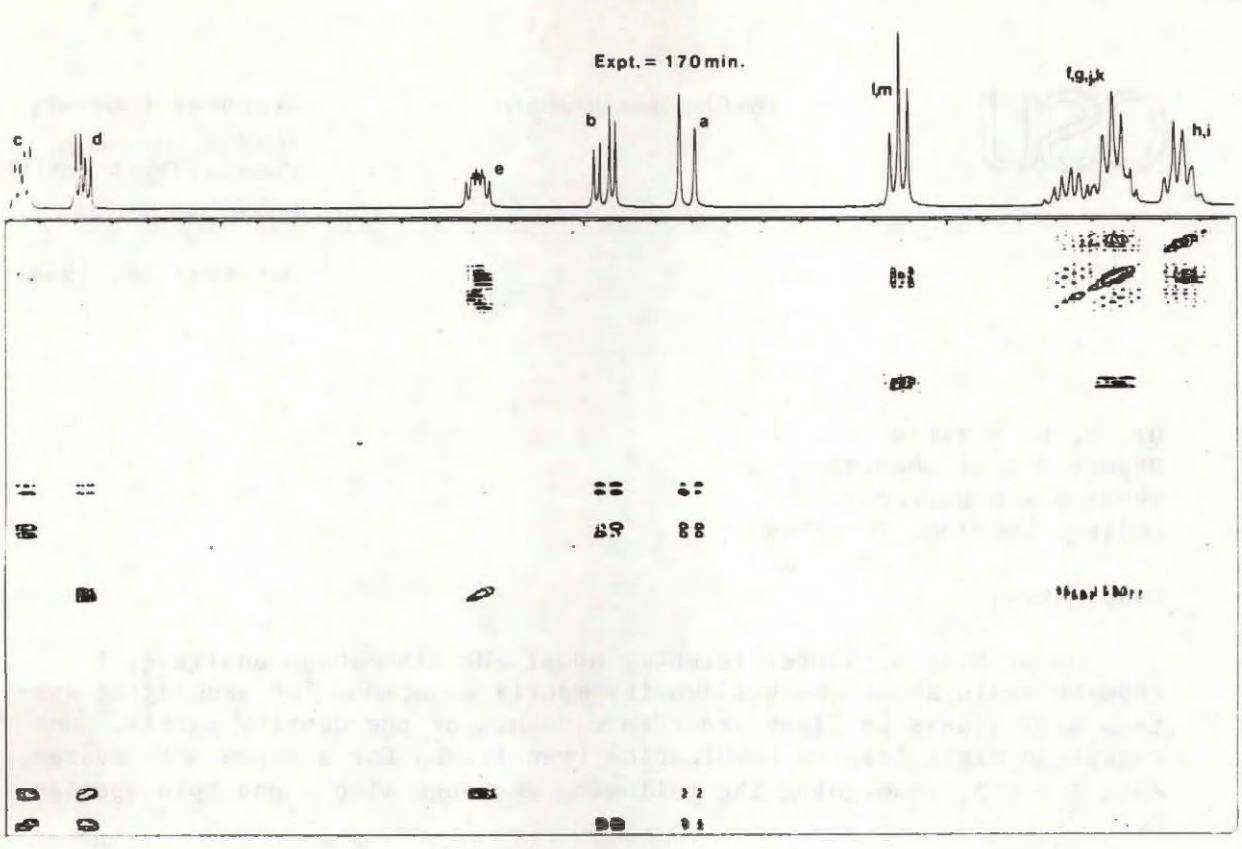
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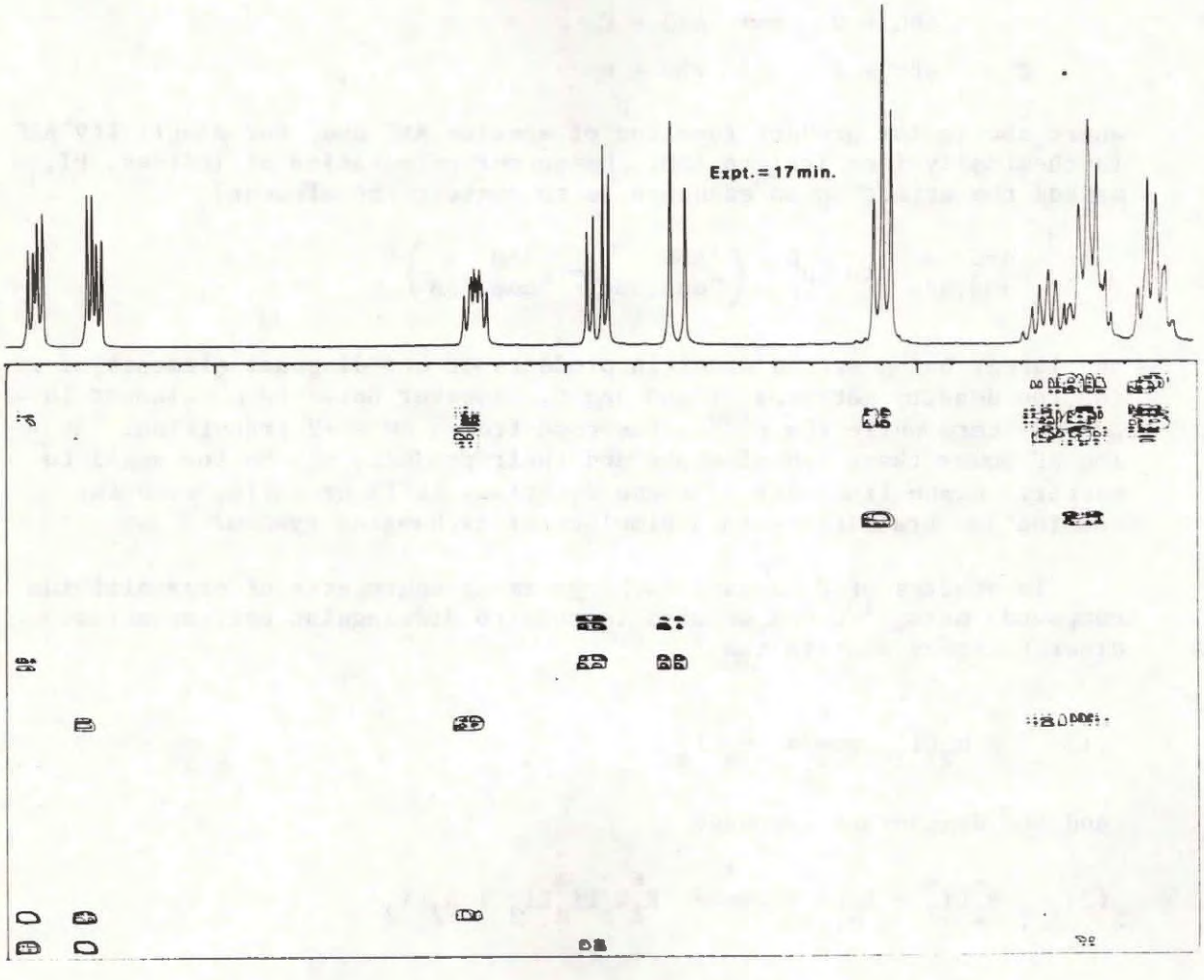
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OSU

The Ohio State University

Department of Chemistry
140 West 18th Avenue
Columbus, Ohio 43210-1173
Phone 614-422-2251

December 28, 1984

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

Dear Barry,

On writing a Chapter recently about NMR line-shape analysis, I thought again about whether density matrix equations for exchanging systems will always be first order in elements of the density matrix. One exception might involve combination transitions for a three spin system, ABC, I = 1/2, undergoing the following exchange with a one spin species, D,

$$\begin{array}{lcl} & \overset{\tau}{\rightleftharpoons} & \\ \text{ABC} + \text{D} & & \text{ABD} + \text{C} \\ \text{abc} + \text{d} & & \text{abd} + \text{c} \end{array} \qquad \emptyset$$

where abc is the product function of species ABC and, for simplicity ABC is chemically identical to ABD. Using our permutation of indices, **PI**, method the effect on an exchange is to convert the element,

$$\rho^{ABC}_{\alpha\alpha\beta,\beta\beta\alpha} \quad \text{to} \quad \rho^{C}_{\beta,\alpha}\left(\rho^{ABD}_{\alpha\alpha\alpha,\beta\beta\alpha} + \rho^{ABD}_{\alpha\alpha\beta,\beta\beta\beta}\right)$$

the latter being second order in products of off-diagonal elements of the two density matrices of ABD and C. However note the ρ^{C} element is a $\Delta M = -1$ term while the ρ^{ABD} terms come from a $\Delta M = +2$ transition. At low RF power these two elements and their products wil be too small to matter. Hence linearity of these equations still prevails, even for combination transitions in a bimolecular exchanging system.

In studies of C,Li bond exchange among aggregates of organolithium compounds using ^{13}C NMR we have learned to distinguish between a fast dimer tetramer equilibrium

$$(1) \qquad 2\ R_2Li_2 \underset{k_t}{\overset{k_d}{\rightleftharpoons}} R_4Li_4$$

and the degenerate exchange

$$(2) \qquad R^*_2Li^*_2 + R_4Li_4 \overset{k_2}{\rightleftharpoons} R^*_2R_2Li^*_2Li_2 + R_2Li_2$$

Our system is $(CH_3)_3CC{\equiv}C^6Li$ in THF. We monitor the ^{13}C NMR line-shape for C_1 (C bonded to ^6Li). The system forms a cubic tetramer, in equilibrium with bridged dimer, (see below). Fast exchange of alkynyls and lithiums among aggregates averages the $^{13}C,^6Li$ couplings. Again we used the PI method to derive the ^{13}C density matrix equations,

$$A\rho_{col} = iCB_{col} \ ,$$

for the two different proposed mechanisms. Algebraically what causes the ^{13}C NMR transitions to average are the off-diagonal (real) terms in τ in the coefficient matrix,A. What is interesting is that array of ratios of the coefficients for the τ's among the different elements within the two A matrices come out the same. So as far as the nuclear spins are concerned, it makes no difference how the $^{13}C,^6Li$ couplings have been averaged. The way one tells the difference is that τ_D in step (1) has the kinetic dependence

$$\frac{1}{\tau_{D(1)}} = k_d(D) \ , \qquad D = \text{dimer}$$

which is what we observe, whereas for degenerate exchange it would be

$$\frac{1}{t_{D(2)}} = k_2(T) \qquad T = \text{tetramer}$$

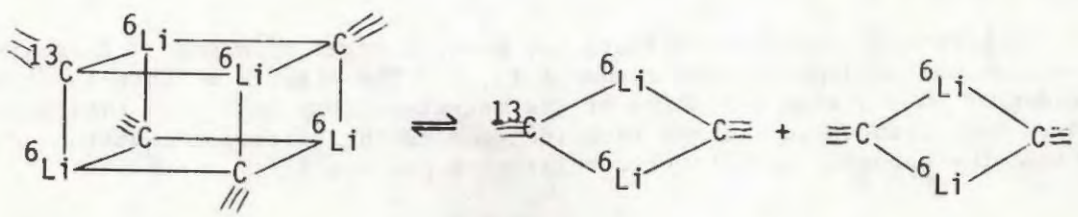
In closing I will not regale you and your readers with the vicissitudes of instrument procurement but announce the successful installation of a Bruker 500 at Ohio State. Both the machine and its users are doing well.

Best wishes for 1985

Yours sincerely,

Gideon

Gideon Fraenkel
Professor of Chemistry



316-27

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Delhi Road, North Ryde, NSW, Australia

A Division of the Institute of Energy and Earth Resources

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Telex AA25817

3rd January, 1985

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

TITLE: Selective Saturation and Domain Structure Analysis

Dear Professor Shapiro,

When cross relaxation occurs between two proton populations the apparent spin-lattice relaxation rates and probabilities observed are complicated functions of the intrinsic relaxation rates (R(1),R(2)), the population fractions (P(1),P(2)) and the cross relaxation rates (K(1),K(2)). Edzes and Samulski, using a pulse sequence of the type (180(SOFT)-Ta-90)(1)(Type 1) have shown how the apparent relaxation processes can be resolved into the intrinsic and cross relaxation contributions. They applied this method to hydrated collagen where the phases are well resolved by their respective spin-spin relaxation times. The soft 180 preparation pulse saturates the mobile water magnetisation, but only partially saturates the magnetisation of the 'rigid' macromolecular phase which rapidly becomes isothermal, at a lower spin temperature than that of the mobile phase, by spin diffusion. Adjustment of the soft 180 pulse varies the initial induced spin temperature or magnetisation difference between the phases and hence the degree of magnetisation flow. Two different initial conditions allows determination of the parameters K(1),K(2) and R(1),R(2) when spin diffusion is rapid compared to the spin-lattice relaxation rates. The results of application of this sequence to the study of a hydrated keratin specimen is shown in Figure (1).

The components of the reduced magnetisations are describable by twin exponential rates, that are equivalent in either phase, but weighted by different pre-exponential factors. Data at small 'Ta' values display the presence of cross relaxation by a matching loss and gain in magnetisation of the two components.

For the Goldman Shen sequence of (90_X-Ta-90_{-X}-t-90_X) (Type 2) (2) used in cross relaxation studies, 'Ta' is chosen so that the rigid population has lost phase coherence, whilst the mobile phase retains a degree of coherence prior to the second pulse. This pulse is responsible for the establishment of a spin temperature difference between the two phases. Results of data collected for the same keratin water system using the Type (2) sequence are shown in Figure (2).

Analysis of the Type (2) data has been in terms of magnetic diffusion processes due to dipolar spin exchange (3,4). The effects of spin-lattice relaxation in the time evolution of the magnetisations have been theoretically considered, with an additional term included in the diffusion equations to include the apparent spin-lattice relaxation process (3).

We have used a sequence (90_X-Ta-90_{-X}-t-90_X) Type (3) different from Type 2 by the change of phase in the second pulse to collect data for the keratin water system. This may be seen in Figure (3).

The data of the Types (2) and (3) sequences follow the behaviour of the signal components evident in the Type 1 and can be readily analysed in terms of a two phase model. Variation of the value 'Ta' in these sequences performs the same function as variation in the duration of the soft pulse in the Type 1 sequence. For the identical choice of dephasing times 'Ta' in these two sequences, the initial magnetisation difference between the phases is equivalent, but the spin temperature gradient has been reversed.

As such, the Type (2) and Type (3) sequences used in conjunction satisfy the required two different boundary conditions in the component magnetisations, from which one may obtain estimates of K(1),K(2) and R(1), R(2). Sequences (Type 2 + 3) create an optimum difference in the initial magnetisations of the two phases and therefore optimum resolution of the decay modes.

This type of analysis is not valid if the spin diffusion is not rapid in comparison to the spin-lattice relaxation rate in that phase. We have derived analytical solutions for the two phase model in which we have incorporated the functionality of the spin-lattice relaxation processes in the diffusion system. We shall report in a later letter on the aspects of this analysis which indicate that the intrinsic coefficients of the system may be defined without the necessity of maintaining that the spin diffusion be rapid in comparison to the relaxation process. A further experimental approach in which a domain size estimate may be made under certain conditions for the two phase model shall also be reported.

COMPLETE REFERENCES:

1. H.T. Edzes and E.T. Samulski, J. Magn. Reson., 31, 207-229 (1978).
2. T.P. Cheung and Gerstein, J. Appl. Phys., 52, 5517-5528 (1981).
3. T.P. Cheung, Phys. Review B., 23, 1404-1418 (1981).
4. R.A. Assink, Macromolecules., 11, 1233-1237 (1978).

Yours sincerely,

Greg M. Simms
Leo J. Lynch
Division of Fossil Fuels

Figure 1

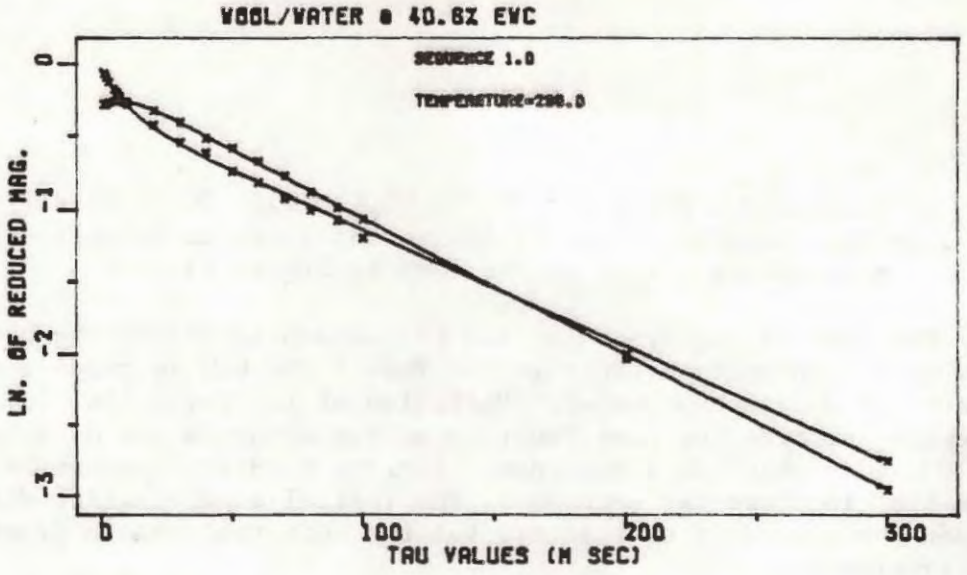


Figure 2

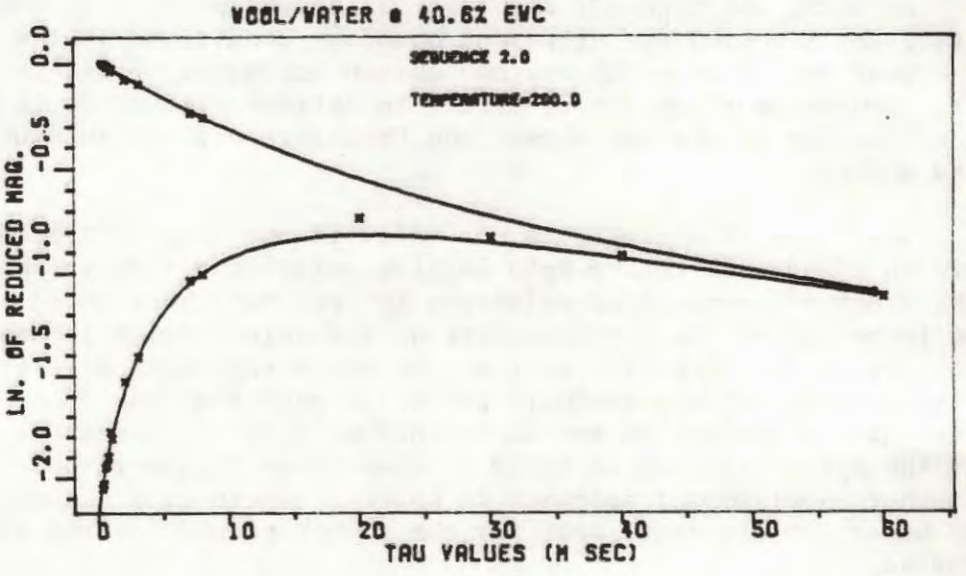
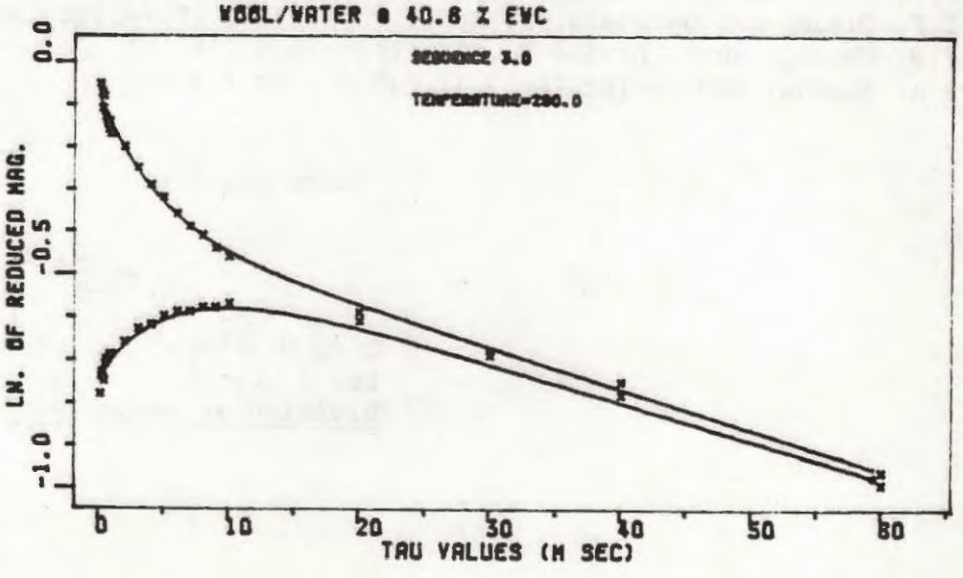


Figure 3



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316-31

TOWSON STATE UNIVERSITY
TOWSON, MARYLAND, 21204

Department of Chemistry (301) 321-3058

January 2, 1984

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

Study of Outer Sphere Complexes by NMR

Dear Barry:

The work in our laboratory involves the study of the formation of outer sphere complexes formed between a transition metal complex ion and various anions. This work is just now getting underway and we are using our newly acquired JEOL FX-90Q spectrometer. Our choice of a transition metal complex $Co(en)_3^{3+}$ (en = ethylenediamine) is based upon the fact that diamagnetic Co(III) complexes show extremely large ^{59}Co chemical shifts due to low lying excited electronic states[1]. Also ^{59}Co NMR is made relatively easy due to its 100% natural abundance.

To date we have measured the ^{59}Co spin relaxation times of several solutions of fixed concentrations of $Co(en)_3Cl_3$. $3H_2O$ and varying concentrations of acetic acid. The pH is adjusted with tetramethylammonium hydroxide to insure that essentially all of the acetic acid added has been converted to the acetate ion. It appears that there is a slight decrease in ^{59}Co T_1's as the acetate ion concentration is increased. More detailed work is about to get underway. We will also be studying ^{13}C chemical shifts and relaxation rates.

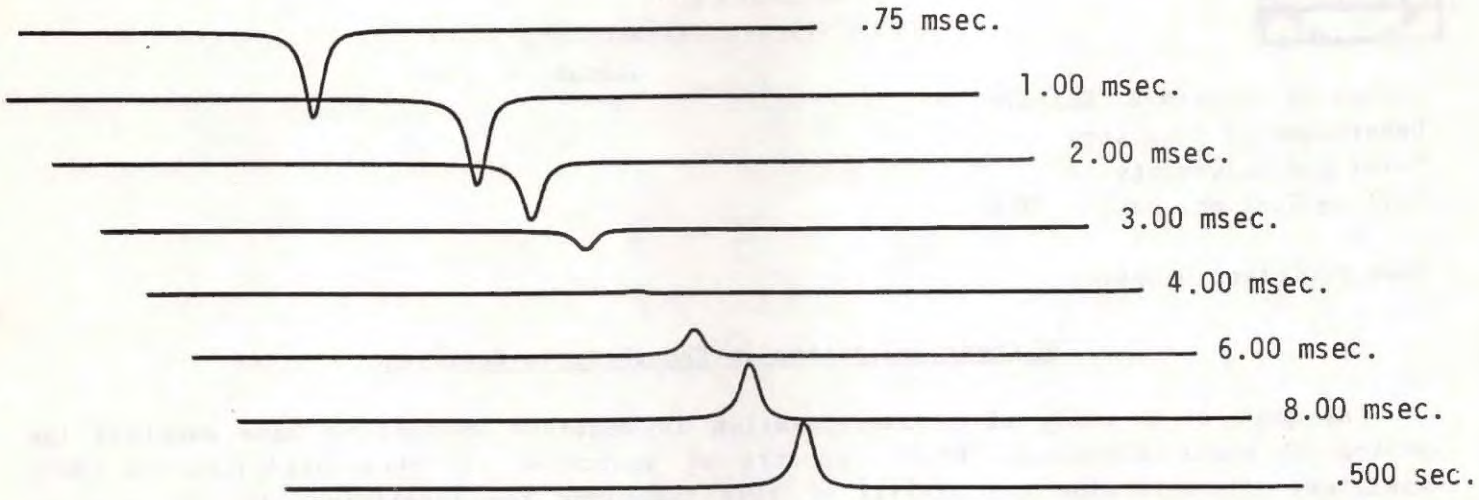
The following is a stacked plot of an inversion recovery measurement of the spin lattice relaxation time of ^{59}Co in .30 M $Co(en)_3^{3+}$ and .20 M $C_2H_3O_2^-$. The delay time between the 180° and 90° pulses are indicated. 100 free induction decays were accumulated for each spectrum and the frequency is 21.39 MHz. For this particular measurement we determined that T_1 = 7.5 ($\pm$.2) msec.

Sincerely yours,

Thomas Martin

Diana Danz

J. W. Emsley, J. Feeney and H. Sutcliffe "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergarthon Press, Oxford, 1966, p. 1178.



316-33

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
McCORMICK ROAD
CHARLOTTESVILLE, VIRGINIA 22901

January 3, 1985

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

Dear Professor Shapiro:

^{1}H Cross-Relaxation in Phospholipid Vesicles

As part of a study of cross-relaxation in membrane systems we have examined the proton 2D cross-relaxation (NOESY) spectra of sonicated egg phosphatidylcholine (EPC) vesicles. To determine the utility of this technique for localizing ligands bound to lipid bilayers we have examined the 2D spectra of EPC vesicles with (Figure 1a) and without (Figure 1b) the hydrophobic ion, tetraphenylborate (TPB). The resonance assignments are shown in Table I.

As expected, conservative magnetization transfer dominates the cross-relaxation in the lipid vesicle system and relatively short mixing times must be used to obtain spacial information. At 50 ms, cross-peaks are seen between the meta and ortho TPB protons and the methyl protons of the EPC choline headgroup (G). In addition, phenyl ring-current shifts of approx. 0.2ppm (due to TPB) are induced in the headgroup resonances G and H as previously noted in 1D work (1). Thus, cross-relaxation appears to provide a good indication of proximity at short mixing times. In the presence of TPB, all cross-peaks are stronger than without TPB, indicating that this hydrophobic ion strengthens dipolar interactions throughout the bilayer. In the present case, TPB does not appear to have a significant effect on vesicle size and we conclude that the increased dipolar interactions are likely due to an increase in lipid order. TPB also increases the order parameter as measured by EPR techniques (2).

Several other interesting features appear in the 2D spectra of lipid vesicles. For example, the diagonal allylic resonance (D) in EPC is split into two peaks, a result not resolved in the 1D spectrum. The intensity ratio of the low-to-high field peak is 2 to 1 and the low field peak relaxes approx. 3 times faster than the high field peak. This allylic splitting was not seen in the NOESY spectra of EPC in $CHCl_3$ nor was it seen for other pure phosphatidylcholine bilayers having homogeneous acyl chain compositions. In addition, these single allylic resonances (for PCs of various saturation) all had approx. the same chemical shift. It seems likely that the EPC resonances of D1 and D2 are due to groups in the outer and inner monolayers of the EPC vesicles, respectively. While relative intensities and relaxation rates are consistent with this interpretation, the allylic splitting could be due to the slow exchange of phospholipid betyween nonequivalent lipid domains in the plane of the bilayer.

In conclusion, proton cross-relaxation spectroscopy provides a means of obtaining information on molecular organization, conformation and dynamics in lipid bilayer vesicles. A more complete account of this work will appear in JACS.

Jeff Ellena, William Hutton, and David Cafiso

Jeff Ellena David J. Cafiso

References

1) Levine, B.A., Sack, J. and Williams, R.J.P. Biochim. Biophys. Acta 1979, 550, 201-211.
2) Seidah, N.G., Roy, G., Laprade, R., Cyr, T. and Dugas, H. Can. J. Biochem. 1976, 54, 327-335.

Fig. 1. 360 MHz ^1H cross-relaxation spectra of a) egg phosphatidylcholine (EPC) vesicles containing 20 mol% tetraphenylborate and b) EPC vesicles at 25°C. ↓ indicates t_1 noise. Although the spectra are displayed in absolute value mode, 1D NOE experiments indicated that all cross peaks are positive.

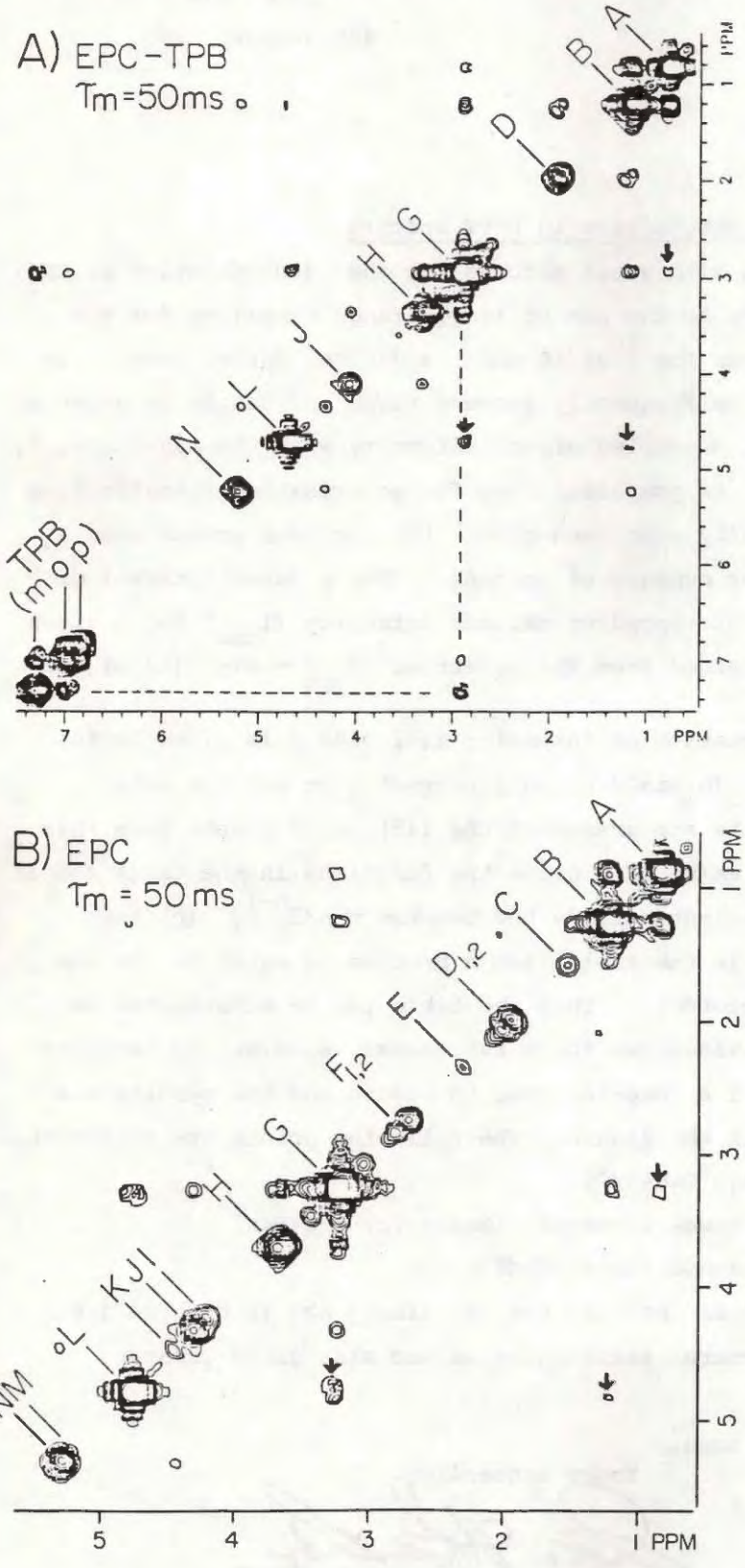


TABLE I

Chemical shift assignments for 2D cross-relaxation spectra

Diagonal Peak (Figure 1)	Group
A	$-CH_3$
B	$-(CH_2)_n-$
C	$-CH_2-C-CO-$
D_1/D_2	$-CH_2-C=C-$
E	$-CH_2-CO$
F_1/F_2	$-C=C-CH_2-C=C-$
G	$-N-(CH_3)_3$
H	$-CH_2-N-$
I	$-CH_2OPO$(glyceride)
K	CH_2OCO
J	$-OPOCH_2-$(choline)
L	HOD
M	CHOCO
N	-HC=CH-

316-35

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4th January 1985.

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

Dear Barry,

Signal intensities in DEPT spectra

Having used the DEPT pulse sequence with great success for the identification of CH_3, CH_2 and CH groups we turned our attention to the use of longer range couplings for the observation of quaternary carbon atoms and for ^{29}Si in $SiMe_2$ and $SiMe_3$ derivatives. In these cases the number of coupling protons frequently exceeds three and can be as great as nine. Although the variation of proton decoupled signal intensity with the magnitude, θ, of the third proton pulse is well known[1] in graphical form for polarisation transfer from one, two and three protons and has recently also been given[2] for the four proton case I am not aware of similar graphs for larger numbers of protons. For a pulse interval of 1/2J the optimum value of θ_{opt} and the corresponding maximum intensity (I_{max}) for a given number (n) of protons can readily be obtained from the equations[3] $\theta_{opt} = \sin^{-1}(1/n)$ and $I_{max} \propto n^{\frac{1}{2}}(1-{}^{1}/_{n})^{\frac{n-1}{2}}$. However, the variation of intensity $I(\theta)$ with θ is given by the more general expression $I(\theta) \propto \Sigma B\{n,M_i,l_i\}M_i \sin 2M_i\theta$ and I suspect I am not the only chemist who cannot instantly visualize the appearance of the $I(\theta)$ vs. θ graphs from this expression. Unravelling this for each value of n gives the functions in the table and it soon becomes evident that (a) the coefficient outside the bracket = $n/2^{n-1}$, (b) the coefficient of the (m)th term (as written in the table) for n protons is equal to the sum of the (m)th and (m-1)th terms for n-1 protons. Thus the table can be constructed in simple manner but I was still unable to visualize these functions. However, my daughter and the recent acquisition of a BBC model B computer came to rescue and the results are presented for values of n from 1 to 10 in the figure. The following points are noteworthy:

(i) There is only one maximum in the range $0<\theta<\pi/2$.

(ii) Polarisation transfer from even n gives inverted signals for $\pi/2<\theta<\pi$.

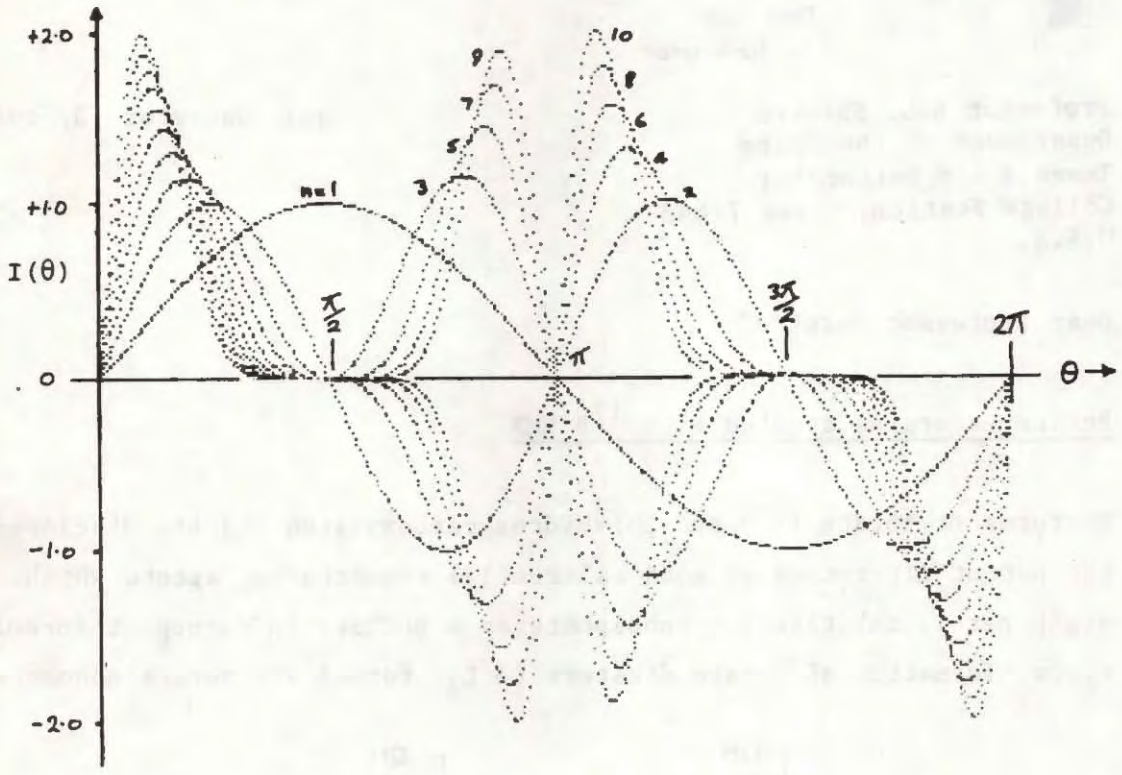
(iii) For $n>4$ very small signals are obtained for $\pi/3<\theta<2\pi/3$.

(iv) A signal intensity of ca 1.3 to 1.4 is obtained for all likely $n>4$ if θ is ca $\pi/6$. This is useful as it can be used as a general starting value and also gives greater tolerance on J.

In the hope that this is useful to some,

Yours sincerely,

Dr. I.H. Sadler.



no of coupled protons n	Relative Intensities I(θ)
1	(sin θ)
2	(sin 2θ)
3	3(sin 3θ + sin θ)/4
4	(sin 4θ + 2sin 2θ)/2
5	5(sin 5θ + 3sin 3θ + 2sin θ)/16
6	3(sin 6θ + 4sin 4θ + 5sin 2θ)/16
7	7(sin 7θ + 5sin 5θ + 9sin 3θ + 5sin θ)/64

Ref. 1. M.R. Bendall, D.M. Doddrell, D.T. Pegg & W.E. Hull, DEPT Bulletin Bruker A.M. Karlsruhe 1982.

2. D.T. Pegg & M.R. Bendall, J. Magn. Res. 1983, 55, 51.

3. D.T. Pegg & M.R. Bendall, J. Magn. Res., 1983, 51, 264.

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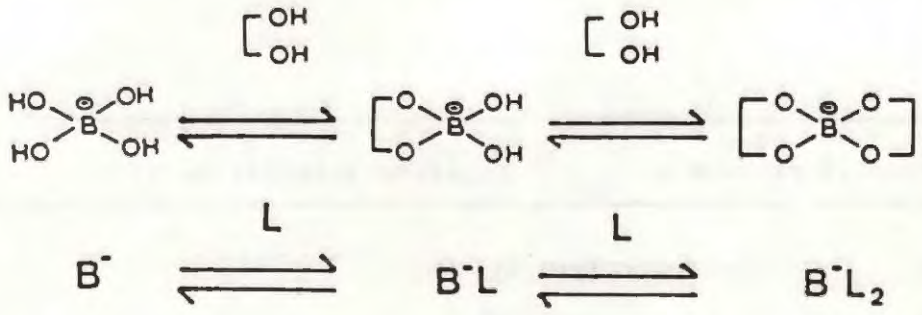
U.S.A.

Delft, December 18, 1984

Dear Professor Shapiro,

Borate esters as studied with ^{11}B NMR

Mixtures of borate (B^-) and polyhydroxycarboxylates (L) are disclosed in the patent literature as good calcium(II) sequestering agents which might partly substitute triphosphate as a builder in detergent formulations. Formation of borate diesters (B^-L_2) formed via borate monoesters



(B^-L) is responsible for this phenomenon. ^{11}B NMR appeared to be a versatile tool in the identification of the various types of borate esters possible in such systems. After inspection of numerous ^{11}B spectra we formulated the following empirical equation for the ^{11}B chemical shifts of borate esters of α,β-diols ($\delta_{B^-L_n}$):

$$\delta_{B^-L_n} = \delta_{B^-} + n * (\Delta + i)$$

δ_{B^-} is the chemical shift of free borate (δ_{B^-} = -17.6 ppm), n the number of polyhydroxy compounds bound by borate (n = 1, 2), Δ the increment per bound diol function (Δ = 3.7 ppm) and i an increment for the combined effect of configuration and substitution of the glycol moiety (Table 1).

Table 1: Configuration and substituent effects

Configuration	Substituents			
X-CHOH-CHOH-Y	X/Y = CH_2/CH_2	CHOH/CHOH	COO^-/COO^-	$CHOH/COO^-$
threo	+0.1	+0.3	+1.3	+0.5
erythro	-0.1	-0.6	+0.8	-0.2
X-CHOH-CH_2OH	X = CH_2	CHOH	COO^-	
	0.0	+0.4	+0.8	

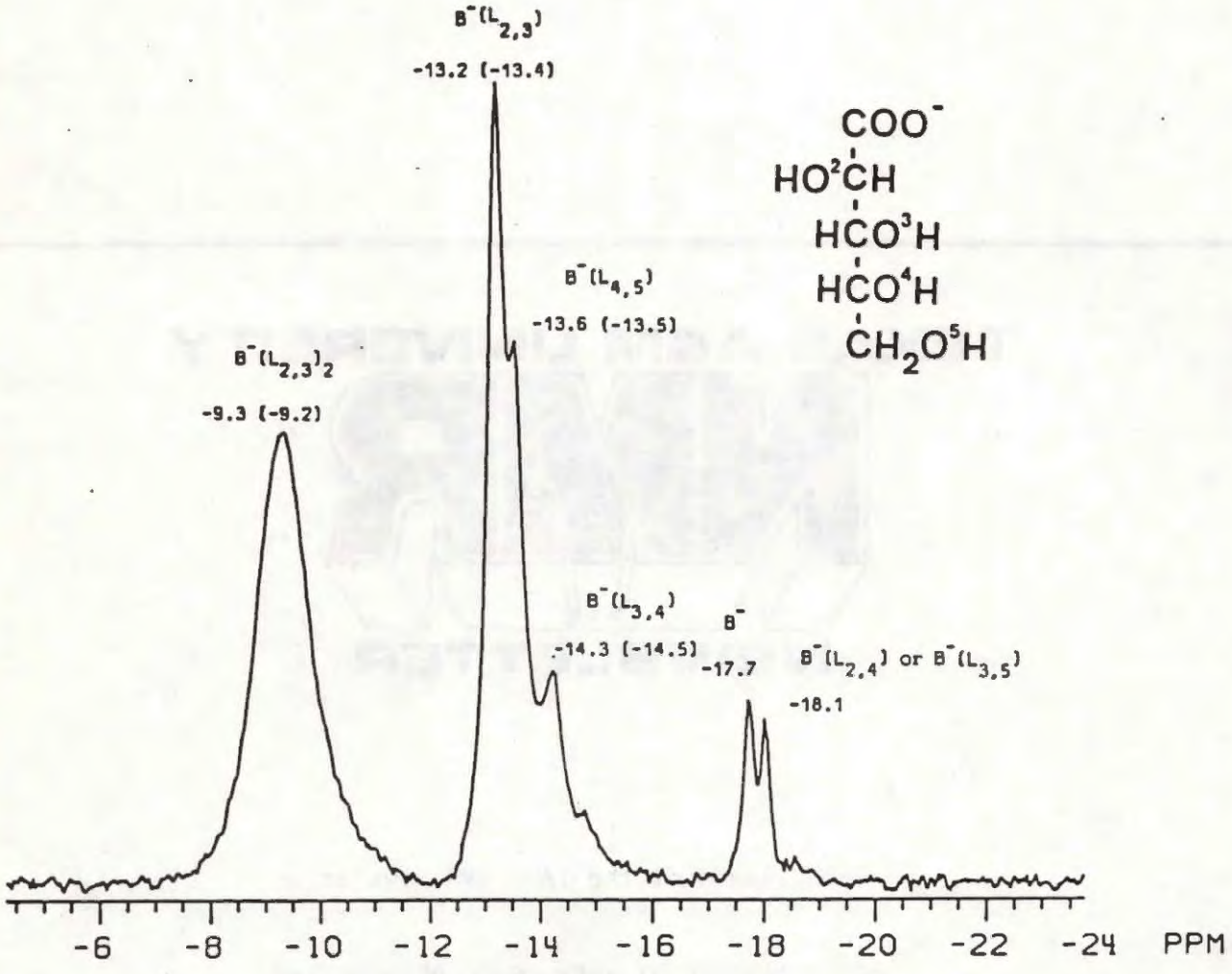


Fig. 1: ^{11}B NMR spectrum of a sample with C_B = 0.04 and C_L = 0.2 mole/l (L = arabinonate; suffixes denote the oxygen atoms bound by the boron atom).

^{11}B chemical shifts can be predicted with an accuracy of $\pm$ 0.2 ppm. Figure 1 shows a ^{11}B spectrum of a sample with C_B = 0.04, C_L = 0.2 mole/l (L = arabinonate) at pH = 11.0. The calculated chemical shifts are given between brackets. Using the data of series of spectra with varying C_B and C_L, the association constants of the borate mono- and diesters for the various diol functions were determined which is not possible with common techniques such as potentiometry or polarimetry.

Yours sincerely,

Martin van Duin. Peters

M. van Duin J.A. Peters

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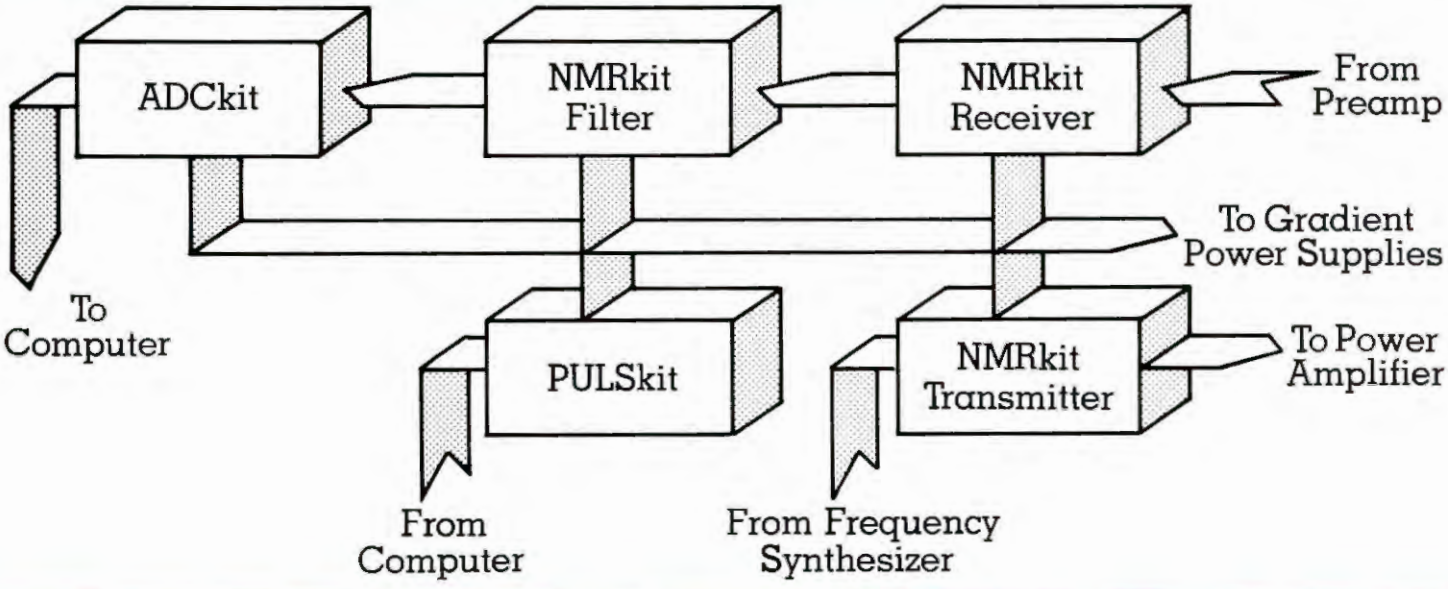

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Physical Chemistry Laboratory, Oxford, U.K.

19 December 1984

Dear Barry,

'MAXIMUM ENTHALPY'

There are certain topics in NMR that can be relied upon to generate the maximum amount of heat in discussion. Those of us who value a quiet life have learned to avoid raising subjects like zero filling and maximum entropy. Nevertheless I am breaking my own rule and venturing some caveats on the latter. A recent paper in Nature (1) later became the subject of a popular science article in the 'Times' of London, which went so far as to imply that the maximum entropy method could so improve NMR sensitivity that natural abundance carbon-13 spectroscopy in vivo would not need time averaging. Since there is an element of magic in the maximum entropy recipe (the procedure is never very clearly explained) readers might well be tempted to believe it has magical powers to improve sensitivity.

NMR spectroscopists are accustomed to working with receivers, detectors and processing schemes that are linear, and may therefore be forgiven for using the terms sensitivity and signal-to-noise ratio essentially interchangeably. Sensitivity really defines the ability to detect a very weak signal comparable in amplitude to the instrumental noise. In a linear system it is sufficient to quote the signal-to-noise ratio obtained with a known concentration of a standard test sample, since by proportion we can calculate the minimum concentration that will just give a detectable signal. This is no longer true in a non-linear system. An improvement in signal-to-noise ratio is then not equivalent to an improvement in sensitivity. In fact we can use all the old tricks -- recorder dead-band, non-linear amplification, 'constant speed' recorder pens, feed-back spectrometers, and so on -- to improve the signal to noise ratio by large factors, provided that it is already significantly greater than unity. Unfortunately these methods make it even harder to find a weak signal hiding under the noise. The maximum entropy method is a non-linear process, so if we wish to analyse the method we should be careful to consider the question of sensitivity rather than signal-to-noise ratio.

A digression may help to illustrate the point. We recently described a data processing method (known familiarly as 'Hogwash') which removed undesirable dispersion-mode components from two-dimensional spectra (2). It is loosely based on a procedure used in radioastronomy (3). A computer search routine finds the coordinates and linewidths of each response in the frequency-domain matrix, taking care to correct for frequency displacements due to overlap, eventually subtracting out all the dispersion-mode contributions from the experimental 2D spectrum. It is not much trouble for the computer (and who cares if it is ?) to present the final spectrum in a completely noise-free form, simply by introducing all the pure absorption-mode responses onto a background matrix which is everywhere zero. We call the result an

'ersatz' spectrum, implying that it is not all it pretends to be. Signals in the raw experimental spectrum that were so weak as to be comparable with the noise do not appear in the ersatz spectrum because the search program fails to find them. By contrast, artifacts in the raw spectrum are promoted to the status of genuine signals, with plausible linewidths and lineshapes. Sensitivity has not been enhanced, although the spectra are very nice for grant proposals.

Although Hogwash is cruder than the sophisticated maximum entropy routine, its purpose is similar -- to improve the presentation of data by removing known artifacts, without significantly degrading the input data. The advantages of Hogwash are that it is easy to see how it works and it needs far less computer time and space. Both methods have undoubtedly useful applications in repairing known distortions of the experimental spectrum, for example the removal of sinc wiggles caused by premature truncation of a time-domain signal (4). The danger is to consider noise as an artifact that can be eliminated in this way.

Successful methods of improving sensitivity exploit some characteristic difference between the nature of noise and that of a genuine signal. If there are different components present in the Fourier spectra, for example if the noise contains higher-frequency components, then these can be filtered out without significantly broadening the NMR signals; the optimum 'matched filter' condition is well-known from the work of Ernst (5). At a corresponding point in two consecutive recordings of a particular spectrum, the noise fluctuates in amplitude and (perhaps) sign, while true signal components maintain the same amplitude and sign. This is the basis of perhaps the only genuine sensitivity enhancement technique -- time averaging. The maximum entropy method does not appear to work on any such criterion.

A suitable test case for the advocates of maximum entropy might be something like this. Ensure that the noise has no higher-frequency components than the signal by using a matched filter. Record an NMR spectrum that has several lines with signal-to-rms-noise ratio of say four, after 64 accumulations. Now take <u>one</u> such transient, corresponding to a signal-to-noise ratio of about 0.5, and manipulate it by any suitable algorithm. See if any of the lines reappear.

Yours sincerely,

Ray

Ray Freeman

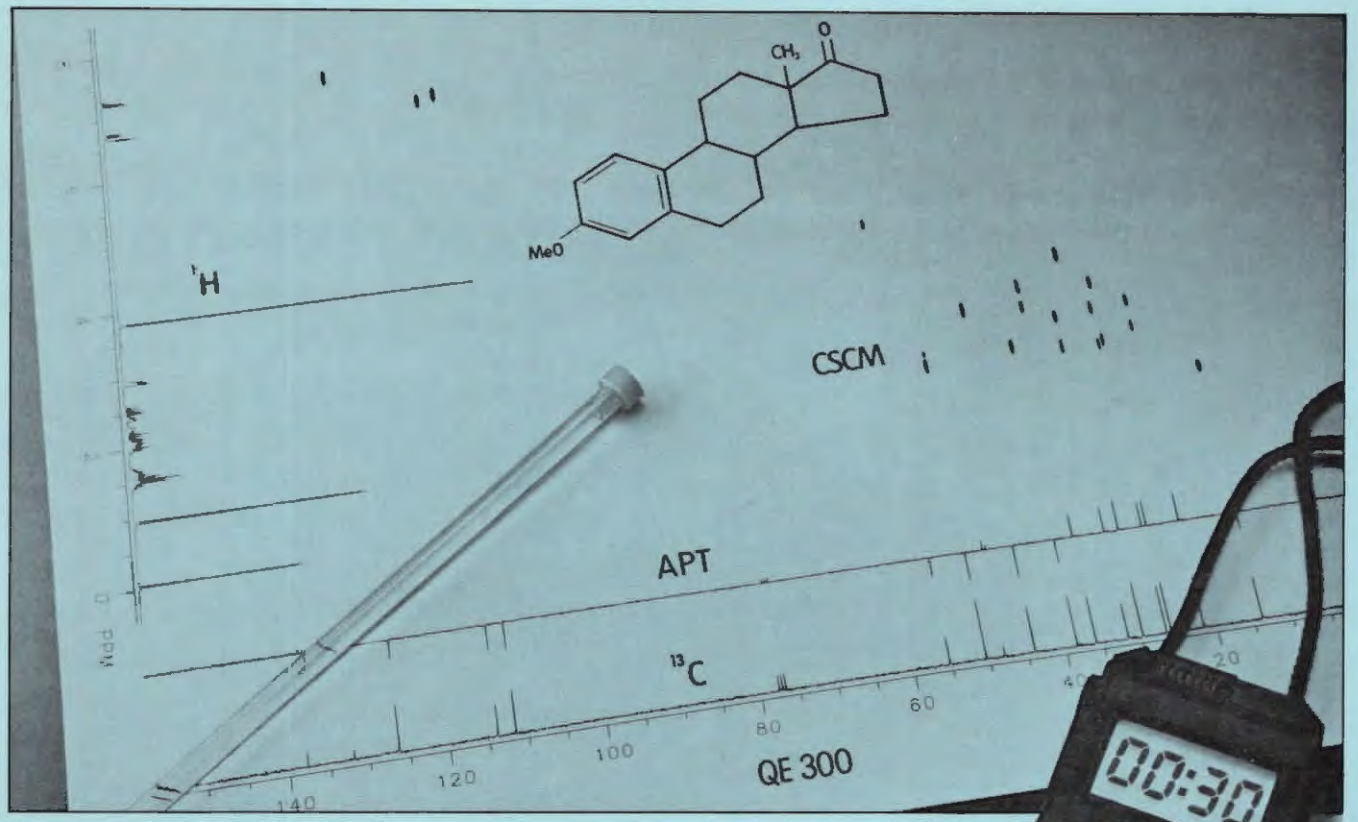
(1) Sibisi, Skilling, Brereton, Laue and Staunton, Nature, <u>311</u>, 446 (1984).

(2) Shaka, Keeler and Freeman, J. Magn. Reson. <u>56</u>, 294 (1984).

(3) Hogbom, Astron. Astrophys. Suppl. <u>15</u>, 417 (1974).

(4) Keeler, J. Magn. Reson. <u>56</u>, 463 (1984).

(5) Ernst, Adv. Magn. Reson. <u>2</u>, (1966).



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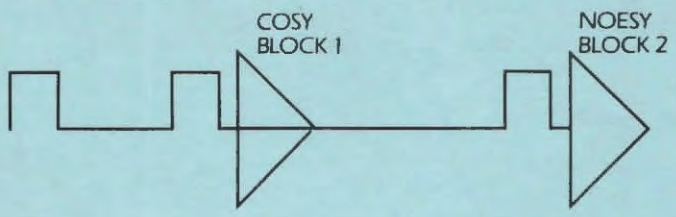

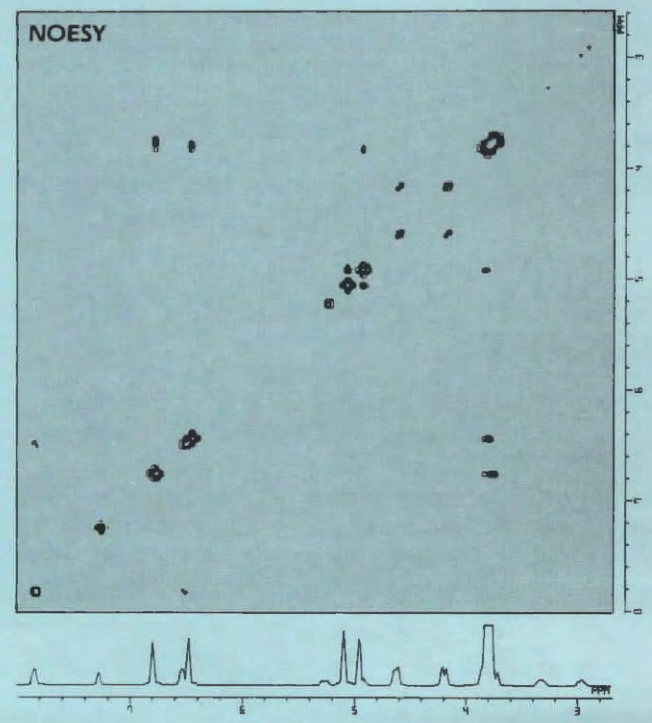

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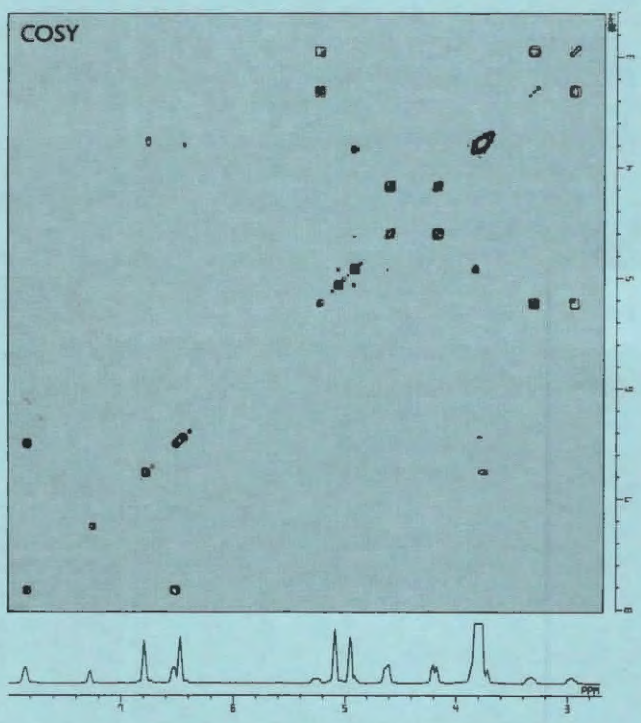

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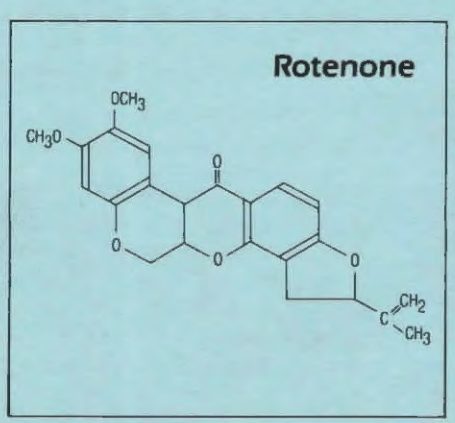

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