BRIAN SYKES

TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

No. 340

January 1987

TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

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AUTHOR INDEX ------ TAMU NMR NEWSLETTER, NO. 340, JANUARY 1987

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FORTHCOMING NMR MEETINGS

28th ENC (Experimental NMR Conference) - April 5-9, 1987; Asilomar, Pacific Grove, California; Chairman: Dr. Lynn W. Jelinski, (AT&T Bell Laboratories); Detailed information, etc., appears on pages 54-57 of this Newsletter issue.

8th International Meeting "NMR Spectroscopy" - July 5-10, 1987; University of Kent at Canterbury, England; For information, contact Dr. John F. Gibson, Royal Society of Chemistry, Burlington House, London W1V OBN, England. See Newsletter #338, p. 55 for information and application.

29th Rocky Mountain Conference - August 2-6, 1987; Radisson Hotel, Denver, Colorado; Program Chair: Michael Reddy, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002, (303) 236-3617; Nuclear Magnetic Resonance Symposium: James Haw, Department of Chemistry, Texas A&M University, College Station, Texas 77843, (409) 845-1966; Preliminary program and pre-registration information available from Sandy Grande, 8780 W. Quarto Circle, Littleton, Colorado 80213.

FACSS XIV - October 4-9, 1987; Detroit, Michigan; For information, contact Dr. Stephen J. Swarin, Publicity Chairman, Analytical Chemistry Department, General Motors Research Labs, Warren, Michigan 48090-9055, 313-986-0806.

29th ENC (Experimental NMR Conference) - April 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For information, contact Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

Additional listings of meetings, etc., are invited.

*Welcome to this new advertiser!

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. 342 (March) ------ 27 February 1987

No. 343 (April) --------- 27 March 1987

McMASTER UNIVERSITY
Department of Chemistry
1280 Main Street West, Hamilton, Ontario, L8S 4M1
Telephone: 525-9140

November 27, 1986
(Received December 11, 1986)

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

Dear Barry:

^{59}Co Solid State NMR

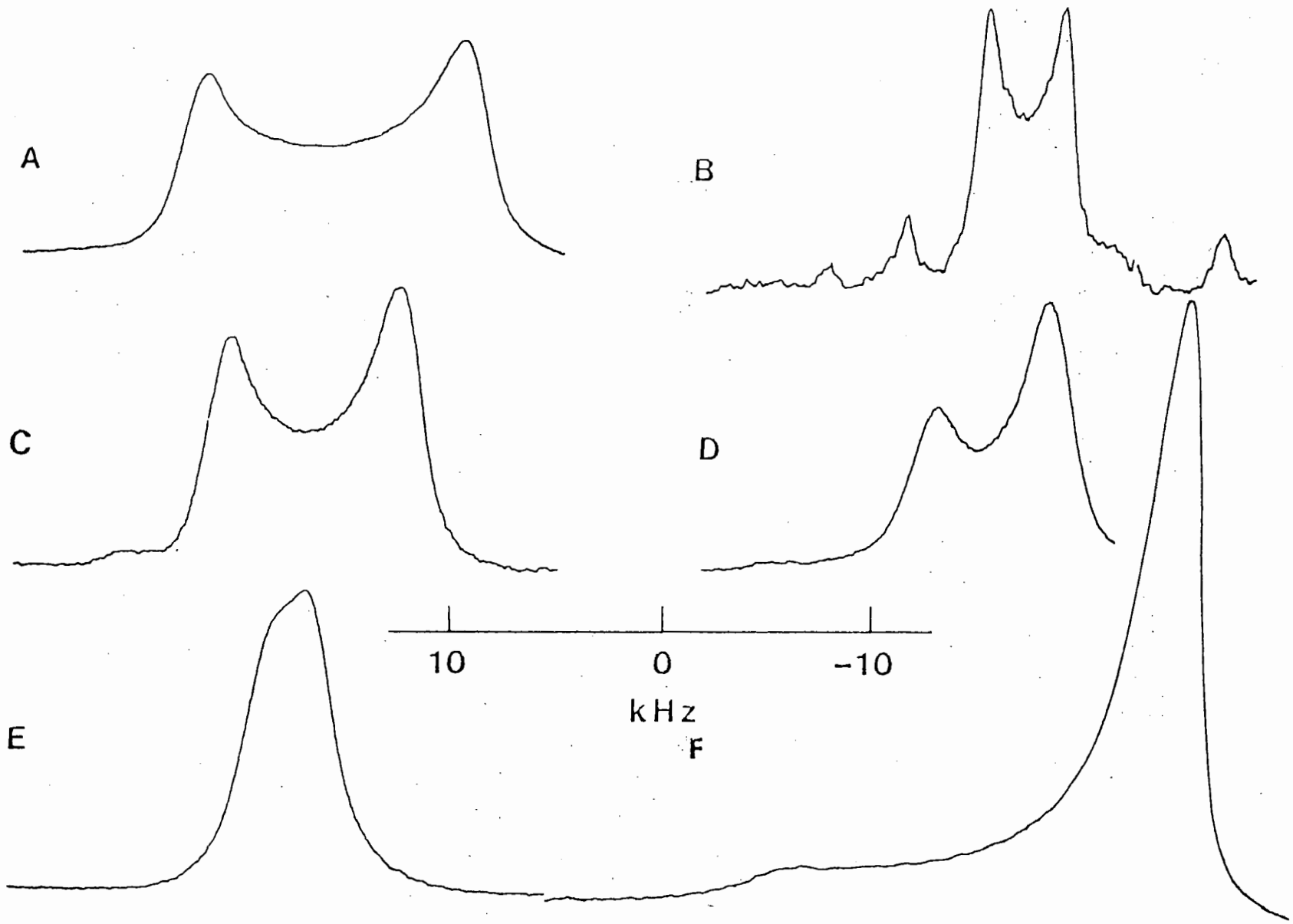
Solid state NMR is rapidly gaining acceptance as a routine tool particularly with the range of MAS probes now available. However, for quadrupolar nuclei, spinning the sample may obscure useful information. The spectra in the figure were obtained (except B) non spinning in conventional "solution probes".

The ^{59}Co nucleus has been extensively studied in solution however very little has been reported in the solid state. In principle the chemical shift anisotropy and quadrupole coupling constants can be determined from solid state spectra. The figure shows the ^{59}Co spectra of polycrystalline sodium cobaltinitrite at different field strengths; A) 4.7T, B) 4.7T + MAS, C) 5.9T, D) 7.1T, E) 9.5T, F) 11.8T.

At low fields the appearance is that expected for a quadrupolar broadened resonance, i.e., a broad doublet; at higher fields this splitting is lost and the spectrum becomes typical of that expected from a molecule with axial chemical shift anisotropy as evidenced by the shoulder to higher frequency in spectrum F. A fuller account will appear in Can. J. Chem.

D. R. Eaton R. J. Buist B. G. Sayer

Please credit this contribution to the account of J.I.A. Thompson



^{59}Co Spectra of Polycrystalline Sodium Cobaltinitrite at Different Field Strengths

GRUPPO MONTEDISON
MONTEDIPE

Professor BERNARD SHAPIRO
Dept. of Chemistry
TEXAS A & M UNIVERSITY
COLLEGE STATION - Tx 77843 - U.S.A.

(Received December 15, 1986)
30 NOVEMBER 1986
MONTEDIPE/PM/CER
Stab.to Petrolchimico
Via della Chimica, 5
30175 - PORTO MARGHERA
(Venezia) ITALY

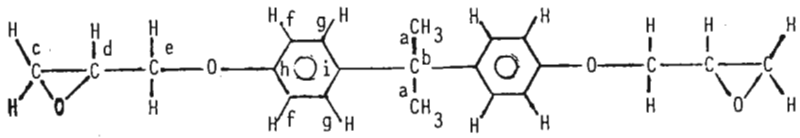
Interpretation of ^{13}C NMR spectra of bisglycidylether of bisphenol A and related molecules.

Dear professor Shapiro,

in a previous note (1) we have reported the ^{1}H NMR spectra of bisglycidylether of bisphenol A (I) and their variation with the temperature.
In this letter we report the full analysis of the ^{13}C spectra of (I) together with that of the condensation product of (I) with phenylisocyanate, i.e. bis-2-oxazolidone (II). Chemical shift assignments of all ^{13}C atoms, one-bond and multibond carbon hydrogen coupling constants are listed in tables 1 and 2.
Despite the relative complexity of the molecules, due to the small substitution effects of the phenylisocyanate group, an exact attribution of each resonance is possible.

TABLE 1

^{13}C parameters of the bisglycidylether of bisphenol A

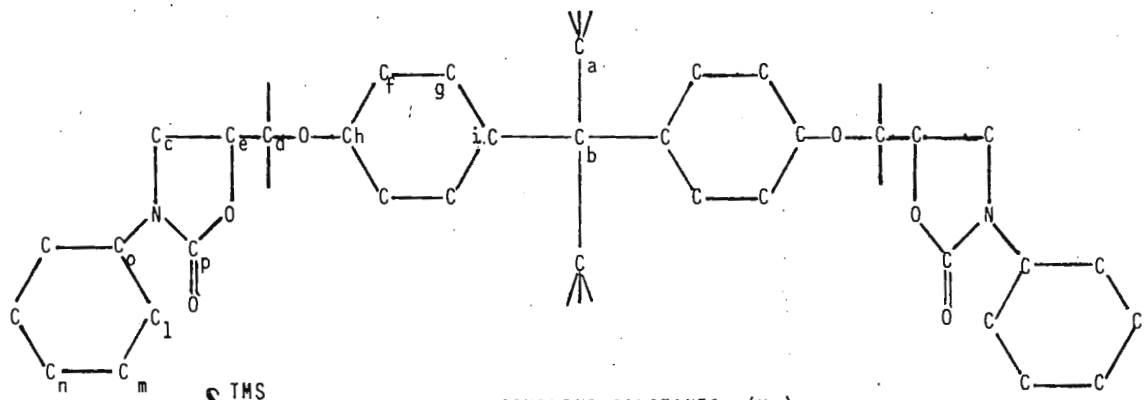


	δ^{TMS}_{ppm}	COUPLING CONSTANTS (Hz)		
C_a	31.00	$J^1_{C_a-H}$ = 126.48	$J^3_{C_a-C_b-C_a-H}$ = 4.38	
C_b	41.72	Unresolved multiplet		
C_c	44.65	$J^1_{C_c-H}$ = 176.49	$J^2_{C_c-C_d-H}$ = 2.94 (3)	
C_d	50.17	$J^1_{C_d-H}$ = 175.02	$J^2_{C_d-C_c-H}$ = 2.94	$J^2_{C_d-C_e-H}$ = 4.41 (3)

	δ^{TMS}_{ppm}	COUPLING CONSTANTS (Hz)			
C_e	68.76	$J^1_{C_e-H}$ = 142.30	$J^2_{C_e-C_d-H}$ = 4.41		
C_f	114.06	$J^1_{C_f-H}$ = 158.84	$J^2_{C_f-C_g-H}$ <1	$J^3_{C_f-C-C_f-H}$ = 4.42 (3)	
C_g	127.77	$J^1_{C_g-H}$ = 157.36	$J^2_{C_g-C_f-H}$ <1	$J^3_{C_g-C-C_g-H}$ = 7.35 (3)	
C_h	156.37 (2)	Unresolved multiplet			
C_i	143.63	Unresolved multiplet			

TABLE 2

^{13}C parameters of bis-2-oxazolidone



	δ^{TMS}_{ppm}	COUPLING CONSTANTS (Hz)		
C_a	30.94	$J^1_{C_a-H}$ = 127.96		
C_b	41.72	Unresolved multiplet		
C_c	47.18	$J^1_{C_c-H}$ = 145.60 *		
C_d	68.11	$J^1_{C_d-H}$ = 143.40		
C_e	70.64	$J^1_{C_e-H}$ = 150,50 *		
C_f	114.12	$J^1_{C_f-H}$ = 160.31 *	$J^3_{C_f-C-C_f-H}$ = 3.73	
C_m	118.35	$J^1_{C_m-H}$ = 161.78	$J^2_{C_m-C_l-H} = J^2_{C_m-C_n-H}$ = 5.88	$J^3_{C_m-C-C_m-H}$ = 7.35

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	δ^{TMS}_{ppm}	COUPLING CONSTANTS (Hz)			
C_n	124.07	$J^1_{C_n-H}$ = 161.80	$J^3_{C_n-C-C_1-H}$ = 7.35		
C_g	127.84	$J^1_{C_g-H}$ = 157.37*	$J^3_{C_g-C-C_g-H}$ = 7.35		
C_1	129.07	$J^1_{C_1-H}$ = 161.05	$J^2_{C_1-C_m-H}$ = 5.88	$J^3_{C_1-C-C_1-H} = J^3_{C_1-C-C_n-H}$ = 7.35	
C_o	138.23	(Triplet of doublet)	$J^3_{C_o-C-C_m-H}$ = 8.82	$J^4_{C_o-C-C-C_n-H}$ = 7.35	
C_i	144.08	Unresolved multiplet			
C_h	154.55	Unresolved multiplet appears like a triplet			
C_p	155.98**	Doublet ^ $J^3_{C_p-N-C_c-H}$ = 8.33			

* Cfr. the corresponding spectral parameters of bisglycidylether of bisphenol A in Table 1.

** Relaxes more fastly than other quaternary carbons, due to quadrupolar coupling with ^{14}N nucleus.

All spectra were obtained in ~33% w/v solution of I and II in $CDCl_3$ at 22.63 and 20.15 Mhz, at room temperature.

References:

(1) G. Gurato - R. Pernice - M.F.Coletta TAMUN NMR LETTERS 328-11-1986

(2) W. Voelter - S. Fuchs - R.H. Sauffer - K. Zech - MONAT. CHEMIE 105-110 (1974)

(3) A.u.Rahman - Nuclear Magnetic Resonance - pg.186 - SPRINGER (1986)

Sincerely Yours

F. COLETTA °

F. Coletta

G. GURATO

G. Gurato

R. PERNICE

R. Pernice

(°) Centro di studio sugli stati molecolari ed eccitati del CNR (c/o DIP. di Chimica Fisica - via Loredan 2 - PADOVA)

The NMR evolution continues:

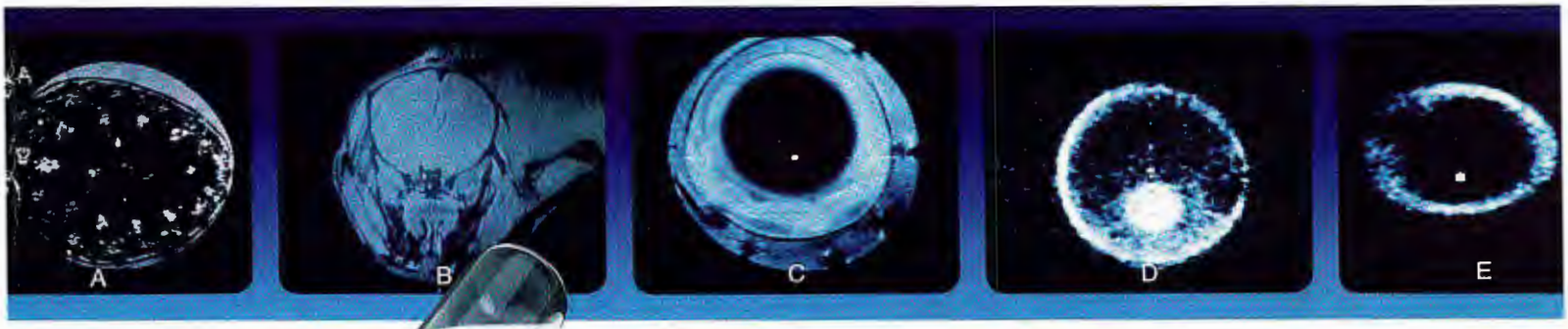

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Fig. A: Cross sectional image of a philodendron stem. Resolution 19μ x 19μ x 300μ.
Fig. B: Cross sectional image of a mouse brain tumor. Resolution 100μ x 100μ x 500μ.
Fig. C: A cross sectional image of a mouse eye, 3 mm in diameter. Resolution 20μ x 20μ x 250μ.
Fig. D: Image of an ovum from laevis (frog egg). Resolution 10μ x 10μ x 250μ.
Fig. E: Diffusion of water through a piece of nylon. Resolution 50μ x 50μ x 1000μ.

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(Received December 11, 1986) November 27, 1986

Prof Bernard L Shapiro
TAMU NMR Newsletters
Department of Chemistry
Texas A & M University
College Station, Texas 77843
USA

NaV NMR

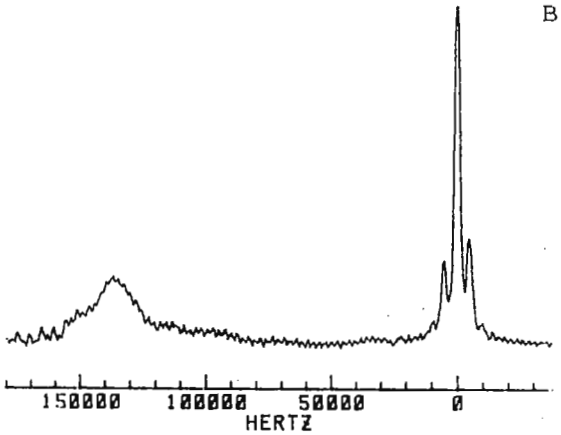
Dear Prof Shapiro,

During the course of our studies of peat and wood pulping in the solid state we occasionally relax ourselves and run samples for other people interested in solid state work.
This was the case when the inorganic department at this institute were interested to see whether solid state NMR could aid in their interpretation of solution and X-ray studies of complex anions containing ^{51}V.
Below you see a ^{51}V MAS NMR spectrum of $Na_6Mo_6V_2O_{26} \times 16H_2O$ obtained at 26.323 MHz with our MSL-100 using the tunable double air bearing probe.
We just wanted to show you this multinuclear observation where both ^{23}Na and ^{51}V resonances appear in the spectrum. In solution the vanadate appears in equilibria of several species but obviously this is not the case in the crystalline form. In the ionic crystal the vanadium resonance appear as a single peak at high field in the spectrum (with sidebands due to incomplete rotational reduction of the quadrupole splitting).
We also see the sodium resonance which is octaedrically coordinated to water and to hexamolybdo-divanadate anion.
Please credit this contribution to the account of Dr Ulf Edlund.

Yours sincerely,

Bo Nordén

Bo Nordén



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Professor Alan P. Marchand

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NORTH TEXAS STATE UNIVERSITY

Center for Organometallic Research and Education

December 2, 1986 (Received December 8, 1986)

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

Dear Barry:

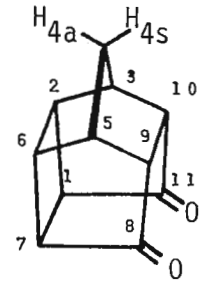
Assignment of Proton and Carbon-13 NMR Resonances in

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione

During the past decade, we have been involved in studies of the synthesis and chemistry of novel, substituted pentacycloundecanes. Recently, we have undertaken detailed 2D NMR studies of symmetrical and unsymmetrical methyl-derivatives of the title compound (**1**, a cage diketone whose structure is shown below). We now report the complete assignment of proton and carbon-13 signals in the corresponding NMR spectra of the parent diketone.

The 2D HETCOR spectrum of **1** reveals the following correlations:

C-13 Chemical Shift		**H-1 Chemical Shift**
δ38.32 (d)	(correlates with)	δ3.19
44.25 (d)		2.95
43.42 (d)		2.80
54.38 (d)		2.70
40.05 (t)		2.06, 1.90
212.03 (s)		- -



1

Note that the C-13 NMR peak at δ 40.05 (C-4, methylene carbon atom) correlates with the ABX$_2$ pattern at δ1.90 and 2.06 (due to H-4s and H-4a; more about these later!). Nuclear magnetic double resonance (NMDR) of H-4s and H-4a produces a major change in the appearance of the peaks at δ 2.95. Although other peaks in the proton NMR spectrum of **1** are also affected, the effect is considerably smaller elsewhere. This observation permits assignment of the proton NMR peaks at δ2.95 to H-3,5, (to which H-4s and H-4a are coupled vicinally). These resonances correlate (HETCOR) with the C-13 NMR peak at δ 44.25, (i.e., C-3,5).

NMDR of the proton NMR peak at δ 2.95 (H-3,5) produces major changes in the appearance of the peaks at δ 2.70 and 3.19. The latter two peaks most likely arise from H-9,10 and H-2,6 (to which H-3,5 are vicinally coupled). Whereas we cannot differentiate between H-9,10 and H-2,6 on the basis of this observation alone, nevertheless we can use this information to tentatively assign the peak at δ 2.80 to H-1,7 (since this is the only set of protons in **1** which is not coupled vicinally to H-3,5). From the HETCOR experiment, we see that the resonance at δ 2.80 correlates with the C-13 NMR peak at δ 43.42 (C-1,7).

Additionally, we observe that NMDR of the proton NMR peak at δ 3.19 produces a greater change in the appearance of the peak at δ 2.80 (H-1,7, to which it is coupled vicinally) than does NMDR of the proton NMR peak at δ 2.70 (which is not vicinally coupled to the peak at δ 2.80). We note that H-1,7 is coupled vicinally only to H-2,6, and we can therefore assign the resonance at δ 3.19 to H-2,6. From the HETCOR spectrum, we see that the peak at δ 3.19 correlates with the C-13 NMR peak at δ 38.32 (i.e., C-2,6).

The remaining unassigned peak in the proton NMR spectrum of **1**, i.e., that which appears at δ 2.70, must be due to H-9,10. From the HETCOR spectrum, we see that the peak at δ 2.70 correlates with the C-13 NMR resonance at δ 54.38, (i.e., C-9,10).

To complete this exercise, it is necessary only to assign H-4s and H-4a in the ABX_2 pattern at δ 1.90 and 2.06. Actually, this can be done by simple inspection of the 300 MHz proton NMR spectrum; such inspection reveals that the lowfield half of the "tripled AB pattern" is clearly broadened. This result is most likely due to the operation of stereospecific long-range (five-bond!) coupling between H-4s and H-1,7. Such long-range five-bond couplings have been reported in similar polycyclic systems by R. M. Coates and J. L. Kirkpatrick, J. Am. Chem. Soc., **90**, 4162 (1968) and by C. W. Jefford, et al., Ibid., **91**, 1532 (1969). The operation of this long-range coupling is possible in **1** for H-4s but not for H-4a. Accordingly, we assign the lowfield half of the "tripled AB" pattern (δ2.06) to H-4s, leaving the corresponding upfield half of this pattern (δ1.90) to be assigned to H-4a. We have observed that double irradiation of the resonance at δ 2.80 (i.e., H-1,7) results in removal of a small coupling to the peak at δ 2.06 with consequent sharpening of the latter signal. This observation is consistent with the foregoing interpretation and confirms our assignment of the signal at δ 2.06 to H-4s.

Sincerely yours,

Alan P. Marchand
Distinguished Research Professor

Arthur D. Earlywine*

* NMR experiments were performed by Dr. Earlywine at the University of Oklahoma, Norman, OK; Present address: Department of Chemistry, University of Wyoming, Laramie, WY 82071

WASHINGTON UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY

December 9, 1986
(Received December 12, 1986)

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

Regional Blood Flow and Tissue Perfusion by Deuterium NMR

Dear Barry,

Knowledge of blood flow rates and changes in this flow due to therapeutic treatment in specific tissues and organs is of vital importance to many investigators, us being no exception. Needing to know the blood flow rate in the tissue of interest at the time of, and following, our NMR analysis of metabolic status prompted us to develop a novel technique using deuterium-NMR to measure regional blood flow and tissue perfusion (1,2). We have been investigating, with very promising results, the use of D_2O as a relatively inert diffusible tracer to measure blood flow and tissue perfusion *in vivo* in a method analogous to currently used radiolabelled tracer techniques. This was accomplished with minimal additional invasiveness, and in some cases without removal of the subject from the magnet.

Upon injection of a small bolus (0.01-0.5 ml) of D_2O directly into the blood supply entering the tissue of interest, or directly into the tissue, the resultant washout of D_2O due to ongoing blood flow is monitored by deuterium-NMR. The integrated deuterium signal intensity decreases exponentially as expected from similar studies using radiolabelled tracers (for reviews, see 1-3), see Fig. 1. The mathematical models developed for radioactive bolus tracer studies are directly applicable to the deuterium washout data. In the case of single compartment modeling, the exponential time constant (T) obtained from fitting the washout curve to a two parameter single exponential decay is related to blood flow by the central volume principle of tracer kinetics:

$$\frac{F}{W} = \frac{\lambda}{T}$$

where F/W is the volumetric blood flow per unit mass of tissue and λ is the blood:tissue partition coefficient, which is easily determined independently of the NMR experiment.

Our preliminary experiments with *in situ* rat liver and muscle and mouse tumor gave blood flow rates determined with single compartment modeling comparable to literature values (hepatic blood flow as 61 ml/100 g/min, muscle blood flow was 6.8 ml/100 g/min, tumor blood flow was 12 ml/100 g/min). We have validated the deuterium NMR technique by measuring the "blood" flow through an *ex vivo* perfused liver and comparing the calculated result to the known perfusion rate. The average error magnitude is 5.5% (n = 8).

Application of this technique to other tissues and to flow-imaging will be the focus of future investigations.

References

1 Ewy, C.S.; Bennett, D.L.; Ackerman, J.J.H.; Deuterium NMR Measurements of Blood Flow in Normal and Tumor Tissue. Soc. Magn. Reson. Med. 5th Ann. Meet., Montreal, Canada (August, 1986).

2 Ackerman, J.J.H.; Ewy, C.S.; Kim, S.-G.; Shalwitz, R.A.; Deuterium Magnetic Resonance In Vivo: The Measurement of Blood Flow and Tissue Perfusion. Ann. N.Y. Acad. Sci., in press.

3 Lassen, N.A.; Hendriksen, O.; Sejrsen, P.; Indicator Methods for Measurement of Organ and Tisue Blood Flow. Handbook of Physiol.; Sect. 2, Vol. 3, Part 1, Ch. 2; Waverly Press (1983).

4 Zierler, K.L.; Equations for Measuring Blood Flow by External Monitoring. Circ. Res., 16, 309-321 (1965).

5 Shipley, R.A.; Clark, R.E.; Tracer Methods for In Vivo Kinetics. Academic Press (1972).

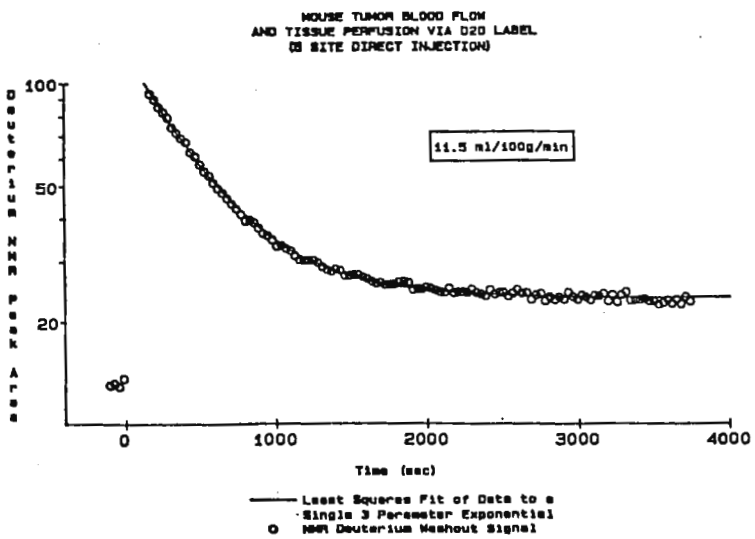


Figure 1. Washout curve of integrated deuterium signal at 55.28 MHz following a 0.05 ml total bolus of 20% D_2O dispersed over 5 injection sites into a mouse RIF-1 tumor. Time resolution was ca. 30 sec. Open circles represent NMR data values. Solid line represents least squares fit of entire data to a 3 parameter single exponential (resulting from consideration of a two compartment model) of the form $y = A + B\,e^{-t/T}$. Calculated blood flow was 11.5 ml/100 g/min.

Sincerely,

Coleen Ewy Seong-Gi Kim Nancy Becker Robert Shalwitz J.J.H. Ackerman

340-14

THE UNIVERSITY OF UTAH

DEPARTMENT OF CHEMISTRY
HENRY EYRING BUILDING
SALT LAKE CITY, UTAH 84112

December 11, 1986

(Received December 16, 1986)

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

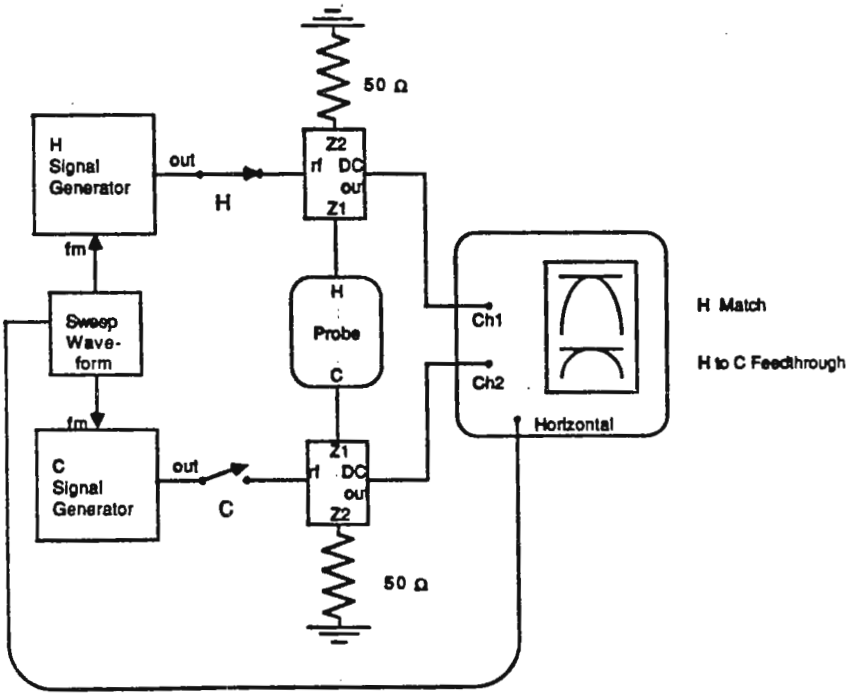
A Setup for Tuning Match and Feedthrough in Double Tuned Probes

Dear Professor Shapiro:

Recently we have built double tuned probes using a design that enables us also to tune the feedthrough of the probe. While adjusting these probes, we use a setup that allows us to observe both the ^{1}H or ^{13}C match and the feedthrough simultaneously. The setup consists of two signal generators, a sweep waveform generator, two Texscan Model RCB-3 reflection coefficient bridges, a dual display oscilloscope and two rf switches. These components are connected as shown in the accompanying diagram.

To match the ^{1}H channel and observe the ^{1}H to ^{13}C feedthrough, switch H is closed and switch C is left open. The ^{1}H match waveform then appears on channel 1 of the oscilloscope and the ^{1}H to ^{13}C feedthrough waveform appears on channel 2 as in the diagram. To match the ^{13}C channel and observe the ^{13}C to ^{1}H feedthrough, switch H is opened and switch C is closed. In this way the probe tuning is done in a very efficient manner.

Two things need to be mentioned about this setup. First, the feedthrough measurement is qualitative. For a quantitative measurement of the feedthrough we still use a conventional setup. Second, the bridge measuring the feedthrough has no power applied to its rf input; thus, its diodes are not biased on resulting in reduced sensitivity. But this decrease in sensitivity is not severe enough to cause us difficulty in tuning the feedthrough.



Sincerely,

Arlen Soderquist — Arlen Soderquist

D. W. Alderman — D W Alderman

David M. Grant — David M. Grant

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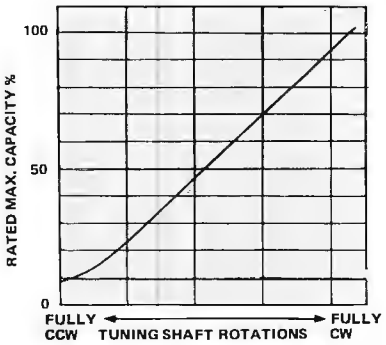
Series VC Trimmers can be provided to meet MIL-Spec requirements. Some units are already available with military part numbers.

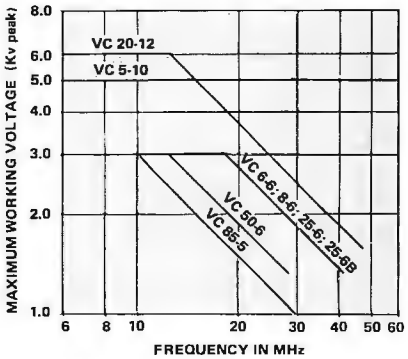
Specifications:

Capacitance Range:	0.7 to 85 pf
Working Voltages:	To 6 Kv
Dielectric Strength:	200% of working voltage, minimum
Quality Factor (Q):	Greater than 5000 to 1 GHz
Insulation Resistance:	10^6 Megohms
Operating Temperature:	−50°C to +150°C*
Temperature Coefficient:	Within 50 ppm/°C
Tuning Torque:	1 to 4 inch ounces

POLYFLON SERIES VC



Typical Adjustment Curve VC Series



Voltage/Current Limits (at maximum temperature)

Consult factory for voltage/current ratings under conditions other than cw, at maximum temperature and maximum capacity.

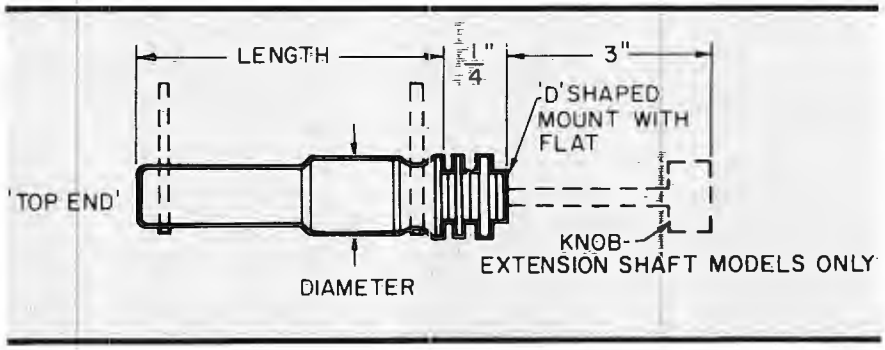
Available as Screwdriver Adjustment or with Extension Shaft. Select Dash No. from Code Table Below.

Model Number	Capacitance Range pf	Peak Working Voltage Kv	Peak Test Voltage Kv	Current (note 1) amps	Nominal Dimensions Inches Length	Inches Dia	Millimeters Length	Millimeters Dia
VC-18-1-(*)	0.7 - 18.	.75	1	1.8	1.13	.43	28.7	10.9
VC-10-12-(*)	0.8 - 10.	6	12	3.3	1.52	0.58	38.6	14.7
VC-5-10-(*)	0.9 - 5.0	5	10	1.65	1.25	0.50	31.8	12.7
VC-6-6-(*)	0.9 - 6.0	3	6	1.25	1.25	0.50	31.8	12.7
VC-8-6-(*)	3.0 - 8.0	3	6	1.7	0.87	0.50	22.1	12.7
VC-25-6-(*)	5.0 - 25.	3	6	5.3	1.43	0.88	36.2	22.4
VC-25-6B-(*)	5.0 - 25.	3	6	4.1	1.48	0.63	37.6	16.
VC-50-6-(*)	5.0 - 50.	3	6	5.3	2.24	1.44	56.9	36.6
VC-85-5-(*)	5.0 - 85.	3	6	5.2	3.25	1.44	82.6	36.6

*Add code number for leads. See Lead Code Number Table below.

Note 1. RMS ampere rating at 16MHz attained by direct connection to capacitor body. Wire leads to straps may limit current to a lower value as a function of application. Most units reactance-limited by working voltage.

Capacitor Outline



Lead Code Number Table

(Unless otherwise specified, units will be supplied as -05 or -06.)

* Code for Screwdriver Adjust Series	Description	* Code for Extension Shaft Series
05	without lead wires	06
15	3" wire, top only—in line with flat	16
25	3" wire, top and bottom—in line with flat	26
35	1½" strap, top only—in line with flat	36
65	3" wire, top only, opposite flat	66
75	3" wire, top and bottom—opposite flat	76
85	1½" strap, top only—opposite flat	86

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Oklahoma State University

DEPARTMENT OF CHEMISTRY
COLLEGE OF ARTS AND SCIENCES

STILLWATER, OKLAHOMA 74078-0447
PHYSICAL SCIENCES 106
405-624-5920

9 December 1986

(Received December 11, 1986)

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

Dear Dr. Shapiro:

Single Pulse and CP-MAS ^{13}C Spectra of Labeled Polystyrene Gels

In efforts to analyze the structures of the cross-link repeat units of styrene-divinylbenzene copolymers, we obtained single pulse ^{13}C spectra of $DCCl_3$-swollen gels with the Varian XL-300 at OSU and ^{13}C CP-MAS spectra of both dry powders and $DCCl_3$-swollen gels with the IBM WP100 at Conoco. The polymers were 99% ^{13}C enriched at the vinyl methine carbon of the *p*-divinylbenzene. The aims were twofold: 1) To determine if the labeled carbon atoms, which must lie at the most rigid sites in the polymer networks, could be detected by single pulse experiments. 2) To determine what fraction of the carbon atoms in the solvent-swollen, more flexible polymer networks could be detected by the CP-MAS method.

The very first single pulse spectra gave us a big surprise: A strong peak at 137 ppm revealed large amounts of unpolymerized vinyl groups of the *p*-divinylbenzene, even in networks prepared with only 1% or 4% DVB. These copolymers are not as highly cross-linked as all of us working with polymer-supported reagents and catalysts thought they were! Analyses of peak areas in the single pulse spectra, and in the powder CP-MAS spectra under optimum contact time conditions, showed 20-28% unpolymerized DVB double bonds in samples prepared by a standard suspension polymerization method. We tried to analyze the residual double bonds by previously reported IR and bromine number methods, but only ^{13}C spectra of labeled polymers detected the unreacted sites well.

We thought that in the gel state there would be insufficient dipolar coupling to detect most of the ^{13}C nuclei by cross-polarization, but the CP-MAS spectra of the gels gave surprisingly strong signals. (The gels were sealed into Kel-F inserts as described in Ford, Mohanraj, Hall, and O'Donnell, *J. Magn. Reson.* ***1985, 65*** , 156). The peak areas in spectra of gels were 0.25-0.5 as large as those in CP-MAS spectra of the same samples in dry powder form. Both the labeled carbon signals and signals from all other carbons present only in natural abundance were detected. The small amount of residual dipolar coupling and the scalar coupling in the gel state must be sufficient for cross-polarization. The results suggest that CP-MAS spectroscopy may be useful also for other kinds of semi-mobile samples such as rubbery polymers, coals in solvents, and liquid crystals.

Sincerely,

Warren T. Ford

Warren T. Ford, OSU
M. Periyasamy, OSU
Frank J. McEnroe, Conoco

CENTENNIAL DECADE
1980 • 1990

December 9, 1986 (Received December 15, 1986)

NMR of Cellulose Triacetate

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

Dear Professor Shapiro:

In the past five years several investigations by ^{1}H- and ^{13}C-NMR have been reported for cellulose esters.[1] In all of these reports assignments of chemical shifts were made by chemical derivations or by comparison to spectra of lower oligosaccharides. Moreover, the resolution in these spectra was generally quite poor and revealed very little detail. As part of an ongoing study of cellulose esters by NMR we needed detailed spectra and unambiguous assignment of these spectra.

We have found that sufficient spectral resolution can be obtained in the 1D spectra by application of a suitably parameterized Lorentzian to Gaussian transformation. The proton spectrum of the ring protons of cellulose triacetate (CTA, Figure 1, 400 MHz, 25°C, $CDCl_3$) very nicely demonstrates the detail which can be obtained by application of resolution enhancement techniques.

Combined use of homonuclear and heteronuclear 2D NMR has provided an unambiguous spectral assignment of CTA. As an example of this work we include the H-H and C-H correlation NMR spectra of CTA (Figures 2 and 3, 270 MHz, $CDCl_3$, 25°C) for the polymer backbone.

A paper describing the full details of this work, including assignments of the appendant acetyls, is in preparation.

Yours very truly,

Charles Buchanan
Research Laboratories
P. O. Box 1972

J. A. Hyatt
Research Associate
Research Laboratories
P. O. Box 1972

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

Reference

1. Miyamoto, T.; Sato, Y.; Shibata, T.; Inagaki, H. J. Polymer Science: Chem. Ed. 1984, 22, 2363. And references cited.

syb/TR40231 cc: Dr. G. E. McGraw, Eastman Chemicals Division, P. O. Box 1972

Figure 1: (a) Resolution enhanced ^{1}H-NMR of the ring protons of CTA. (b) Normal spectrum of the same region shown in a.

Figure 2: COSY spectrum of CTA.

Figure 3: C-H correlation spectrum of CTA. Although the cross-peak for C6 does not appear, the resonance for this carbon is easily assigned by an elimination process.

Figure 1

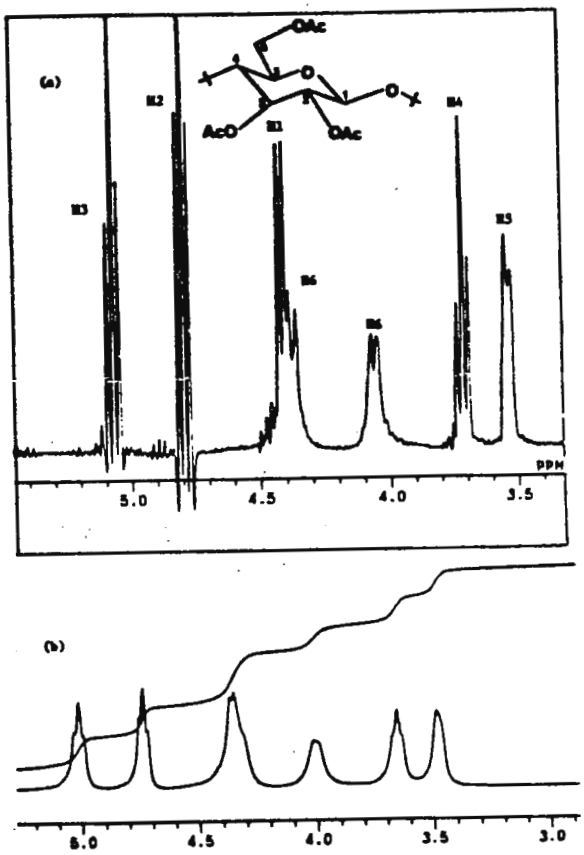


Figure 3

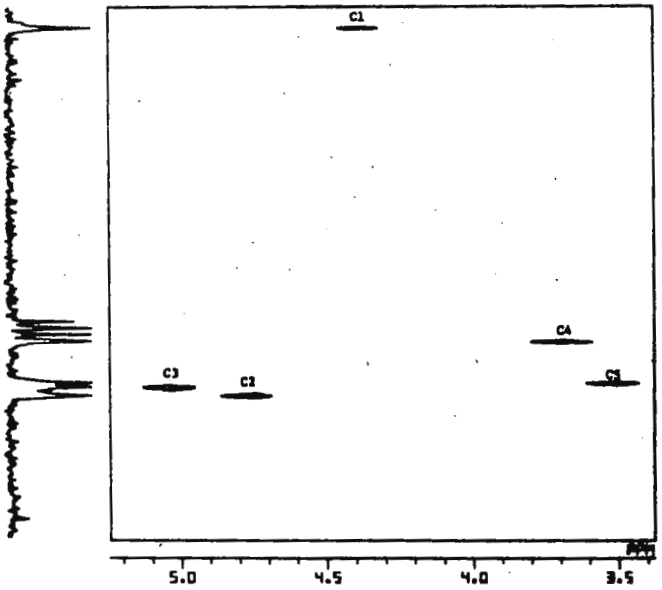
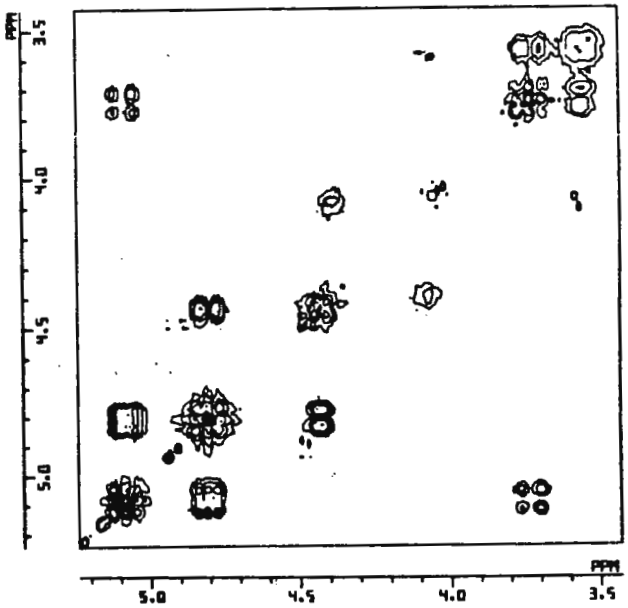


Figure 2



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Canada Centre for Mineral and Energy Technology,
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Coal Research Laboratories
Laboratoires de Recherches sur le Charbon

P.O.Bag 1280
Devon,Alberta Canada TOC 1EO

Carbon-13 CPMAS Studies of Coal and Related Materials

Your file Votre référence

Our file Notre référence

(Received December 12, 1986)

Dec. 10, 1986

Dear Prof.Shapiro,

As applications of solid state nuclear magnetic resonance spectroscopy to problems in heavy oil/bitumen upgrading of tar sands have yet to be demonstrated, this letter will outline some preliminary results in the context of our on-going studies into the factors that influence emulsion stability. Several specific areas of interest can be noted. For instance, during hydrocarbon processing several variables/processes may be involved including : variations in temperature, pressure, concentration, pH and physical / mechanical separation (e.g., froth flotation, centrifugation). In the present context, interest lies in the characterization of the insoluble organic matter (IOM) associated with the clay minerals, heavy metal minerals and quartz.

The general problem is complex in nature. It has been noted that losses of bitumen to tailings increases dramatically as the amount of fines (< 44 μm) increases. This, in turn, correlates with a large increase in the amount of residual IOM bound to the fines. Furthermore, heavy metal and inorganic carbon concentrations increase as particle size decreases. Increased bitumen losses in the presence of higher concentrations of IOM bound to the clay minerals presumably occurs as a consequence of the change in the naturally occurring hydrophilic nature of the clay surfaces to hydrophobic in the presence of the bound IOM. Consideration must also be given to the question of synergistic interactions among the species present that contribute to the extent of binding of the IOM to clays as well as the irreversibility of the process. Selective adsorption may occur among the solids present and the various bitumen components (e.g., saturates, aromatics, resins and asphaltenes). Catalytic conversion of some species may occur as a result of the interaction of the organic material with the clays present.

Possible advantages of CPMAS ^{13}C nmr analysis include the fact that the sample is studied with a minimum of preparation; severe extraction conditions may substantially alter the chemical composition of the organic material. Through the careful study of relaxation properties of the interacting materials, it may be possible to draw conclusions concerning the nature, site(s) and extent of binding. The conditions under which both qualitative and quantitative nmr data may be obtained must also be considered from the point of view of sensitivity considerations and the possible deleterious effects of large amounts of paramagnetic/ferromagnetic minerals.

The ^{13}C CPMAS spectra of many samples obtained from the Dean and Stark extraction procedure have been acquired but Figure 1 will be used to illustrate the technique. It has an appearance characteristic of humic acids. Although the 1 ms contact time spectra do indeed yield information concerning the nature of the IOM, they may be complex and relatively featureless; only aliphatic, aromatic and carboxylic acid species are

defined to any extent. However, the longer contact time (5 ms) spectrum shown in Figure 2 for same sample reveals a wealth of chemical shift information The abundance of oxygenated carbons as well as olefinic resonances is consistent with the nature of the species which have been hypothesized or observed in oil sands derived solids. The features noted in Figure 2 are associated with those chemical structures exhibiting relatively long proton rotating frame spin-lattice relaxation times, $T_{1\rho}^{H}$. The results also emphasize the importance of using differences in relaxation properties in complex materials to simplify spectra.

Results obtained to date illustrate several points of interest. Of prime importance is the fact that the IOM associated with the clay mineral and silica component of the bitumen varies in composition. Differences in the composition of the organic matter have important implications with respect to the efficiency of the separation of the bitumen. The nature of the various surfaces (surface area, charge density, cation excahnge capacity, charge distribution, distribution of hydrophilic and hydrophobic functional groups, etc) is the dominant factor in determining the nature of emulsions formed, their stability, and the ease with which they may be broken. Electrophoretic mobility and surface tension studies of these same clay-organic complexes derived from bitumen (after various physical/mechanical treatments) indicate a high correlation with structural changes in functional groups observed by nmr.

The effect of various magnetic impurities on the acquistion of C-13 CPMAS data is also under investigation. Finally, it is important to note that 5 - 10 mg quantities of clay-organic complexes comprising less than 10% (by weight) organic matter can be studied with standard probe sensitivity.

Figure 1

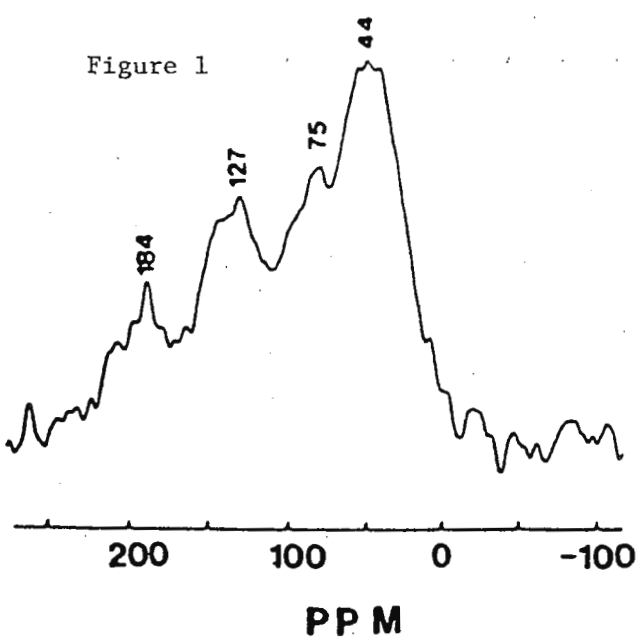
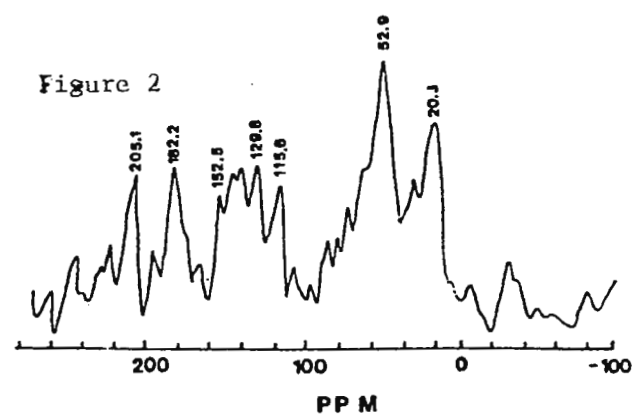


Figure 2



Sincerely,

Dave Axelson

David E.Axelson

UNIVERSITY OF MINNESOTA
TWIN CITIES

Department of Chemistry
Kolthoff and Smith Halls
207 Pleasant Street S.E.
Minneapolis, Minnesota 55455

December 15, 1986
(Received 19 December 1986)

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

SAMPLE CHANGERS IN ACADEMIA; EQUIPMENT FOR SALE

Dear Dr. Shapiro:

We have spent much of the past year absorbing two new NMR instruments from IBM: an NR-300, which is used for walk-up proton and carbon spectra, and an NR-200 with an automatic sample changer, which runs mostly proton. The system we have developed for using the sample changer is unusual and somewhat different from what was expected. The normal view of these devices is that they allow a trained operator to set up a number of samples to run overnight, resulting in efficient use of the spectrometer when no one is around. We planned to use ours in this way to run large numbers of spectra for undergrad laboratories; researchers would be expected to learn to run the instrument in the traditional way. Instead we have come to rely on the sample changer for research work as well, and it has become an invaluable addition to the lab.

During the day, the sample changer is left running continuously, and anyone needing a proton spectrum can bring down their sample and leave it in line to be run; they put it in the appropriate spot themselves and set up the experiment they want run with fairly simple dialog; they then return later to pick up their spectrum and sample. Even the most unsophisticated users can begin generating NMR spectra in just a few minutes. We run about 50 samples a day this way--over 90 on several occasions--and NMR has become dramatically more accessible to chemists in the department. In the evening and on weekends carbon may also be run with the sample changer; the protocol is slightly more complex, since we do not want any samples left un-run the next day. Time may be reserved for special experiments and other nuclei, but there is not much demand for this, and the instrument is run almost exclusively with the sample changer.

Of course, it is to a large extent the automation of spectrometer functions--independent of the sample changer--that is responsible for the increased accessibility. In a situation like ours, however, where we want the highest possible throughput, the changer seems more and more indispensible. Without it every person must schedule a slot of time--inevitably more than is really needed, since both acquisition and processing must be done in that period--and the person spends most of the time simply waiting while the spectrometer does its work. With the sample changer the only instrument time wasted is when there are no samples to be run, which for us is fairly unusual during normal weekdays; no researcher time is wasted at all.

Some might argue that the easy access made possible by automation has the disadvantage that users do not learn as much about NMR as they should. Our experience in the past has been that when large numbers of users are

(continued on page 25)

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(continued from page 22)

involved--we have over 100 at any given time--the vast majority of them simply learn what operations they need to produce spectra, without necessarily understanding just what those operations are doing or the underlying principles of NMR. Thus the problem of teaching people about NMR is a separate one from providing them with NMR spectra.

I believe automatic sample changers have a place in many environments for which they are not even considered. Certainly our experience has been that they are almost addictive--so pleasant to use that more and more of your valuable instrument time gets devoted to them.

We have just retired two Varian CFT-20's and anyone interested in purchasing them or any parts should contact me at 612-625-8374 or the above address for details. There is one fully functional instrument and one with several malfunctioning boards; probes for 5 mm proton, 8 mm carbon, and 5/10 mm H/C (switchable inserts), a VT unit, a Sykes cassette unit, extra computer power supply, etc.

Cordially,

Stephen B. Philson

Stephen B. Philson
Director, NMR Lab

PHILIPPS-UNIVERSITÄT MARBURG
FACHBEREICH CHEMIE

Priv. Doz. Dr. Stefan Berger

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

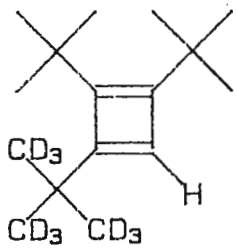
(Received 26 December 1986)

Temperature Dependent Deuterium Isotope Effects

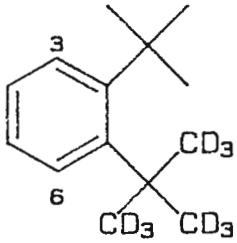
Dear Professor Shapiro,

The isotopic perturbation of equilibrium[1] is now a well known method to distinguish between double and single minimum potentials. Although mainly used in cations with a large chemical shift difference between the exchanging carbon atoms it can be applied to other systems like 1[2].

We have now looked at tert.butylated benzenes e.g. 2[3] with one tert.butylgroup perdeuterated. We find distinct temperature dependent deuterium isotope effects as shown in the figure for carbon atoms 3 and 6. At present we are not able to explain these results since suitable model compounds do not show temperature dependence.



1



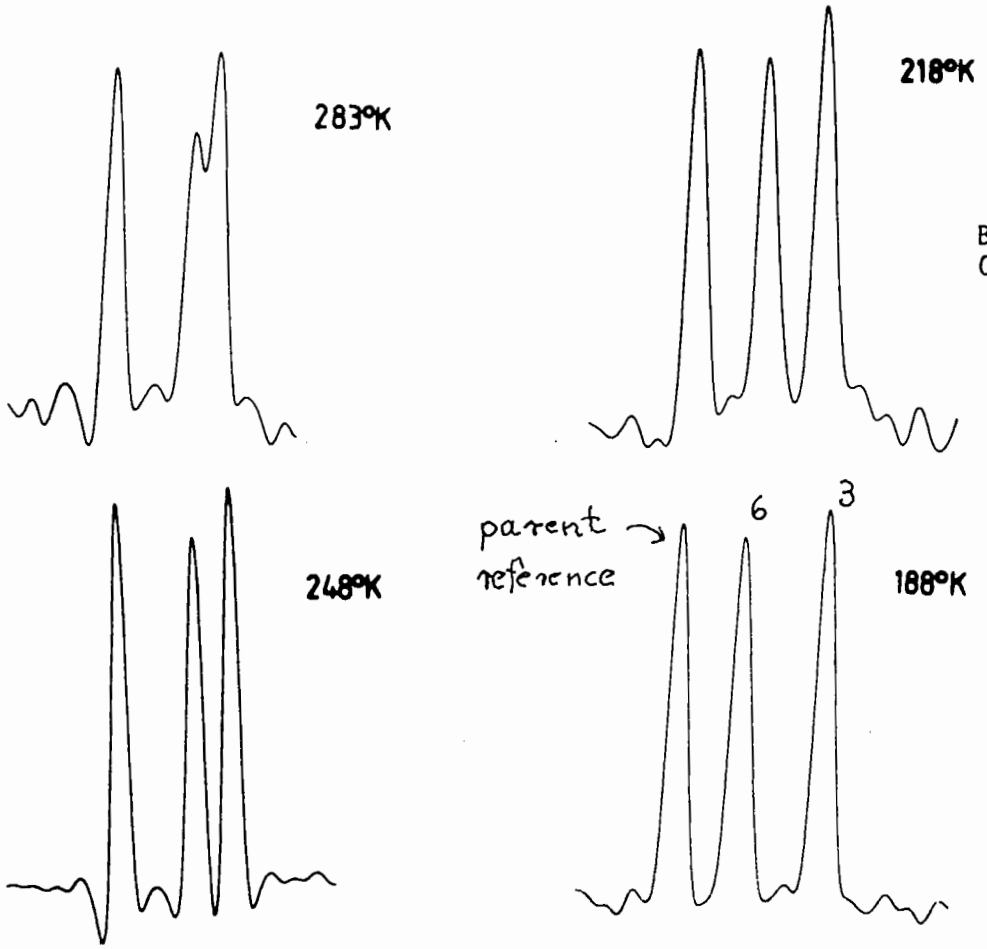
2

Sincerely Yours

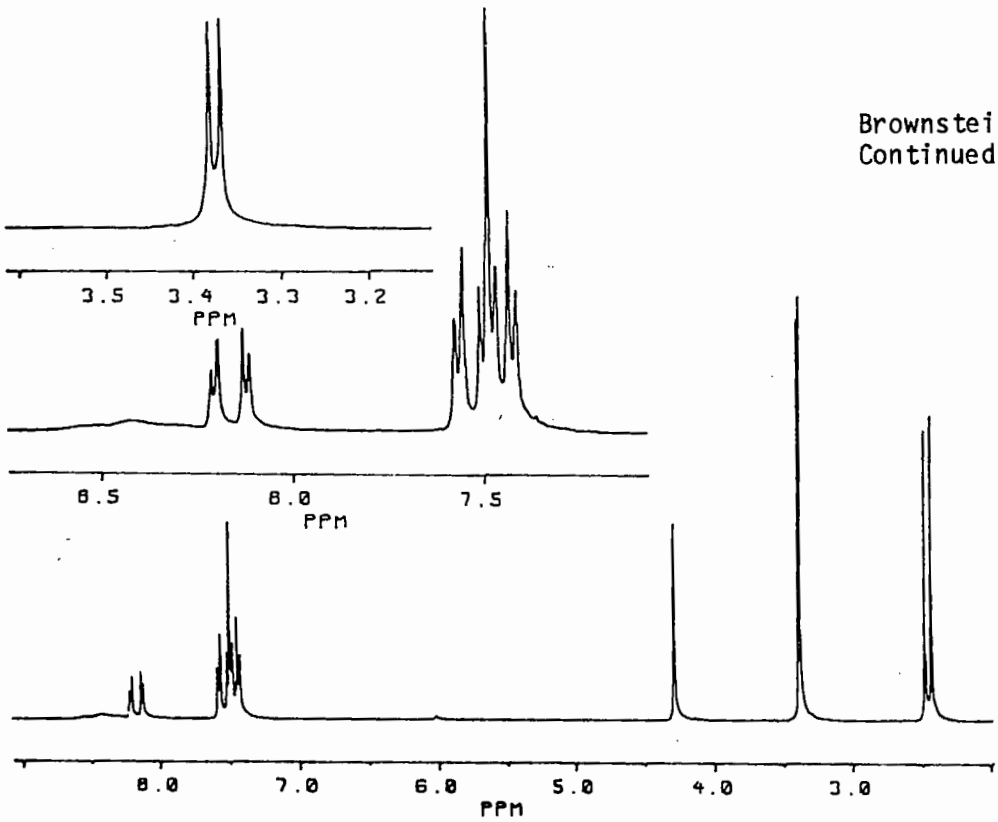
Stefan Berger

Bernd W. K. Diehl

1) M. Saunders und M. R. Kates, J. Amer. Chem. Soc. 99, 8071 (1977).
2) G. Maier, H. O. Kalinowski und K. Euler, Angew. Chemie 94, 706 (1982).
3) H. Künzer und S. Berger, J. Org. Chem. 50, 3222 (1985).



Berger letter;
Continued from page 26



Brownstein letter;
Continued from page 28

National Research Council Canada
Conseil national de recherches Canada

Division of Chemistry
Division de chimie

Ottawa, Canada
K1A 0R6

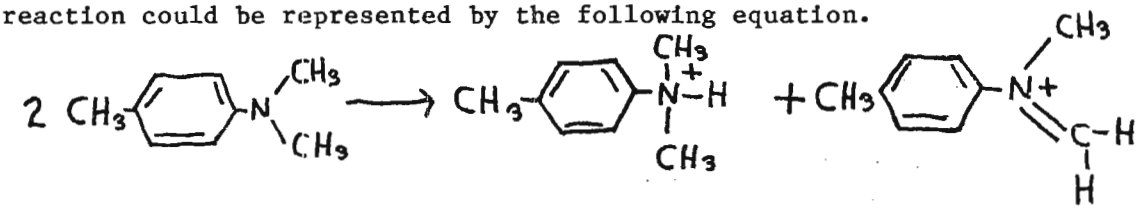
December 17, 1986
(Received 29 December 1986)

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

A Deceptively Simple Spectrum

Dear Barry,

In some work on the reaction of BF_3, NO and N,N-dimethyl-p-toluidine we obtained the 400 MHz proton spectrum shown on the accompanying Figure. The relative areas of the peaks in the aromatic region are 10, at 4.3 p.p.m. 3, at 3.4 p.p.m. 6, and at 2.4 p.p.m. also 6. Altering the solvent, investigating after partial reaction, and ^{13}C spectroscopy led to the conclusion that the organic part of the reaction could be represented by the following equation.



The chemical shifts for the aminium and iminium phenyl ring protons overlap just enough to reinforce the central line and give the impression that all of these signals come from a single spin system. The $N-CH_3$ of the aminium ion at 3.4 p.p.m. is spin coupled to the very broad N-H line at 8.5 p.p.m. A well resolved $^{13}C-^{14}N$ spin coupling is observed for the iminium $N-CH_2$ while the N-CH3 iminium line is broadened by an unresolved $^{13}C-^{14}N$ coupling.

Yours truly,

(Figure on page 27.)

Syd

S. Brownstein

/mr

The University of Western Ontario

Department of Chemistry
Chemistry Building
London, Canada
N6A 5B7

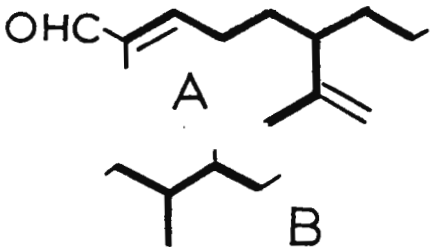
December 4, 1986
(Received December 10, 1986)

Dear Barry:

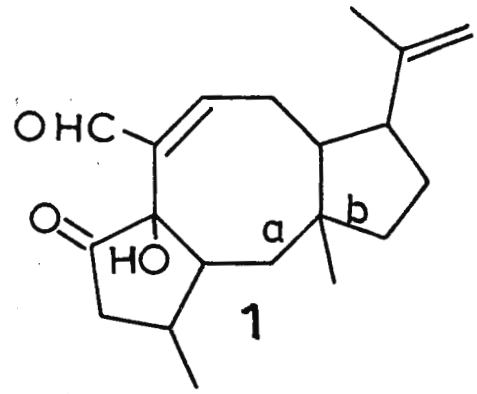
NMR Structural Elucidation of a Fungal Metabolite Aided by Biosynthetic Incorporation and ^{13}C COSY

Here is my response to your colored reminders to "renew" my subscription.

A fungus recently isolated as a pathogen from a standing crop of fenugreek was identified as Cercospora traversiana. Because of an interest in the metabolites of other Cercospora spp, Albert Stoessl and I wished to examine its metabolites. The initial experiments furnished a colorless compound which readily crystallized from EtOAc or C_6H_6 solutions of the extracts. The ^{13}C spectrum showed 20 nonequivalent carbons, including a conjugated aldehyde, a tert-alcohol and a cyclopentanone moiety, and ms gave its formula as $C_{20}H_{28}O_3$ while ^1Hmr indicated two major fragments, A and B, and an angular methyl. Directly bonded carbons and hydrogens were identified by heteronuclear correlation. An incorporation experiment with [1,2-$^{13}C_2$] acetate furnished 8 mg of material whose ^{13}C spectrum readily revealed the intact acetate units and led to assemblage 1 as a probable structure. Since the incorporation level was satisfyingly high (4.4%), a ^{13}C COSY spectrum was recorded to try to establish the linkages between labelled units. The use of ^{13}C COSY was illustrated in an earlier newsletter, #325, Oct. '85, p. 28. Also a 2D INADEQUATE spectrum was obtained. From these data all but two linkages (a and b in 1) were confirmed. (For the missing links, the signals involved appear at δ_C 42.8, 44.0 and 44.4, so this is not surprising.) In any event the COSY experiment was a valuable assignment aid for this problem (and will be for many other cases). The stereochemistry of 1 was also defined by n.O.e. difference spectra.



Finally it may be noted that 1 has the ring system of the fusicoccins and the sesterterpenoid ophiobolins, both of which have been well studied to unravel their biogenesis. In fact, 1 bears a more striking resemblance to the latter but lacks the additional isopentenyl unit in the side-chain. To illustrate a possible relationship to either, an incorporation experiment with $CD_3{}^{13}CO_2^-$ was carried out leading to 1-$^{13}C_x$,^2H_y whose ^{13}C and ^2H spectra showed its biosynthesis to be analogous to that established for the ophiobolins.



Sincerely,

J.B. Stothers.

December 12th 1986
(Received December 16, 1986)

University Chemical Laboratory
Lensfield Rd.
Cambridge, CB2 1EW, U.K.

The Nuclear Overhauser Effect in Strongly Coupled Spin Systems

Dear Prof. Schapiro,

It is widely recognized by NMR spectroscopists who use the NOE that in strongly coupled systems one must exercise some caution in the interpretation of the observed enhancements. The root of the problem is that in a such spin systems one cannot assign individual lines in the spectrum to specific spins. Of course, unless the spetrum is very strongly coupled, one can always say that certain lines are *mostly* associated with certain spins, and by proceeding in this way it should be possible to begin to interpret to NOE enhancements found in such systems.

Recently, we have been following up this assertion with both calculations and experiments, and have turned up some results which we think you may find interesting. The system we chose to study was that of three spins, ABX, where A and B are strongly coupled, and X is not coupled to A or B, but is spatially close to A. This kind of arrangement is one which is often encountered.

Figure 1 shows a series of calculated steady state NOE difference spectra of this system at ever increasing degrees of strong coupling. The three spins are assumed to be in a line (B-A-X) and the X spin is the irradiated one. The top row are the "control" spectra, and show the AB part of the spectrum undergoing the familiar collapse of the AB "quartet". Underneath are the NOE difference spectra. In the weak coupling limit we see the expected positive enhancement of the A lines, and a negative enhancement of the B lines (three spin effect). As the strength of coupling increases, the different lines of the AB quartet behave in rather different ways. The B lines are especially interesting: the outer line of B rapidly shrinks to zero whereas the inner line of B soon changes sign to a positive enhancement and grows in strength towards that of the inner A line. At intermediate coupling strengths "triplet" patterns are produced.

Figure 2 shows an excellent example of the effect "in practice". The β protons of the peptide shown are quite strongly coupled, and irradiation of the methyl group gives this triplet like pattern in the NOE difference spectrum. With the aid of the previous calculations we can now rationalize this very easily - but without this knowledge one would be rather hard pressed to make a confident assignment from this spectrum. We have seen very similar effects in many more complex systems.

We can make the following generalizations about the NOE spectra of strongly coupled spin systems:

1. Strong coupling acts to transfer an enhancement expected at one resonance into its strongly coupled partner. This may become such a strong effect as to over turn a negative (three spin) enhancement on a spatially remote site.
2. At intermediate extents of strong coupling the "roof effect" on the directly enhanced multiplet is reduced (easily visible on all the spectra shown here).
3. These are no substantial flip angle effects on steady state NOE spectra. However, transient NOE spectra and two-dimensional NOESY spectra show a strong dependence of the observe pulse flip

(continued on page 33)

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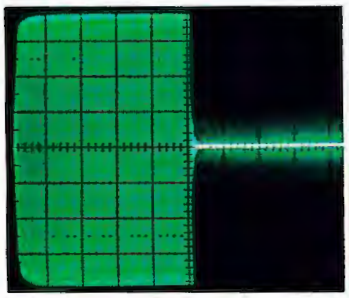
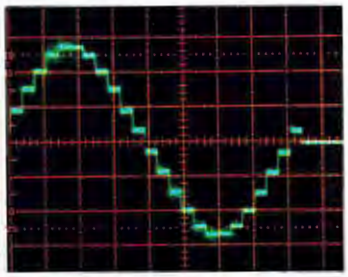
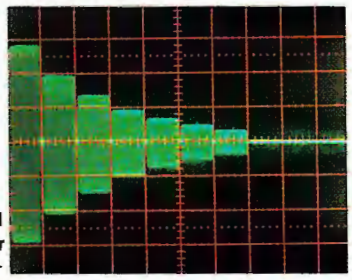




15° phase shift through 360°. ►



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(continued from page 30)

angle. In such experiments it is possible to reduce greatly the apparent transfer to the remote spin by reducing the flip angle to, say, 30°.

A fuller account of this work has recently been accepted by the *Journal of Magnetic Resonance*. Please credit this contribution to Jeremy Sanders' account !

Yours Sincerely

James David Mike

James Keeler
Univ. Chem. Lab.
Cambridge

David Neuhaus
Parke Davis Research Unit
Cambridge

Mike Williamson
Roche Products
Welwyn Garden City

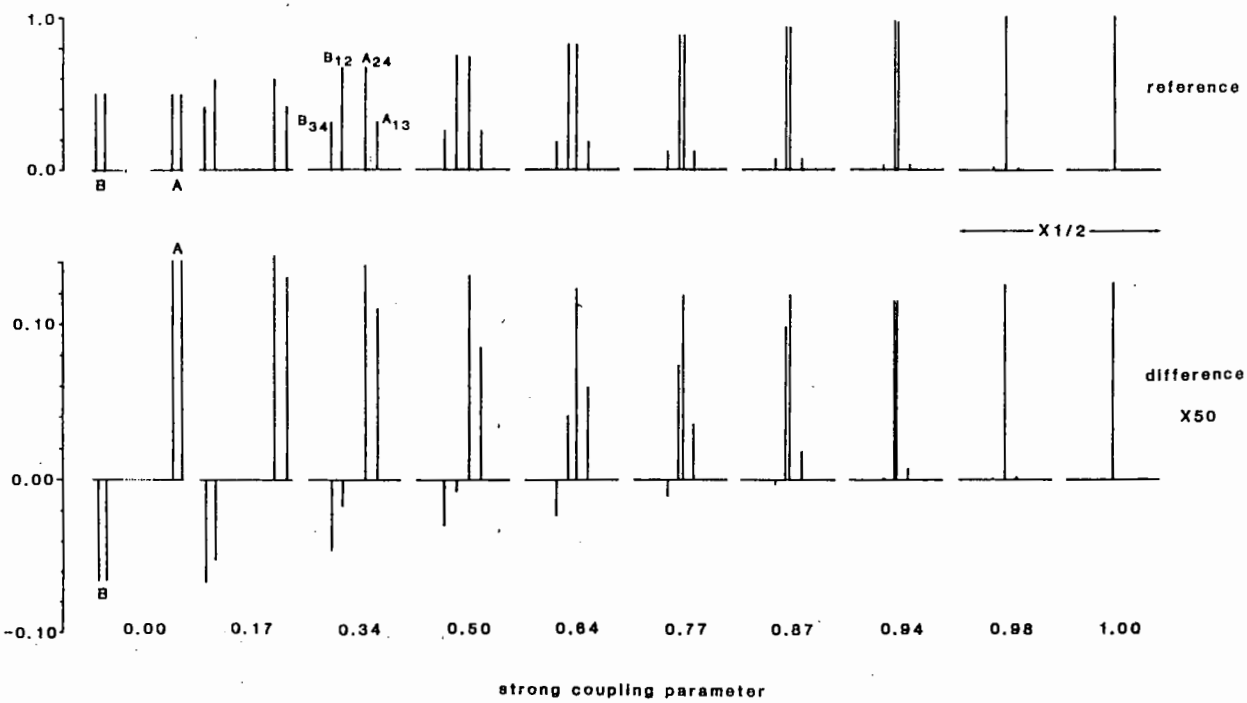


Figure 1

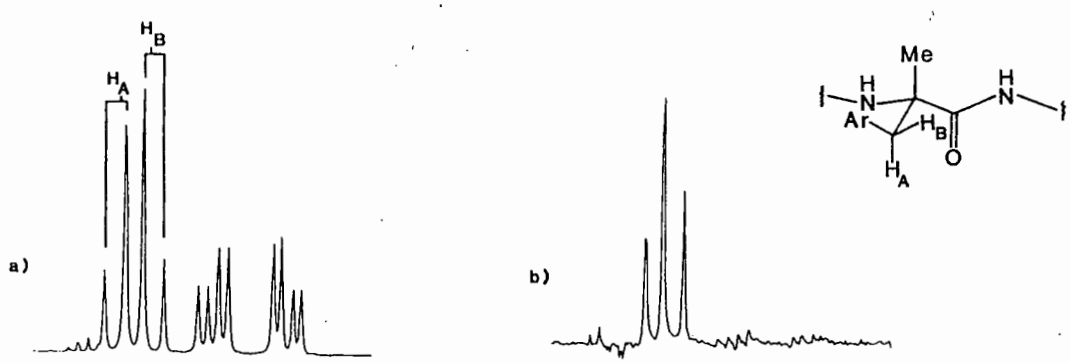


Figure 2 (a) Reference Spectrum, (b) NOE difference spectrum, Me irradiated.

LOVELACE MEDICAL FOUNDATION

18 December 1986
(Received 22 December 1986)

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

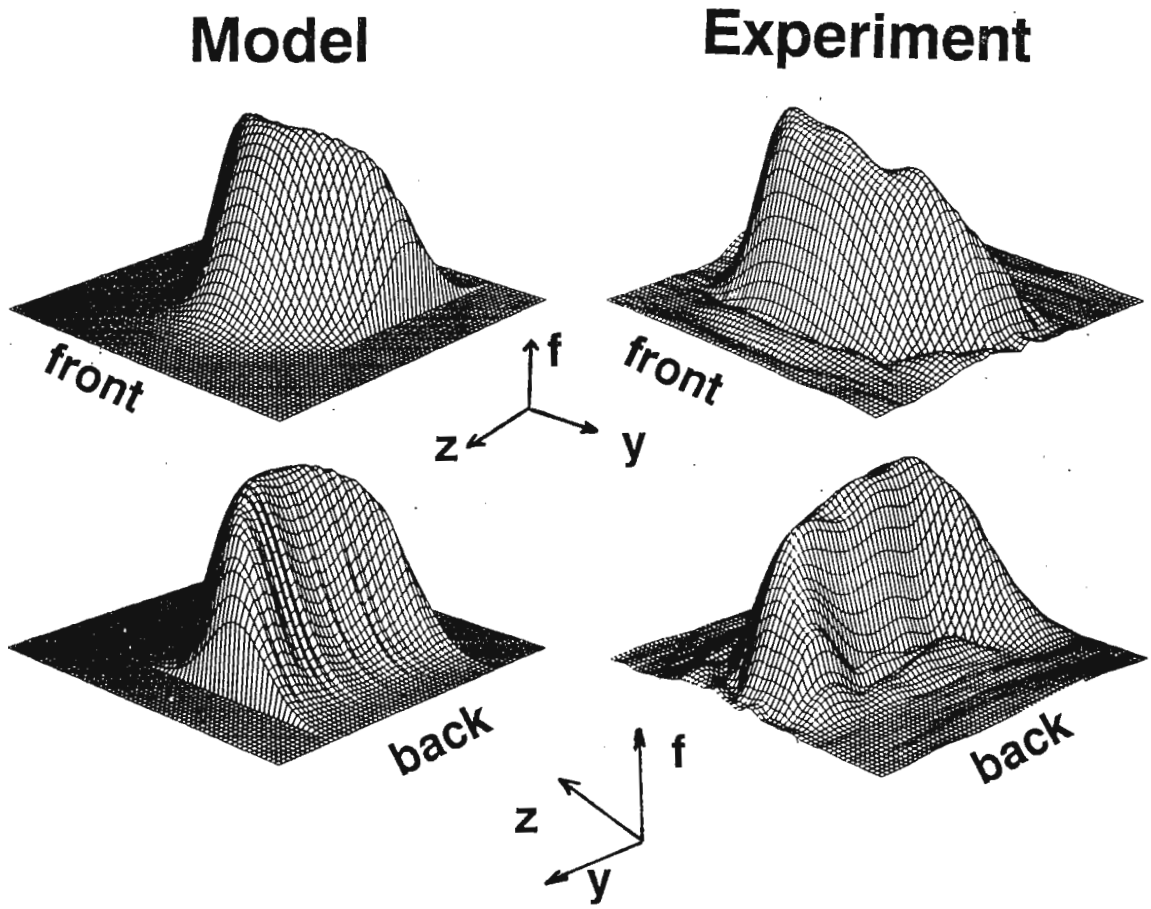
Velocity Distributions in Small Tubes

Dear Professor Shapiro:

In the course of work aimed at *in vivo* NMR blood velocity measurement some interesting pictures have been generated recently. The idea is to tag a transverse slice flowing in the z-direction (the velocity and static field are parallel) and subsequently read-out the position of the slice with an even echo. A 1-D FT of the echo produces what we call a 1-D velocity distribution (VD) [1]. If a series of 2nd echoes is collected with a stepped, phase-encoding gradient pulse applied during the first echo, and the data set is subjected to a 2-D FT, 2-D VD's are produced: experimental and simulated 2-D VD's are shown below. The naive simulation shown is a numerical integration of:

$$f(y, z) = \int_{-\infty}^{\infty} M(\, z - T \cdot v(x,y)\,) \cdot dx \quad .$$

where f(y, z) is the distribution of spins (proportional to the distribution of velocities), M(·) is the magnetization profile of the slice, T is the time between slice selection and the 2nd echo, v(x, y) is the axial velocity profile, y is the phase-encoding direction, and x is perpendicular to y and z. Note that z - T·v(x,y) is the initial position of the fluid subsequently detected at x, y, z.



The figure shows a calculated distribution (labelled Model) and an experimental distribution. Each is shown from the "front" and "back". In the calculated distribution function, slice profile was Gaussian, and velocity profile was parabolic. The experimental distribution was calculated from 33 echoes obtained from water flowing in an 0.95 cm ID tube, with Reynolds number approximately 2000 (mean velocity ≈ 20 cm/s).

Please credit this contribution to the subscription of Eiichi Fukushima.

Sincerely,

Stephen Altobelli

1. Caprihan A., J.G. Davis, S.A. Altobelli, and E. Fukushima. A New Method for Flow Velocity Measurement Frequency Encoded NMR. Magnetic Resonance in Medicine, 3:352-362, 1986.

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December 22, 1986
(Received 30 December 1986)

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77834

Re: A SOLUTION FOR A WATER SIGNAL

Dear Professor Shapiro:

In ^{1}H NMR spectra of millimolar solutes in aqueous solution the inhomogeneous "hump" from the water solvent causes spectral distortions and can also interfere with 2D data (solvent t_1 noise). In some cases the static magnetic field shim currents can be adjusted to cause the "hump" to appear as wings of the main water signal. Recent results in our laboratory show that this interference can be eliminated by a probe modification. This modification (patent pending) comprises an electromagnetic shield positioned between a portion of the lower part of the sample area and the rf coil leads. For certain probe coil designs the shield also isolates part of the conductive material forming the coil. A full report is scheduled to appear in the March, 1987 issue of J. Magn. Reson.

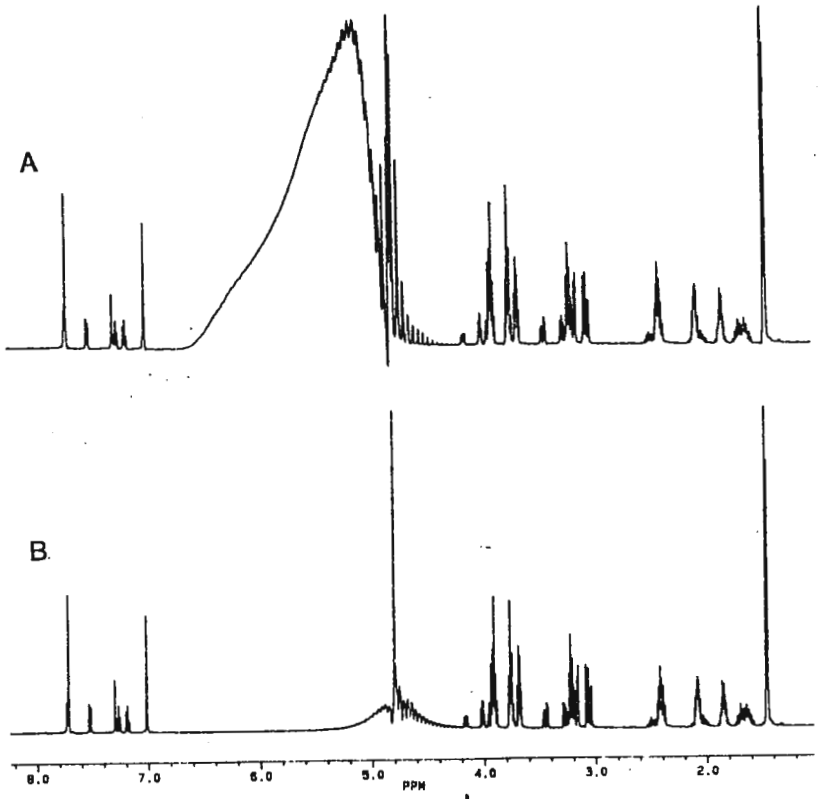

Figure 1

The spectra shown in Figure 1 are from a sample containing a mixture of amino acids (7-23 mM) in 90% H_2O. Both spectra result from identical presaturation experiments. The spectra are phase corrected Fourier transforms - no other data manipulation was used. The residual peak at 4.8 ppm is truncated at 50% of its intensity. A is from a standard probe, B is from the same probe after the modification.

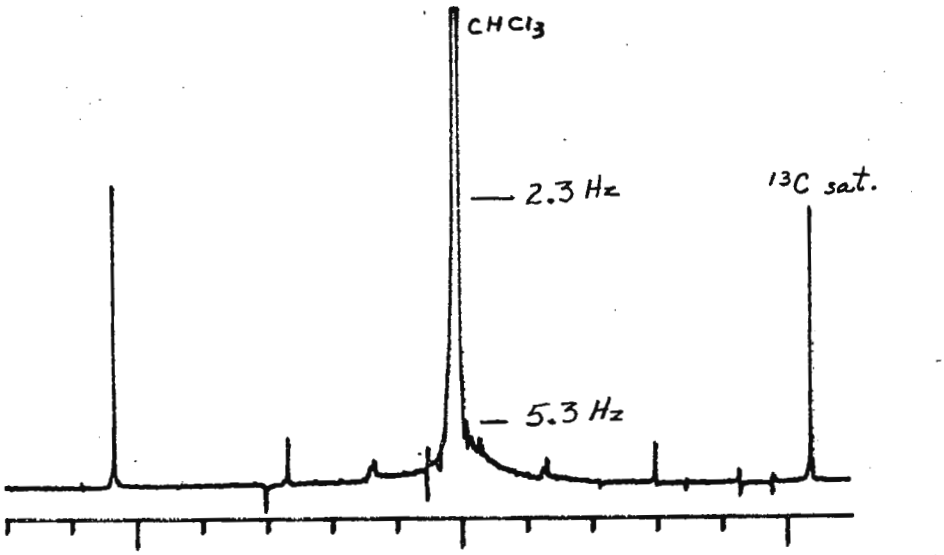

Figure 2

Prior to this modification to our NT-300 GN series ^1H probe, a considerable effort was required to achieve results which met the lineshape specification of 10 and 25 Hz at 0.55% and 0.11% of the intensity of a chloroform signal. Now, 2.3 Hz and 5.3 Hz are attainable (see Figure 2), and a spin rate of 23 Hz leaves only a trace of spinning sideband signals.

Sincerely,

Robert W. Dykstra

RWD/msw

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Dr. B. L. Shapiro, Editor/Publisher
TAMU NMR Newsletter
Department of Chemistry
Texas A&M University
College Station, Texas 77843-3255

November 25,1986
(Received December 2, 1986)

PUMPING THE SUPERCON MAGNET

Dear Dr. Shapiro:

Recently we had made a significant improvement in prolonging the liquid helium refill time for our Varian XL 300 magnet from ~3 to 9 weeks by pumping the magnet dewar while the field was still active. The entire pumping operation turned out not so dreadful as we first thought. Indeed,we now feel that it can be easily accomplished,provided that certain precautions are taken. The followings are the set up and procedures we have used which may be of interest to some of the Newsletter readers.

1). Connect a high efficiency diffusion pump to the magnet dewar and install a sensitive vacuum gauge(capable of measuring the vacuum down to at least 10^{-7} torrs) near to the dewar valve. Always use metal fittings, tubings and teflon ferrules or O-rings in making all the connections. DO NOT use rubber hoses.

2). DO NOT open the dewar valve until the vacuum line is pumped down to $<3\times10^{-6}$ torrs. If rubber hoses were used, the vacuum can only go down to $\sim10^{-5}$ torrs even after 2 days pumping. (This is presumably due to the chemicals in the rubber hose which has high vapor pressure.)

3).After the dewar valve is opened there are several ways to monitor the progress of the pumping. a). If the vacuum of the dewar is poor (i.e. $>3\times10^{-6}$ torrs) a sudden increase in the pressure reading will be noticed right after the valve is opened. The pressure will then gradually go back down again as the vacuum is steadily improved. b). If a helium gas leak detector is also hooked up into the pumping line, a high helium gas leak will be detected when the valve is first opened and then the leak gradually decreases. c). An inexpensive yet imformative way for monitoring the progress is to monitor the helium flow rate at the vent port of the magnet using a gas flow meter. A high helium flow rate of ~24 cc/hr was recorded for our system before the valve was opened. The flow rate dropped down to ~3 cc/hr after pumping the magnet for 2 hrs,(the pressure reading reached 2.5×10^{-6} torrs).

Sincerely yours,
Herman J. Yeh
LAC/NIDDK

P.S. Please credit this contribution to Dr. E. D. Becker's account.

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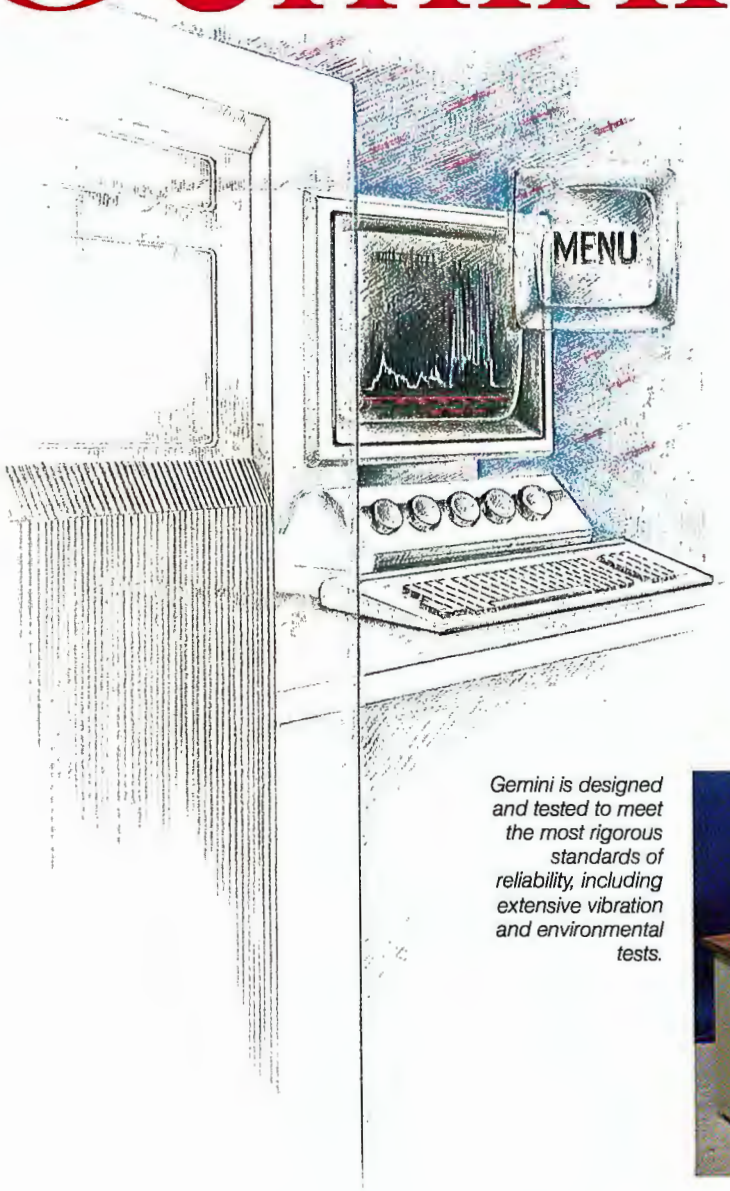

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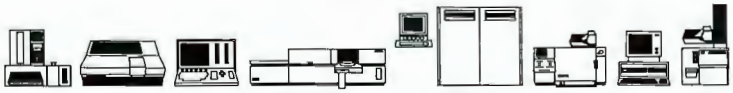

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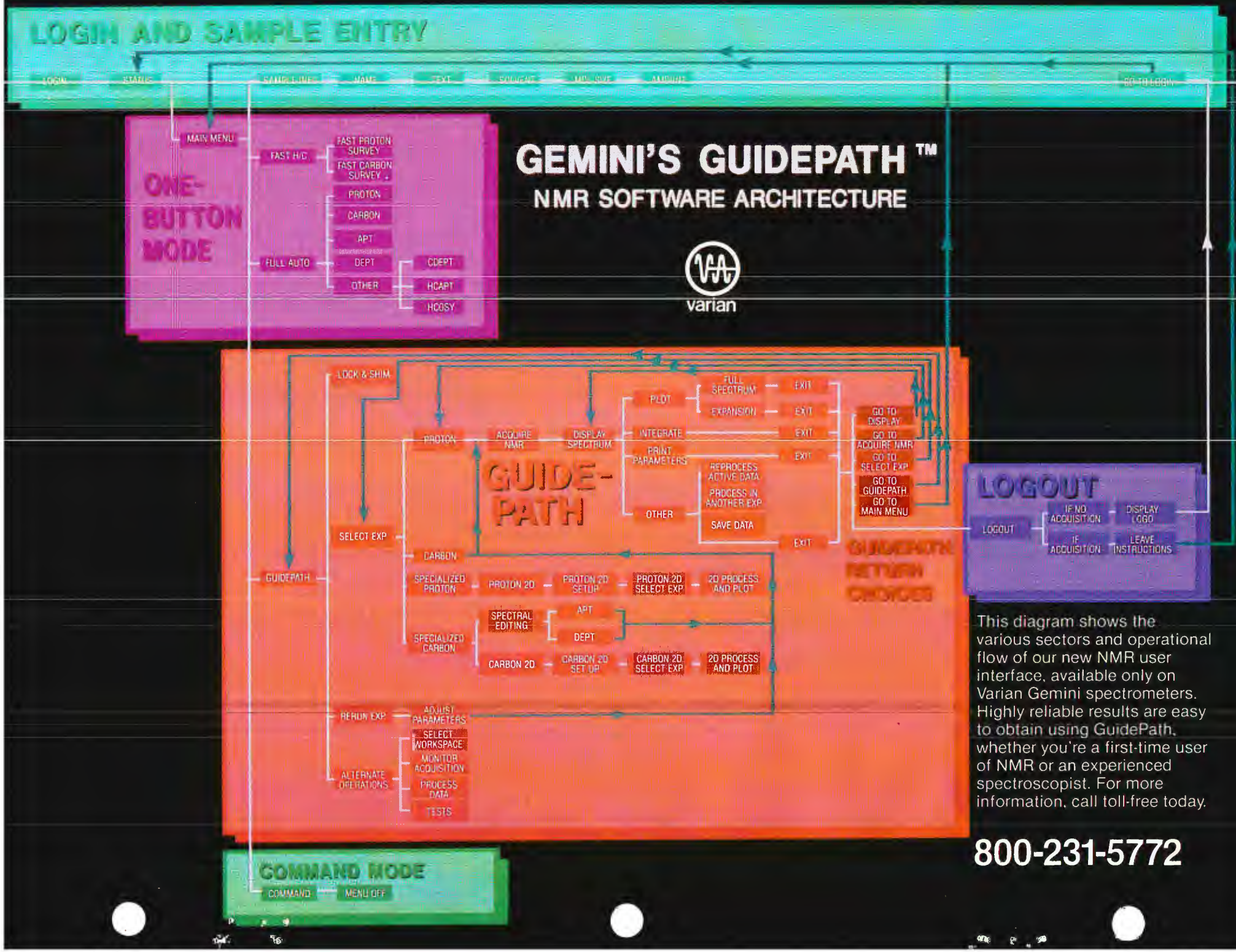

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December 23, 1986
(Received 29 December 1986)

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

Evidence for the Detectability of Weak Resonances Near Peaks Which Are 10,000 Times Larger, Without Suppression of the Large Peaks

Dear Barry:

Although many papers have been published in the last 25 years on the subject of "elimination" of large unwanted resonances, such as the H_2O signal in ^1H NMR, refinements are still being reported practically every month. For example, the last six issues of the Journal of Magnetic Resonance (July - November, 1986) contain 5 articles on this subject.[1-5] Obviously, this activity is motivated not only by the importance of NMR for studying minor (low-molarity) components in the presence of major ones such as H_2O, but also by the various limitations and difficulties associated with each available solvent -suppression technique. Peak suppression may be difficult, inconvenient, or undesirable (i) when there are many large peaks, (ii) when one or more of the small peaks is very close to a large one, and (iii) when the relative intensities of small and large peaks are being studied. Here we show that careful attention to dynamic range and lineshape quality enables the NMR spectroscopist to study minor components without suppression of the major resonances, even when each minor peak has only 10^{-4} the intensity of a major one and when the separation between the two peaks is only 100 Hz or even less.[6]

Our studies involve the use of ^{13}C NMR to observe minor components whose resonances are very close to those of major ones. Because the signal-to -noise ratio (per scan) of the major resonances is much lower than that of the ^1H resonance of H_2O, a 12-bit digitizer appears to be adequate, even for 1.4 M D-[1-^{13}C]glucose (see below). We present two examples. In the first one, the observation of the ^{13}C resonance of $^{13}CH_2D$-CO-CH_3 of acetone of natural isotopic composition, the linewidth (after introduction of some digital Lorentzian broadening) of the large resonance of $^{13}CH_3$-CO-CH_3 is about 0.08 Hz. In the second case, the detection of the hydrated aldehyde anomer of aqueous glucose, the linewidth of the major resonances (of the pyranose anomers) is about 1 Hz. We feel that these two examples cover the range from very narrow to typical linewidths in ^{13}C NMR spectroscopy of simple and complex organic molecules.

Figure 1 shows the methyl carbon resonance of acetone of natural isotopic composition (with 20% v/v cyclohexane-d_{12}) at 26.5°C, after 6000 scans. The main peak, that of $^{13}CH_3$-^{12}CO-$^{12}CH_3$ is truncated at 0.06% of its full peak height. The two smaller truncated peaks, at about ±20 Hz

from the main peak, are the $^{13}C-^{13}C$ satellites which arise from $^{13}CH_3-^{13}CO-^{12}CH_3$. Peaks 1, 2, and 3 arise from $^{13}CH_2D-^{12}CO-^{12}CH_3$.[6] The integrated intensity of Peak 1 is difficult to measure, but those of Peaks 2 and 3 are 0.014% and 0.012%, respectively, of the main peak intensity. These values agree, within experimental error, with the expected 0.015%, the natural isotopic abundance of deuterium. The three-fold loss of intensity caused by $^{13}C-^{2}H$ scalar splitting is fully compensated by the three-fold increase in intensity as a result of equal probabilities of substitution by deuterium at each of the three equivalent hydrogens. Peak 4 of Fig. 1 arises from the two equivalent methyl carbons of $(CH_3)_2C(OH)-CH_2-CO-CH_3$, commonly called "diacetone alcohol", which is the aldol condensation dimer of acetone. Integrated intensities, corrected for differences in NOE values, indicate that our sample of reagent grade acetone contained about 0.005% diacetone alcohol. This amount is three orders of magnitude less than the equilibrium proportion. We speculate that the glass wall and/or traces of impurities catalyze the slow formation of diacetone alcohol in commercial "pure" acetone.

The equilibrium composition of aqueous reducing sugars has been investigated by carbohydrate chemists for the last 140 years. It is well known that each aldopentose or aldohexose in aqueous solution exist as an interconverting mixture of at least six species ("anomers"): the two pyranoses, the two furanoses, the acyclic aldehyde form, and the acyclic hydrated aldehyde (*gem*-diol or aldehydrol) form. The equilibrium proportions and rate constants of interconversion are of considerable interest, because they are major determinants of chemical and biochemical behavior. The equilibrium proportions of five of the six anomers mentioned above are known with varying degrees of accuracy for most of the aldopentoses and aldohexoses. The exception is the hydrated aldehyde form. The detailed anomeric composition of aqueous ***D-glucose*** is undoubtedly the greatest challenge of the remaining gaps of knowledge about anomeric equilibria, not only because of the biological importance of glucose, but also because of the overwhelming dominance of the two pyranose anomers.

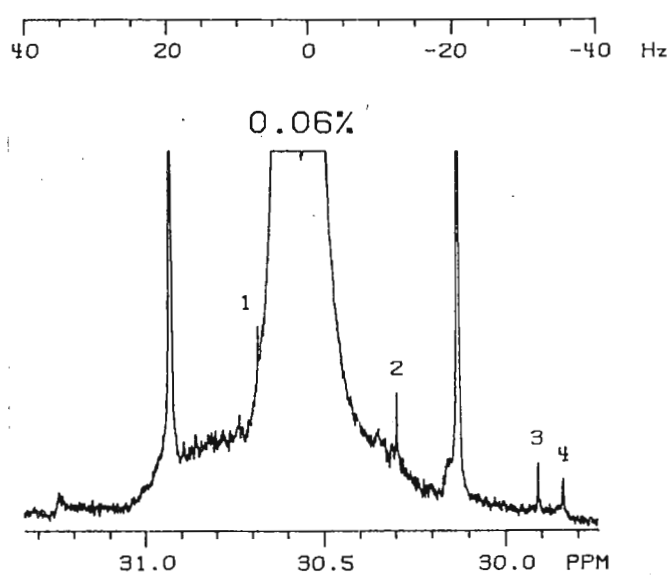

Figure 1

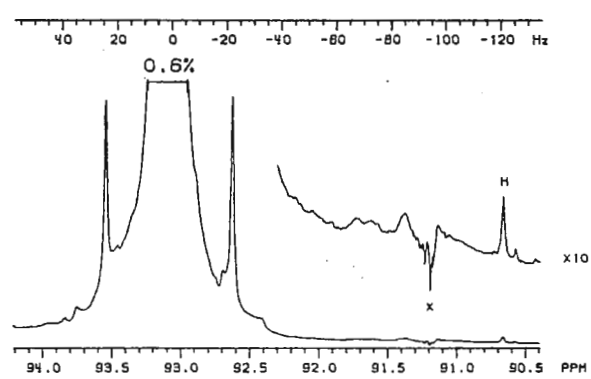

Figure 2

With the use of the same ultra-high resolution methodology which yielded the spectrum of the methyl carbon of acetone shown in Fig. 1, we observed all six anomers of a sample of aqueous D-[1-^{13}C]glucose, and we obtained equilibrium proportions as a function of temperature. Figure 2 shows the available resolution and dynamic range. The spectral segment shown in Fig. 2 contains (i) the resonance of the anomeric carbon of the α-D-glucopyranose anomer, truncated at 0.6% of its full peak height, (ii) the $^{1}J_{CC}$ satellites of the α-pyranose resonance, at about ±23 Hz from the main peak, which arise from molecules with ^{13}C nuclei at C-1 and C-2, (iii) the aldehydrol resonance at -121.7 Hz from the α-pyranose peak, labeled *H* in Fig. 2, and (iv) an artifact at about -95 Hz (see below). The proportion of the aldehydrol anomer is 0.006% under the conditions of Fig. 2.

Finally, we wish to comment on the question of artifacts. Peak *X* in Fig. 2 is an instrumental artifact. It is well known that very large signal-to-noise ratios (for the large resonances) reveal spurious peaks caused by imperfect accumulation and processing. Although these artifacts are very small relative to the major resonances, they are potentially troublesome if they are mistakenly identified as real peaks of minor components. We are confident that artifacts can be reduced to levels even lower than in Fig. 2, and that systematic procedures can be developed for distinguishing residual artifacts from real peaks.

Best regards,

Adam Allerhand

Steven R. Maple

AA/tam

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E3-43 Chemistry Building East, Telephone (403) 432-3254

December 1, 1986

(Received December 11, 1986)

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

Non-Magnetic - It ain't necessarily so

Dear Barry:

Recently we had it forcibly brought to our attention that the appellation "non-magnetic" applied to such things as tuning capacitors does not imply that all magnetic properties have been magically eliminated.

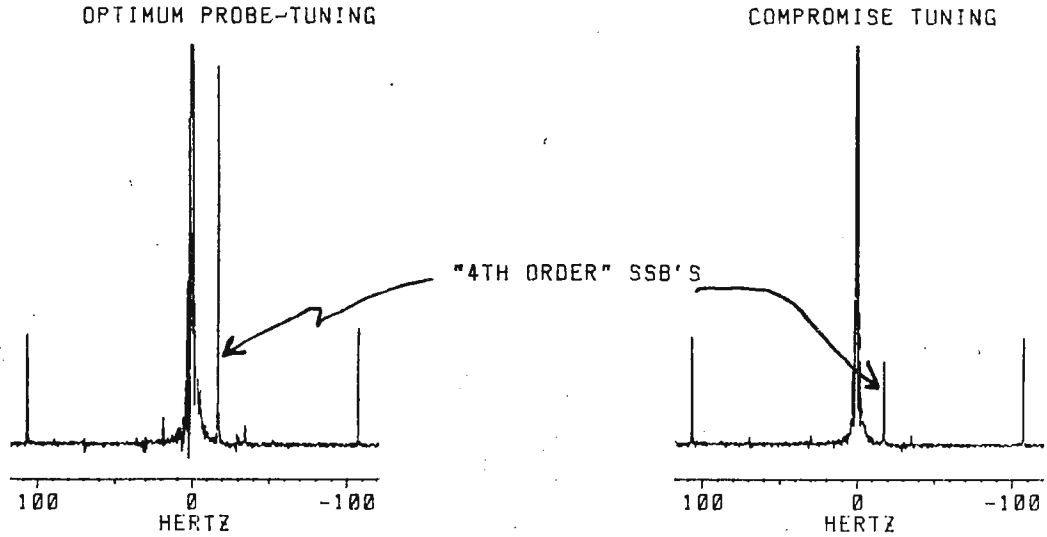
A few months ago we found it necessary to retune some of the traps in one of our WH-400 probes. This probe had always had excellent lineshape and small spinning sidebands (~ 0.3%); however, on retuning, a 3% sideband was found on one side of the peak and about 0.1% on the other side. Several shimming marathons finally convinced us that this was due to a high even order gradient in the x-y plane (e.g., r^4 or r^6) over which we had no control. The likely culprits (or the only ones we could imagine) appeared to be three Johanson 5761 Non-magnetic tuning capacitors located about 4 cm below the centre of the receiver coil. Indeed, deliberate detuning reduced the spinning sideband. Exchanging capacitor tuning slugs with some other "non-magnetic" ones on the off-chance that somebody had goofed produced no improvement. In the end, we found it possible to sacrifice some tuning range for acceptable spinning sidebands (< 0.5%).

We issue a caveat, then, to all probe designers, amateur or otherwise, to be wary of the placement of "non-magnetic" materials in your probes. To those people afflicted with "one-sided" spinning sidebands, try retuning your probe.

Please credit this to Tom Nakashima's subscriptions.

Sincerely,

Glen Bigam



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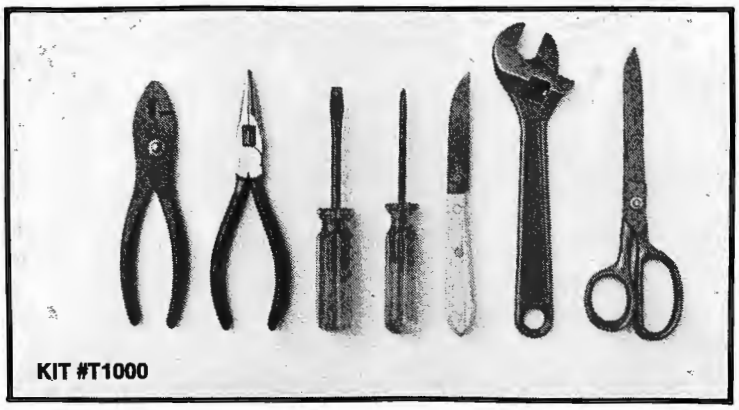

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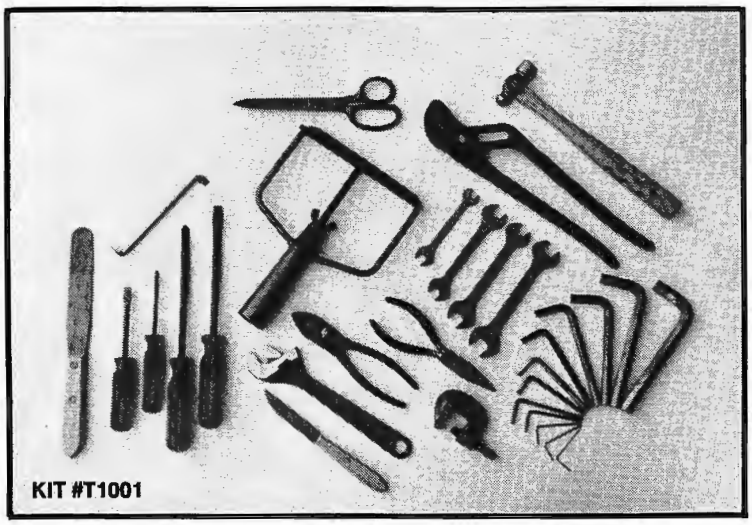

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- 5/16"
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- C clamp, ¾" opening
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KIT #T1002 - 9 piece hex nutdriver set. SAE

- 1/8"
- 5/32"
- 3/16"
- 7/32"
- 1/4"
- 5/16"
- 3/8"
- 7/16"
- 1/2"

KIT #T1002M - 9 piece hex nut driver set. Metric

- 3.5mm
- 4mm
- 5mm
- 6mm
- 7mm
- 8mm
- 9mm
- 10mm
- 11mm

KIT #T1003 - 10 piece ¼" drive socket set. SAE

- Ratchet wrench, reversible
- Extension bar, 4" length
- Socket, 3/16"
- Socket, 7/32"
- Socket, 1/4"
- Socket, 9/32"
- Socket, 5/16"
- Socket, 11/32"
- Socket, 3/8"
- Socket, 7/16"

KIT #T1003M - 10 piece ¼" drive socket set. Metric

- Ratchet wrench, reversible
- Extension bar, 4" length
- Socket, 4mm
- Socket, 5mm
- Socket, 5.5mm
- Socket, 6mm
- Socket, 7mm
- Socket, 8mm
- Socket, 9mm
- Socket, 10mm

KIT #T1001M
30 Piece Deluxe Metric Hand Hand Tool Kit

Same as T1001 with exception of:

- Allen Wrenches 2mm thru 16mm 9 pieces
- Combination Wrenches 6mm thru 16mm 6 pieces

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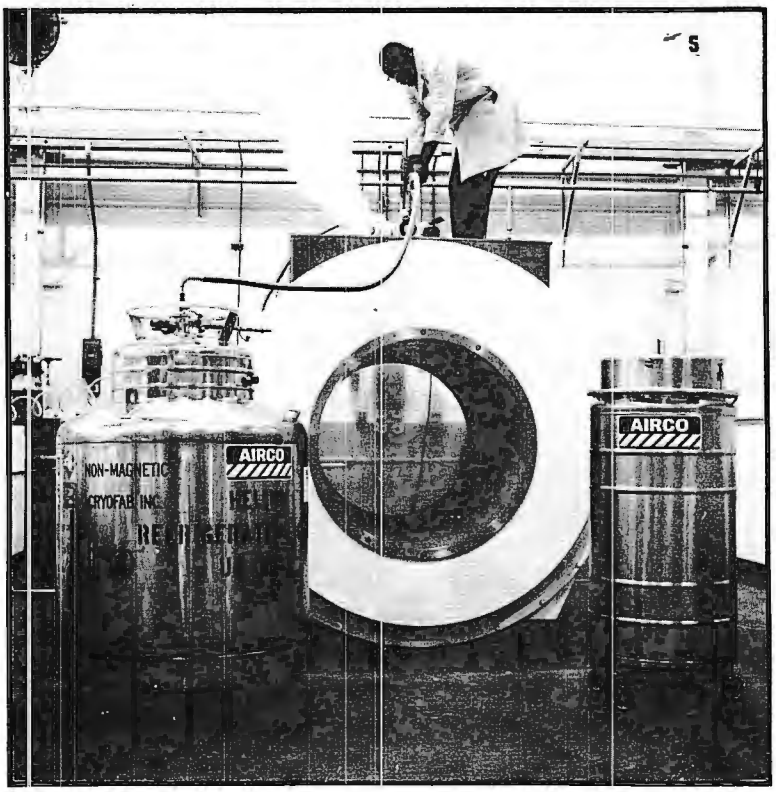

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Professor B. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

(Received December 8, 1986)

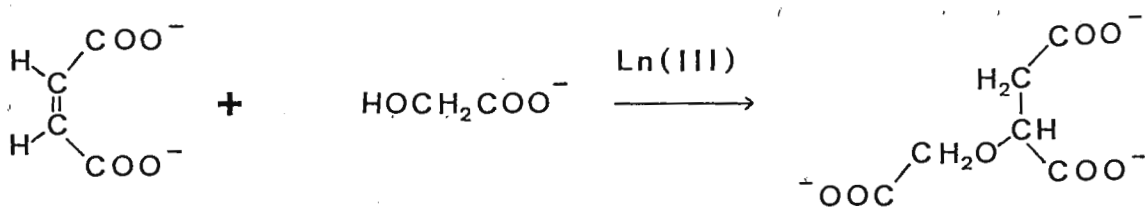
Your reference and date	Our reference	Office telephone	Date
	JAP/mk/493	(015) 78 5892	27-11-1986

Subject
Investigation of intermediates of the reaction between glycolate and maleate by multinuclear NMR spectroscopy

Sub-division
Lab. of Organic Chemistry

Dear Professor Shapiro,

It is known that carboxymethoxysuccinate (3) can be synthesized from maleic acid (1) and glycolic acid (2) by refluxing an aqueous slurry of these compounds with calcium hydroxide (1.8 eq) at pH 11.4.[1] By replacing the calcium hydroxide by lanthanide salts we were able to perform the addition under relatively mild conditions: namely at pH 7-8 and 90 °C.



1 2 3

An additional advantage of the use of paramagnetic Ln(III) cations instead of "NMR-silent" Ca(II) is that it enables us to study the intermediate coordination compounds in this reaction by multinuclear NMR spectroscopy.[2-3] Upon addition of Gd(III) to a mixture (1:1) of glycolate and maleate at 25 °C, an enhancement of the relaxation rates (T_1) of the ^{13}C nuclei in both glycolate and maleate is observed. The magnitudes of these enhancements are about the same as those obtained with the individual carboxylic acids (Figures 1 and 2). It may be concluded that a mixed ligand complex is formed from Ln(III), glycolate and maleate. No reaction to 3 occurs at 25 °C. Upon extrapolation to p 1, the relaxation rates from Figures 1 and 2 can be related to the molecular structure of the complexes via eqn (1):

$$(1/T_1)_i = k.n\tau_R/r_i^6 \qquad (1)$$

wherein i is the nucleus under study, k is a constant, n is the number of coordinated ligands, τ_R is the rotational correlation time and r is the distance between nucleus i and Gd(III). An optimal fit of the experimental

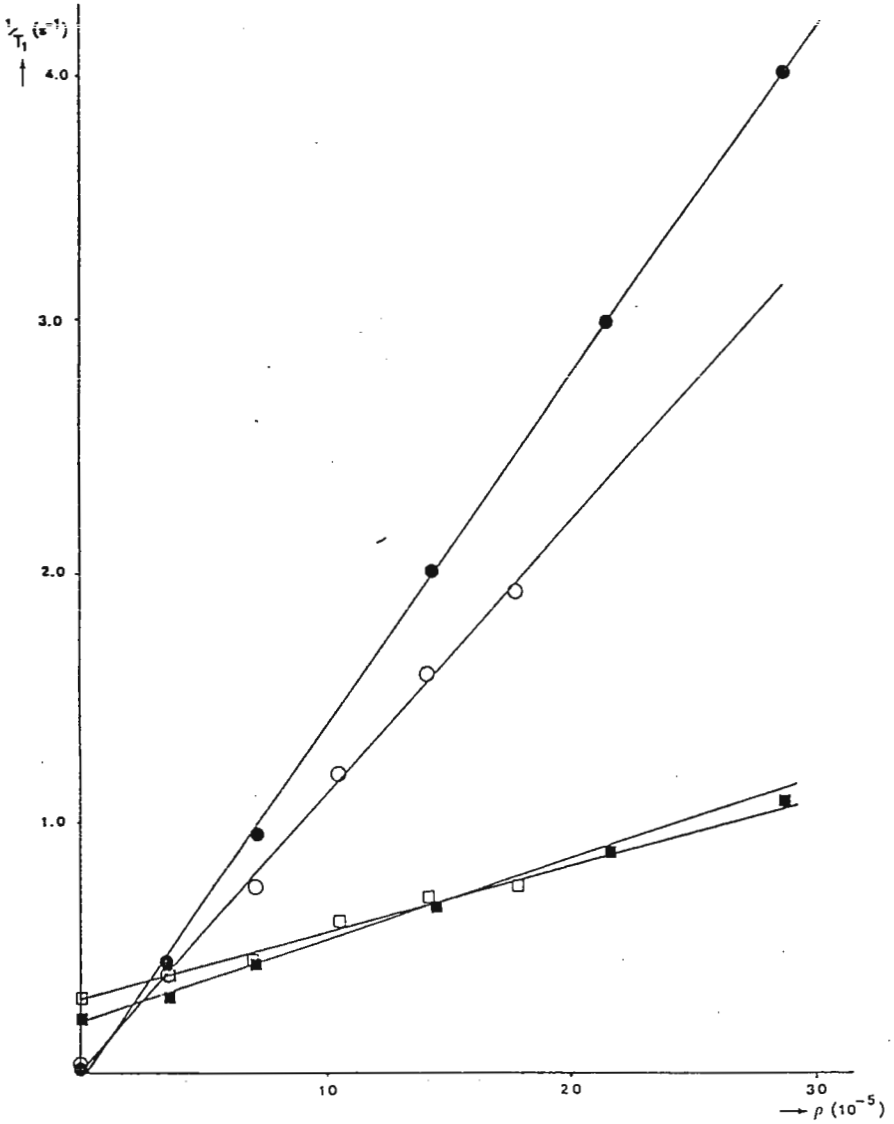


Fig. 1. The longitudinal relaxation rate ($1/T_1$) of the ^{13}C nuclei of maleate (● COO, ■ C=C) and maleate in a mixture (1:1) of glycolate and maleate (o COO, □ C=C) as a function of the Gd(III)/maleate ratio (ρ) at 50.3 MHz in D_2O and pD 7.9; [maleate] = 1.0 M in both experiments.

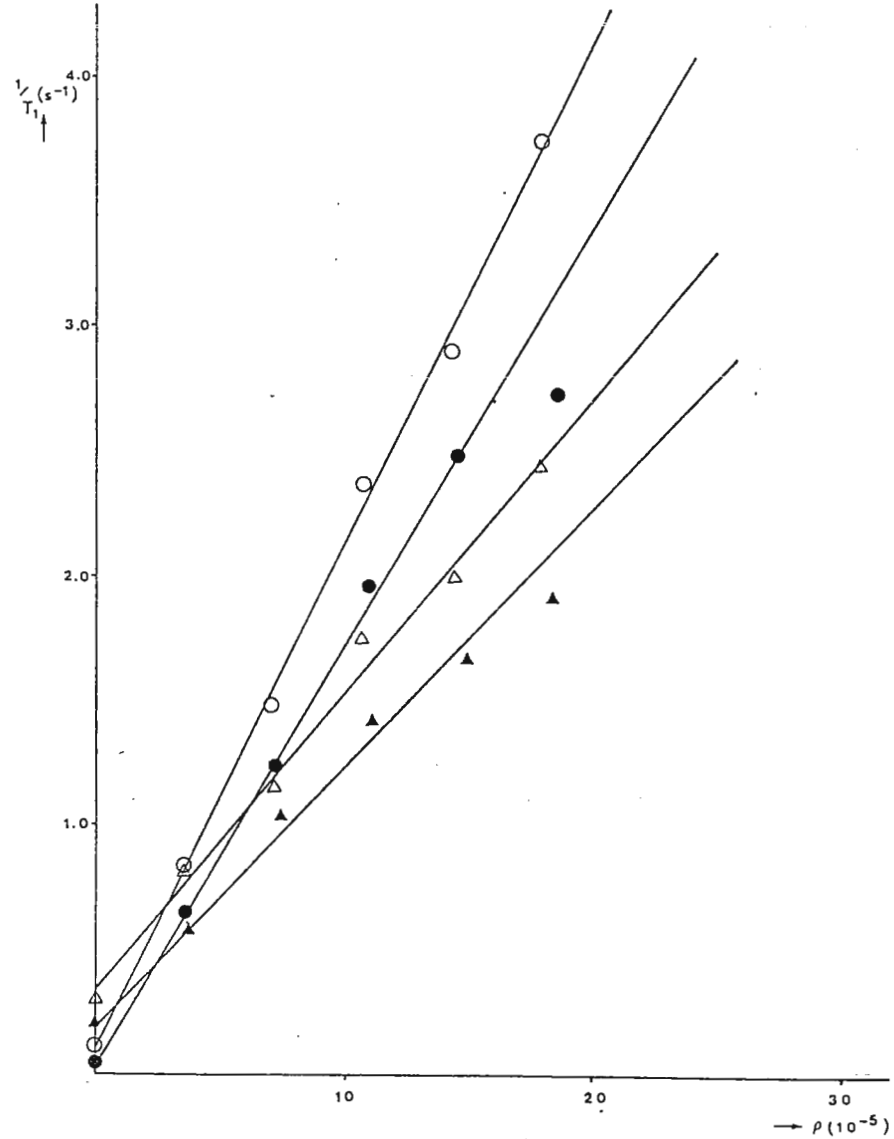


Fig. 2. The longitudinal relaxation rate ($1/T_1$) of the ^{13}C nuclei of glycolate (● COO, ▲ CH_2OH) and glycolate in a mixture (1:1) of glycolate and maleate (o COO, Δ CH_2OH) as a function of the Gd(III)/glycolate ratio (ρ) at 50.3 MHz in D_2O and pD 7.9; [glycolate] = 1.0 M in both experiments.

data with eqn (1) was obtained for a mixed ligand complex, in which three glycolates are coordinated bidentately via the hydroxyl and the carboxylate groups, and in which one maleate is coordinated bidentately either via its two carboxylate groups or acetate-like with one carboxylate group. These conclusions were confirmed by Dy(III) induced ^{17}O shift measurements also performed at 25 °C.

Yours sincerely,

J. van Westrenen J.A. Peters H. van Bekkum

[1] V. Lamberti, M.D. Konort, and I. Weil, German Patent 2,057,258; Chem. Abstr. 75 (1971) 89458z.

[2] J.A. Peters and A.P.G. Kieboom, Recl. Trav. Chim. Pays-Bas 102, 381 (1983).

[3] C.A.M. Vijverberg, J.A. Peters, A.P.G. Kieboom, and H. van Bekkum, Tetrahedron 42, 167 (1986).

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11 December 1986

(Received 22 December 1986)

POSITIONS IN SPECTROSCOPY

Our Spectroscopy section, in the Analytical Chemistry Department, has two new positions. One is for a PhD with experience in NMR and/or mass spectrometry; the other is for a graduate with similar experience or interests. Both people will work in a well equipped lab providing a range of spectroscopic and problem-solving services to chemists, biologists and others in our pharmaceutical research laboratories.

We have a Bruker WM-250 and a General Electric QE-300. We are about to install a GE GN-500 and to upgrade the Bruker to an AM-250. We also have two double-focussing mass spectrometers, a VG 7070F and a VG 7070-E-HF, and other instruments for IR, uv-vis, etc.

Anyone interested in either post could write or phone me at the above address.

Yours,

David V. Bowen

UNIVERSITY OF STOCKHOLM
Physical Chemistry

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

Stockholm, December 22, 1986 (Received 29 December 1986)

PROTON RELAXATION IN AQUEOUS SOLUTION OF THE Ni(II) ION

Dear Dr Shapiro,

We have for many years been interested in the nuclear spin relaxation in paramagnetic systems and have pursued experimental as well as theoretical work in the area (1). On the theoretical side, we are mainly concerned with the problems that arise if the electron spin relaxation is on the same time scale as the lattice motions that lead to the relaxation - the situation denoted as "slow motion". On the experimental side, we are interested in model systems, from which we hope to learn about the validity of our theoretical models. The approach of choice in this type of work is to measure the nuclear spin-lattice relaxation rate as a function of the magnetic field or the nuclear magnetic resonance dispersion (NMRD) curves. A "classic" model system with slow motion is the aqueous nickel(II) ion (2). We have recently extended the low field work of Hertz and Holz (3) in acidic solutions to high fields and fitted the data to the conventional Solomon-Bloembergen-Morgan (SBM) theory (1) and to the pseudorotation model developed at this laboratory (1,4). The results are illustrated in the figure and the table, where the parameters are the nickel - proton distance (R), the rotational and distortion correlation times (τ_R and τ_D) and the magnitude of the transient zero field splitting (Δ). Both models give a fit of similar quality. The advantage of the slow motion theory is that it gives a longer R. Friedman et al (2) estimate R at 2.66 Å, but it is reasonable to assume that the NMRD determined distance might be 2-4% shorter due to the paramagnetic relaxation outside of the first coordination sphere.

A more complete account of the work has been submitted to the Journal of Magnetic Resonance.

REFERENCES

(1). J. Kowalewski, L. Nordenskiöld, N. Benetis and P.-O. Westlund, Progr. NMR Spectr., 17, 141 (1985).
(2). H.L. Friedman, M. Holz and H.G. Hertz, J. Chem. Phys., 70, 3369 (1979).
(3). H.G. Hertz and M. Holz, 63, 64 (1985).
(4). P.-O. Westlund, H. Wennerström and N. Benetis, Mol. Phys., in press.

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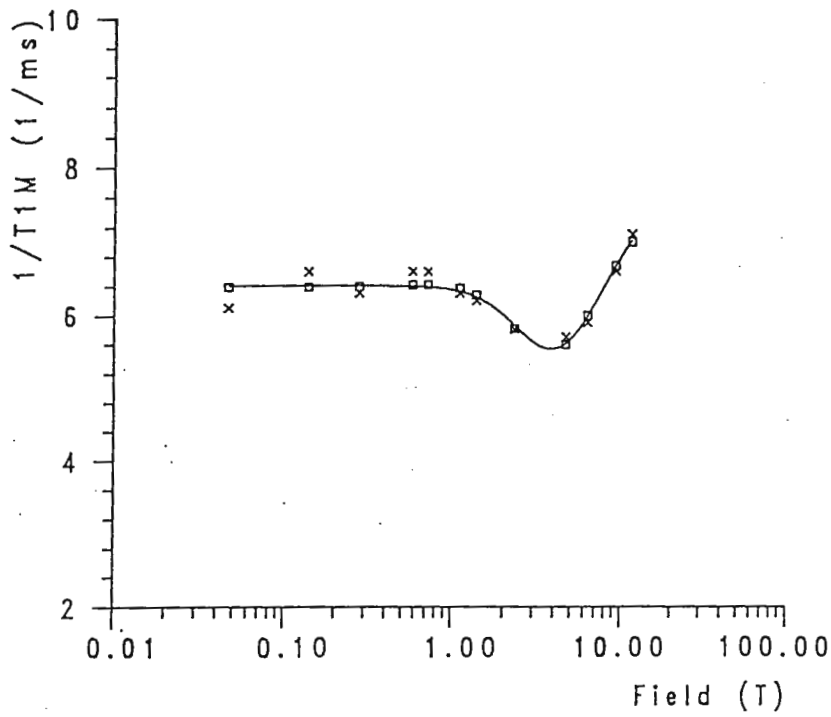


Figure 1. Proton spin-lattice relaxation rate in the $Ni(H_2O)_6^{2+}$ complex (pH = 0.1, 51°C) as a function of the magnetic field. The crosses are experimental points, the squares are the points calculated by the slow motion theory and the solid line corresponds to the SBM theory.

Table 1. Least-squares fit parameters in the SBM and slow motion theories.

	MSB	Slow motion
R, pm	2.45±0.05	2.53±0.04
τ_R, ps	7.0±0.6	8.3 ±0.6
τ_D, ps	1.1±0.2	1.8±0.3
$\Delta \cdot 10^{-12}$, rad s^{-1}	0.63±0.10	0.59±0.07

Yours sincerely

Jozef Kowalewski Tomas Larsson Per-Olof Westlund

340-52

State University of New York
Health Science Center
Syracuse

College of Medicine

Department of Radiology
Division of Radiological Sciences
(315) 473-8469

December 24, 1986
(Received 30 December 1986)

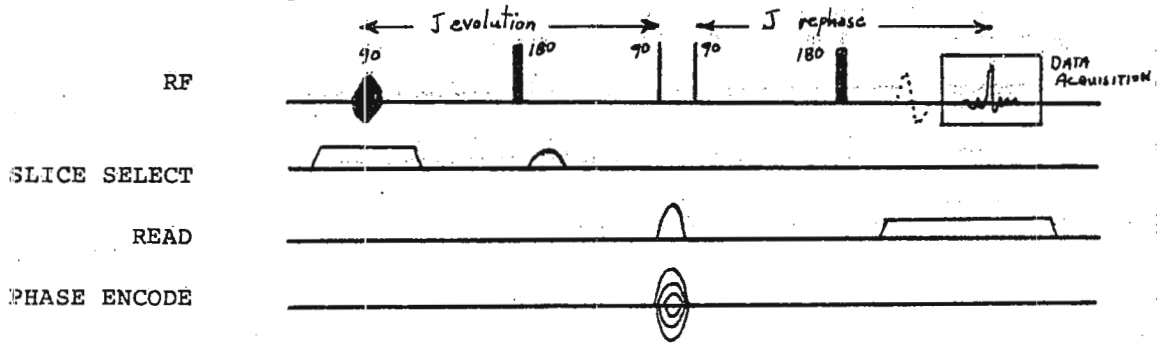
Professor B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Double Quantum Filter for Imaging Studies

Dear Barry,

We have just installed and have operating a 2T. GE animal imaging/spectroscopy system. After going through the normal (I am told) fruit and vegetable imaging phase, we are starting to do more relevant experiments. One of the ideas being evaluated by us involves the use of multiple quantum filters for *in vivo* proton spectroscopy and imaging. The experiment below outlines how a homonuclear proton double quantum filter can be employed to suppress water signal and isolate the signal arising from fat (or other metabolites that have scalar coupled protons).

The sequence goes like:



The J evolution and J rephase interval are each 30 ms (which was found to be optimal for lactic acid). The phase of the excitation pulses are stepped by 90 degree increments with the receiver having the reverse phase cycling. A 30 minute experiment on the "tail end" of a rat with a 10 mm slice and 1 second repetition time gives the image shown below. A normal T1 weighted image of the same slice is given for comparison. It is primarily fat that responds in this example -- this experiment does not work at a lower field strength of 0.5 T. for fat. Currently we are extending these ideas to selective volume spectroscopy experiments.

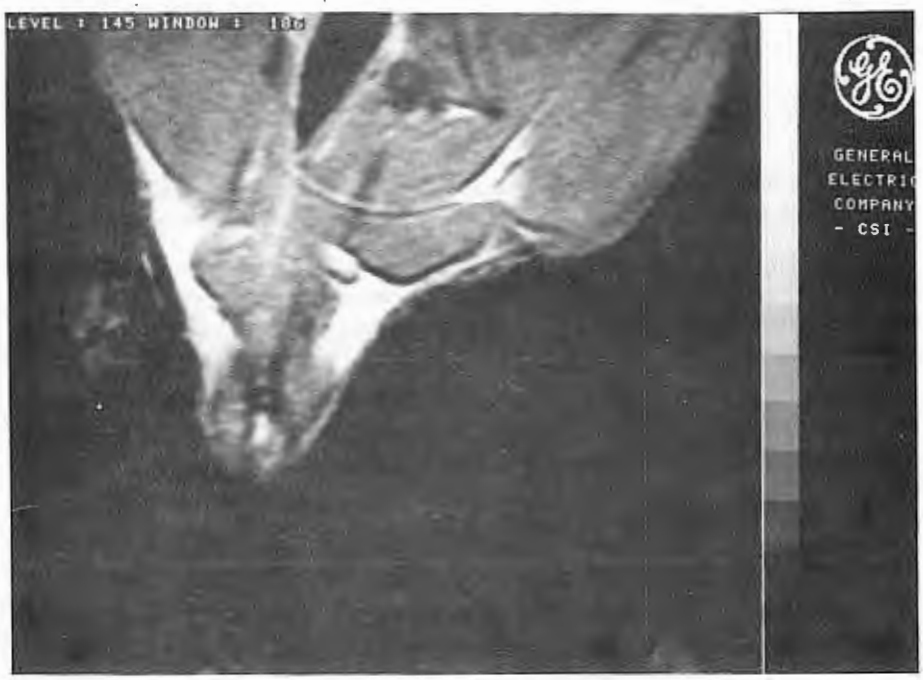
Best regards,

Nikolaus M Szeverenyi

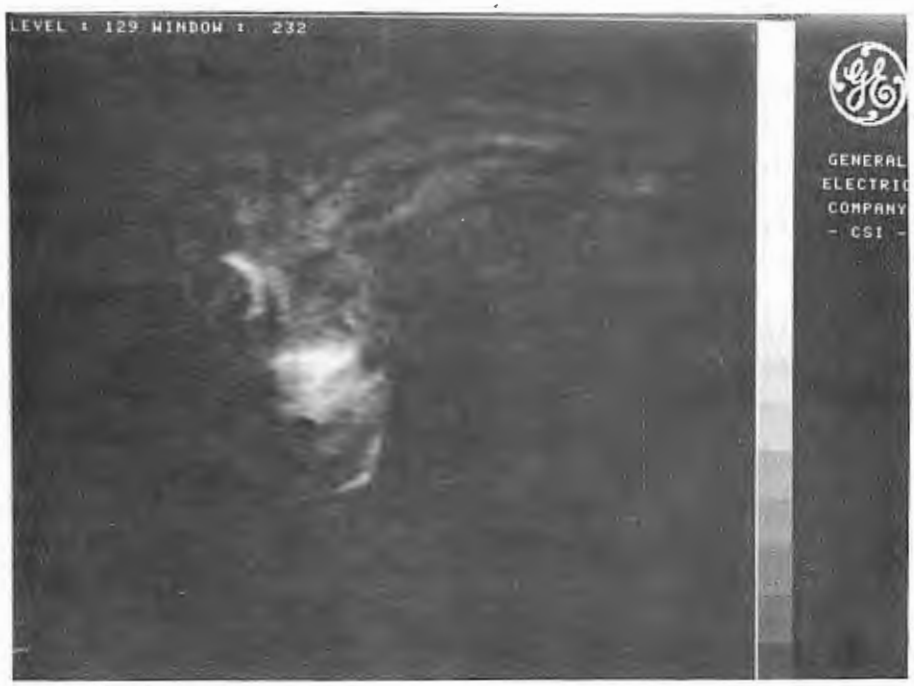
Nick

Martin Ruocco

Marty



A T1 weighted image of the tail end of a rat obtained with an ordinary proton imaging experiment.



An image through the same slice as above, but using a double quantum filter to isolate signals arising from materials other than water

ENC, Inc.

28th Experimental Nuclear Magnetic Resonance Spectroscopy Conference
Asilomar, California, April 5-9, 1987

December 24, 1986

Dear Barry:

This letter is to remind your readers that the 28th Experimental NMR Conference will be held from April 5 - 9, 1987, at the Asilomar Conference Center near Monterey, California.

This year we're trying a number of new ideas in an attempt to re-capture the intimate nature of the conference, to bring in new speakers, and to give young people a chance to speak before the group. We're also trying to deal with the overcrowding and the lousy audio-visual facilities, and at the same time have a smoother operation. Here's what is new:

- The first technical session will be held on Sunday night, both to relieve the overcrowding on Monday morning, and to get the ENC off to an early start. We are pleased that Professor Ernst has accepted our invitation to present the Opening Lecture.
- The session chairs have agreed to provide a brief (5 - 10 minute) overview of their sessions, describing what is new and why it is important, thereby putting the subsequent talks in perspective. We hope that this exercise will provide a more global perspective than we've been able to get before.
- The speakers for each day have been asked to localize their geographical coordinates for the first hour after that evening's session, so that interested persons can find them for additional discussions.
- There will be two sessions that are intended as "pointers" to the posters, in which young people will be asked to give a 10-minute overview of their posters.
- People bringing families or non-attending spouses will be asked to arrange for their own accommodations off the Asilomar site.
- Registration will be limited, if necessary, to those who meet the registration deadline (which was January 15; see the Information Sheet for late registration information). Professors with large groups are asked to help us in this respect.
- We have retained a professional Conference Management Service to handle the details of the local arrangements. We've already observed that this arrangement is going to require a lot of patience from all parties until we get to know each other!

I think you'll agree that the Technical Program is exciting and varied (see the Preliminary Program, which is enclosed). That's largely because all members of the Executive Committee provided ideas for sessions and volunteered to assemble speakers in their areas of expertise.

I've also enclosed an Information Sheet for those who may not be on the mailing list and did not receive the early December mailing.

Finally, we are very pleased that Prof. Herbert S. Gutowsky has agreed to be our banquet speaker. (Watch out Herb — we've been successful in collecting pictures of you at earlier conferences!)

We are looking forward to seeing you in Asilomar!

Lynn Jelinski

Executive Committee

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Murray Hill, NJ. 07974
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Princeton, NJ. 08544
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Robert B. Bryant
R. Andrew Byrd
Paul Cope
Colin Fyfe
A. N. Garrowsy
Edward O. Stejskal
Linda Sweeting
Nikolaus Szeverenyi
David VanderHart
Nicholas Zumbulyadis

Information Sheet — 28th ENC
April 5 - 9, 1987

Preregistration. All conferees must register, whether staying at Asilomar or not. The registration fee is $50 ($30 for *bona fide* predoctoral students) and must be paid by check with your application for attendance. **Your application for attendance may not be accepted if your preregistration material is postmarked later than January 15, 1987.** There will be no on-site registration.

A waiting list (which will close on February 15, 1987) will be compiled of late registrants. Registration information can be obtained by calling or writing to:

Mary Bradford (301-377-8181)
Convention Management Services
5814 York Road
Baltimore, MD 21212

Accommodations. The Asilomar Conference Grounds has a variety of excellent cottages. The rates vary from $ 136 to $ 340 and are per person for four nights. They include all meals except the banquet, starting with dinner on Sunday and ending with lunch on Thursday. Asilomar can accomodate vegetarian meals. All payments will be handled by mail. All rooms are not available in all combinations, and conferees are encouraged to share rooms because of the limited number of single rooms. Families and non-attending spouses are required to stay in private motels near Asilomar; these arrangements may be made through Convention Management Services. Off-site conferees may purchase meal tickets for $ 23/day.

All Asilomar accommodations must be handled through Convention Management Services.

Banquet. Banquet tickets may be purchased for $ 15. The banquet will be held on Wednesday evening; Prof. H. S. Gutowsky is the after dinner speaker. Please include your payment for the banquet with your preregistration material.

Conference Schedule. See Preliminary Program. The conference starts with check-in on Sunday between 3:00 and 6:00, and ends after lunch on Thursday. The first technical session begins at 7:00 on Sunday night.

Conference Materials. Conference badges, abstracts, the final program, vendor literature, and other conference materials will be available during check on Sunday.

Posters. Poster abstracts must be submitted to Mary Baum prior to January 15, 1987. We are limited by space concerns, and if poster submissions exceed our space limitations, a jury will evaluate posters according to scientific content. Professors are asked to prioritize poster submissions from their groups.

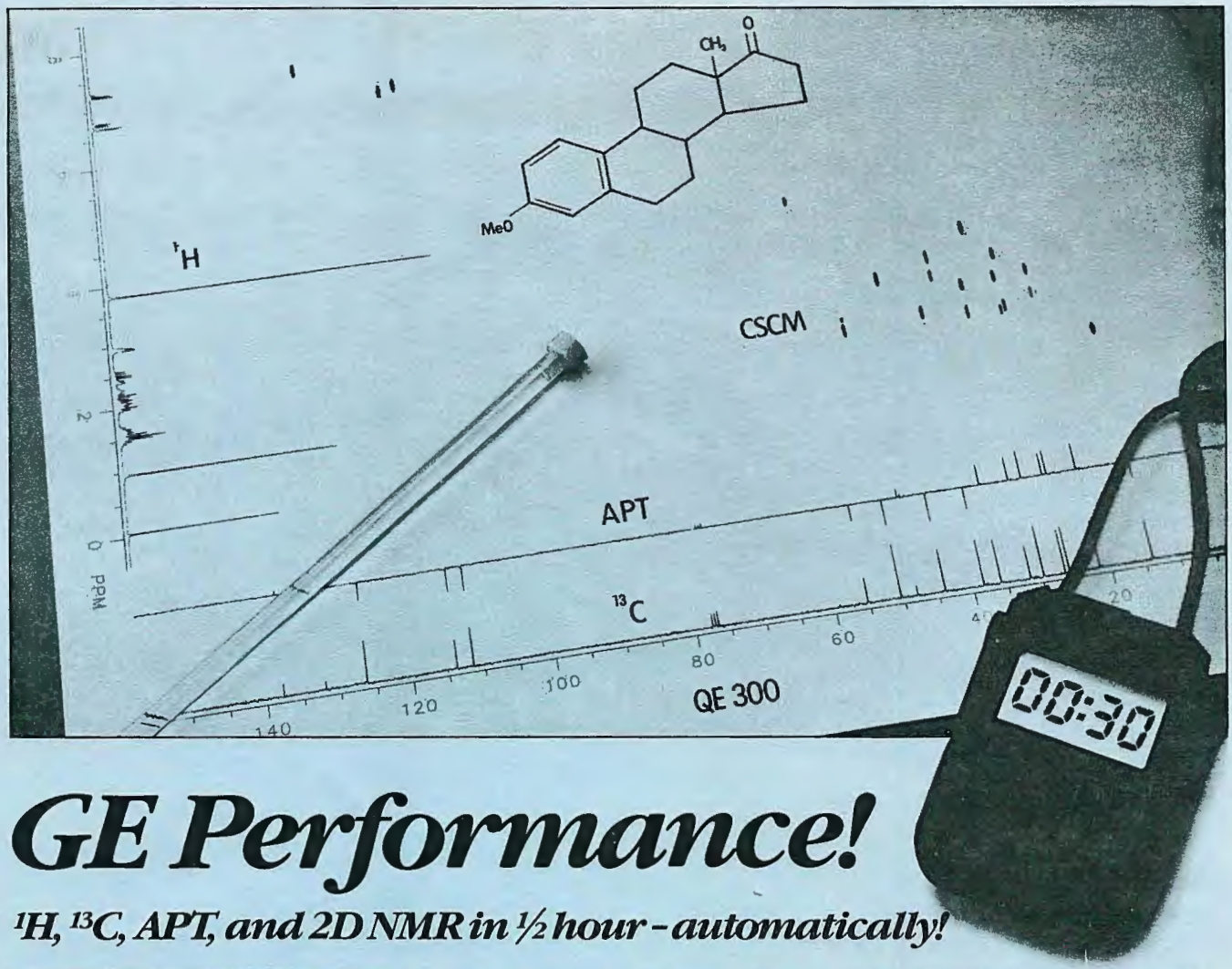
Travel Information. *By air:* Monterey Airport is serviced by several flights daily from San Francisco and Los Angeles. Both air transportation and ground transportation from the Monterey Airport to Asilomar can be arranged through Convention Management Services. *By automobile from San Francisco:* drive south on US 101, take 156 west to Monterey, then follow signs for Pacific Grove, which will take you to Lighthouse Avenue. Turn left off Lighthouse Avenue onto Forest, then right onto Sinex. Sinex terminates at the Asilomar main gate. The distance from San Francisco Airport is about 115 miles. *From Los Angeles or Salinas:*, follow US 101 north to State Highway 68, and follow 68 to its termination at the Asilomar main gate. *From the north or south on State Highway 1:* turn onto 68 just north of Carmel, and proceed as above.

Weather. The weather along the ocean can be chilly, breezy, foggy, or even damp on occasion. Warm sweaters and jackets may help make your visit more pleasant, but be prepared also for warm, sunny afternoons inland. Dress at Asilomar tends to be very casual; comfortable walking shoes are recommended.

28th ENC — Preliminary Program

April 5 - 9, 1987

Date	*Time*	*Session*
Sunday	3:00 - 6:00pm	Check - In, Mixer
	7:00 - 9:00pm	Opening Lecture (*chair - Sweeting*) R. R. Ernst
		POSTERS - **P**reviews **O**f **ST**ellar Post**ERS** (*chair - Baum*)
Monday	8:30 - 10:00am	Protein NMR (*chair - Opella*)
		Kurt Wüthrich, Chris Dobson, Angela Gronenborn
	10:30 - 12:00n	2D NOE of Biomolecules (*chair - Maddox*)
		Phil Bolton, NOE and Site-Specific Enzymes in DNA
		Niels Andersen, Conformation of Molecules in the Protein - Bound State
		Tom James, Structure and Dynamics using Complete Relaxation Matrix Analysis of 2D-NOE Spectra
	2:00 - 5:00pm	Poster Session A (*chair - Baum*)
	7:30 - 9:00pm	Gizmos (*chair - Szeverenyi*)
Tuesday	8:30 - 10:00am	Data, MEM, Automated 2D, and Recognizing Patterns (*chair - Byrd*)
	10:30 - 12:00n	How to Sense your Low Gamma's (*chair - Bax*)
		Cowburn, Wagner
	7:30 - 9:00pm	Gauss Meets Angstrom: Spatial and Spectral Spin Diffusion (*chair - Zumbulyadis*)
		John Waugh, Computer Simulation of Spin Diffusion in Crystals
		Robert Wind, Suppression of Dipolar Broadening by Magic Angle Spinning
		Dieter Suter, Diffusion of Spin Order in Resolved Solid State NMR Spectra
		POSTERS (*chair - Baum*)
Wednesday	8:30 - 10:00am	CPMAS, And then Some (*chair - Stejskal*)
		Gerry Harbison, Jim Yesinowski, Bob Griffin
	10:30 - 12:00n	NMR With or Without a Magnet (*chair - Batchelder*)
		Paul Ellis, W. S. Veeman
	2:00 - 5:00pm	Poster Session B (*Chair - Baum*)
	evening	Banquet, Prof. H. S. Gutowsky, after dinner speaker
Thursday	8:30 - 10:00am	Spatially Resolved Spectroscopy (*chair - Bryant*)
		David Hoult, Overview of the Experiment
		Gary Glover, Beating Back Eddy Current and Transient Problems
	10:30 - 12:00n	NMR in Mobile Systems: Mobile Samples and Mobile Spectrometers (*chair - Garroway*)
		William Rollwitz, NMR for the Detection of Explosives
		Ann Nicol, The NMR Gyro: Application of NMR in a Slowly Rotating Frame



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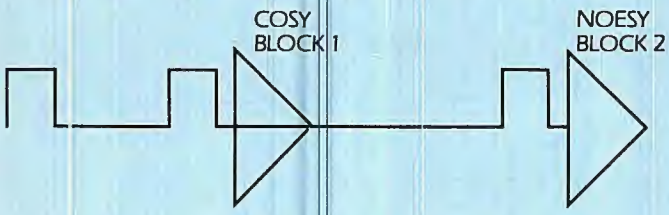

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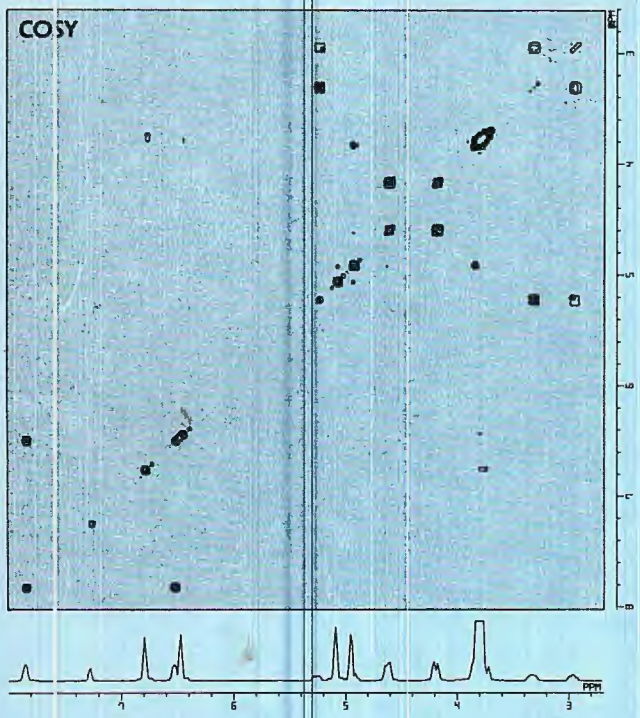

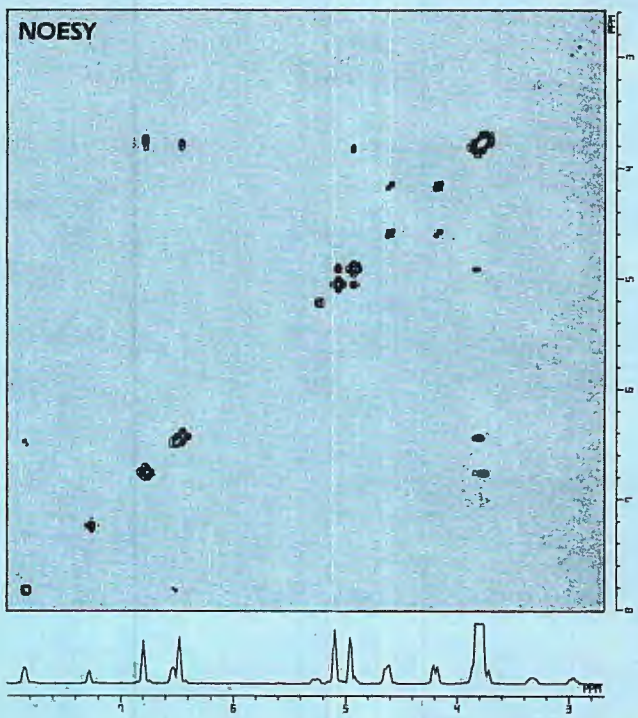

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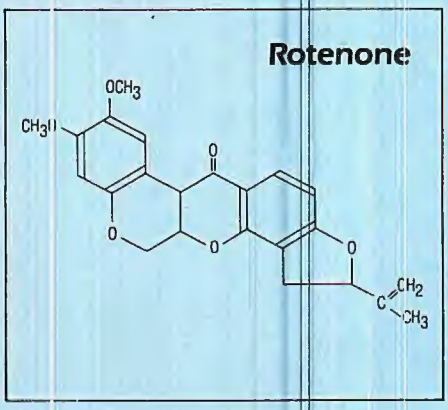
*COCONOSY (Haasnoot, et. al., J. Magn. Reson., 56,343 [1984])



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