BRIAN SYKES

TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 357

June 1988

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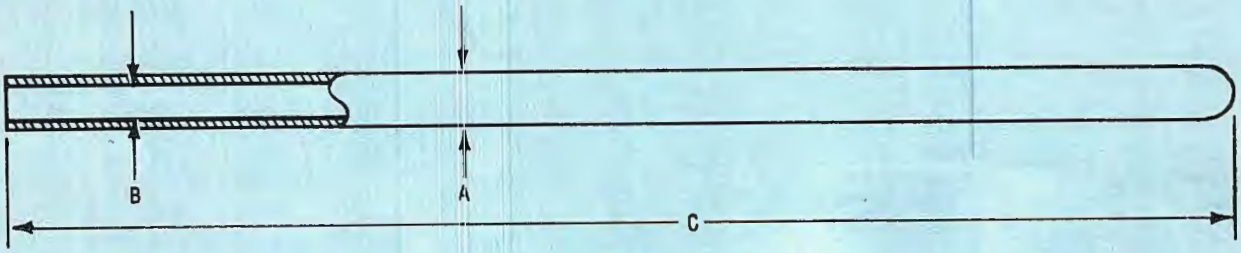

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FORTHCOMING NMR MEETINGS

30th Rocky Mountain Conference, July 31 - August 5, 1988; Radisson Hotel, Denver, Colorado; NMR and EPR symposia; contact M. M. Reddy, U.S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002, (303) 236-3601.

XIII Intl. Conference on Magnetic Resonance in Biological Systems, Aug. 14-19, 1988; Madison, Wisconsin. See Newsletter 349, 60.

NATO Summer School: "A Methodological Approach to Multinuclear Magnetic Resonance in Liquids and Solids: Chemical Applications", August 22 - September 2, 1988; Maratea, Italy; See Newsletter 353, 76.

XXIV Ampere Congress on Magnetic Resonance and Related Phenomena, August 29 - September 3, 1988; Poznan, Poland; Dr. S. Hoffmann, Instytut Fizyki Molekularnej PAN, ul. Smoluchowskiego 17/19, 60-179 Poznan, Poland.

Teaching Course on Nuclear Magnetic Resonance, September 5 - 9, 1988; Trondheim, Norway; Ms. I. S. Gribbestad, The MR Center, N-7034, Trondheim, Norway.

European Workshop on Nuclear Magnetic Resonance: Seminar on Contrast in MRI and MRS, September 12 - 13, 1988; Trondheim, Norway; Ms. I. S. Gribbestad, The MR Center, N-7034, Trondheim, Norway.

27th Annual Eastern Analytical Symposium and Exposition, October 2 - 7, 1988; New York Hilton Hotel, New York; General Chairman - Dr. Harvey S. Gold, Polymer Products Dept., E256/308, E. I. du Pont de Nemours & Co., Wilmington, DE 19898; (302) 695-3669.

International Post-Graduate Course 'NMR in Agriculture, Plants and Products', October 3 - 15, 1988; Wageningen, The Netherlands; Dr. Ir. J. H. de Ru, Foundation for Post-Graduate Courses, Agricultural University, Hollanseweg 1, NL-6706 KN Wageningen, The Netherlands.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence
Should Be Addressed To:

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303, U.S.A.

(415) 493-5971

DEADLINE DATES

No. 359 (August) ———— 22 July 1988
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No. 361 (October)——23 September 1988
No. 362 (November)——21 October 1988

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Friday the 13th (of May) (received 5/17/88)

Simulation of NMR Experiments by Embedded Density Matrix Operators

Dear Barry,

The CUNY NMR Facility's most recent contribution to the world at large was ready in February -- the birth to Ruth Stark and husband Abe Malz of daughter Aliza Ilana. Assuming that this does not count as a technical contribution, we also provide the following.

As the repertoire of 2D experiments grows, so does the size of the molecule to which they can be applied. Since we are dealing with biopolymers which have rather messy spectra, it would be helpful to us if we could simulate a variety of two-dimensional spectra; the catch is, of course, that diagonalization of a 2^N x 2^N Hamiltonian matrix takes up an enormous amount of computer memory and greater amounts of computer time. We have developed a scheme whereby a 2^N x 2^N matrix, made up of Sorensen's product operators operating on simple product wave functions, can be stored as a one-dimensional character string list, the length of which is proportional to the number of non-zero elements in the matrix. By simple analysis of symmetry based on the two-state Pauli spin matrices, using four character strings, it is possible to manually write down the Hamiltonian matrix for a system of N spins (where N is unlimited) in as little time as it takes to physically write the symbols on a sheet of paper; the one-dimensional computer representation of this is "calculated" as trivially. Whereas this representation is a saving in memory size, it is of course worthless unless an efficient diagonalization scheme be developed. Using a series of embedded Jacobi transforms, both the storage space and time requirements for diagonalization are compressed substantially. For example. using this method, it is straightforward to manually diagonalize a 16 x 16 matrix, corresponding to a 4-spin system; the time involved was again simply that of writing everything down step by step (virtually no calculation). We are finishing up the Fortran program for the entire scheme now, so we cannot yet send an example of the finished product. We therefore promise to send another contribution before we get a reminder or an ultimatum from you.

W Chen
Chen Wenqiao

Michelle
Michelle S. Broido

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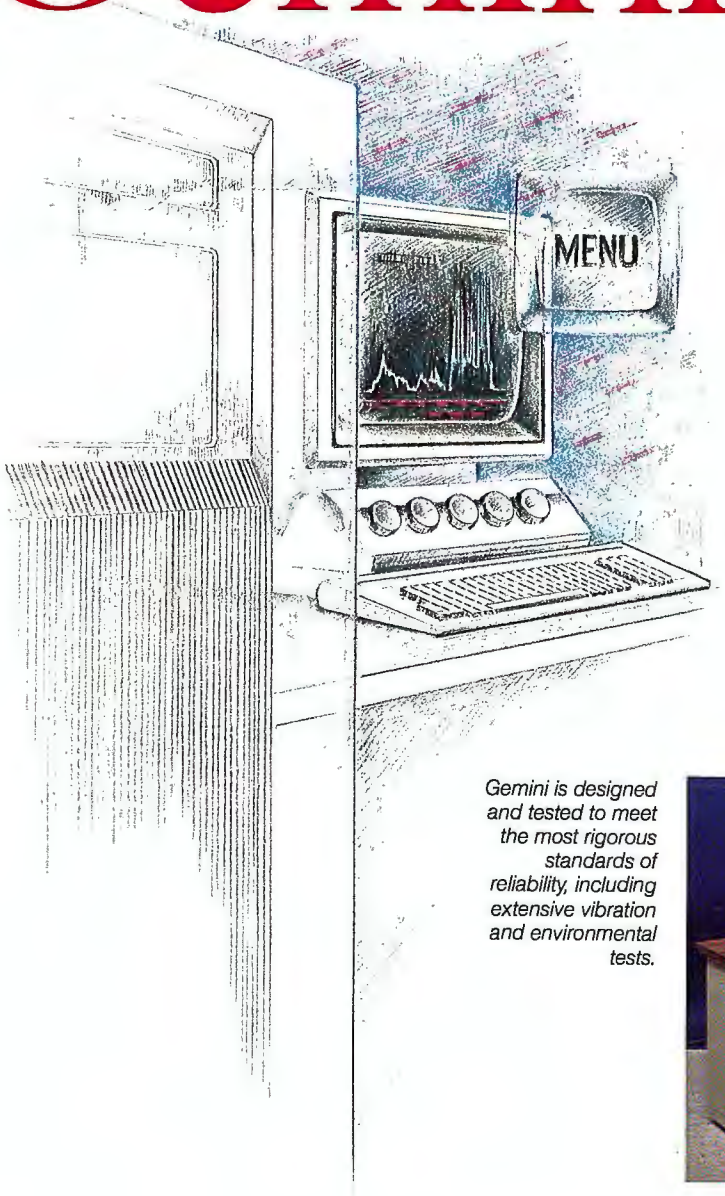

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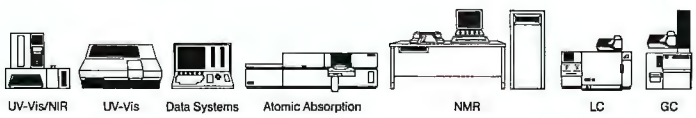

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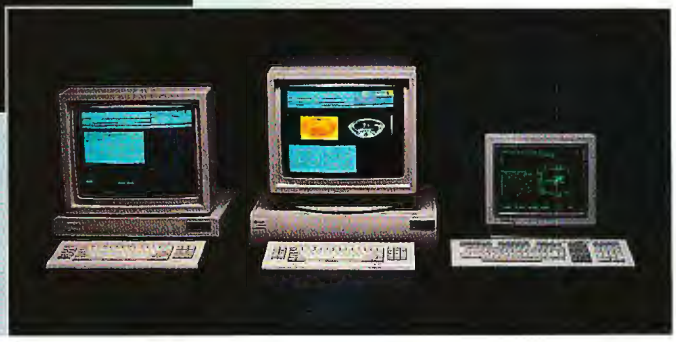

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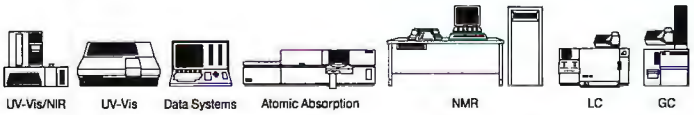

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Professor B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto
California 94303
USA

14 May 1988
(received 5/21/88)

Dear Professor Shapiro,

Yet another crystallographic inconsistency indicated by ^{119}Sn MAS n.m.r.

In collaboration with Dr. Angelika Sebald of the University of Bayreyth, we have been looking at the ^{119}Sn MAS spectra of sodium and potassium hexahydroxystannates, $M_2[Sn(OH)_6]$ (M = Na, K). These compounds are reported to be isostructural with a unique octahedrally coordinated tin (C.O. Björling, Arkiv. Kemi, Min., Geol., 1941, 15, No. 2). However, whilst the ^{119}Sn MAS spectrum of the potassium salt exhibits a single sharp (Γ_{ht} = 20 Hz) resonance at $\delta(^{119}Sn)$ = -569·7 ppm, the spectrum of the sodium salt comprises *two* peaks at $\delta(^{119}Sn)$ = -563·4 and 564·4 ppm. The solid state structure of the latter salt must therefore contain two chemically distinct tin sites, contrary to the (albeit rather old) crystallographic report. As expected, the $\delta(^{119}Sn)$ shifts in solution (0·2*M* in water) are identical (-595·3 ppm (Na), -595·5 ppm (K)).

Yours sincerely,

Philip G. Harrison
Reader in Inorganic Chemistry

Please credit this contribution to the account of Dr. Harold Booth of this Department.

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04/27/88
(received 4/30/88)

Dr. Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
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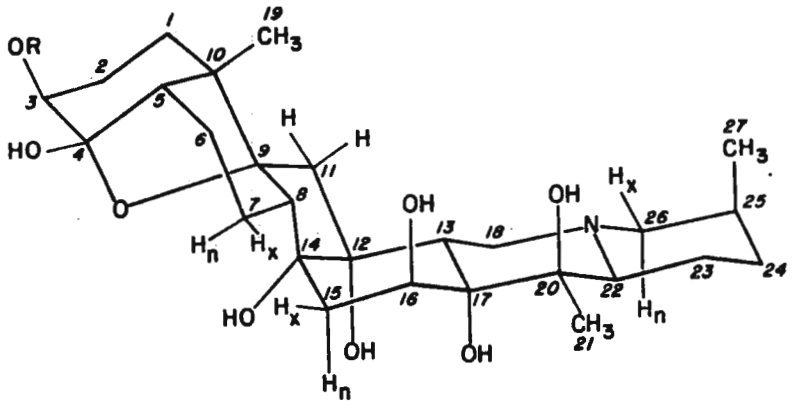
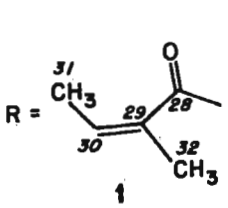
Use of Double Quantum Coherance 2D NMR (DQC2D) in spectral assignment of Cevadine and Veratridine:

Dear Dr. Shapiro:

In our recent investigation of complete spectral peak assignment of Cevadine (1) and Veratridine (2) (as a 2:1 mixture, also called





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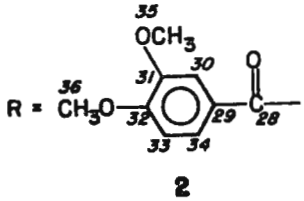
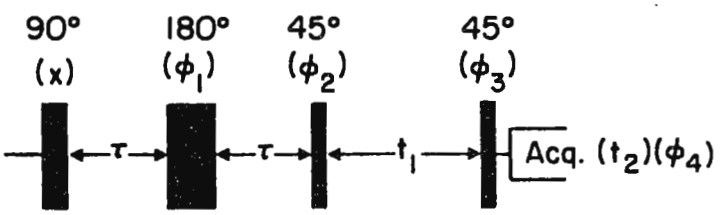


2

Veratrine), we made use of the DQC2D for the unequivocal assignment of H_2 and H_{24}. While the sequence of 90°(x)- 1/2J - 180°(y)- 1/2J -90°(x) could be used for the generation of double quantum coherance, we used instead the the sequence: 90°(x)- τ - 180°(y) - τ -45°(y) which essentially generates the terms $2I_{kz}I_{lz} + 2I_{kx}I_{lx}$.

The latter is a linear combination of both zero and double quantum coherances and by proper phase cycling of the "read" pulse one can choose either one of them. The actual sequence and the phase cycling used are given below.

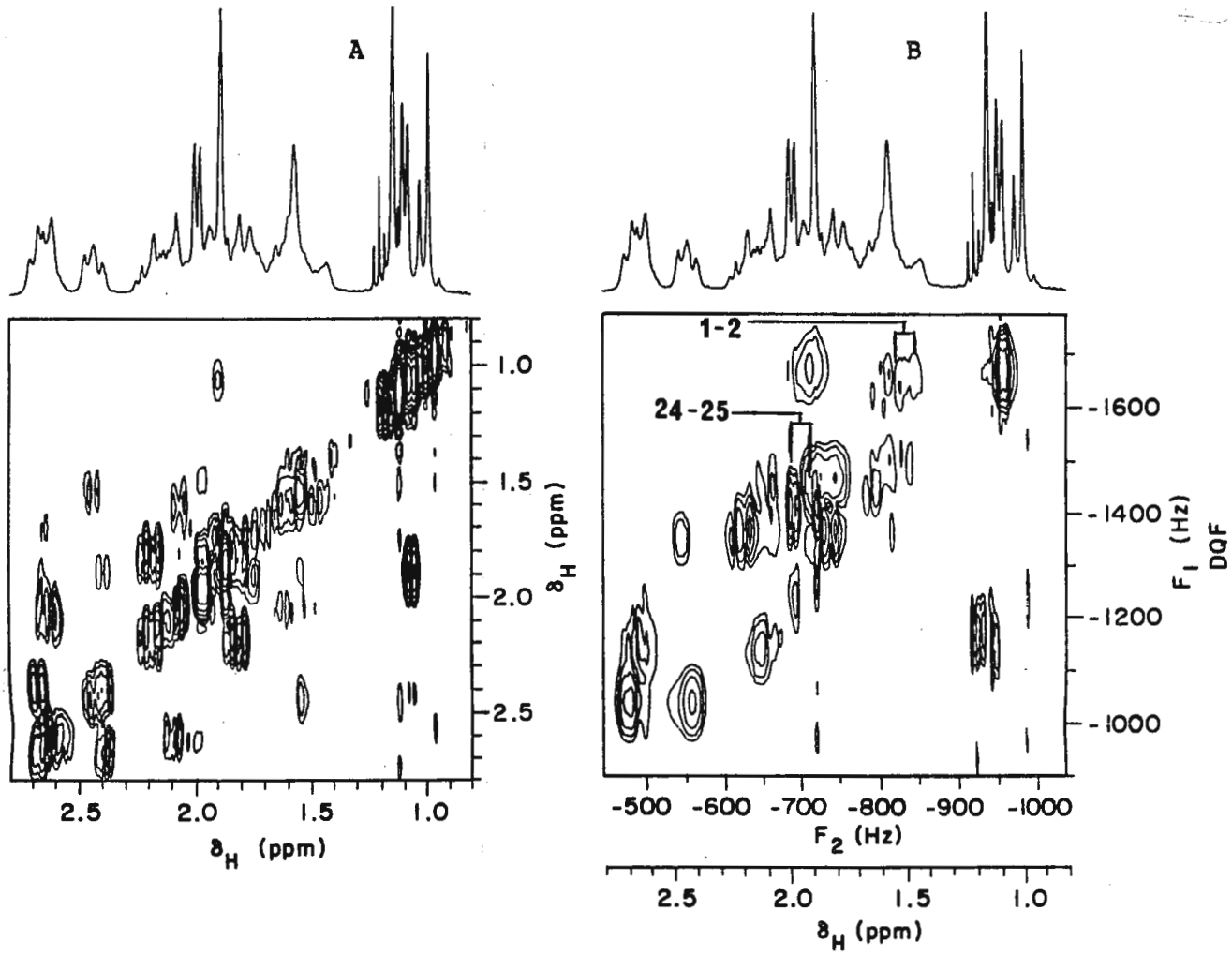


ϕ1	+y	+y	+y	+y	-y	-y	-y	-y	+y	+y	+y	+y	-y	-y	-y	-y
ϕ2	+y	+y	+y	+y	+y	+y	+y	+y	-y	-y	-y	-y	-y	-y	-y	-y
ϕ3	+y	-x	-y	+x	+y	-x	-y	+x	+y	-x	-y	+x	+y	-x	-y	+x
ϕ4	+x	+y	-x	-y	+x	+y	-x	-y	+x	+y	-x	-y	+x	+y	-x	-y
ZQC2D	+x	+y	-x	-y	+x	+y	-x	-y	+x	+y	-x	-y	+x	+y	-x	-y
DQC2D	+x	-y	-x	+y	+x	-y	-x	+y	+x	-y	-x	+y	+x	-y	-x	+y

As can be seen, the receiver phase cyclings are similar for both ZQC2D and DQC2D except that the alternate pulse are added for ZQC2D while they are substracted for DQC2D. Single acquisition could be performed with the alternate scans being stored in separate computer memory locations. Addition of these two data sets gives the FID's for the ZQC2D spectrum while subtraction gives the FID's for the DQC2D spectrum. This technique is exactly similar to that recently reported by Hall and Norwood[1] for ZQC2D and DQC2D and to that reported earlier by Müller[2] for relayed ZQC2D and DQC2D.

The routine use of one-bond CH correlation experiment, HH COSY and long-range CH Correlation experiment and the analysis of the respective spectra completely assigned all but two methylene (2 and 24) resonances. The two CH_2 carbon resonances at 18.7 and 18.1 ppm and the corresponding proton resonances at 1.93 and 1.43 ppm posed some problem in unambiguous assignment. The H_3 ("equatorial") resonances (at 5.14 ppm in veratridine and 5.00 ppm in cevadine) did not show coupling to either one. The only coupling observed (in the 1D spectrum and in the COSY) for H_3 is the one due to the methine proton, H_5. The proton resonance at 1.93 ppm did show a COSY cross peak to another proton around 1.55 ppm. However, H_1 (1.58 ppm) and H_{23} (1.55 ppm) were 'too close for comfort'. The H_{25} resonance is at 1.90 ppm and did not show any correlation with 1.43 ppm, indicating that this could probably be H_2 and the one at 1.93 ppm be H_{24}. Any possible COSY correlation between 1.43 and 1.58 ppm (H_1) or between 1.93 and 1.90 ppm (H_{25}) is masked by the diagonal peaks. The final assignment for these two peaks were made using DQC2D which showed clear double quantum peaks for H_{24}-H_{25} (1.90 to 1.93 ppm) and H_2-H_1 (1.43 to 1.55 ppm) methylene pairs. The COSY and the DQC2D (obtained using the above sequence) contour spectra of the aliphatic region are given in the figure.

Figure: (A) Partial COSY (unsymmetrized) and (B) partial DQC2D spectra of Veratrine in $CDCl_3$.



The ZQC2D spectrum (not shown) obtained from the same raw data, though did not confirm these two correlations (due to interference from peaks at $F_1=0$), gave complimentary evidence for the total assignments. The complete details of spectral peak assignments are discussed in a paper submitted to MRC[3]. Please credit this contribution to my account.

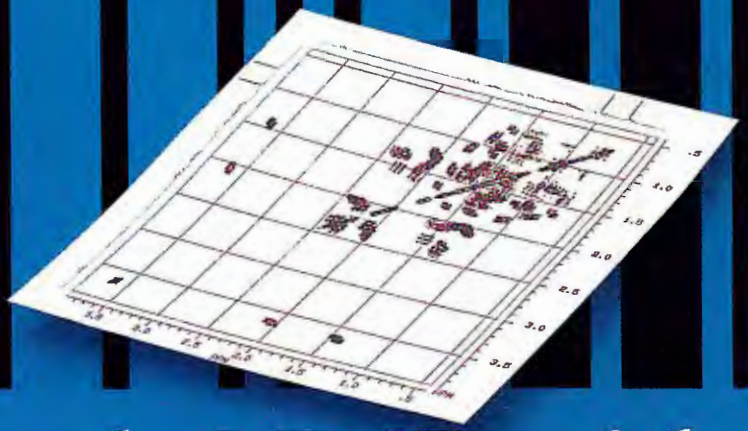
Sincerely,

V.V. Krishnamurthy
NMR Specialist.

References:
1. L.D. Hall and T.J. Norwood, J. Magn. Reson., 76, 241 (1988).
2. L. Muller and A. Pardi, J. Am. Chem. Soc., 107, 3484 (1985).
3. V.V. Krishnamurthy and J.E. Casida, Magn. Reson. Chem., submitted.

Start NMR Experiment

^{13}C



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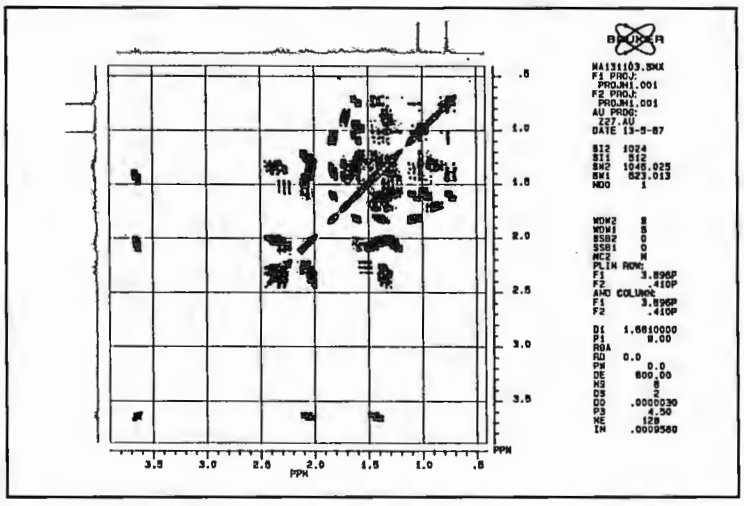

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Lichtenbergstraße 4
Ruf-Nr. (089) 3209-
Telex: 17898174
Teletex: 898174

May 3, 1988
(received
5/6/88)

Dear Prof. Shapiro:

^{127}I - QUADRUPOLE COUPLING IN PERIODATES WITH ETHYL-SUBSTITUTED CATIONS OF MAIN GROUP V

^{127}I solid state NMR studies of metaperiodates with ethyl-substituted cations of main group V in the compounds $Et_4E^+IO_4^-$ (E = P, As, Sb and Et = C_2H_5) revealed second order quadrupole effects from their lineshapes (s. Fig.1) with measured quadrupole coupling constants in the range of 5 - 7 MHz.

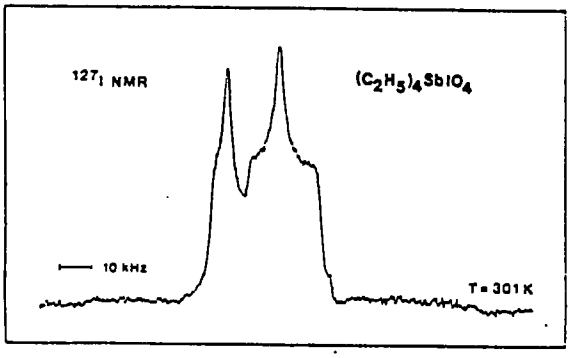

Fig. 1. ^{127}I NMR spectrum of polycrystalline $(C_2H_5)_4SbIO_4$. Larmor frequency: $\nu_L = 40.30$ MHz; sweep range: SW = 151.5 kHz; pulse program: one cycle pulses; pulse width: 5 µs; recycle time: 20 ms.

In $(C_2H_5)_4PIO_4$ and in $(C_2H_5)_4AsIO_4$ the ^{127}I-quadrupole coupling constants show normal negative temperature coefficients $\bar{\alpha}$ in the order of -10^{-4} K^{-1} for 180 K < T < 300 K.

In contrast to this behaviour in tetraethylstiboniummetaperiodate $(C_2H_5)_4SbIO_4$ a case of an anomal positive temperature coefficient $\bar{\alpha} = + 9.0 \cdot 10^{-4}$ K^{-1} is observed.

The relevance of possible mechanisms [1] for this anomalous temperature coefficient, like breakdown of d_π-p_π-backbonding, effect of the cation-radii, reorientational motions and orientational change of the electric field gradient tensor axes system is discussed. The temperature dependence of the asymmetry parameter η reveals the dominance of the latter mechanism.

Reference

[1] D.G. Klobasa, P.K. Burkert, Proc. XXIII.Congress Ampere, Roma 1986, p.424

Please credit this contribution to Prof. Dr. F.H. Köhler's subscription.

Sincerely,

P. K. Burkert

(Dr. P.K. Burkert)

THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA 85721

COLLEGE OF ARTS & SCIENCES
FACULTY OF SCIENCE
DEPARTMENT OF CHEMISTRY

May 2, 1988
(received 5/6/88)

Dr. B. L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Dear Barry:

"Non Equivalence of Glycine α-Hydrogens in Cyclic Enkephalin Analogues"

We have been interested in studying the conformational properties of the highly potent and delta opioid receptor selective cyclic peptide Tyr-D-Pen-Gly-Phe-D-Pen, [D-Pen^2, D-Pen^5]enkephalin (DPDPE) (Pen = ββ-dimethyl-cysteine) by the use of one and two-dimensional NMR spectroscopy.

These studies in combination with molecular mechanics calculations have led to a conformational model for this peptide which is consistent with all the data obtained in these laboratories. A striking feature of the NMR spectra of DPDPE is the large chemical shift non-equivalence (0.8 ppm) of the diastereotopic Gly^3 α-hydrogens. In most peptides and proteins the chemicals of these protons are less than 0.15 ppm. We ascribe these chemical shift differences to the anisotropic environment of these protons in the reasonably rigid 14-membered ring system, in which one hydrogen is in the shielding region, the other in the deshielding region, of the adjacent peptide bond. In our model the aromatic rings are not close enough to lead to such a large difference.

Recently, we had occasion to prepare [p-NO_2-β-MePhe^4]DPDPE and have separated the corresponding enantiomers and diastereoisomers (I-IV). The D-erythro, D-threo and L-erythro, L-threo-containing isomers exhibited dramatic changes in their biological activity and in ^{1}H chemical shift data. We have made complete ^{1}H chemical shift assignment of these isomers and noted curious chemical shift differences for the two glycine-Hα, Phe^4-Hα and Phe^4-NH (Table). These results clearly suggest that the side chain rotamer populations of the aromatic residues, particularly Phe^4, could play an important role in understanding the NMR characteristics of these molecules. The large chemical shift differences for the two Gly^3-Hα and Phe^4-NH between the D and L isomers can be explained by the fact that in the D series only the aromatic ring can now interact with the Gly^3 α-protons such that one of the Gly^3 α-protons is in the shielding cone and the other in the deshielding cone of the aromatic ring dramatically decreasing their nonequivalence. Consequently the ^{1}H chemical shifts of Phe^4-Hα and Phe^4-NH are also affected.

Table: ^1H Chemical Shifts (ppm)

	Peptide	Gly^3-Hα	Phe^4-Hα	Phe^4-NH
I.	[L-erythro-p-NO_2-β-$MePhe^4$]DPDPE	4.13; 3.10	4.31	8.40
II.	[D-erythro-p-NO_2-β-$MePhe^4$]DPDPE	3.65; 3.51	4.76	7.62
III.	[L-threo-p-NO_2-β-$MePhe^4$]DPDPE	4.47; 3.24	4.42	8.68
IV.	[D-threo-p-NO_2-β-$MePhe^4$]DPDPE	3.80; 3.70	4.72	7.74

These observations confirm the more rigid conformation of the peptide backbone in the 14-member ring. All the ^1H chemical shift assignments were confirmed by recording the 2D ^1H-^1H COSY and COSYLR NMR spectra at 298K in DMSO-d_6 on a Bruker AM 500.

Sincerely yours,

Victor J. Hruby

Om Prakash

Géza Tóth

Geza Toth

Terry Matsunaga

Terry Matsunaga

P.S. Please credit this to the account of Professor Mike Barfield

T. J. Watson Research Center
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May 9, 1988 (received 5/17/88)

Dr. Barry Shapiro
TAMUNMR Newsletter
966 Elsinore Ct.
Palo Alto, CA 94303

"Nmr at Yorktown; Goodbye to Sine Lookup Tables"

Dear Barry:

Now that I've finally settled here at Yorktown, I'm writing to get out of the pink and back into your good graces. Here at Yorktown, we have an IBM AF-250 (AC-250) with the IBM solids accessory just installed, and are working to install PCNMR as well and connect it to the Token Ring Network throughout the building.

In addition, the Lab Automation group is concerned with support of a number of experiments, some migration to Windows type graphics environments and remote experimental monitoring. I'll keep you posted on all of the above.

Meanwhile, I've been experimenting with Microsoft's QuickBASIC 4.0 for scientific data manipulation. Since the program automatically uses the PC's math coprocessor if it is present, the problem of the sine lookup table is essentially eliminated. In a poster at the 21st ENC, I described how you could reverse the inner and middle loops of the FFT so that each sine is only looked up and interpolated once. In a similar fashion, once the sines are calculated by the math coprocessor, you can calculate the butterflies of the points in each cell so that they need only be calculated once per pass. We found that the calculation times of an FFT with calculated since versus one with looked-up and interpolated since differed by only about 2%. Thus, the old question of the length of a lookup table is now moot: don't bother with one and do your FFT's in floating point. This FFT, incidently, is given in my text on QuickBASIC, to be pusblished by Wiley this fall.

Best regards,

Jim

James W. Cooper,
Research Staff Member,
Laboratory Automation

Richard R. Thomas
Research Staff Member,
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84-70001	$^{1}H_2O$ [Deuterium-depleted Water]	99.985	99.99995	1/2	500.133	25g	25.
						4 x 25g	90.
						10 x 25g	200.
						20 x 25g	300.
						30 x 25g	400.
						1kg	500.
82-70001	D_2O ($^{2}H_2O$) [Deuterium Oxide]	0.015	99.9	1	76.778	100g	45.
						5 x 100g	215.
						10 x 100g	425.
						1kg	400.
						5 x 1kg	1950.
						10 x 1kg	3875.
82-70901	D_2O ($^{2}H_2O$) [Deuterium Oxide]	0.015	99.8	1	76.778	min. 10kg	3500.
						25kg	8500.
						50kg	16250.†
82-70002	D_2O ($^{2}H_2O$) [Deuterium Oxide "100%"]	0.015	99.96	1	76.778	10g	15.
						5 x 10g	50.
84-70000	$H_2{}^{16}O$ [^{17}O- and ^{18}O-depleted Water]	99.759	99.98			10g	100.
						25g	125.
						50g	150.
87-70003	$H_2{}^{17}O$ [Water-^{17}O, normalized]	0.037	20	5/2	67.805	1g	155.
						5g	575.
						10g	1100.
87-70004	$H_2{}^{17}O$ [Water-^{17}O, normalized]	0.037	40	5/2	67.805	0.5g	300.
						1g	450.
88-70023	$H_2{}^{18}O$ [Water-^{18}O, normalized]	0.204	10			50g	190.
						100g	365.
						500g	1775.
						1kg	3500.†
88-70005	$H_2{}^{18}O$ [Water-^{18}O, normalized]	0.204	95			1g	85.
						5g	410.
						10g	800.
						25g	1950.
						50g	3800.†
81-70002	$D_2{}^{18}O$ ($^{2}H_2{}^{18}O$) [Water-^{18}O, not normalized]	0.204 (^{18}O) 0.015(^{2}H)	97 (^{18}O) 70 (^{2}H)	1	76.778	1g	140.
						5g	550.

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Dr Bernard L Shapiro,
Editor/Publisher,
TAMU NMR Newsletter,
966 Elsinore Court,
Palo Alto, CA 94303
U.S.A.

13 May 1988

Dear Dr Shapiro,

I wonder if you could bring the following two graduate studentships to the attention of your readers.
Yours sincerely

David G Reid

1. Drug Interactions with Deuterated calmodulin - Hatfield Polytechnic
   The protein calmodulin is an important modulator of the intracellular effects of calcium in most mammalian cell types. A number of medicinal compounds, including trifluoperazine, felodipine and oxmetidine bind to calmodulin and interference with calcium mediated cellular functions may be a direct consequence of such interactions. NMR and other spectroscopic techniques can be used to study drug binding to proteins but considerable difficulties arise when trying to distinguish the resonances of a ligand from those of its biological 'receptor' molecule. To overcome this problem this project will prepare calmodulin in a fully deuterated form which will be invisible in an ^1H NMR spectrum. The proposed programme of research includes the following:

1. Growth of algae in D_2O followed by hydrolysis of the culture to release deuterated nutrients and amino acids.
2. Constructs containing the calmodulin gene in an expression vector in E.coli are available. Growth of E.coli in deuterated media will produce deuterated calmodulin which will be purified for use in NMR studies.
3. Drug-calmodulin interactions will be studies using ^1H NMR spectroscopy and heteronuclear spectroscopy where appropriate. The student will have access to state-of-the-art molecular graphics and computational facilities for modelling these interactions.

Applicants should hold, or expect to obtain, a first or upper second degree in an appropriate subject.
Informal enquiries or applications (no forms) to:
Dr John Walker, Biological Sciences, Hatfield Polytechnic, Herts OR
Dr David Reid, SK&F Research Ltd, The Frythe, Welwyn, Herts.

2. Binding of cAMP Analogues to cAMP Receptor Protein - (MRC) at NIMR, Mill Hill
   cAMP receptor proteins (CRP) control the expression of a number of genes in prokaryotic cells. The apo-protein binds weakly and non-specifically to DNA. When the cAMP is bound, the protein binds tightly and specifically to clearly characterised sites on genes and either increases or decreases their expression. This change in affinity has been shown to depend upon a conformational change in the protein on binding cAMP.
   The project will involve the use of biophysical techniques to observe and quantitate the binding of cAMP analogues to CRP, and elucidate the molecular basis of analogue specificity and induced conformational changes. These studies will be greatly assisted by the fact that CRP has been cloned and can be expressed in high yields. This will enable NMR-active nuclei to be incorporated biosynthetically, as well as the preparation of fully deuterated, spectroscopically "silent" protein. This will allow the signals of bound ligands to be assigned unambiguously and their protein bound conformations to be determined without interference from protein signals.

Applicants should hold, or expect to obtain, a first or upper second degree in an appropriate subject.
Please direct informal enquiries to:
Dr Rodney King, NIMR, The Ridgeway, Mill Hill, London, NW7 1AA (01 959 3666) OR
Dr David Reid, SK&F Research Ltd, The Frythe, Welwyn, Herts, AL6 9AR (0707 325111 Ext 3533)

LOVELACE MEDICAL FOUNDATION

May 2, 1988
(received 5/5/88)

Distortions of Flow Images due to Stimulated Echoes.

Dear Dr. Shapiro,

Stimulated echoes (STE; Hahn) have been the 'focus' of much recent research in NMR imaging because of their interesting T_2 and phase dependencies (see Merboldt, *et al.*, and its references). However, undesired STE's are always present in experiments containing three or more rf pulses (often due to nonideal π refocussing pulses) and they can lead to severe distortions of the image obtained from the second primary spin echo (SE) (Zur and Stokar). One manifestation of the STE is a sinusoidal modulation of the SE image, the frequency of which is inversely proportional to the separation of echoes according to the modulation theorem (Bracewell). Another manifestation is an STE image superimposed on the SE image.

Consider the flow phase-compensating imaging experiment (Caprihan, *et al.*) shown in Fig. 1. In order to collect the SE in exclusion of the STE, we can vary the timing of the rf pulses to separate the SE and STE temporally. This is easy to accomplish for non-flowing samples, but for flow experiments, the gradient amplitude G_{flow} during the various intervals must be carefully adjusted to eliminate the velocity dependence. We calculate these gradient values to be $G_1 = G_3(2m^2+m)/(m+2)$ and $G_2 = G_3 3m/(m+2)$ where $m = \frac{T}{\tau} - 2$ and τ is the time between the first two pulses, T is the interval from the first to the third pulse as defined by Hahn, and G_1, G_2, and G_3 are the amplitudes for G_{flow} defined in Fig. 1.

Another strategy is rf pulse phase cycling to cancel the STE, and involves the alternation of the phase of either π pulse by 180°, *i.e.*, $(\pi/2)_x - G_{PE} - \pi_y - \pi_{\pm y}$ or $(\pi/2)_x - G_{PE} - \pi_{\pm y} - \pi_y$, where G_{PE} is the phase-encoding gradient. However, this requires the repetition and coaddition of each G_{PE} increment at least twice (at least 6 times with QPC) thus possibly increasing the experimental time. Because the modulation effect is prominent even when the STE is very small relative to the SE, this technique requires high reproducibility making electronic drift and sample movement intolerable. Fig. 2a is the transverse projection image of a slice in a tube of water (no flow) using the sequence in Fig. 1. Fig. 2b was obtained using the first phase-cycling scheme listed above and the image modulation is diminished.

Finally, the STE image can, in principle, be compressed into one dimension by placing the phase encoding (PE) gradient G_{PE} after the first π pulse where the STE spins will not "see" it, rather than after the $\frac{\pi}{2}$ pulse (see Fig. 1). The compressed STE image runs through the center of the image window, but it is a sharp feature, and can be easily accounted for (Fig.2c). It can also be shifted to the edges of the window in the PE dimension (Fig.2d) by alternating either π pulse on alternate PE steps, *i.e.*, $(\pi/2)_x - \pi_y - G_{PE} - \pi_{(-1)^n y}$ or $(\pi/2)_x - \pi_{(-1)^n y} - G_{PE} - \pi_y$ (where n is the PE increment number), because the STE signal is then modulated at the Nyquist frequency. This rf phase-cycling scheme requires no co-addition of signals, so that the experiment time is not increased. The STE image in Figs.2c and 2d show a significant width which we tentatively attribute to eddy currents from the G_{PE} pulse which survive until after the final π pulse. The remaining artifacts are due to quadrature imperfections.

Please credit this contribution to the account of Dr. Eiichi Fukushima.

Sincerely,

Paul Majors

Paul D. Majors

Bioengineering Research
2425 Ridgecrest S.E., Albuquerque, New Mexico 87108 505/262-7155

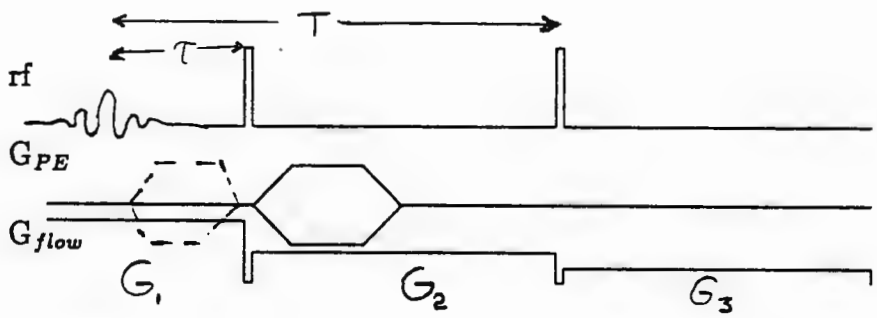

Figure 1

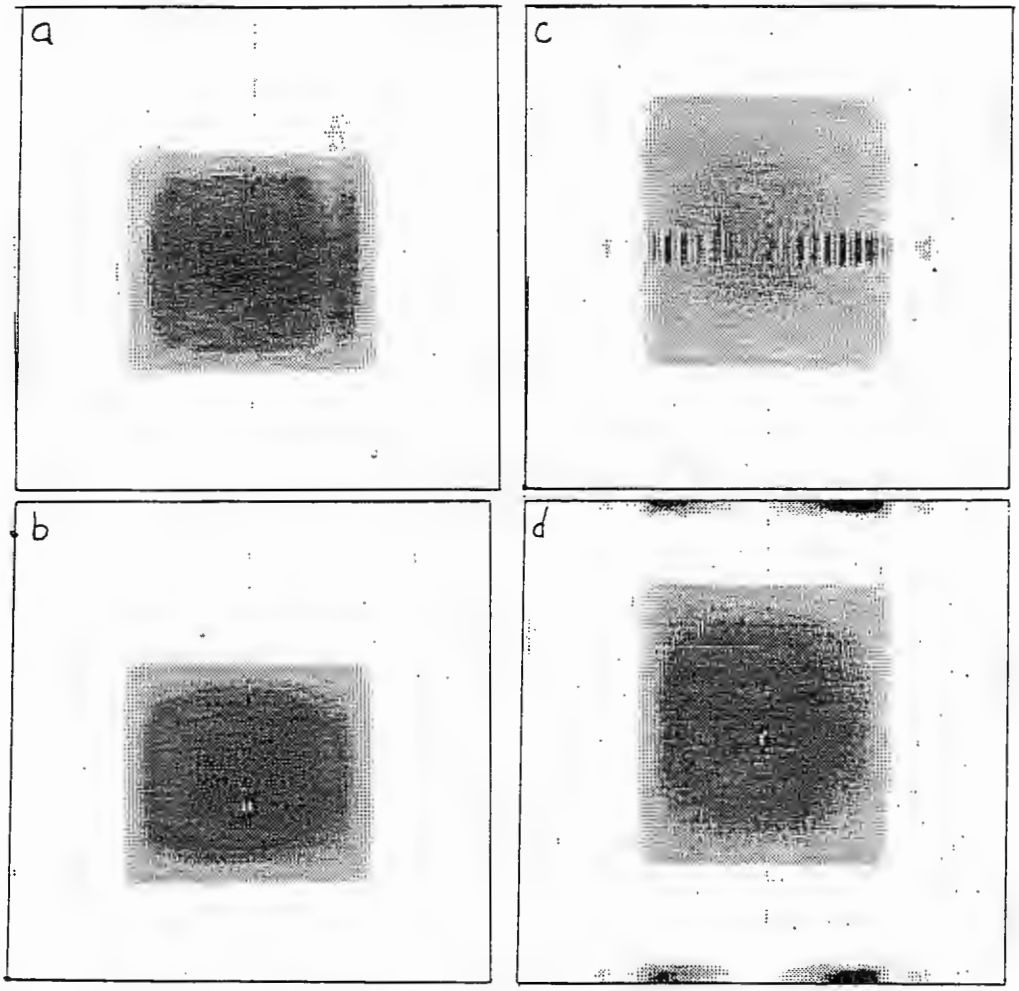

Figure 2

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Zur, Y., and Stokar, S., *J. Magn. Reson.* **71**, 212-228 (1987).

357-20

GEORGETOWN UNIVERSITY HOSPITAL

Department of Radiology

April 29, 1988 (received 5/19/88)

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

Use of hydraulic devices in magnets

Dear Barry:

The use of horizontal bore magnet instruments in in vivo nmr is becoming quite common. Although the wide bore size allows the study of larger animal systems, it is quite cumbersome to tune the nmr probes. This is because of the increased lengths from the edge of bore to the center of the magnet. Typically, this problem is circumvented by the use of rather long capacitor tuning linkages or transmission cables to external tuning boxes. The first choice can become difficult when more than one or two capacitors need to be tuned and the second method incurs transmission line losses. We have used an hydraulic device to tune an inductively coupled probe. The hydraulic device was essentially used to move the coupling loop back and forth from the sample coil. A couple of 5 ml plastic syringes and a length of plastic tubing were used to construct the device. The syringe barrels were fastened to a rigid plexiglass plate, which in turn was mounted on the animal holder cradle. The syringe plungers were mounted on another plate onto which the coupling loop was fastened with tie wraps. The syringes were connected with plastic tubing and Y-connectors to the third syringe placed outside the magnet. By adjusting the position of the plunger in the syringe outside the magnet the coupling loop could be moved back and forth precisely. This rather crude contraption has worked remarkably well in our single and double tuned probes. Although water was used as the hydraulic fluid, no detrimental effects were observed. This technique is quite general and can conceivably be used to move objects remotely inside the magnet bore.

S. Sunder Rajan

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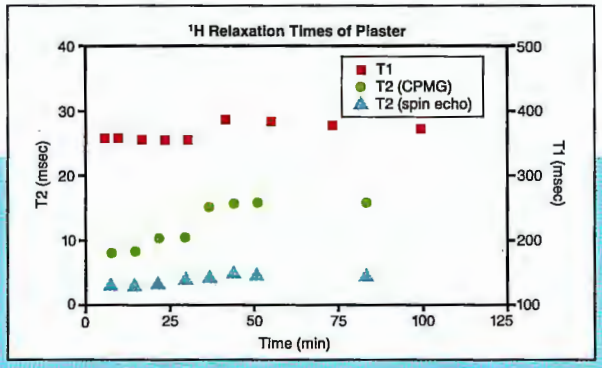

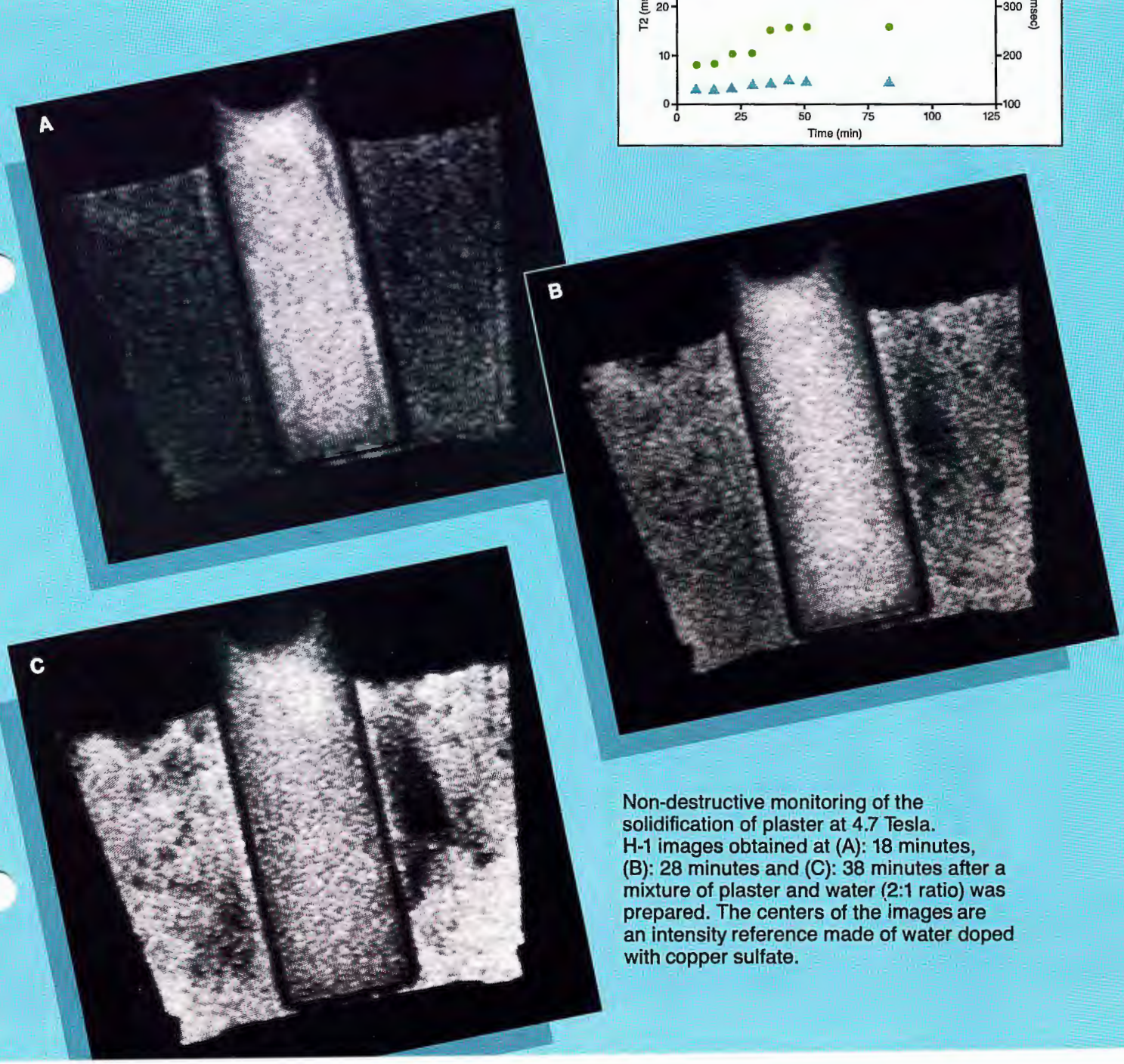

Non-destructive monitoring of the solidification of plaster at 4.7 Tesla. H-1 images obtained at (A): 18 minutes, (B): 28 minutes and (C): 38 minutes after a mixture of plaster and water (2:1 ratio) was prepared. The centers of the images are an intensity reference made of water doped with copper sulfate.

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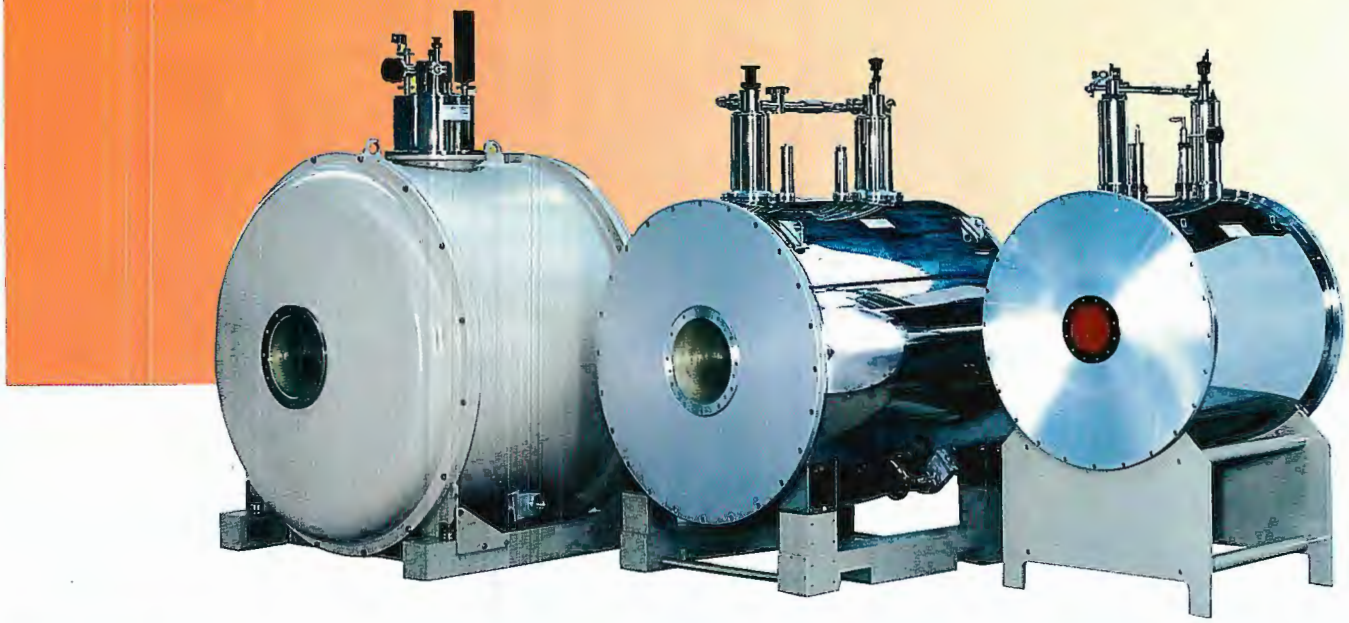
85/310	2.0T	310 mm	225 mm	3.0 G/cm	100 mm DSV ± 5 ppm	70 mm DSV 0.1 ppm	4.50 m	3.63 m

DSV = Diameter Spherical Volume
HHLW = Half-Height Line Width
PPM = Parts Per Million



200/400, 200/330, and 300/180 magnets for the NMR Imaging Spectrometer System.
(Photos courtesy Oxford Instruments.)

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Note: Equipment described is intended for investigational purposes, and is not approved by the FDA for clinical use.

TOWSON STATE UNIVERSITY

COLLEGE OF NATURAL AND MATHEMATICAL SCIENCES

TOWSON, MARYLAND 21204

Department of Chemistry (301) 321-3058

May 2, 1988
(received 5/16/88)

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

Strategies for ^{19}F-NMR Acquisition

Part I. Subdividing the ^{19}F-NMR Spectral Range

Dear Professor Shapiro,

This letter outlines a "divide and conquer" strategy for the acquisition of fluorine-19 NMR spectra, which enables a small segment of the fluorine spectral range to be viewed in more detail. Fluorine NMR data can be readily collected on most spectrometers, requiring only minor adjustment to instruments used to run proton samples. Proton and fluorine NMR's can be quickly acquired for the same sample using the same number of scans and receiver gain settings. Fluorine-19 sample preparation requires similar sample size and deuterated solvent as proton NMR, with the addition of a small amount of a fluorine reference (0.5% $CFCl_3$, 0.3% CF_3CO_2Et, or 0.2% C_6F_6 by weight).

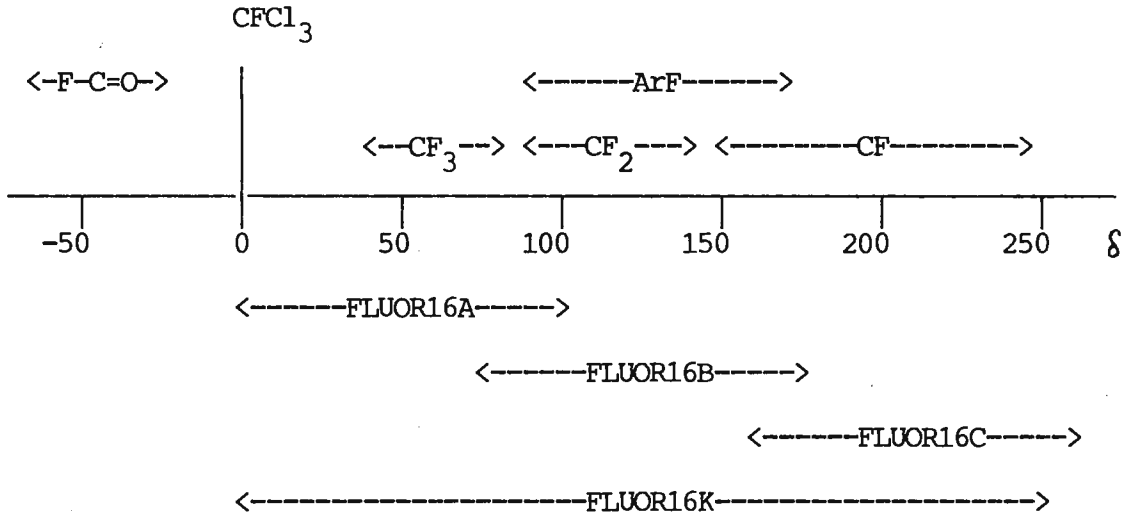
The wide spectral range of fluorine chemical shifts minimizes chances of signals overlapping. But this can create a problem when a wide spectral sweep and high resolution (to show detailed splitting patterns) are desired at the same time. This situation often arises with selectively fluorinated organic compounds, where the coupling constants J_{HF} and J_{FF} are important structural evidence, requiring resolution of 1 Hz or less. A partial solution to this problem is to subdivide the fluorine spectrum into three 100 ppm sections, each with its own reference.

The majority of chemical shifts for fluorines bound to carbon are detected upfield from $CFCl_3$, the most common reference, and fall in a 250 ppm range, shown in the accompanying correlation diagram. For unknowns, reaction mixtures with multiple fluorine signals, and single compounds with multiple fluorine signals, start with a maximum sweep of 250 ppm (using FLUOR16K) then narrow the sweep width as required. Three standard sets of parameters, each covering 100 ppm, serve for the following situations:

FLUOR16A	0-100δ	for CF_3 compounds and similar trihalomethyls.
FLUOR16B	75-175δ	for CF_2 compounds and aromatic fluorides.
FLUOR16C	160-260δ	for most CF compounds.

Even so, these programs give only fair resolution at best. Narrowing the sweep width to 1200 Hz gives excellent resolution of 0.15 Hz/pt for individual signals and coupling within each multiplet. Using the same sweep width for proton and fluorine spectra at this stage allows a direct visual connection between the spectra of two different nuclei with J_{HF} serving as the link.

FLUORINE-19 NMR CORRELATION DIAGRAM



FLUORINE-19 NMR PARAMETERS - IBM NR/80 (16K memory, spectral freq. 75.39 MHz)

program	FLUOR16K	FLUOR16A	FLUOR16B	FLUOR16C	(Narrow)
delta range	0-250	0-100	75-175	160-260	10
reference	CFCl3	CFCl3	CF3CO2Et	C6F6	
ref. value	0.0	0.0	75.8	162.2	
SW (sweep width)	19000	7600	7600	7600	1200
AQ (acquis. time)	0.43	1.08	1.08	1.08	6.82
Hz/pt (resolution)	2.35	0.92	0.92	0.92	0.15

Water-soluble samples can be run in D_2O containing 0.3% CF_3CO_2H. A complete list of fluorine-19 NMR parameters for the IBM NR/80 is available upon request.

T. Stephen Everett

T. Stephen Everett

P. S. Please credit this contribution to Linda Sweeting's account.

CALIFORNIA INSTITUTE OF TECHNOLOGY

Mail Code 164-30, Pasadena, CA 91125

May 18, 1988
(received 5/20/88)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Calculation of MAS-NMR Spectra of Paramagnetic Solids

Dear Barry,

Despite increasing interest in the magic-angle spinning NMR spectra of paramagnetic solids, no quantitative interpretation of the effects of paramagnetic ions upon the intensity of the spinning sidebands has been made. We therefore chose to study the ^{1}H MAS-NMR spectrum of copper chloride dihydrate in its paramagnetic (room temperature) phase. The sample was partially deuterated in order to reduce the large homonuclear dipolar couplings. The 200 MHz ^{1}H MAS-NMR spectrum at a spinning speed of 8.3 kHz is shown in the Figure, superimposed upon a theoretical simulation described below.

The predominant contribution to the numerous intense spinning sidebands in the spectrum is the dipolar interaction between the proton and the thermally-averaged electron magnetic moments of the Cu^{2+} d^9 ions (since the electron T_1^{-1} is rapid compared to the "full" dipolar interaction). An expression for this interaction was originally given by Bloembergen; it is an atypical dipolar interaction since it depends linearly upon the magnetic field strength and inversely upon the temperature! We have shown that even in the presence of many electron spins coupled to a given nucleus, g-tensor anisotropy of the unpaired electron(s), and a chemical shift anisotropy of the nucleus, the net inhomogeneous interaction responsible for the sideband intensities is formally equivalent to a chemical shift tensor. Thus the approach of Herzfeld and Berger can be used to calculate the sideband intensity patterns. The theoretical simulation carried out using this approach with *no adjustable parameters*, but only atomic coordinates from diffraction studies, electron g-tensor information from EPR studies, and an assumed chemical shift tensor, correctly predicts the approximate spectral width of the sideband pattern. However, in order to improve the agreement between the theoretical and experimental spectra, we allowed for delocalization of the electron spins from the copper atoms to the neighboring chlorine atoms (ca. 15%), as suggested by other studies. This simulation (incorporating dipolar couplings to neighboring ^{2}H nuclei) is shown in the Figure, and is in close agreement with the experimental spectrum.

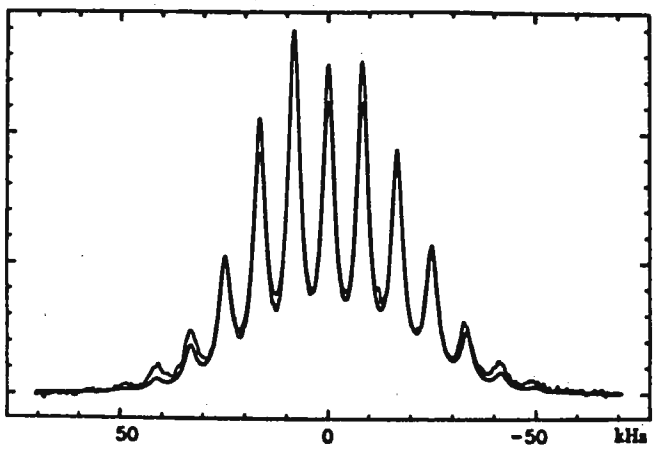
We believe that this quantitative approach to paramagnetic interactions in MAS-NMR will provide useful structural information, and will enable one to separate the contact shift from the pseudo-contact shift, since the latter can be calculated from the known geometry in the solid state. A detailed discussion of the theory and the latter points, along with the sources of linebroadening in such spectra, are found in a paper which has been submitted to *J. Chem. Phys.*.

Sincerely yours,

Akbar Nayeem

James P. Yesinowski

200.27 MHz ^1H MAS-NMR spectrum of $CuCl_2 \cdot 2H_2O$-d_4, spinning speed 8.3 kHz, and theoretical spectrum superimposed to show detailed agreement (Lorentzian linewidth of 3.5 kHz used in simulation).



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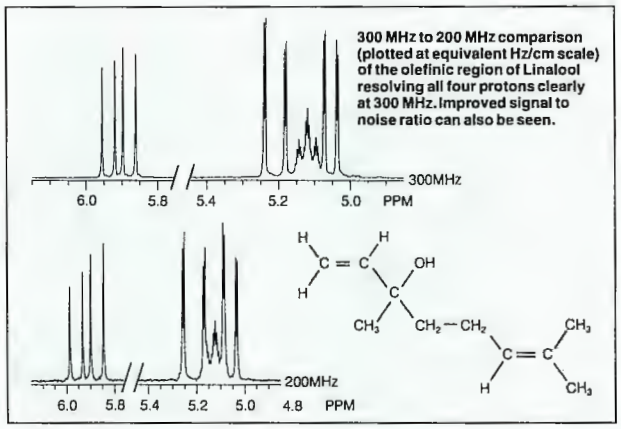

300 MHz to 200 MHz comparison (plotted at equivalent Hz/cm scale) of the olefinic region of Linalool resolving all four protons clearly at 300 MHz. Improved signal to noise ratio can also be seen.

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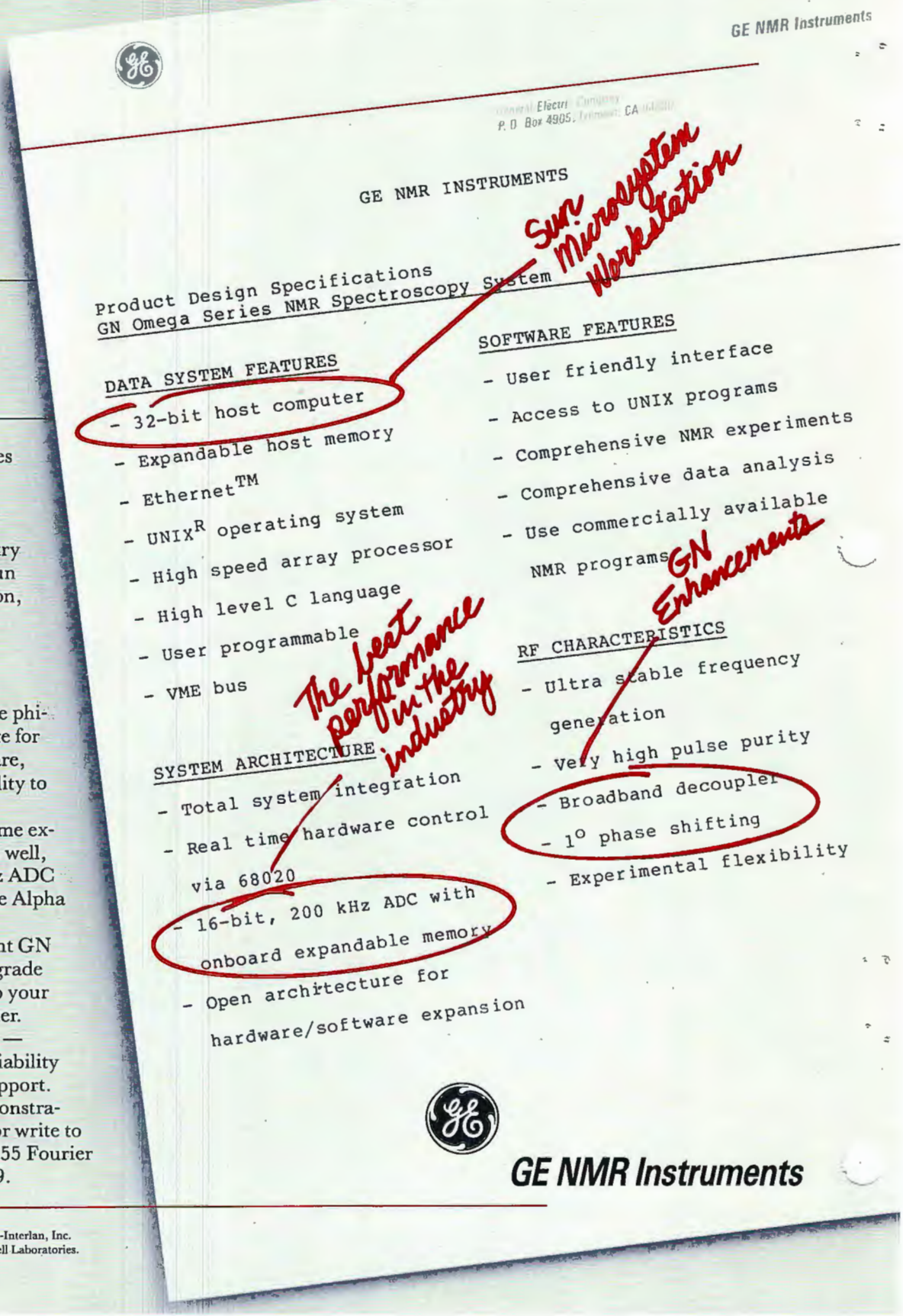

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713.749.3476

Department of Medicinal Chemistry and Pharmacognosy

X-Band MLEV Decoupling for Nicolet NT Spectrometers

May 3, 1988
(recd.5/12/88)

Dr. Bernard L. Shapiro, Editor / TAMUNMR Newsletter / 966 Elsinore Court / Palo Alto, CA 94303

Dear Barry:

We have noted with great interest your desire to save space in the TAMU NMR Newsletter. In lieu of sending nothing at all (a rather Draconian way to save space) we have elected instead to 1) use smaller type, 2) use smaller margins, 3) use smaller vertical spacing increments, and 4) do away with paragraph indentations. In this latter case, we have replaced indendations with paragraph symbols (¶). We are sure you will be delighted with these modifications and request all contributors to adopt them! ¶Now, we get into more serious things. To keep pace with developments in two-dimensional NMR spectroscopy, we have found it necessary to make frequent alterations on our NT-300 instrument. Recently, we described modifications(1) which allow the performance of Bax's long-range heteronuclear multiple bond chemical shift correlation experiment(2). While quite useful in and of itself, this still is limiting if you are unable to obtain a one-bond correlation experiment on the sample available. Ideally, you would like to be able to run a proton-detected direct heteronuclear correlation experiment as well. While the former does not require X-band decoupling, the latter does. We have thus modified our poor NT-300 still further to accomplish this task. ¶Quite simply, we have taken the output of the decoupler, nominally about 300.455 MHz, and have mixed this with the doubled 112.5 MHz output of a Fluke 160 frequency synthesizer to afford the requisite 75.455 MHz. The 75.455 MHz rf is then amplified using an ENI power amplifier and run to the probe. To clean up the output when the amplifier is not being used to actaully generate pulses, it was necessary to insert a pair of back-to-back diodes in line. A further cleanup is provided by a MiniCircuits BHP-150 filter in line ahead of a Janel 300 MHz narrow band preamplifier. ¶At this point, all well and good, but does it work? Well, the pulses off the system were calibrated using a 99%-13-C-enriched (in the 2-position) sample of sodium acetate using the pulse method of Bax(3) which gave a 39 microsecond 90° pulse at a power level of 10 J/s ("watts" to the uninitiated). (The ENI is capable of running at a much higher power output and is also equally capable of melting the solder on picofarad capacitors in our probe from past experience! However, this is sometimes to one's advantage in colder climates if the lab needs heating.) ¶The results obtained using MLEV16 decoupling of the carbon resonances are shown in Figure 2. At 7 kHz off resonance, there is still adequate decoupling of the heteronuclear coupling; but at 8 kHz--as you will note--we are sufficiently far off resonance to begin seeing residual couplings. ¶Saying big things in a small way we are

Sincerely yours,

Milt Larry Gary

Milton D. Johnston, Jr., Larry D. Sims, and Gary E. Martin

1. A. S. Zektzer, L. D. Sims, R. N. Castle, and G. E. Martin, Magn. Reson. Chem., **26**, 287 (1988).
2. A. Bax and M. F. Summers, J. Am. Chem. Soc., **108**, 2093 (1986).
3. A. Bax, J. Magn. Reson., **52**, 76 (1983).

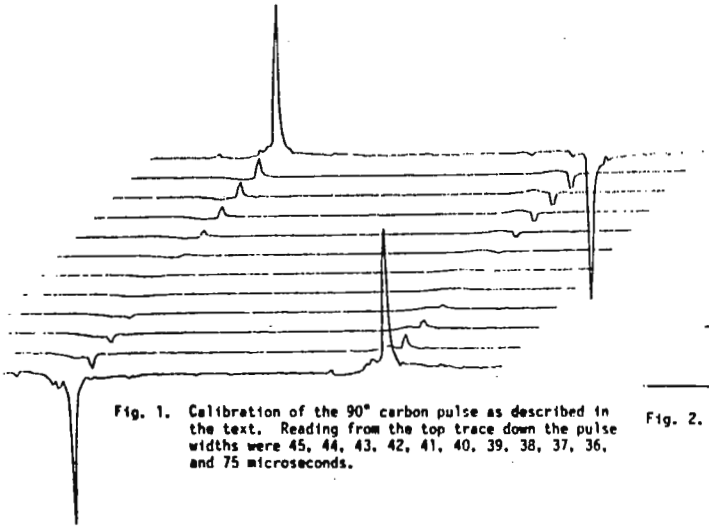

Fig. 1. Calibration of the 90° carbon pulse as described in the text. Reading from the top trace down the pulse widths were 45, 44, 43, 42, 41, 40, 39, 38, 37, 36, and 75 microseconds.

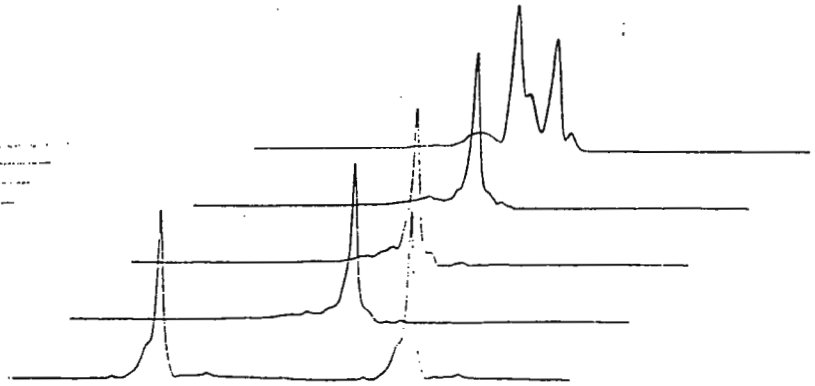

Fig. 2. Carbon decoupling via the MLEV16 sequence as described in the text. The bottom trace was recorded with the decoupler off. The next trace (going up) was with decoupling exactly on resonance. The final three traces are for offsets of 5, 7, and 8 kHz, respectively.

"If you face is dirty, wash it - don't cut your head off".(Shaw)

Please credit this contribution to Milt Johnston's Account. BLS

357-30

WESTERN RESEARCH INSTITUTE
P.O. Box 3395, University Station
Laramie, Wyoming 82071
(307) 721-2011

May 5, 1988
(received 5/11/88)

Professor Bernard L. Shapiro, Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

RE: ^{1}H CRAMPS NMR Spectra of Pyrolyzed Tar Sand Residues

Dear Barry:

In our quest to applied new NMR techniques as they become available to us to study fossil fuel materials, we made arrangements with the NMR Regional Center at CSU to have ^{1}H CRAMPS spectra run on several samples of tar sand residues obtained from the pyrolysis of native tar sand at three temperatures.

A modified Fischer Assay retorting method was used to produce tar sand residue samples nonisothermally at maximum temperatures of 280°, 380° and 440°C. The ^{1}H CRAMPS spectrum for each temperature is shown in Figure 1. The aromatic hydrogen are assigned to the broad band a ~7.0 ppm and the aliphatic hydrogen to the resonances at ~1.5 ppm. The resonance signal at about 5.0 ppm in the spectrum of the 440°C tar sand residue is assigned to hydrogens of interstitial water resulting from the mineral chert ($SiO_2 \cdot xH_2O$). This signal is also visible in the 280 and 380°C spectra.

The ^{1}H spectra at 280 and 380°C are similar to the ^{1}H CRAMPS spectrum of native tar sand. As the pyrolysis temperature is increased, the overall amount of organic residue on the surface of the sands decreases. However, the major change in ^{1}H spectrum of the tar sand residue at a pyrolysis temperature of 440°C is the greater loss of paraffinic hydrogens with regards to aromatic hydrogens.

Additional experiments are in progress and we hope to publish a full report in the near future. I would like to acknowledge Dr. Chuck Bronnimann who did the work to obtain the ^{1}H CRAMPS spectra.

Sincerely,

Dan

Daniel A. Netzel

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Spurious Outputs: −70dB

Phase Noise: −63dBc, (0-15KHz)
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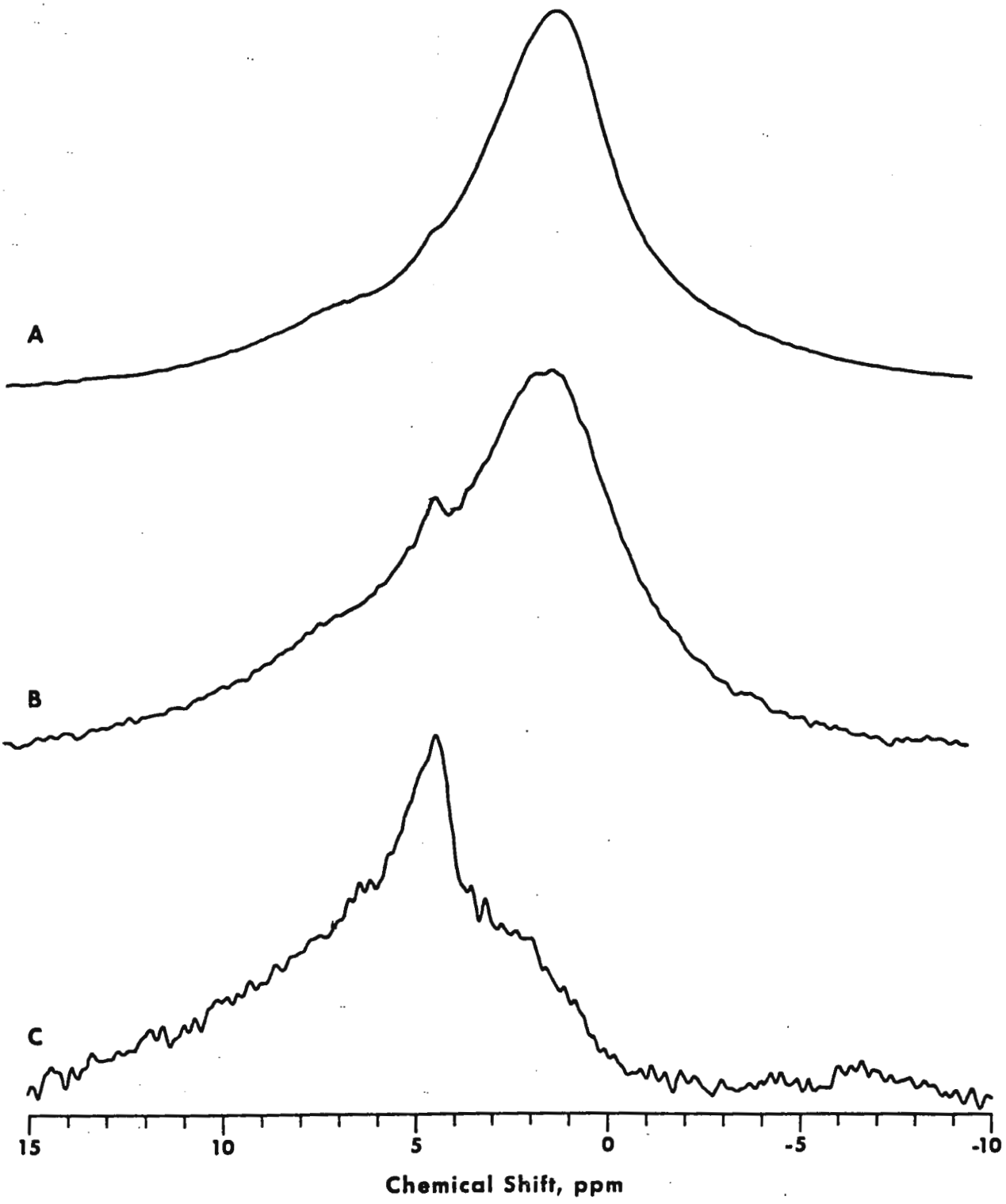

Figure 1 ^{1}H CRAMPS Spectra of Asphalt Ridge Tar Sand Residues from the Nonisothermal Pyrolysis of Native Tar Sands (A) 280°C, (B) 380°C, and (C) 440°C

Lawrence Livermore National Laboratory

May 3, 1988
(received 5/7/88)

Dr. Bernard L. Shapiro
TAMU NMR News Letter
966 Elsinore Court
Palo Alto, CA 94303

Re: ^{1}H NMR of Isotopically Labeled PhIP

Dear Barry,

One project of interest to our lab is to understand the synthesis mechanism of the mutagen 2-amino-1-methyl-6-phenylimidazole[4,5-6] pyridine (PhIP) produced in griddle-fried ground beef*.

PhIP

Dry heated binary mixtures of phenylalanine and creatine result in high yields of PhIP. Large amounts can also be produced if phenylalanine is replaced by β-phenylethylamine plus D-glucose. These facts aided studies with heavy-isotope-labeled precursors (^{15}N and ^{13}C).

Amounts of labeled material are usually in the 20-80 μgm range. The samples can readily be dissolved in 0.5 ml of acetone-d_6 in a 5 mm tube which makes homogeneity adjustments and maintaining a lock for relatively long periods relatively easy. However, we have had problems at the low concentration range in obtaining satisfactory spectra with our 200 MHz instrument. Decreasing the volume much in a 5 mm tube usually makes the homogeneity adjustments trying, while spherical μ-cells or capillaries positioned in a 5 mm NMR tube were difficult to deal with in a reproducible manner. We obtained the best spectra in a fairly reproducible way by using Wilmad concentric tubes containing a capillary tube at the bottom of the inner tube. Sample volumes of at least 50 μl are routinely used.

Labeled PhIP was synthesized from isotopically labeled phenylalanine or creatine. Creatine labeled with ^{13}C in the methyl position yields PhIP that exhibits a ^{1}H spectrum characterized by an N-Methyl doublet with $J^{1}_{^{13}C,H}$ = 139.6 Hz. Creatine labeled with ^{15}N in the N-methyl nitrogen position yields PhIP that exhibits a ^{1}H spectrum characterized by

*Project directed by Dr. R. T. Taylor, LLNL

an N-methyl doublet splitting with $J^2_{^{15}N,H}$ = 1.4 Hz. If phenylanine is labeled with ^{15}N the synthesized PhIP exhibits a ^1H spectrum with an aromatic 5-CH position doublet due to an adjacent ^{15}N heteroatom $J^2_{^{15}N,H}$ = 11.5 Hz. PhIP produced from phenylalanine labeled with a $^{13}CH_2$ group yields a ^1H spectrum containing an aromatic 5-CH proton doublet, $J^2_{^{13}C,H}$ = 7.6 Hz, due to an adjacent ^{13}C. No spin coupling between ^{13}C and the 7-CH proton is resolved, but the 2',6' ^1H resonance of the PhIP phenyl ring clearly broadens consistent with an unresolved 3-band coupling to a ^{13}C nucleus in the adjacent ring.

Sincerely,

James A. Happe

Please credit this to R. L. Ward's account.

1AH:pah/1728R

Scripps Clinic and Research Foundation
10666 North Torrey Pines Road
La Jolla, California 92037

Dr. Walter J. Chazin, MB-2
telephone: (619)-457-9860

Research Institute of Scripps Clinic
Department of Molecular Biology

May 18, 1988

I have an opening for a postdoctoral fellow in my laboratory to work on a unique project to study the structure of synthetic Holliday junctions, which are proposed intermediates for genetic recombination and DNA repair. The candidate will work at the interface between molecular biologists (directed by Dr. Fred Heffron) and physical biochemists (directed by myself) and will involve coordinating efforts in the two laboratories, a limited amount of oligonucleotide synthesis and purification, and extensive use of NMR spectroscopy and molecular graphics. Facilities include oligonucleotide synthesizers, four Bruker spectrometers (MSL 300, two AM 500s, AM 600), dedicated workstations, the department's network of CONVEX C1s, and the Scripps Institute CRAY XMP.

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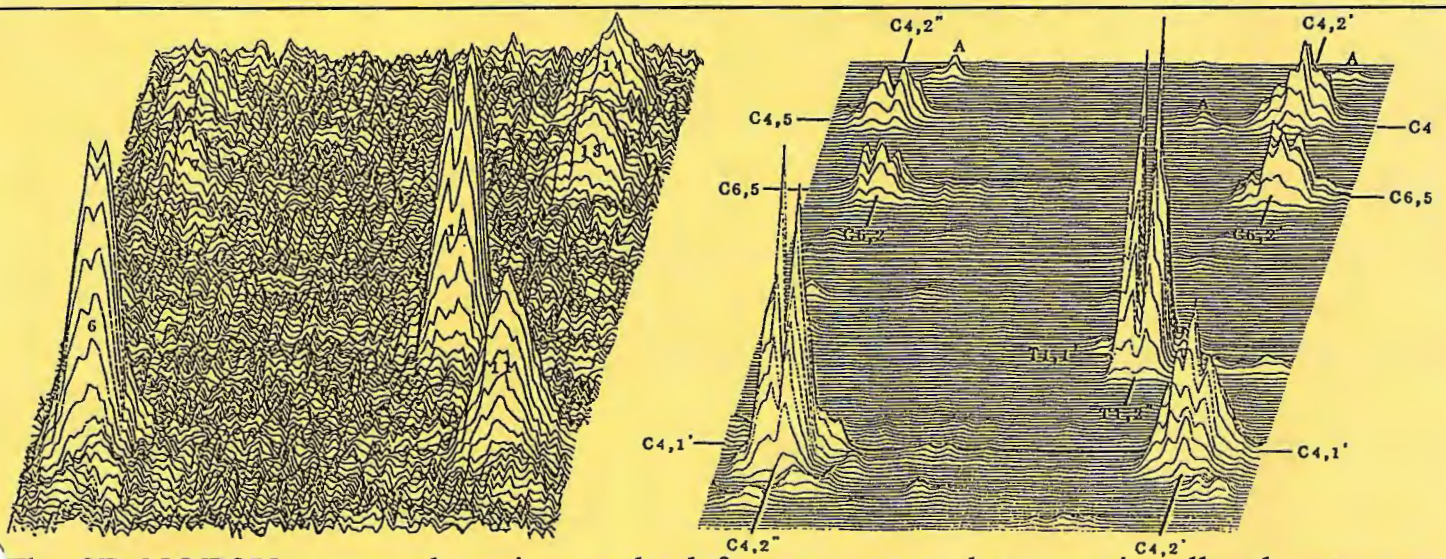

The 2D NOESY crosspeak region at the left was processed conventionally; the same region processed by 2D maximum likelihood deconvolution is shown at the right.

New Methods Research, Inc., 719 E. Genesee Street, Syracuse, New York 13210 (315) 424–0329

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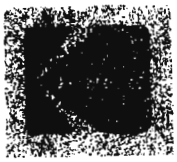


May 13, 1988 (received 5/16/88)

Professor Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Diffusion of Sodium in an Aggregated Surfactant; ^{23}Na NMR

Dear Dr. Shapiro:

While tidying up various loose ends recently, I came across some ^{23}Na NMR work that I did with Peter Kilpatrick[1] (Dept. Chem. Eng. NCSU). This work involves observing the diffusion of ^{23}Na in an aqueous two-phase environment by NMR. A double tail surfactant, sodium 4-(1-heptylnonyl)benzene sulfonate (SHBS), was used as the aggregated phase (lamella phase). The experiments involved a series of four counter ions; Uranyl acetate, Cesium acetate, Potassium acetate, and Ammonium acetate. The effects of temperature and the history of the surfactant were also investigated.

The ^{23}Na NMR spectra consisted of two overlapping peaks, that were decomposed into a broad peak ($\upsilon_{\frac{1}{2}}$=70Hz), corresponding to sodium in the aggregated phase, and a sharp peak ($\upsilon_{\frac{1}{2}}$=16Hz), corresponding to sodium in the isotropic phase, Figure 1. We have shown that these two peaks are due to two distinct chemical environments, and are not due to the phenomenon described by Alan Marshall[2]. Our evidence for this is 1) that the relative areas of the two peaks change with time, (from 70%/30% to 12%/88%), and 2) addition of shift reagent (Dysprosium(III) tripolyphosphate) moves the isotropic peak upfield, leaving the aggregated peak unaffected.

Our results indicate that the rate of exchange of sodium on addition of a counter ion, depends strongly on temperature, and on the size (and charge) of the counter ion, but only slightly on the initial relative concentrations of the two ions. However, the initial relative concentration of the two ions does appear to determine the final equilibrium concentration. Several rate curves are shown in Figure 2 for the Uranyl acetate/SHBS system at four different relative concentrations. At the present time we are still number crunching, and hope to have some fully crunched numbers in the not too distant future.

Sincerely

D Mark Naylor

D. Mark Naylor
Research Laboratories
P.O. Box 1972

Please credit to Doug Lowman's account.

[1]Kilpatrick, P.K., and Miller, W., J.Phys.Chem., 88, 1649(1984)
[2]Marshall, A.G., TAMU NMR Newsletter, 284, 35 (1982)

Figure 1.

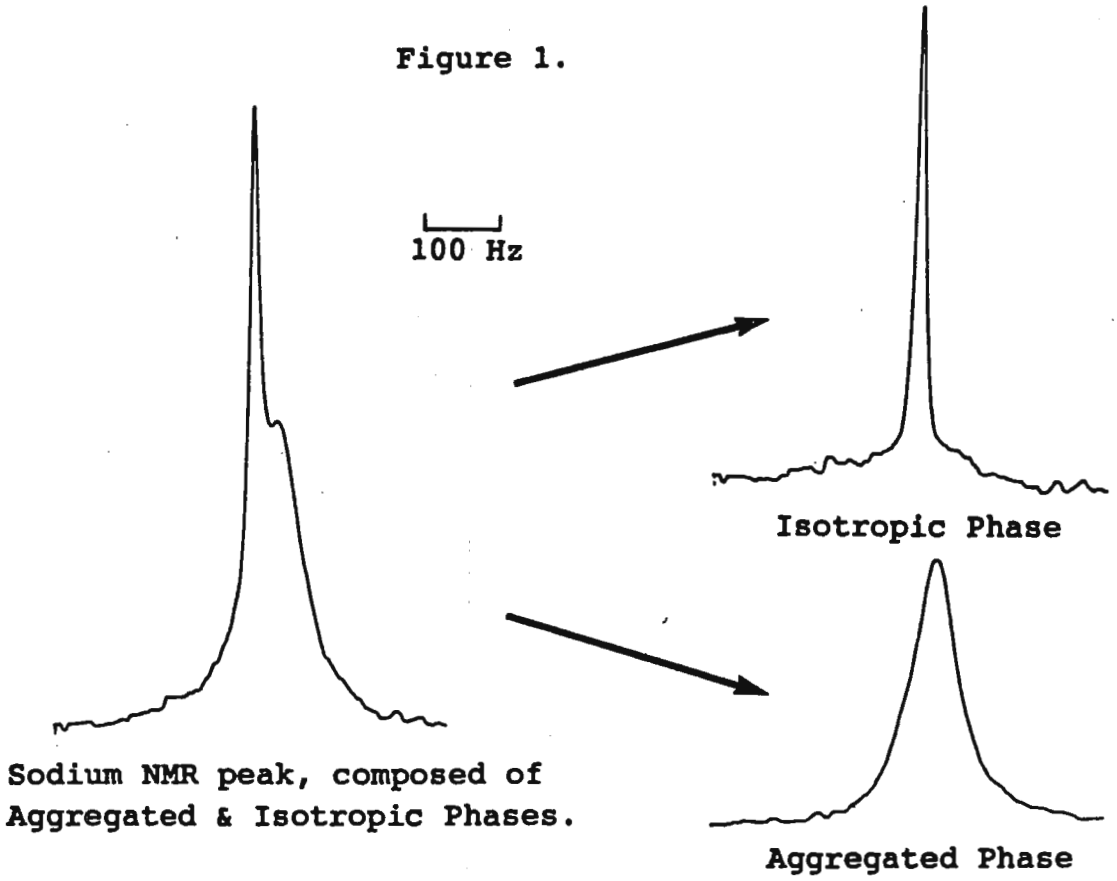
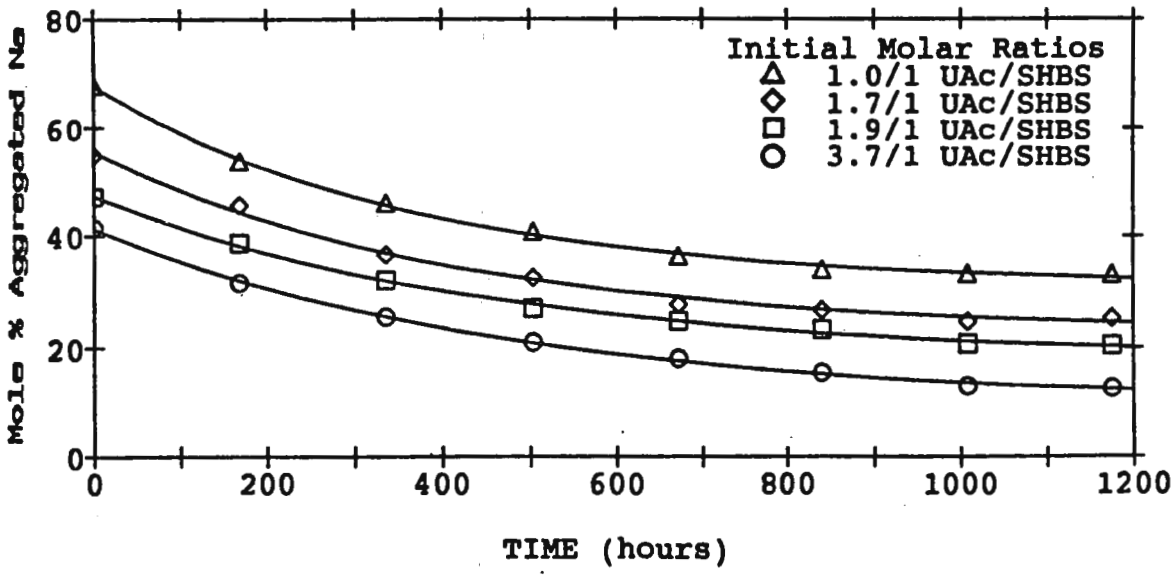


Figure 2. Diffusion of Na out of Aggregated Phase (RT, 0.05M)



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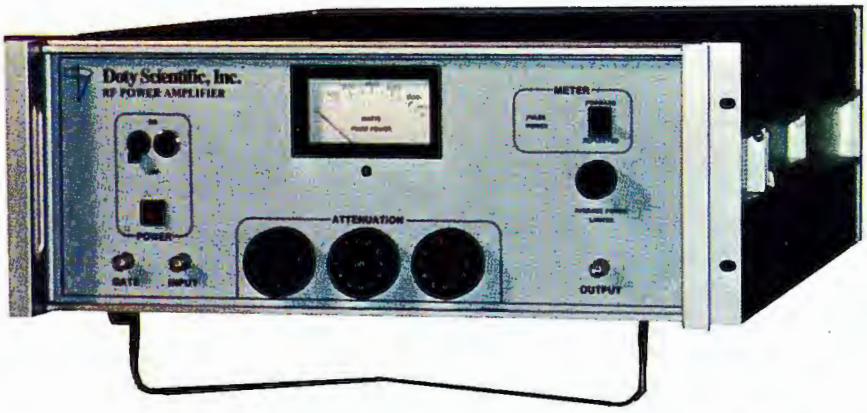

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500A	8-130	56	500	57	9,800
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Fall Time : less than 50ns to -70dB.
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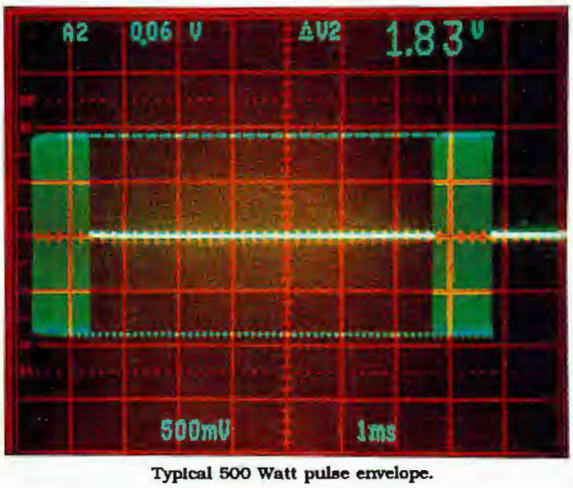
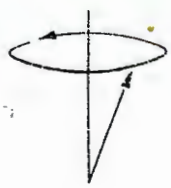


Typical 500 Watt pulse envelope.



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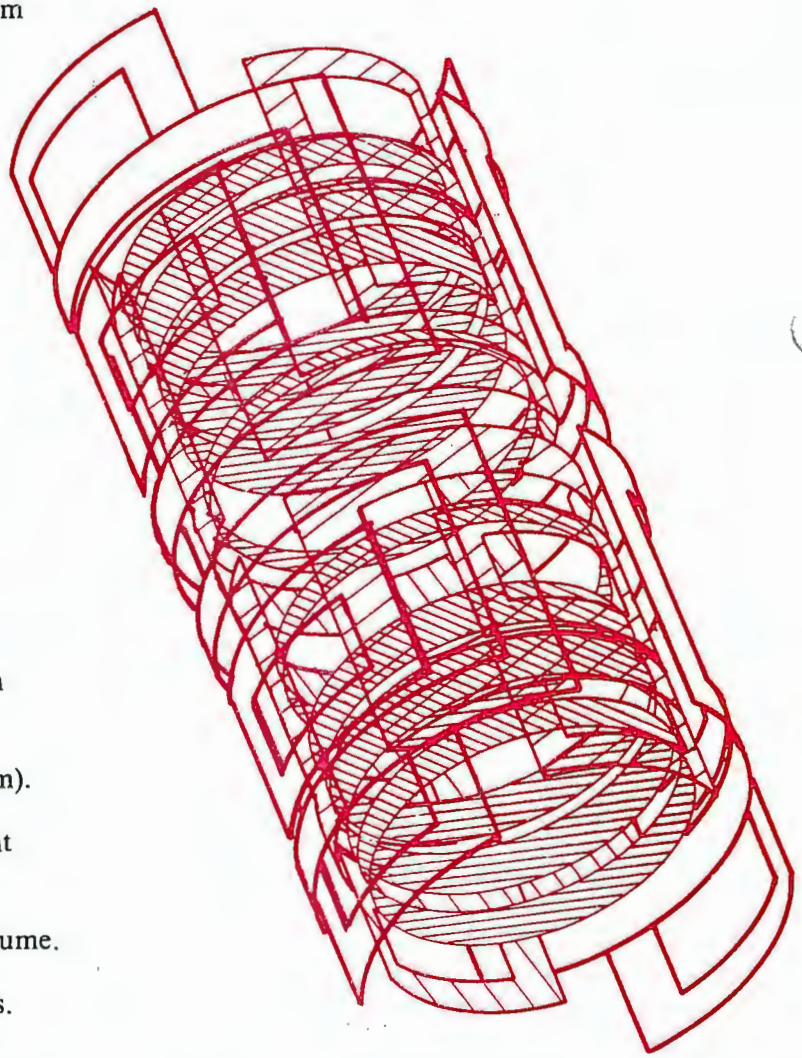

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DEPARTMENT OF CHEMISTRY, BOWNE HALL, SYRACUSE UNIVERSITY, SYRACUSE, N.Y. 13244-1200

Dr. Barry Shapiro
TAMU NMR Newsletter
966 Elsinore CT.
Palo Alto, CA 94303

11-May-1988
(received 5/17/88)

Dear Barry:

QUANTITATION AND CONTRAST ENHANCEMENT IN NOESY SPECTRA

Several months ago we sent you an early qualitative look at our attempts to improve the appearance of 2D NOESY spectra. We now have some quantitative results to share with your readers. The data shown is from a 400 ms NOESY spectrum of 13mM $[d(TAGCGCTA)]_2$ obtained in D_2O on our GN-500 by Steve LaPlante and Marc Delsuc (2k x 512 x 2 zero-filled to 2k x 2kx 2, SW = 4310 Hz, cosine bell apodization, hypercomplex pure absorption, not symmetrized). A 256 x 256 region below the diagonal containing H1' & H5 - H2' & H2" cross-peaks (see Fig. 1) was extracted along with the corresponding region above the diagonal. These two regions were contrast enhanced using Feng Ni's DECO2D program which performs optimized spectral deconvolution using a constrained maximum likelihood method. With 7 Hz linewidth reduction in f1 and f2, and 75 iterations specified as the input parameters, each DECO2D run took about 25 minutes on a VAX 8800 (Ultrix; this would take about 10 minutes on Sun-4 workstation).

One question is whether the program conserves the ratios of crosspeak volumes. Shown in Fig. 2 are histograms indicating the relative volumes of the 14 crosspeak domains noted in Fig. 1 (the volume of peak 2 is taken as 1.00). The open bars show volumes prior to enhancement; after enhancement the volumes are shown by hatched bars. We see that cross-peak volumes are superbly conserved over a 10-fold dynamic range as in this example. The deviations between the enhanced and unenhanced volumes are so small that they cannot affect distance determinations. Further, the average deviation in volume between corresponding peaks on both sides of the diagonal is 12% before, and 7% after enhancement. An apodization such as the cosine-bell, causes no large distortions in the relative peak volumes, and is okay to use prior to enhancement. It would not be a good idea to use other shifted sine bells or Gaussians since DECO2D is currently designed for Lorentzian lineshapes. As with any deconvolution method, distortions occur when the dynamic range is very large (as in regions that include the diagonal).

We don't need to conjure up maximum entropy reconstructions of late, distinguished scientists to prove once again that you can't get something from nothing -- any feature that is clear in the contrast enhanced version of a spectrum can also be recognized, however weakly, upon careful examination of the unenhanced spectrum. This is demonstrated with the small peaks (7, 8, 13 & 14) and by examining the fine structure on the peaks shown in the stacked plots of Figs. 3 & 4, which show the boxed region of Fig. 1. As expected, some noise peaks get enhanced, but most do not correlate on both sides of the diagonal and are easily excluded (e.g., the three small peaks labeled "A" at the top of Fig. 4). Likewise in unsymmetrized spectra, noise ridges in f1 and f2 are easily recognized and it takes no special talent to realize when they may cause a problem. The fine structure on the enhanced peaks is consistent from one slice to the next and between peaks at the same frequency (e.g., compare the two crosspeaks involving C4,2" as well as the two C4,2' peaks). With $[d(TAGCGCTA)]_2$, the enhanced NOESY spectra may be sufficient to obtain deoxyribose coupling constants, without the need to measure COSY spectra.

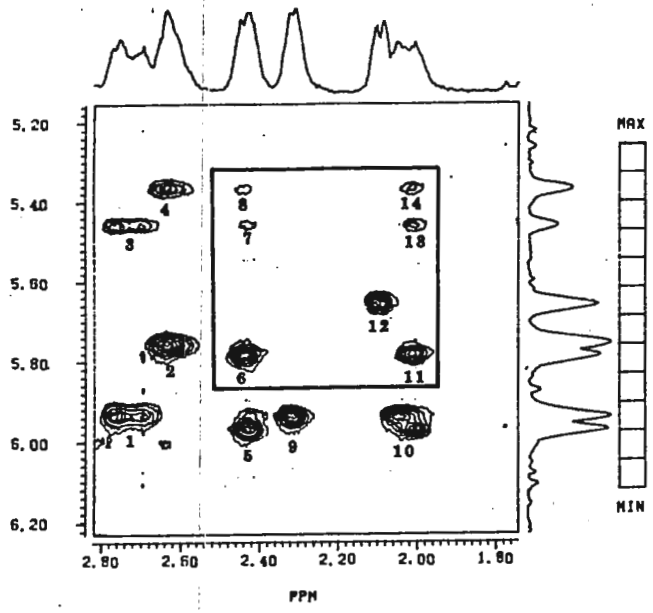
Sincerely,

Karl D. Bishop
Research Assistant

Philip N. Borer
Associate Director

George C. Levy
Science & Technology Professor

Figure 1



T1-A2-G3-C4-G5-C6-T7-A8
• • • • • • • •
A8-T7-C6-G5-C4-G3-A2-T1

Figure 2

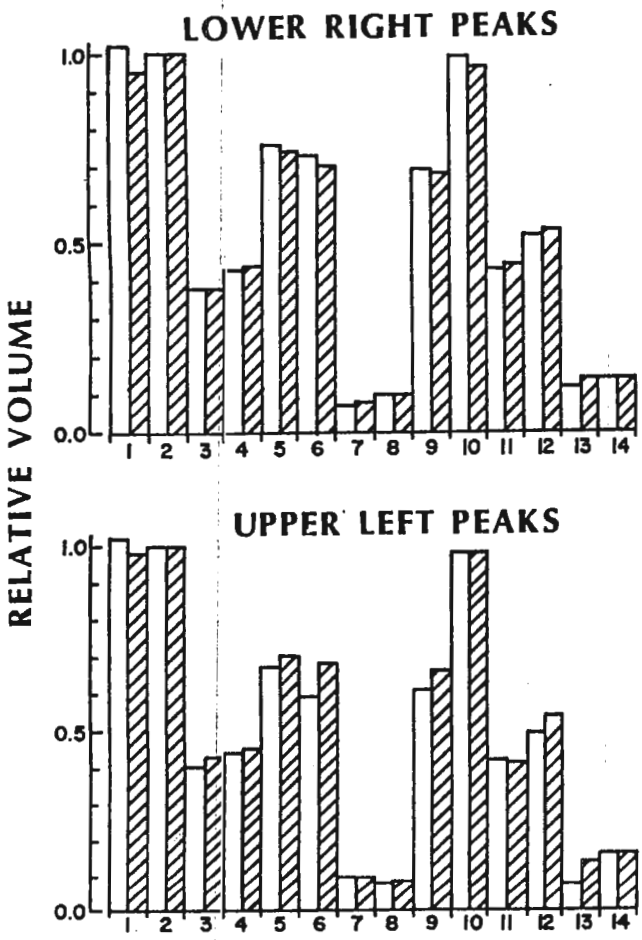


Figure 3

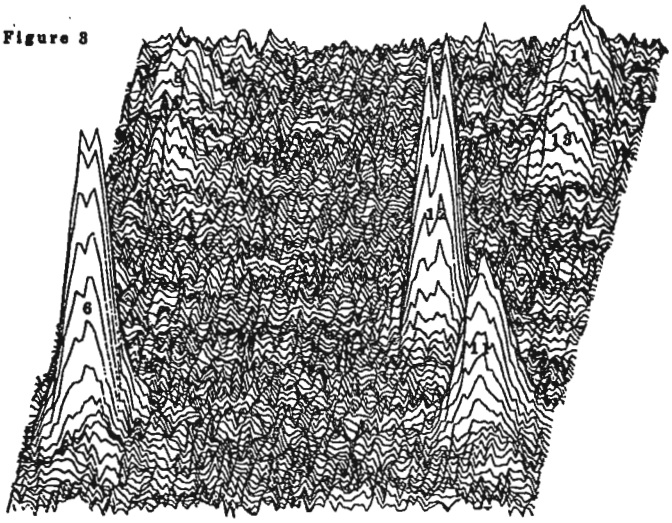
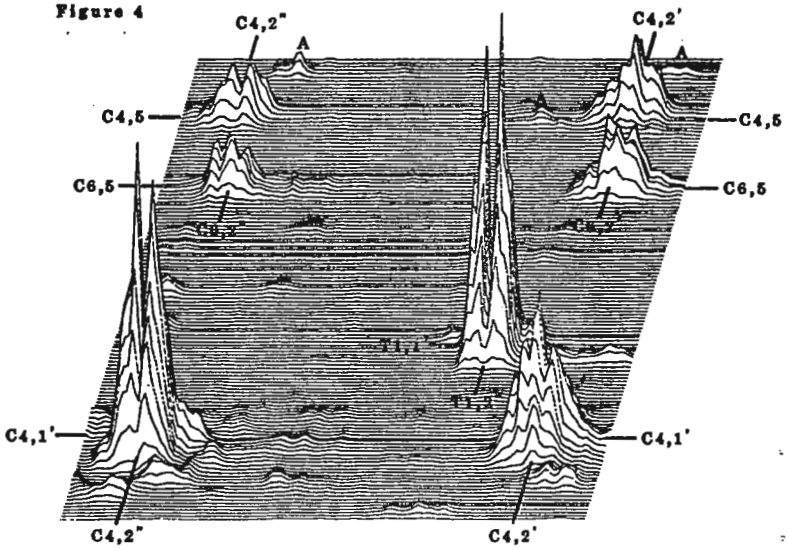


Figure 4



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9 May 1988 (received 5/16/88)

Dr Bernard L Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto,
California 94303
USA

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Dear Barry

Jolted into action after your last pink letter, I thought I would mention some work carried out recently during my association with Queen's University, Belfast as Visiting Professor. By some elegant 1,3-dipolar addition chemistry Harriet Ardill, a Ph.D student of Professor Ron Grigg made, among other interesting compounds, the eight-membered ring (I). Although the x-ray structure had been determined[1] showing an irregular tub conformation for (I), the ^1H nmr spectrum at ambient temperature was unusual, in that the olefinic proton multiplets and the methyl ester peaks were sharp whereas the 3 ring CH_2 groups appeared as very broad indistinguishable peaks. This suggested slow ring inversion between mirror image forms. All was revealed at 233°K, at which temperature all six protons of the $-CH_2\ CH_2\ CH_2-$ fragment were clearly resolved as individual multiplets (Figure), assigned and analysed to determine all ten vicinal coupling constants (including the $= CH.CH_2$) fragment (Table).

Using the torsion angles from the x-ray structure and a simple Karplus relationship the ^3J values are very much as expected, and we confirm that the irregular tub conformation is also that seen at low temperature in solution. At higher temperatures the ring flips to its mirror image form, the energy barrier $\Delta G^{\ddagger}$ being 13.0 $\pm$ 0.5Kcal/mole.

At the lowest temperature examined, about 10% of another conformation is visible in the ^1H nmr, with different olefinic proton shifts. As the nitrogen appears to be planar in the crystal, this may well reflect partial double bond character in the side chain N -- CH = bond, and consequent slow Z/E isomerism.

Previous work by Anet on cylocta-1,3-diene using ^{13}C nmr spectroscopy suggested that interconversion is occurring between two forms, a twist boat and a twist boat-chair, with somewhat lower barriers ($\Delta G^{\ddagger}$ 7.1 and 9.1Kcal/mol)[2]. Perhaps the introduction of the nitrogen atom in (I) and the side chain substituents is responsible for the differences we observe.

I hope this contribution keeps us solvent for a while.

Yours sincerely,

Tom Ian

W A Thomas I W A Whitcombe

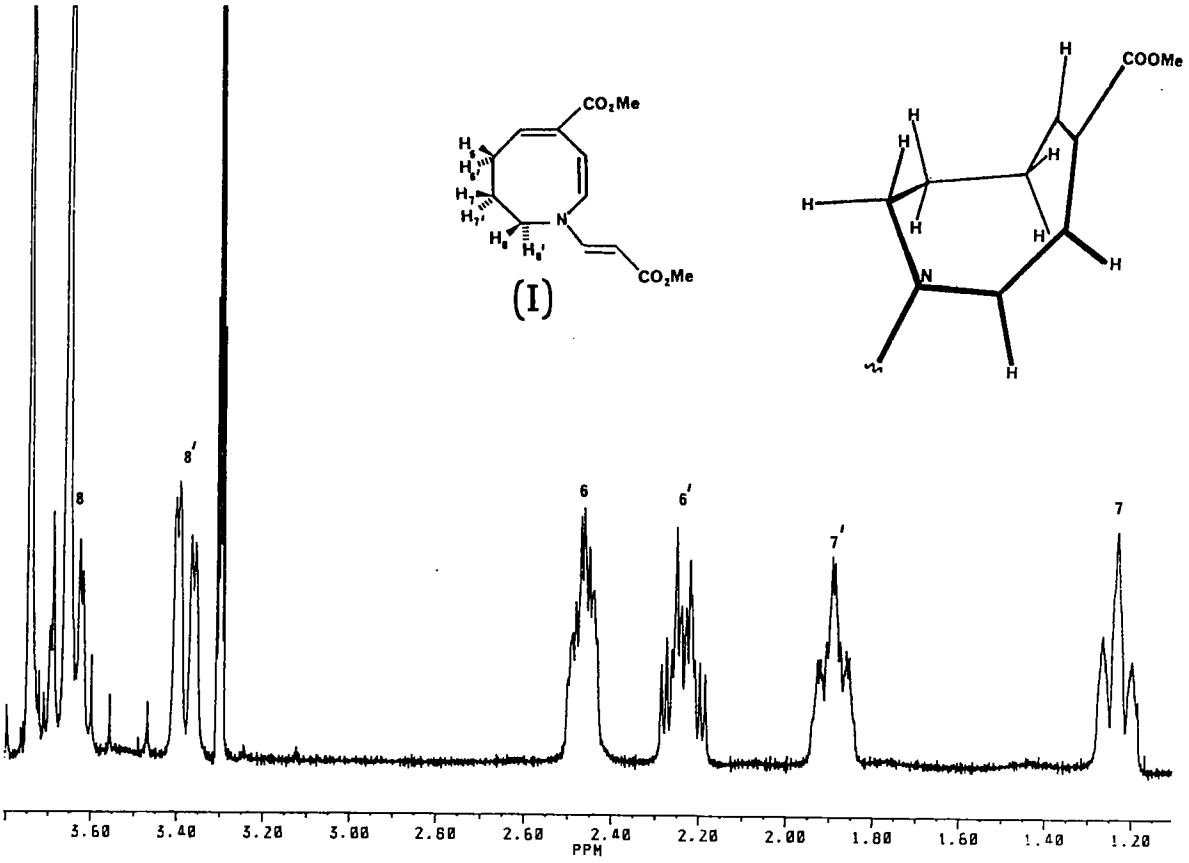

Figure: The ^1H spectrum in CD_3OD at 233°K showing the CH_2 multiplets.

Table Observed and Calculated Vicinal Coupling Constants for (I) Assuming the Crystal Conformation

Coupling Protons	ø[a]	$Cos^2ø$	Calc ^3J[b]	Obs ^3J
H_7H_8	-53.1	0.36	4.7	3.1
H_7,H_8	185.5	0.99	12.9	13.2
$H_7H_{8'}$	47.4	0.46	6.0	3.9[c]
$H_7,H_{8'}$	-74.1	0.08	1.0	<1.5
H_6H_7	-52.6	0.37	4.8	~3.0
H_6,H_7	184.5	0.99	12.9	12.4
$H_6H_{7'}$	64.0	0.19	2.5	2.3
$H_6,H_{7'}$	-58.9	0.27	3.5	4.8
H_5H_6	35.7	0.66	8.6	7.9
$H_5H_{6'}$	145,1	0.69	9.0	9.8

(a) Torsion angle

(b) Assuming $^3J_{max} \simeq 13.0$

(c) This value is reduced as it is trans to the electronegative nitrogen atom.

1. H. Ardill et al, J.C.S Chem. Comm. 1987, 1296
2. F.A.L. Anet and Y. Yavari, Tetrahedron Letters 1975, 1567

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May 20, 1988
(received 5/20/88)

Dr. Bernard L. Shapiro
TAMU NMR News Letter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry:

RE: Improvement in RF Phase and Amplitude Stability of NT-360WB

Research at Du Pont has been increasingly directed toward 2D NMR in biological systems. Sensitivity in 2D experiments is determined not only by signal-to-(thermal)-noise but also by long-term instabilities which contribute to t_1 noise. Particularly important in the observe channel are the phase and amplitude stability of the receiver and transmitter.

Since we are in the process of evaluating new higher field instrumentation, we used slight variants(!) of tests published by Varian (*Varian Instruments at Work*, March 1987, NMR-31) to measure various instrument RF stabilities and compare these with our eight-year old NT-360WB. The tests utilize a paramagnetically doped (0.1 mg/ml $GdCl_3$), 5% H_2O, sample thermostatted at 30°, and not spun. The 90° pulse test collects 32 single-transient experiments to determine the precision and reproducibility of the signal amplitude (magnitude calculation). Analysis of the results is statistically more reliable with 32 data (cf. 10 or so). The 1µs test is identical except it uses a smaller tip angle. The 13° test is two $90°_x$ pulses delivered 1 msec apart 37 Hz off resonance, and measures the phase jitter during typical 2D evolution times by converting phase to amplitude error (again 32 experiments). Table I shows that more modern instruments do indeed deliver better RF stability than the NT-360.

After some head scratching as to the source of the RF instabilities, we hypothesized there were two primary causes: multiplying the 10 MHz master clock to 600 MHz, and frequency impurities in the transmitter at non-linear amplification stages. To test these theories we modified the receiver to bypass the 588 MHz IF stage, thereby eliminating the 600 MHz signal in the receiver. This produced marked improvements in the 90° amplitude stability test, a result which we attribute to improved mixing in the receiver. The transmitter was then filtered before and after the Class C power amplifier. Marked improvements

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David A. Wright has been active in the NMR field since 1968, and a designer of probes since 1971. He received his doctorate in Physical Chemistry at Michigan State University in 1974. After several years as a postdoc, he joined the staff at the University of Illinois as a spectroscopist, where he designed and built NMR instrumentation. He was co-founder of Probe Systems Inc., where he designed numerous solids and cp/mas probes. In 1984 he joined GE-NMR Instruments, where he held the position of Engineering Manager, Probes and Coils. In addition to managing, he personally designed several of the more successful probes, including the GN-500 5mm 1H UHS probe, the GN-500 RPT probe, and the CSI/2T 6" imaging coil.

Woodrow W. Conover has been using and designing NMR equipment since 1969. He received his doctorate in Organic Chemistry in 1973 and did 2 years postdoctral studies at The University of Chicago doing ^{13}C NMR studies. He was Operations Manager for the NIH National Resource at Stanford University for 3 years where he was involved in early development of Correlation and 2DFT NMR, redesigning, improving the facility instrumentation to be broadbanded and capable of state of the art NMR experiments. In 1978 he joined Nicolet to help develop new high field instrumentation and probes. During his tenure he participated in applications, engineering, manufacturing and marketing functions as well as managing both the engineering and manufacturing operations. He managed the all engineering efforts for GE NMR Instruments until formation of FMR in 1988.

Product List

^{1}H Observe Unit for Nicolet NT Series Spectrometers

A ^{1}H Observe Unit which is user and software transparent for ^{1}H spectrometer operation when replacing the Nicolet 5-500 MHz Broadband Observe Unit. The unit is specifically designed to provide *today's* state of the art receiver and transmitter phase and amplitude stability. This high level of stability is necessary for the demanding 2DFT experiment. This upgrade provides a 100 milliwatt pulse to the existing power amplifier and an 11.25 MHz IF output to the existing spectrometer control unit utilizing the existing preamp or an optional proton optimized preamp.

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^{1}H Observe Unit.

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sample	^{1}H EB sens	^{1}H p(90)	γH_3 (15N)	γH_3 (13C)
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5,10,12,15,20mm Broadband probes

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30 cm	85MHz	400	1 kW

^{2}H wideline probe

We have extensive experience in extracting the highest performance for this type of experiment. For each bore size we give careful consideration to optimizing pulse power, recovery time, p(90), and sensitivity. Solenoid coil with diameters from 1mm to 25mm, depending on probe diameter. Standard v/t is 5-60 C; extended v/t range of -170 - +100, or 20 - +300 is also available. Example:

size	frequency	p(90)	t_r	power
5 mm	76 MHz	2.8 μs	15μs	700W

were observed in the 13° test, presumably because phase jitter is related to the spectral purity of the transmitter signal. The results before and after the modifications are shown in Table I.

An additional benefit of an 80% increase in ^1H S/N was also observed due to better mixer driving. Overall the NT-360's utility for more demanding 2DFT experiments is improved. These results also indicate that the useful life of an old instrument has been extended. We anticipate that the 360 will now be used for many of the preliminary experiments before further study on our higher field instruments.

Please credit Don Bly's account for this contribution.

Peter Domaille
Du Pont

Chris Roe
Du Pont

Woody Conover
Fremont Magnetic
Resonance

Table I

Test	Typical Industry	NT-360 Before	NT-360 After
90° pulse	0.05*	0.2	0.07
1 usec pulse	0.4	3	0.6
13° test	0.8	3	0.9

* Numbers represent 1 standard deviation as a % of signal amplitude.

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SUNY Stony Brook
Stony Brook, NY 11974-3400
[516] 632-7994

May 18, 1988
(received 5/20/88)

Professor Bernard L. Shapiro
Editor, TAMU NMR Newsletter
California somewhere.

Dear Barry,

Having been persuaded by the Springer group to do our part to keep the Stony Brook subscription alive, we would like to report on our attempts, using solid-state NMR, to adjudicate a dispute between crystallographers. Solution NMR is of course a currently fashionable method of obtaining structures of small bits of biological stuff and ensuring crystallographic honesty in the field of molecular biology; our work concerns somewhat simpler and more inert materials; namely, the nitrate salts of several metals.

An early X-ray structure of silver nitrate gave a centrosymmetric structure with eight molecules per unit cell, related by two-fold x, y and z screw axes and pairwise by the center of symmetry. The nitrates of Ca, Sr, Ba and Pb, which are isomorphous with each other, gave in early studies a different structure but with the same point symmetry elements. More recent and sophisticated (?) x-ray and neutron diffraction analyses have in each of these compounds removed the center of symmetry and replaced the eight symmetry-related molecules with two sets of four molecules, each set being unrelated to the other by any exact symmetry operation. On the other hand, other physical techniques sensitive to the presence or absence of a center of symmetry (e.g. second harmonic generation, piezoelectric and electro-optic measurements) have tended to come down in favor of the earlier, simpler structures, precipitating a fairly heated debate in the literature.

Our contribution to the discussion consists of a series of ^{14}N single crystal NMR studies of the nitrate anion of several of these compounds. The ^{14}N spectrum at the frequency of our newly completed home-built 6 Tesla spectrometer is of course dominated by the electric quadrupolar interaction, which, like other nuclear spin interactions, is invariant to a center of symmetry. It, however, can very sensitively distinguish between molecules which differ even slightly in either their environment or their orientation. It is thus ideal for settling disputes about the existence or absence of a center of symmetry.

A ^{14}N spectrum of a 600 mg single crystal of $PbNO_3$ is shown on the next page. The spectrum isn't in any way typical; a rather special orientation of the crystal had to be chosen in order to get all the lines within the bandwidth of the spectrometer. Because of the fairly large quadrupole coupling, most of the time our spectra must in fact be taken piecewise, with much laborious retuning of probes between measurements. It is clear that there are 8 lines, two from each of the NMR-inequivalent spin-1 nitrogens in the unit cell. An analysis of the rotation plots (next page) shows that the four quadrupolar splittings arise from the four screw-axis related molecules. No evidence of additional NMR inequivalence is detected; in particular there is no sign of an additional set of eight lines with a different QCC as is predicted by the later diffraction results. The existence of four, rather than eight, distinct quadrupolar splittings, at this and at all other orientations examined, means that the early centrosymmetric structure is the correct one. It's simply a question of arithmetic.

We can put limits on how sensitively we can detect NMR-inequivalent nitrate anions in these compounds. The ^{14}N-NMR linewidth in our samples is typically 100 Hz, while the quadrupolar coupling constant for $PbNO_3$ is 0.54 MHz, with a maximum quadrupolar splitting of 0.81 MHz. We could therefore potentially detect differences in the QCC of putative inequivalent nitrate anions to about 1 part in 8000, or differences in the orientation of their unique axis of less than 0.01 degree. No such differences are observed.

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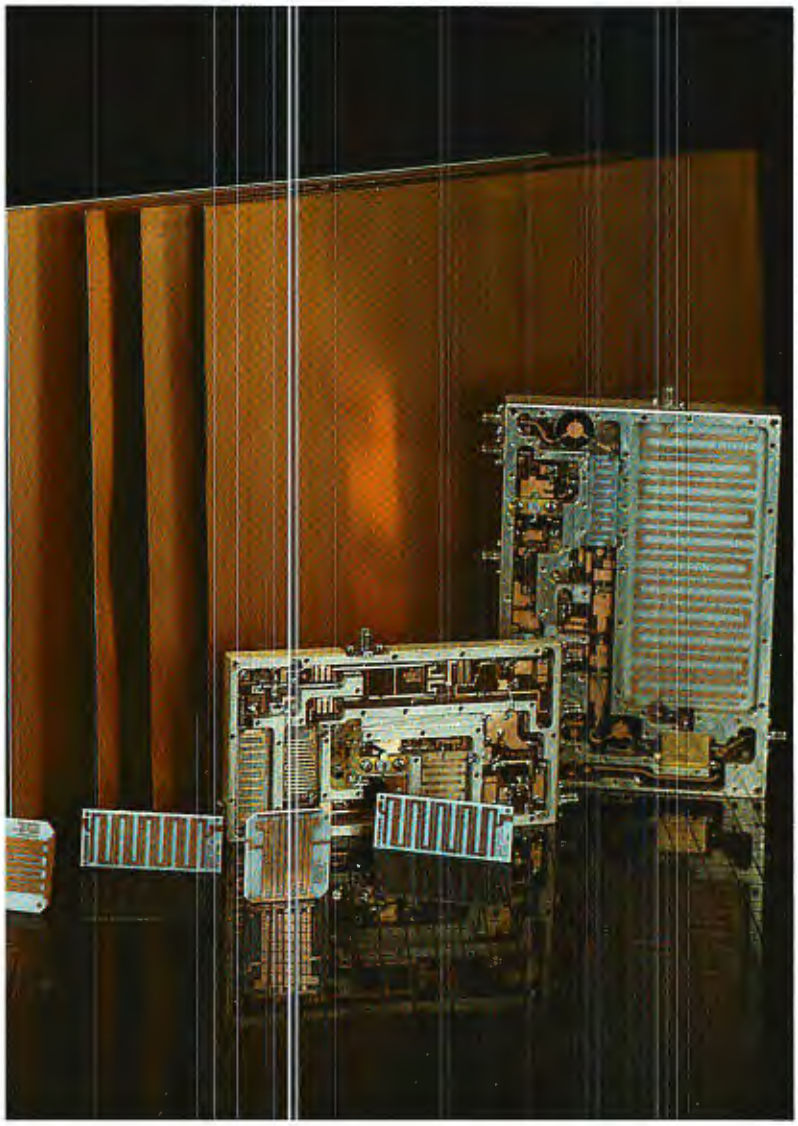
Material Technology for NMR Product Applications



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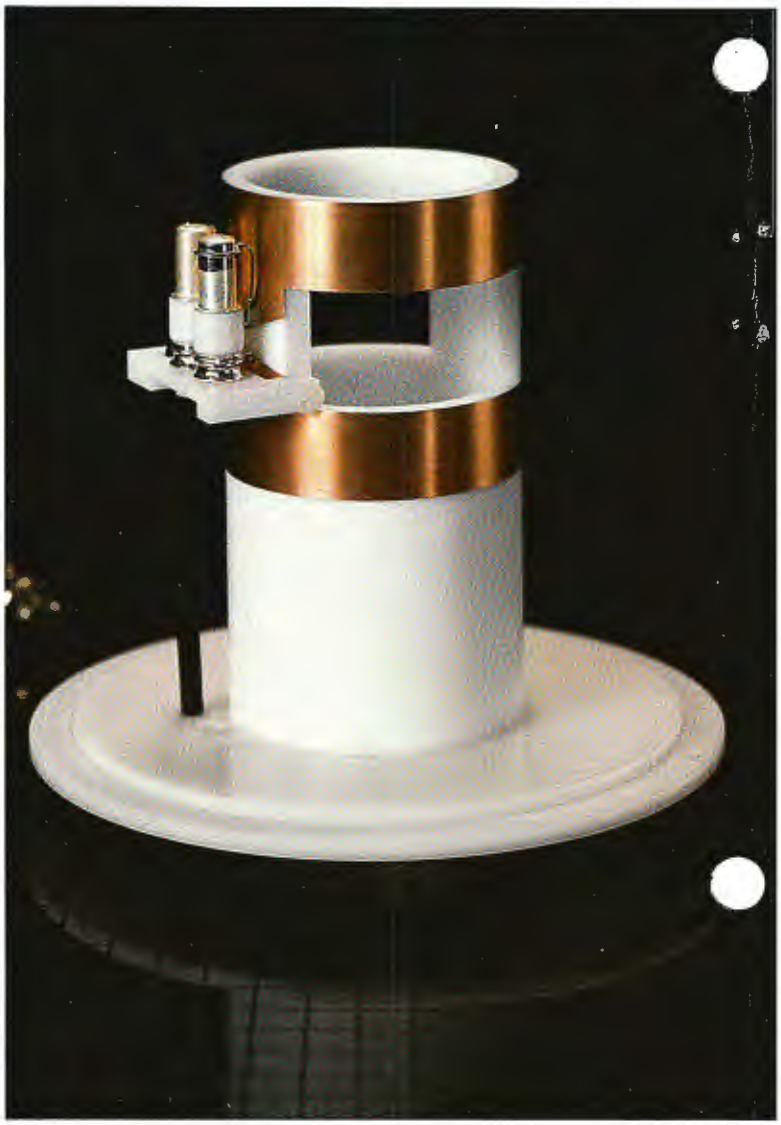

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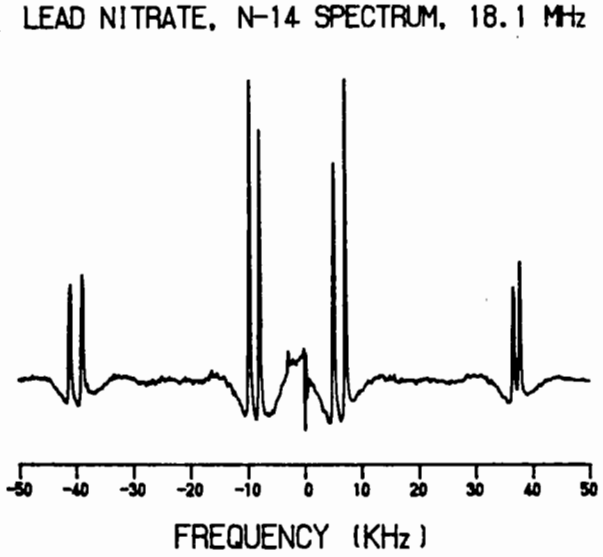

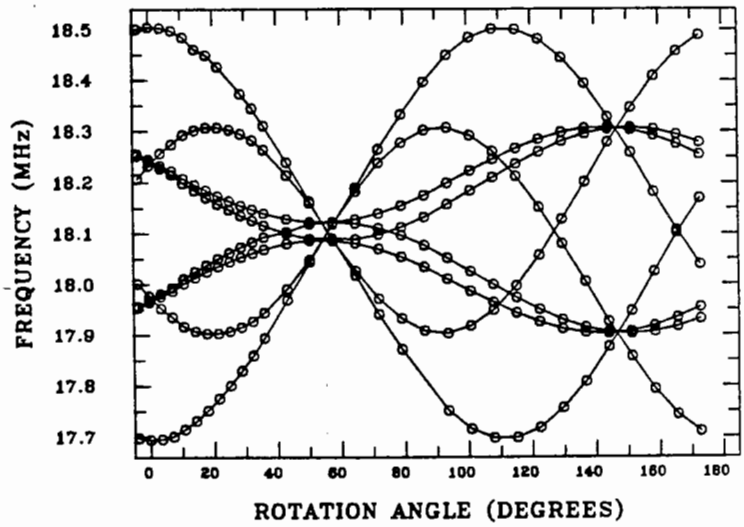

Incidentally, for those who are concerned with these matters, the QCCs we observe in these compounds are uniformly much smaller than those for the only previously reported nitrate, $NaNO_3$. The latter may be quite atypical, and the lower values we obtain may be more appropriate in calculating solution T_1s, for example. The chemical shielding anisotropies, on the other hand, are about 200 ppm; quite consistent with earlier literature values for ammonium nitrate obtained using the ^{15}N isotope. The T_1s are fairly long, typically 30 – 60 s; on the other hand, usually only a few (4–8) transients need be collected to give good signal-to-noise.

As Haeberlen suggested some years ago, NMR may in fact be the most accurate method available for obtaining orientational information from all sorts of materials. This work shows that all one needs to decide authoritatively between crystal structures which otherwise may be almost impossible to distinguish, is a NMR spectrometer and the ability to count. Crystallographers (one of them may pick this issue up by mistake) take note!

Sincerely,

Pei Tang, Rudy Santos, Wei-Jyun Chien,
Graduate Research Assistants

Steven Kwan,
Undergraduate Research Assistant

Gerard S. Harbison,
Assistant Professor of Chemistry

GSH/gsh

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U.S.A.

Compensated ROESY on an AM 600

Zürich, May 18, 1988
(received 5/21/88)

Dear Prof. Shapiro,

Recently, Griesinger and Ernst proposed an elegant method for partial compensation of off-resonance effects in ROESY by the use of a high power $\pi/2$-pulse both before and after the mixing spin lock which is applied with reduced power.[1] However, our Bruker AM 600, delivered last year, does not yet have the fast power switching capabilities of today's Bruker decouplers. The conventional programming with S1, S2, etc. is useless in this case, because power switching times of 400 μs are by far too long. Here we would like to communicate an alternative approach which does not require a fast power switch of the decoupler. The concept is simply to use the transmitter for the high power pulses and the decoupler for the mixing spin lock. F1 is used as the frequency source for both the transmitter and the decoupler to provide the necessary phase coherence between F1 and F2. Before entering the cascode, the transmitter and decoupler channels are recombined with a power combiner. With this setup the resulting 90 degree pulse width of the transmitter was 10 μs. In the Microprogram the phases of the decoupler pulses have to be specified after a delay before the pulse. Phases of the transmitter are entered as usual after the transmitter pulse. The relative phase difference between decoupler and transmitter channel must be determined before the experiment and is then accounted for in the phase program of the decoupler phase. In the microprogram given below the decoupler phase had to be adjusted by 100 degrees to correspond to phase 0 of the transmitter. A DANTE pulse train was used in the preparation period to saturate the water signal.

Please credit this contribution to the account of K. Wüthrich.

Best regards

G. Otting

1) C. Griesinger and R.R. Ernst, J. Magn. Reson. 75, 261-271 (1987).

```
1 ZE
2 D4 S2                  ;S2=25H, D4=0.4MS
3 (D5 PH5 P5):D          ;P5=5US, D5=15US
  L1 TO 3 TIMES 10
  L5 TO 3 TIMES UPR      ;L5=5000 FOR 1 SECOND OF H2O SATURATION
  D4 S1                  ;S1=3H
  P1 PH1
  DO
  P1 PH2
  (D2 PH3 P3 D2):D       ;P3= CW SPIN LOCK , D2=3μs
  P1 PH2
  GO=2 PH0
  WR #1
  IF #1
  IP1
  IN=6
EXIT

PH5=0
PH1=0 2 1 3 2 0 3 1
PH2=0 0 1 1 2 2 3 3
PH3=(360) 100 100 190 190 280 280  10  10
PH0=R0 R2 R1 R3 R2 R0 R3 R1
```


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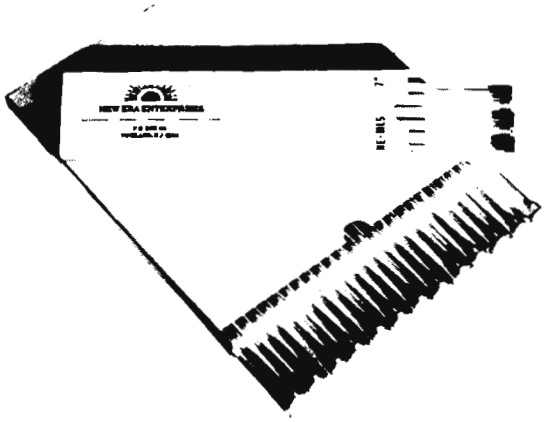

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TEXAS A&M UNIVERSITY
NMR NEWSLETTER

No. 357
June 1988

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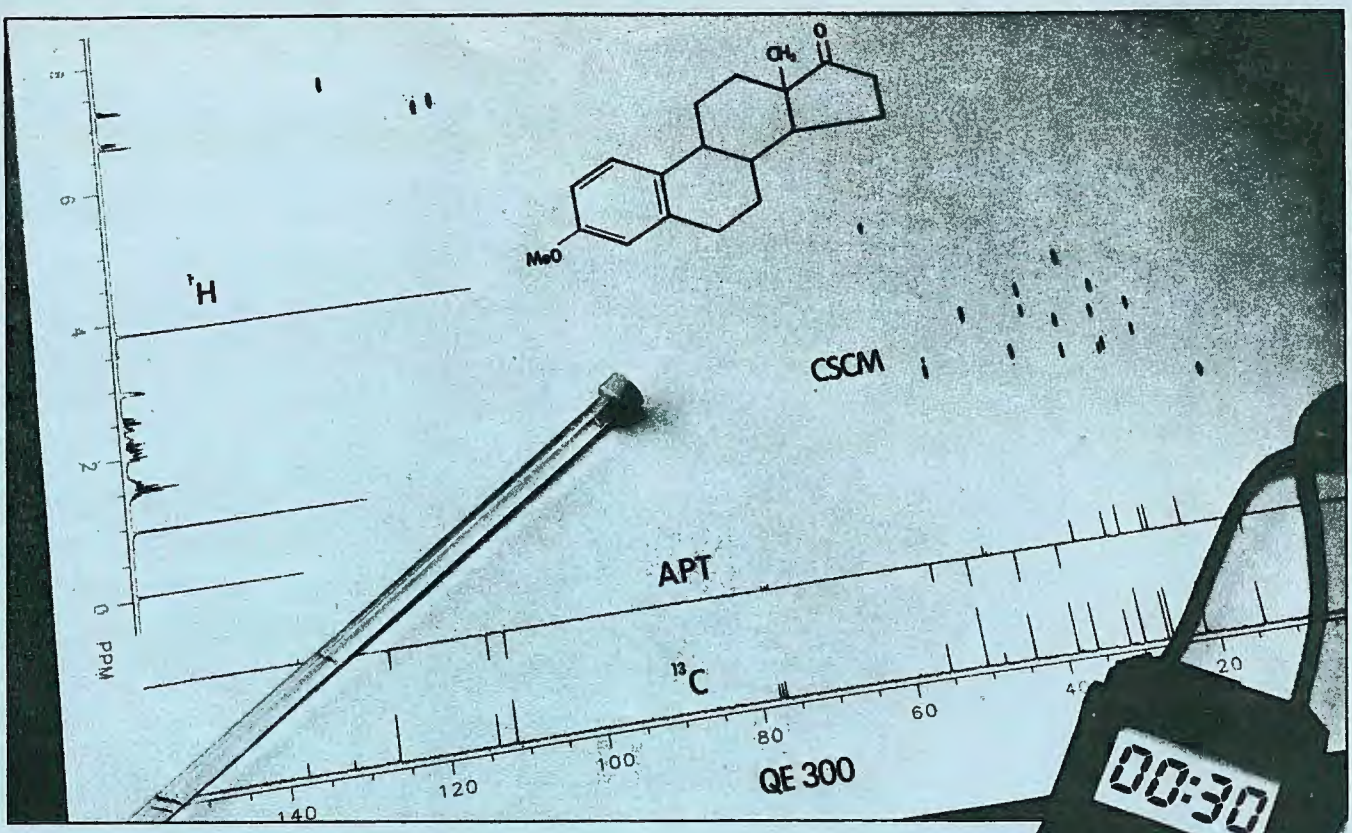
* * * * *

Reminder re New Subscription Rates

You are respectfully reminded (see Newsletter No. 356. p. 75) that **effective for the October 1988 - September 1989 Newsletter year, the annual subscription rate for the TAMU NMR Newsletter will be US$120.00**. The new rate applies to all new and renewed subscriptions. The 50% academic/personal discounts will continue to be applicable. The new rate will continue to include mailing at Printed Matter (Third Class) rates. First class, Air Mail, or other special posting services are available, and I will be happy to provide firm quotations on request.

Invoices for the 1988-89 Newsletter year will be mailed out early in July. If you do not receive an invoice by, say, mid-July, please let me know. It will be greatly appreciated if you will see that these invoices are processed promptly, in order that the costs of operating the Newsletter can be 'contained'. Fiscal considerations require that subscription **payment must be received** (or clear indication given me that payment is in the works) **by October 1, 1988** if your Newsletter mailings are to continue without interruption.

B.L.S.
1 June 1988



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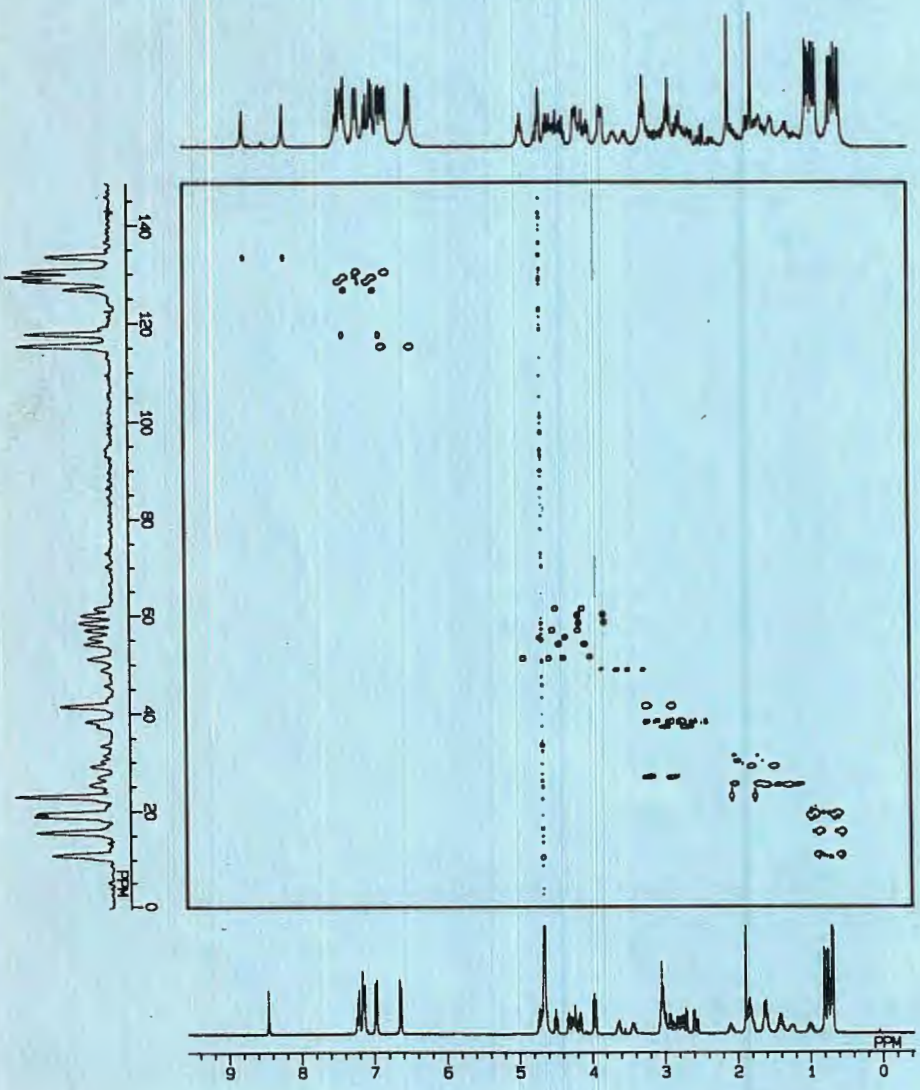

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