BRIAN SYKES

TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 349

October 1987

Widespread Chemical Shift Changes in Response to a Single Amino Acid Replacement . . . . . Fry, D. C., Greeley, D. N., and Pitcher, R. G. 2

NMR Dispersion Curves for Two Paramagnetic Chelates . . . . . Muller, R. N., Van Haverbeke, Y., Vander Elst, L., and Maton, F. 4

Inversion Transfer *In Vivo*; Biomedical Symposium . Saunders, J. K., Rydzy, M., and Smith, I. C. P. 6

Defects in Dealuminated Y Zeolites . . . Ray, G. J., Donohue, J. A., and Nerheim, A. G. 7

NOESY Spectra Lacking Diagonal Symmetry . . . . . Andersen, N. H. and Lai, X. 11

Monitoring the Effect(s) of Anesthetics on Plant Membrane Lipids *In Situ* . . . . . Gerasimowicz, W. V., Kurantz, M. J., and Pfeffer, P. E. 14

Automatic Fan Control . . . . . Koehler, F. H. and Scheer, U. 16

Positions Available . . . . . House, P. 17

Generation of E.COSY Spectra from Interleaved Multiple Quantum Filtered COSY Spectra; 'NMR-88 Meeting': Thredbo, New South Wales, Australia . . . . . Gray, B. N. and Brown, L. R. 18

Position Available . . . . . Hunt, A. H. 20

Book Review . . . . . Neilson, R. H. 21

2D Maximum Entropy Spectral Deconvolution . . . . . Borer, P. N. and Levy, G. C. 25

Adventures with $^{1}H/^{1}H$ NOE Experiments . . . . . Bigler, P. 22

Long-Range C-H Correlations Through Oxygen . . . . . Ralph, J. 28

Precision and Accuracy of SNIF-NMR; Position Available . Martin, G. J. and Martin, M. L. 30

Position Available; Equipment Available . . . . . Marzilli, L. and Live, D. 33

Positions Available . . . . . Brainerd, K. 33

Position Available . . . . . Santini, R. E. 34

Position Available . . . . . Weiner, M. 35

Solid State NMR Potpourri . . . Knight, C. T. G., Phillips, B. L., and Turner, G. L. 36

- continued on page 64 . . .

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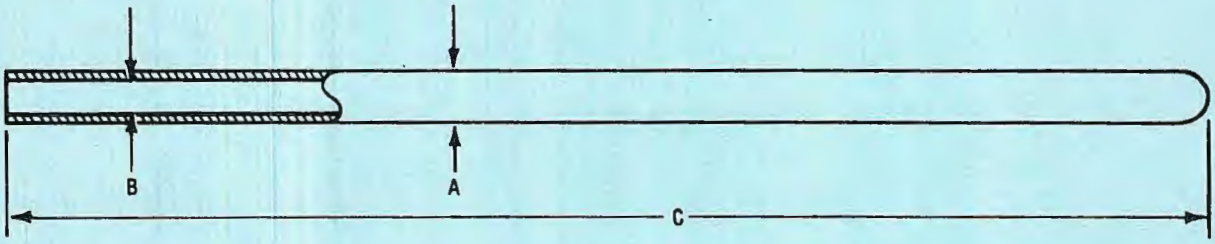

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TEXAS A&M NMR NEWSLETTER NO. 349, OCTOBER 1987

AUTHOR INDEX

Andersen, N. H. . . 11
Arumugam, S. . . 54
Bigler, P. 22
Blum, F. D. . . . 43
Borer, P. N. . . . 25
Brainerd, K. . . . 33
Brown, L. R. . . . 18
Delaglio, F. . . . 39
Donohue, J. A. . . 7
Doverspike, M. A. . 56
Fraenkel, G. . . . 52
Fry, D. C. 2
Garroway, A. N. . . 56
Gerasimowicz, W. V. . 14
Gray, B. N. . . . 18
Greeley, D. N. . . 2
House, P. 17
Hunt, A. H. . . . 20
Knight, C. T. G. . . 36
Koehler, F. H. . . 16
Komoroski, R. A. . . 38
Kurantz, M. J. . . 14
Lai, X. 11
Lauterbur, P. C. . . 58
Levy, G. C. . . . 25
Live, D. 33
Markley, J. L. . . . 62
Martin, G. J. . . . 30
Martin, M. L. . . . 30
Marzilli, L. . . . 33
Maton, F. 4
McGrath, K. J. . . 56
Miller, J. B. . . . 56
Muller, R. N. . . . 4
Neilson, R. H. . . 21
Nerheim, A. G. . . 7
Pfeffer, P. E. . . . 14
Phillips, B. L. . . . 36
Pitcher, R. G. . . 2
Ralph, J. 28
Ray, G. J. 7
Riddell, F. G. . . . 54
Rydzy, M. 6
Sadler, I. H. . . . 47
Santini, R. E. . . . 34
Saunders, J. K. . . 6
Scheer, U. . . . 16
Seger, M. R. . . . 49
Shapley, J. R. . . . 42
Shurts, J. 62
Siatkowski, R. E. . . 56
Smith, I. C. P. . . . 6
Sole, P. 39
Sparks, S. . . . 62
Torchia, D. . . . 62
Tschudin, R. . . . 62
Turner, G. L. . . . 36
Van Haverbeke, Y. . 4
Vander Elst, L. . . 4
Weiner, M. . . . 35
Winchester, W. R. . 52
Yue, H. J. . . . 49

TEXAS A&M NMR NEWSLETTER NO. 349, OCTOBER 1987

ADVERTISER INDEX

Bishop Instruments, Inc. 37
Bruker Instruments, Inc. 9
General Electric Company, Medical Systems Group, NMR Instruments . . 23, inside back cover
JEOL . . . . . outside back cover
New Era Enterprises 53
Programmed Text Sources 31
Varian. 45
Wilmad Glass Company, Inc. . . . inside front cover

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FORTHCOMING NMR MEETINGS

Southeastern Regional American Chemical Society Meeting - Nov. 4-6, 1987; Orlando, Florida. See pp. 41-42 of this Newsletter.

First Annual Missouri Magnetic Resonance Symposium - Nov. 17, 1987; University of Missouri, Rolla, Missouri, See pp. 43-44 of this Newsletter.

1987 Materials Research Society, Fall Meeting - Nov. 29 - Dec. 5, 1987; Boston Marriott Hotel, Boston, Massachusetts. Short course on NMR Spectroscopy - Wednesday, December 2. Course Instructor: James P. Yesinowski (Cal Tech). For further details, contact: Materials Research Society, 9800 McKnight Road, Suite 327, Pittsburgh, Pennsylvania 15237.

Fritz Haber International Workshop on Modern Techniques in Magnetic Resonance - Dec. 13-17, 1987; Weizman Institute of Science, Rehovot, Israel; See page 7 of Newsletter #341, February 1987, for additional information.

NMR-88 - Feb. 14-18, 1988; Thredbo Alpine Hotel, Thredbo, N.S.W. Australia. Chairman: Dr. L.R. Brown, The Australian National University. For further information, contact: Leslie Harland, Research School of Chemistry, The Australia National University, Canberra, A.C.T. 2601, Australia. Telex: AA62172. Facsimile: (61-62)-49-7817. Telephone: (61-62)-49-2863. See page 20 of this Newsletter.

29th ENC (Experimental NMR Conference) - Apr. 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Dept. of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For information, contact Professor Edward O. Stejskal, ENC Secretary, Dept. of Chemistry - Box 8204, North Carolina State University, Raleigh, North Carolina 27695-8204; telephone (919) 737-2998.

9th EENC (European Experimental NMR Conference) - May 16-20, 1988; Bad Aussee, Austria; For further information, write Professor H. Sterk, Karl-Franzens-Universität Graz, Institut für Organische Chemie, Heinrichstrasse 28, A-8010 Graz, Austria. See Newsletter 348, 15 (1987).

XIII Intl. Conference on Magnetic Resonance in Biological Systems - Aug. 14-19, 1988; Madison, Wisconsin. See pp. 60-61 of this Newsletter.

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, California 94303 U.S.A.

(415) 493-5971

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No. 351 (December) -- 20 November 1987
No. 352 (January) ---- 18 December 1987
No. 353 (February) ----- 22 January 1988
No. 354 (March) ------ 19 February 1988

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Widespread Chemical Shift Changes In Response To A Single Amino Acid Replacement

May 29, 1987
(received 9/8/87)

Dear Barry:

One of the major interests in our laboratory is trying to understand the interdependent relationships which exist among sequence, structure, NMR characteristics, and activity for peptides and small proteins. We are presently studying a series of analogs of human growth hormone releasing factor (GRF) which exhibit dramatic changes in activity and structure upon single amino acid substitutions. We have made complete assignments and catalogued NOEs for a fragment of native GRF comprised of residues 1-29, and for an analog of this peptide in which glycine residue 15 has been replaced by alanine, in 75% CD_3OH/25% H_2O at pH 6.

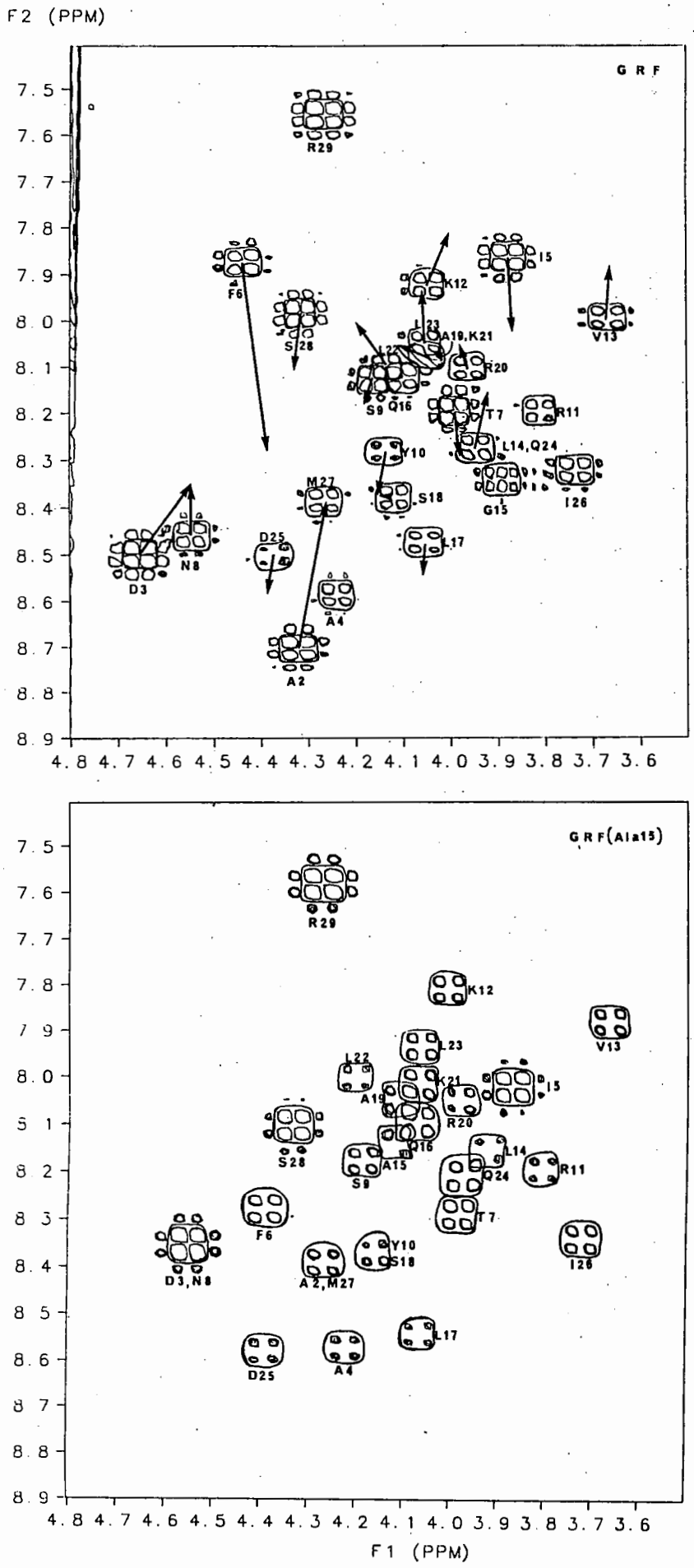
The amino acid substitution at position 15 causes substantial changes in the NH chemical shifts of residues throughout the peptide (Figure 1). However, the largest such changes are observed for residues located far from position 15 in the primary sequence, while some of the smaller changes occur close to position 15 (Figure 2). The pattern of observed NOEs is also altered throughout the peptide, and in an irregular manner, such that interpretation of the structural changes based on NOEs appears as if it will be quite complicated. Changes in CD spectra, which suggest a 20% increase in helicity for the Ala^{15} analog, apparently are due to a combination of structural alterations along the peptide, not simply formation of new α-helix. We are beginning a detailed structural evaluation according to our current approach, which is to apply NOE-derived distance constraints in molecular dynamics calculations, using the program CHARMM. It is only the NH protons which exhibit major effects, probably reflecting their sensitivity to structural changes and not the presence of extensive ring-current shifting. Despite this potentially useful sensitivity, we cannot discern a clear correlation between structure as determined by backbone NOE patterns and NH chemical shifts.

This example points out considerations which, we realize, are becoming obvious to those using NMR to study sequence variants of proteins: subtle changes in sequence can have widespread effects along the molecule; these changes are hard to predict; therefore, sequence-vs.-activity surveys cannot be accurately evaluated in the absence of structural data; NMR provides a sensitive method for analyzing such structural problems; single site replacement does not necessarily lead to NMR resonance assignment by direct comparison of spectra.

Sincerely yours,

Dave Dave Ross

David C. Fry, David N. Greeley, and Ross G. Pitcher
Department of Physical Chemistry



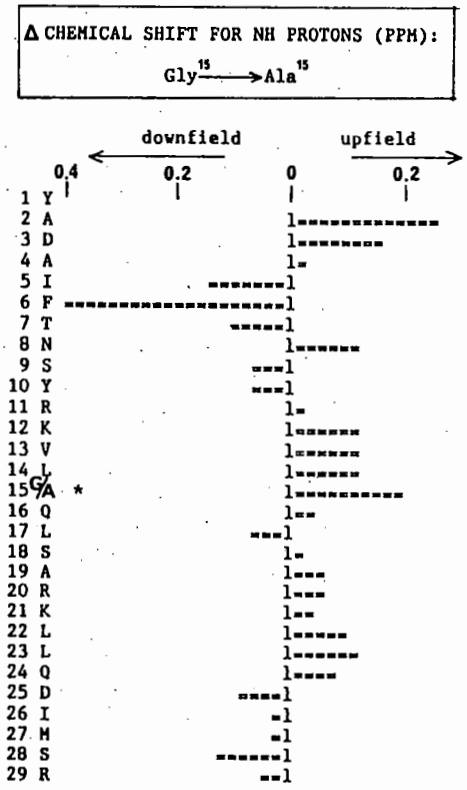


FIGURE 1 (left): COSY fingerprint regions for GRF 1-29 and GRF[Ala^{15}] 1-29, showing the chemical shift changes which accompany replacement at position 15.

FIGURE 2 (above): Graph showing the change in NH chemical shift observed for each residue. An asterisk marks the location of the amino acid replacement.

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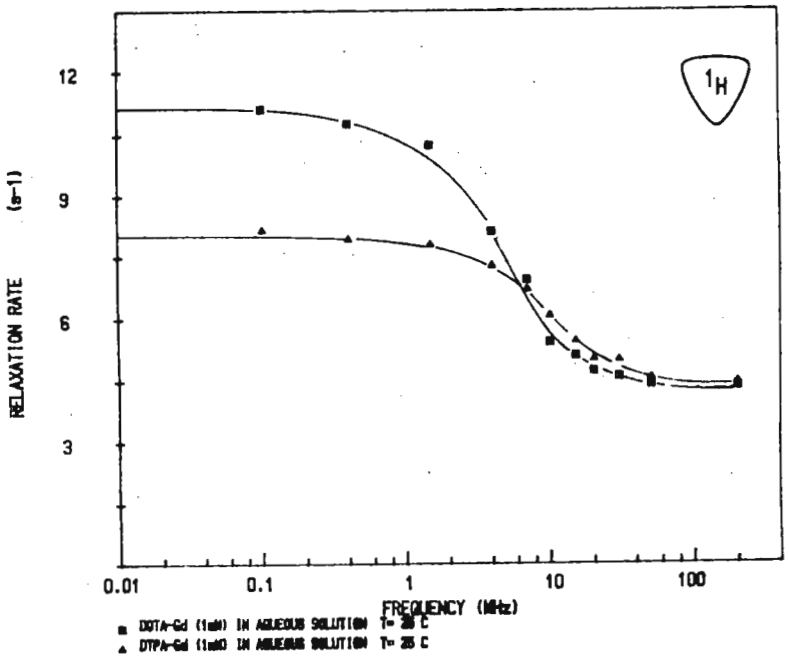
Dear Professor SHAPIRO,

Nuclear relaxation rates of mapped nuclei are of paramount importance in Magnetic Resonance Imaging contrast. Free paramagnetic aquoions (Fe(III), Mn(II), Gd(III),...) are quite efficient in increasing nuclear relaxation rates but are of limited use as in vivo contrast media because of their toxicity. Complexation by multidentate chelates helps in decreasing toxicity but also affects the paramagnetic contribution to the proton relaxation.
Intensively investigated today is the development of paramagnetic macrocyclic complexes characterized by high stability constants.

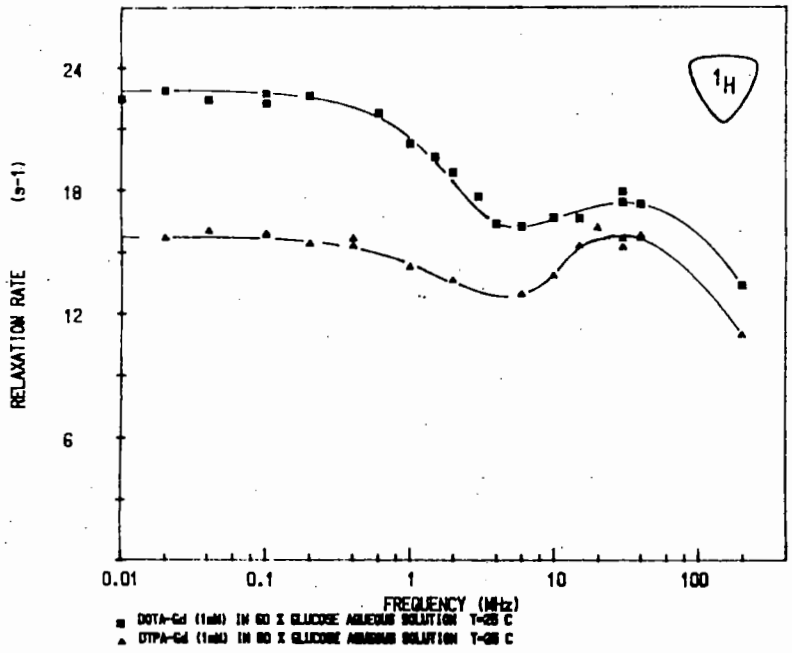
Since proton relaxation enhancement provided by paramagnetic centers is strongly field dependent, observation of Nuclear Magnetic Relaxation Dispersion curves (NMRD) over a wide range of magnetic field extending well below the usual imaging window is useful not only to measure their efficiency at any imaging frequency, but also to understand and improve mechanisms by which they contribute to the proton relaxation.

We report here some results about two paramagnetic chelates, DOTA-Gd and DTPA-Gd which both are tested as MRI contrast agents. Samples were supplied by GUERBET (Aulnay-Sous Bois, France).

T_1 measurements were performed at (25 ± 0.5) °C on an IBM Research Relaxometer and on a Bruker MSL-200 Spectrometer.



The most striking observation is that while DOTA-Gd and DTPA-Gd have similar relaxivities at proton Larmor frequencies higher than 4 MHz, the former presents a higher relaxivity in the lower frequencies range. This can be attributed to different Gd(III) electronic relaxation time (τ_s) when the ion is chelated either by DOTA or DTPA. Lower symmetry of DTPA-Gd may be responsible for a shorter electronic relaxation time competing with rotational correlation time (τ_r) of the complex in the low field zone.
In order to check this hypothesis, we increased τ_r by addition of D-Glucose to aqueous solutions.
Comparison of the profiles confirms the validity of the hypothesis concerning larger influence of electronic relaxation time in the DTPA-Gd structure.



Further experimental work and quantitative analysis of the profiles are in progress.
These observations stress once again the importance of NMRD profiles in research related to MRI contrast media.

Sincerely Yours,

Robert N. Muller, Dr.Sc

Prof. Y. Van Haverbeke, Dr.Sc

Luce Vander Elst, Dr.Sc

Frédéric Maton, Lic.Sc.

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Our ref: 7022-1
11 September 1987
(received 9/25/87)

Dr. B.L. Shapiro
Editor, TAMU NMR Newsletter
966 Elsinore Court
PALO ALTO, Calif. 94303

Dear Barry,

Inversion Transfer In Vivo;
Biomedical Symposium

The transfer of NMR methodology from chemical to in vivo systems tends to baffle us chemists sometimes. An example is the use of inversion transfer experiments. These work well in controlled chemical systems and even in perfused organs. The situation is complicated in vivo since we must localize on a particular organ and hence use surface coils. The problem therein is that the B_1 field in these coils is not homogeneous. The way we have overcome this is to use a relatively large bird cage coil either to saturate or to invert a particular resonance in tissue within the coil. The observe pulse is then transmitted and received on a relatively small coil using localization techniques. The coil was designed and built in collaboration with Paul Morris of Morris Industries, Ottawa. Since the two coils are mutually orthogonal they do not couple.

On October 15 we are having a joint one-day symposium with the Ottawa General Hospital on NMR in medicine. This is to mark the installation of the Siemens 1.5T clinical imager at the hospital and an animal physiology NMR laboratory at NRC. The latter represents the culmination of a change for us from a biological NMR group to a biomedical one. The physiological laboratory has two spectrometers, one with an 8.4 Tesla vertical magnet (89 mm), the other with a 4.7 Tesla (30 cm) horizontal magnet. This laboratory is located at our Montreal Road campus whereas both the spectrometers dedicated to the membrane and cancer projects are located at Sussex Drive.

Yours sincerely,

John K. Saunders Marek Rydzy Ian C.P. Smith

Canada

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August 19, 1987 (received 8/28/87)

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

Defects in Dealuminated Y Zeolites

Dear Barry:

Dealumination of zeolites with reagents such as $SiCl_4$ has become a routine method for preparing zeolites that are more stable than their higher aluminum counterparts. We have been using ^{29}Si NMR to study dealuminated NaY zeolites (DAY's) by both Bloch decay (BD) and cross-polarization (CP) techniques. The dealumination process is presumed to proceed with silicon migrating into lattice positions vacated by the aluminum to give a highly crystalline product. However, this silicon substitution process is not always complete and defect sites consisting of -SiOH moieties can occur.

The BD (Figure 1A) and CP (Figure 1B) spectra of a DAY consist of five peaks at -101, -103, -104, -107, and -111 ppm. The BD spectra were taken with a sufficiently long relaxation delay that the intensities can be used quantitatively. The most intense peak occurs in the BD spectrum at -107 ppm and is assigned to $Si(OSi)_4$ sites in the crystalline sieve structure. By analogy to the literature results on silica gels[1], the peak at -111 ppm is assigned to $Si(OSi)_4$ sites in detrital amorphous silica formed during dealumination. The remaining three peaks are assigned to $Si(OSi)_3OH$ groups. Although comprising but a small fraction of the intensity (ca 15%) of the BD spectrum, they are substantially more prominent in the CP spectrum because of their proximity to the proton of the OH group. The -111 and -107 ppm peaks in the CP spectrum are caused by the same structures that give rise to these peaks in the BD spectrum. The intensity of these two peaks is attributed to cross-polarization from casual water in the zeolite interstices or the proximity of defects.

The intensity of the peaks assigned to SiOH defects is greatly reduced in the spectra of the samples that have been steamed or reacted with Me_3SiCl. In the case of steaming, it is believed that conditions are favorable for further rearrangement of silicon that results in a healing of the defects. In the case of Me_3SiCl treatment, the reagent reacts with the defect site to convert it to $Me_3SiOSi(OSi)_3$, which has a chemical shift under the -107ppm peak. The Me_3Si fragment has a shift (not shown) of 14.8 ppm.

Our assignments differ substantially from those recently reported in the literature[2]. We will publish a more full accounting of this work in the near future.

Sincerely,

Joe
G. J. Ray

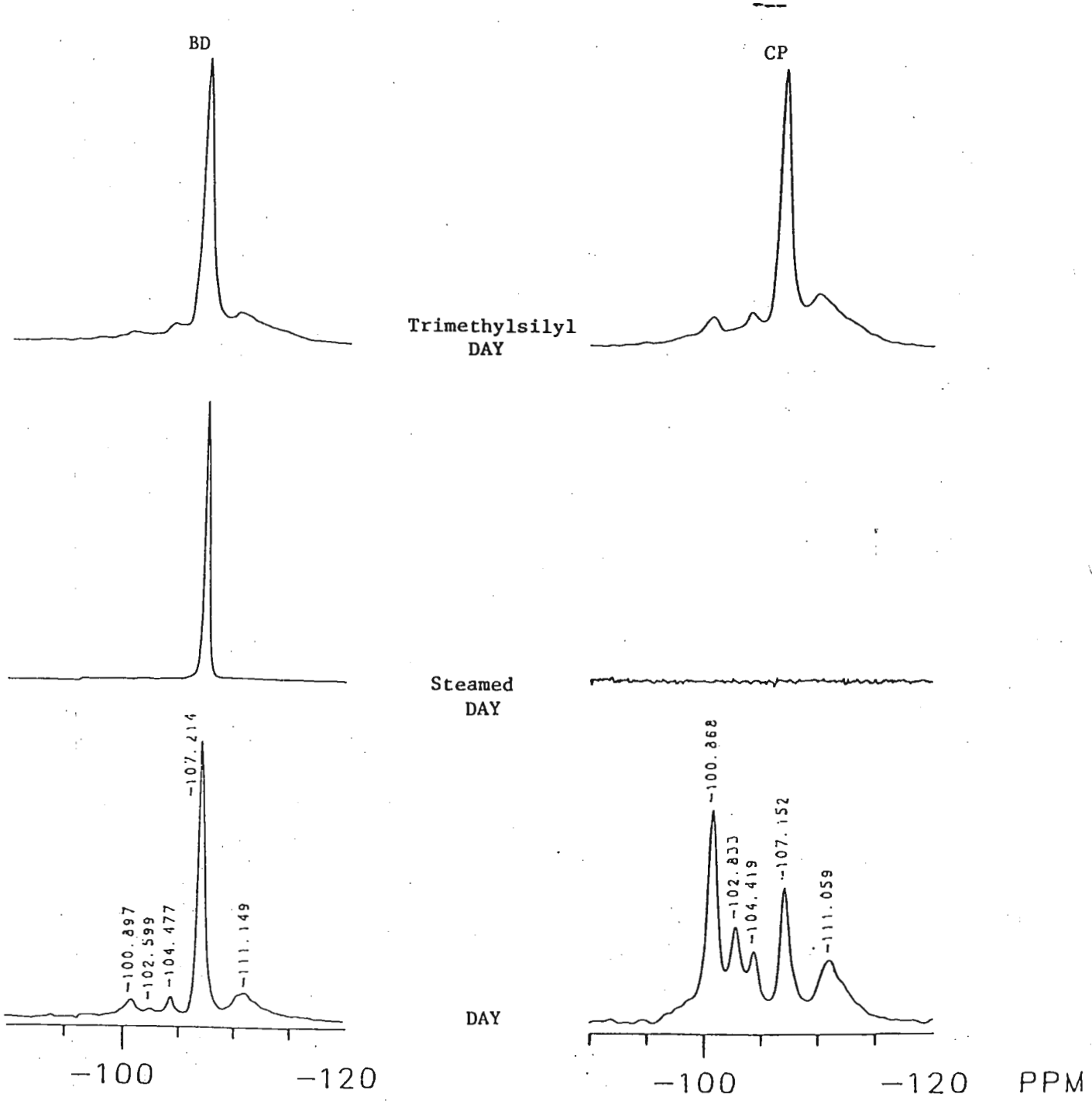
J. A. Donohue
J. A. Donohue

A. G. Nerheim
A. G. Nerheim

1. C.A.Fyfe, G.C.Gobbi and G.J.Kennedy, J. Phys. Chem., 89, 277 (1985)
2. P.J.Grobet, P.A.Jacobs and H.K.Beyer, Zeolites, 6, 47 (1986)

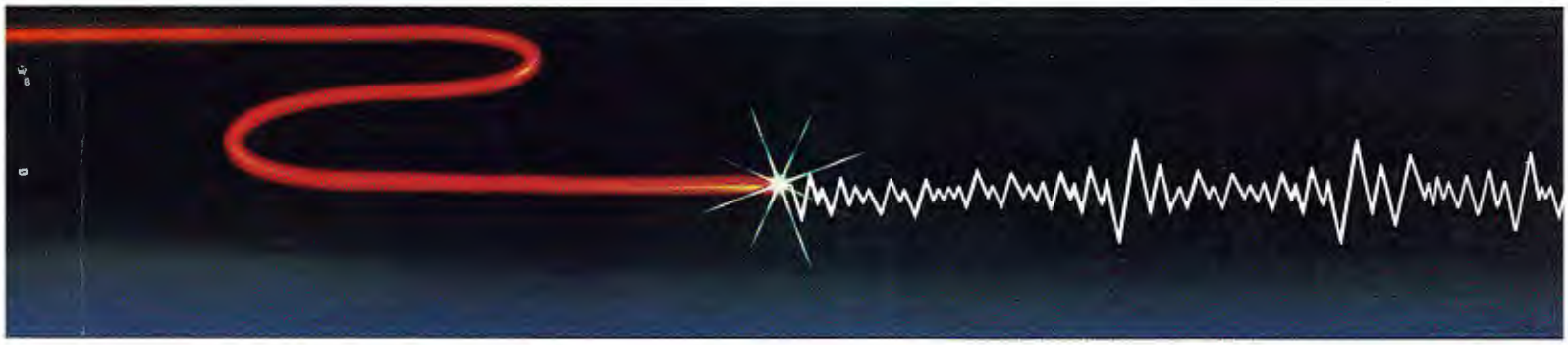
Figure 1A

Figure 1B



BD and CP ^{29}Si NMR spectra of dealuminated NaY (DAY) and its steamed and trimethylsilated products

The NMR evolution continues:



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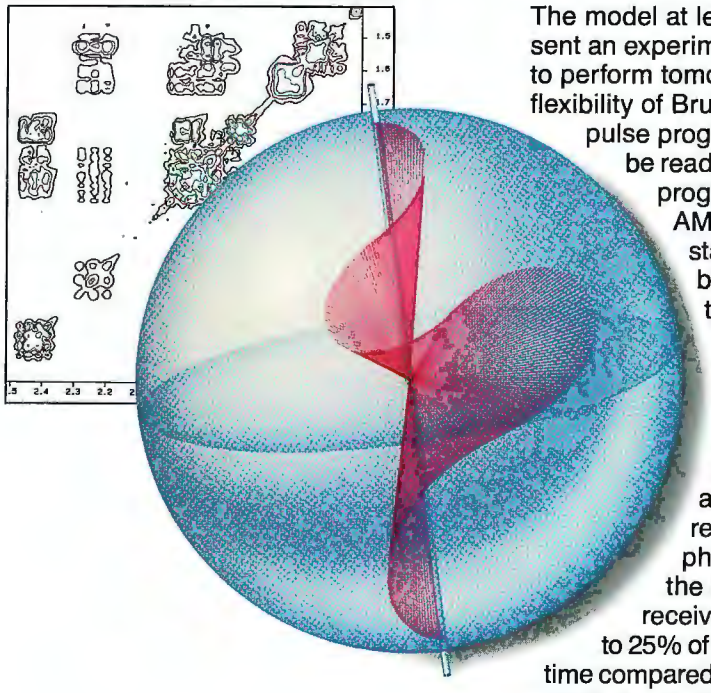

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August 28, 1987
(received 9/5/87)

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

Dear Professor Shapiro:

Subject: **NOESY Spectra Lacking Diagonal Symmetry**

The subject of how to properly extract cross-relaxation rates (and thus distance estimates) from NOESY data sets is one of continuing interest and controversy. At this point, we will not get involved in the "isolated spin-pair" *versus* "relaxation matrix" analysis controversy, but rather wish to point out the problems associated with the inherent non-symmetry present in most NOESY spectra of small molecules. Although we are relatively well-blessed with access to NMR time at U.W.; we rarely can afford more than a 14-16 hr period for a NOESY experiment. Given the long phase program for pure absorption phase data collection and the need for 200^{+} t_1s for resolution, we typically use cycle times of 1.6-2.5 sec for NOESY experiments. These values are far short of 3 times the longer T_1 values observed for protons in small molecules (MW = 200-500). Under such conditions— truncated preparatory delay (PD) experiments, the NOESY signal matrix is no longer symmetric about the diagonal [1], see Figure 1.

The subject of NOE experiment symmetry has also been discussed by others. Williamson and Neuhaus recently restated [2] the basis for non-symmetry — $f_j[i] \neq f_i[j]$ — in steady state and other driven experiments, and contrasted that situation with the "fundamental symmetry" of all transient NOE experiments (including NOESY). This analysis, and Williamson's program for experiment simulation *via* numerical integration [3], however assumes an effectively infinite PD. In our program [4] the PD is included; our simulations revealed that $f_j[i] \neq f_i[j]$ even for transient experiments when the PD period is insufficient. Restated in terms of NOESY signal intensities: $|S_{ij}| \neq |S_{ji}|$. (Note: S_{ij} corresponds to magnetization at δ_i in t_1 that is detected at δ_j in t_2). These results prompted us to proposed eqn.1 as a basis for analysis of NOE experiments [4].

$$\sigma_{ij}^{est} \cong \frac{1}{2\tau_m}\left(\frac{S_{ij}}{S_{ii}} + \frac{S_{ji}}{S_{jj}}\right) = \sigma_{ij} + \frac{\tau_m}{2}\sum_k \sigma_{jk}\,\sigma_{ki} \qquad \text{[eqn. 1]}$$

The non-equivalence of S_{ij} and S_{ji} is reminiscent of the SKEWSY experiment [5] and has a similar source: the frequency labeled magnetizations of spins i and j are not identical if $R_{ii} \neq R_{jj}$. When spin i is the more rapidly recovering member of the pair, $|S_{ij}| > |S_{ji}|$ due to the larger value of M_i (more nearly recovered to its full equilibrium value prior to the first 90° pulse of the NOESY sequence) which governs all net transfers which are initiated at i:

$$S_{ij} \propto \mathbf{M}_i\left(\sigma_{ij} + \frac{\tau_m}{2}\sum_k \sigma_{ik}\,\sigma_{kj} + \ldots\right)\tau_m$$

The extent of intensity shifting about the diagonal that can be introduced by delay truncation in small molecule NOESYs is illustrated by simulation results collected in Figure 1.

Figure 1. The effect of PD truncation on NOESY symmetry. Computer-simulated NOESY signal matrices and the relaxation rate matrix from which they were derived.

The relaxation rate matrix (1/sec), off-diagonal elements are W_0-W_2

0.8042	−0.1662	−0.0986	−0.0080	−0.0260	−0.0050	−0.0080
−0.1662	2.2878	−0.0260	−0.0986	−0.4700	−0.1662	−0.0080
−0.0986	−0.0260	0.5260	−0.0020	−0.0610	−0.0040	−0.0010
−0.0080	−0.0986	−0.0020	1.8596	−0.0040	−0.1662	−0.4700
−0.0260	−0.4700	−0.0610	−0.0040	1.4713	−0.0260	−0.0020
−0.0050	−0.1662	−0.0040	−0.1662	−0.0260	1.1122	−0.0080
−0.0080	−0.0080	−0.0010	−0.4700	−0.0020	−0.0080	1.4077

Calculated NOESY signal matrix comparison at τ_m = 0.9 s, using the relaxation matrix above with recycle times set at 2.1 s, a typical value for time-efficient data collection, and 20 s. The t_c = 20 s signal matrix is symmetric about the diagonal and corresponds to 0.01 times the fractional enhancement values shown in parentheses. For each i,j matrix entry: the top-value is the peak intensity (at t_c = 2.1 s, τ_m = 0.9 s) expressed as fractions of a unit proton intensity, the next entry is the percent fractional enhancement ($-S_{ij}/S^o_{jj}$), and lowest set are residual-driver normalized NOEs ($-S_{ij}/S_{ii}$).

parenthetic values are those calculated at t_c = 20s

					S^o_{jj} at t_c = 2.1 s
−0.3428	0.0277	0.0338	0.0002	−0.0005	
39.3 (49.0)	2.67 (3.97)	4.63 (4.84)	0.02 (0.03)	−0.05 (−0.07)	−0.8726
——	8.08 (8.10)	9.86 (9.87)	0.06 (0.06)	−0.15 (−0.14)	
0.0417	−0.1546	0.0017	0.0127	0.0860	
4.78 (3.97)	14.9 (14.7)	0.23 (0.17)	1.24 (1.21)	8.83 (8.18)	−1.0360
27.0 (27.0)	——	1.10 (1.16)	8.21 (8.23)	55.6 (55.6)	
0.0262	0.0009	−0.3388	0.0001	0.0119	
3.00 (4.84)	0.09 (0.17)	46.4 (62.6)	0.01 (0.03)	1.22 (2.19)	−0.7304
7.73 (7.74)	0.27 (0.27)	——	0.03 (0.05)	3.51 (3.50)	
0.0003	0.0120	0.0003	−0.2091	−0.0029	
0.03 (0.03)	1.16 (1.21)	0.04 (0.03)	20.5 (21.0)	−0.3 (−0.3)	−1.0201
0.14 (0.14)	5.74 (5.76)	0.14 (0.15)	——	−1.4 (−1.4)	
−0.0007	0.0728	0.0195	−0.0026	−0.2540	
−0.08 (−0.07)	7.03 (8.18)	2.67 (2.20)	−0.3 (−0.3)	26.1 (28.5)	−0.9744
−0.28 (−0.25)	28.7 (28.7)	7.68 (7.71)	−1.0 (−1.0)	——	
−0.0012	0.0255	0.0009	0.0310	0.0000	
−0.14 (−0.15)	2.46 (3.26)	0.12 (0.11)	3.04 (3.96)	0.0 (0.0)	−0.9168
−0.41 (−0.40)	8.72 (8.73)	0.31 (0.29)	10.6 (10.6)	0.0 (0.0)	

The last column lists the relative intensities that would be observed in a control spectrum with the same recycle time. These correspond to diagonal intensities at τ_m = 0. The sign convention of 1D ΔNOE spectra has been employed. Positive cross-peak values correspond to enhancements (+ve NOEs due to mutual accelerated relaxation, $W_2 > W_0$).

In the short PD theoretical spectrum illustrated (at τ_m = 900 ms), "symmetry-related" cross-peak intensities can differ by as much as 50% due to the truncations effects. However, residual-driver normalized intensities, S_{ij}/S_{ii} are identical to the values that would be observed with an infinite recovery period. It has been suggested [6] that column normalized NOESY data be used for the derivation of rate (and thus distance) matrices by diagonalizing for an eigenvalue solution. Such a normalization procedure is the 2D equivalent of classical fractional enhancement— % NOE = S_{ij}/S^{o}_{jj}. As can be seen in the middle entries in the lower matrix of **Figure 1**, this produces even greater distortions from diagonal symmetry for the short PD experiment. Fractional enhancement matrices are symmetric about the diagonal only when all initial (τ_m = 0) auto-peaks have intensities in proportion to their equilibrium populations. (The S^{o}_{jj} values for the short PD NOESY are also given in **Figure 1**).

Based on these simulations (and practical cases using actual data), we consider the residual-driver normalized signal matrix—

$$\begin{bmatrix} S_{ii} & S_{ij} & S_{ik} & S_{il} \\ S_{ji} & S_{jj} & S_{jk} & \vdots \\ S_{ki} & \vdots & \vdots & \vdots \end{bmatrix} \Longrightarrow \begin{bmatrix} 1 & (S_{ij}/S_{ii}) & (S_{ik}/S_{ii}) & (S_{il}/S_{ii}) \\ (S_{ji}/S_{jj}) & 1 & (S_{jk}/S_{jj}) & \vdots \\ (S_{ki}/S_{kk}) & \vdots & \vdots & \vdots \end{bmatrix}$$

to be the best format for experimental NOESY data. The resulting row-normalized matrix lacks diagonal symmetry even with an infinite PD period, but each row can be readily calculated from a structural model [4]; and this data format is suitable for a direct application of **eqn.1** for obtaining cross-relaxation rate estimates. Macura *et al.* [7] have suggested "scaling cross-peak intensities relative to the weighted diagonal peak intensities within the same experiment". Their function, $a_2(\tau_m)$, in contrast to **eqn.1**, is still cycle time dependent.

Details of our NOESY simulation program will be provided upon request.

Yours sincerely,

(Niels H. Andersen) (Xiaonian Lai)

References and Notes:

[1] This is independent of the obvious sources of asymmetry: different resolution in w_1 and w_2, and the different nature of noise in the two dimensions – t_1 streaks.

[2] M.P. Williamson and D. Neuhaus, *J. Magn. Reson.* **72**, 369 (1987).

[3] M.P. Williamson, *Magn. Reson. in Chem.* **25**, 356 (1987). We wish to thank Dr. Williamson for confirming (by a different program) the general features of PD-truncation induced NOESY asymmetry noted in this letter.

[4] H.L. Eaton and N.H. Andersen, *J. Magn. Reson.*, in press.

[5] J. Bremer, G.L. Mendz and W.J. Moore, *J. Am. Chem. Soc.* **106**, 4691 (1984).

[6] E.R. Johnson, M.T. Dellwo, and J. Hendrix, *J. Magn. Reson.* **66**, 399 (1986).

[7] S. Macura, B.T. Farmer II and L.R. Brown *J. Magn. Reson.* **70**, 493 (1986).

United States Department of Agriculture | Agricultural Research Service | North Atlantic Area Eastern Regional Research Center | 600 East Mermaid Lane Philadelphia, Pennsylvania 19118

August 4, 1987 (received 8/24/87)

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

Dear Professor Shapiro:

Monitoring the Effect(s) of Anesthetics on Plant Membrane Lipids in situ.

Our laboratories have been engaged in the study of plant tissue metabolism using a variety of spectroscopic approaches with a particular emphasis on in vivo ^{31}P NMR spectrometry. A variety of organic acids, phenols, alcohols, secondary and tertiary amines, as well as anesthetics are known to alter animal membranes and have been studied rather extensively. However, the molecular mechanism(s) whereby anesthetics affect the membrane expansion and composition of plant cells and tissues is still largely unexplored and not clearly delineated. Anesthetics are known to be able to overcome dormancy and to stimulate germination of seeds through their ability to modify plant membrane properties.

One such anesthetic, dibucaine, is known to cause root membrane expansion as well as structural changes. ^{31}P NMR was utilized in following intracellular phosphorus metabolite levels in perfused maize root tip tissue[1] upon exposure to dibucaine as a function of Ca^{2+} ion concentration at pH's 7.5 and 4.0, respectively. The pKa of dibucaine = 8.5. Figure 1 shows the effect of dibucaine on the ^{31}P NMR spectra of the maize tissue as a function of time when no calcium is present at pH = 7.5. (No such spectral change occurs at pH = 4 with or without Ca^{2+}.) When Ca^{2+} is present at 0.1 mM or higher levels, the effects of dibucaine are suppressed, i.e. ^{31}P resonance signals from G6P, Pi, NTP, NADP, and UDPG do not diminish significantly.

Figure 2 provides an indication of the stability Ca^{2+} affords to the tissue. Such spectroscopic changes have been correlated with desaturase inhibition by dibucaine resulting in an increased ratio of saturated/unsaturated fatty acid comprising the root tissue. In particular, a marked decrease in linoleate (18:2) concomitant with increases in more saturated fatty acid species was observed.

The relatively higher potency of the uncharged form (as seen at pH = 7.5) of the anesthetic can be attributed to its increased membrane lipid solubility. A full accounting of this work has been submitted for publication.

Walt Mike Phil

WALTER V. GERASIMOWICZ MICHAEL J. KURANTZ PHILIP E. PFEFFER

[1]P. E. Pfeffer, S. Tu, W. V. Gerasimowicz, J. R. Cavanaugh, Plant Physiology 80, 1986, pp. 77-84.

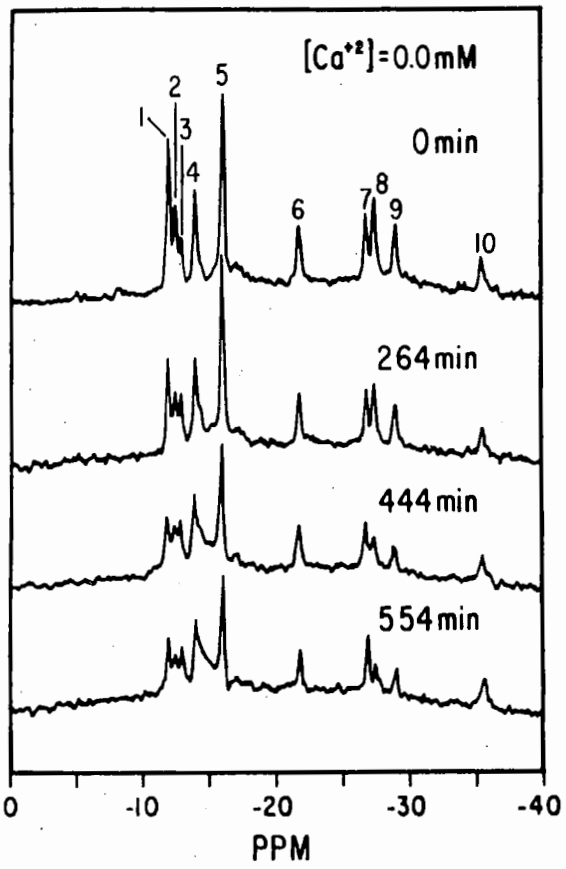

Figure 1. ^{31}P NMR spectral responses of maize root tip tissue upon exposure to 0.05 mM dibucaine at pH = 7.5, 50.0 mM glucose, O_2 saturated perfusate, 10.0 mM MOPS buffer.
(1.) G6P (2.) F6P(?) (3.) AMP(?)
(4.) Pi cytoplasm (5.) Pi vacuole
(6.) γ-NTP (7) α-NTP (8 and 9.) UDPG, NADP
(10.) β-NTP. Scale referenced to HMPA (capillary) at 13.78 ppm relative to MDP at 0.0 ppm.

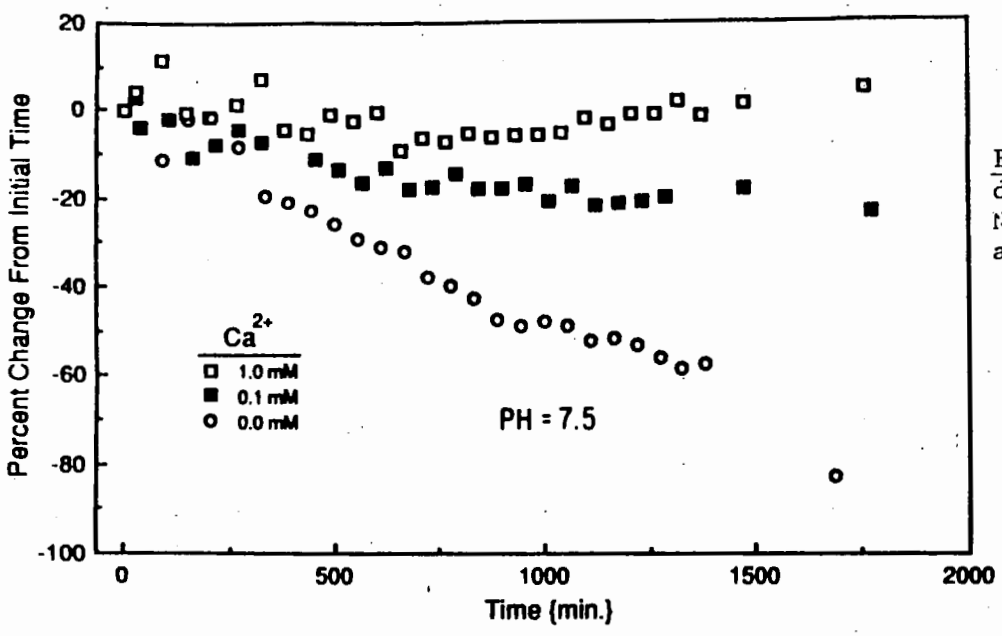

Figure 2. Effect of dibucaine on total NMR-visible phosphorus at pH = 7.5.

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Prof. Dr. F. H. Köhler

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(received 8/31/87)

DR. BERNARD L. SHAPIRO
TAMU NMR NEWSLETTER
966 ELSINORE COURT
PALO ALTO, CALIFORNIA 94303
U. S. A.

Automatic fan control

Dear Dr. Shapiro,

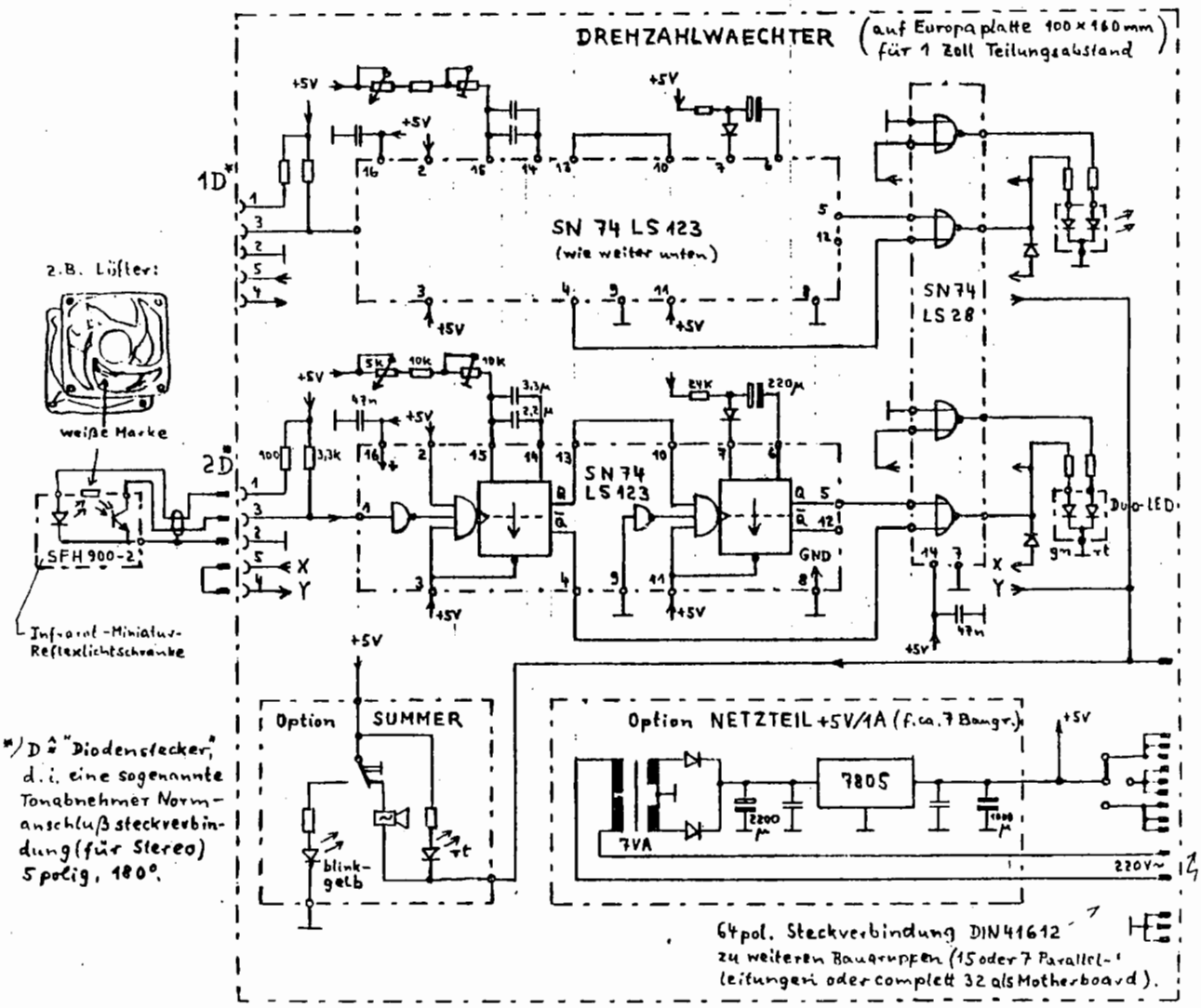
manufacturers of high quality shirts note on their packing material how many needles you should find before you first wear that shirt. Similarly, manufacturers of equipment like NMR spectrometers should provide a listing of fans which must be checked at times in order to avoid a major break-down. The far best solution to the annoying problem is an automatic control. U. Scheer who joined us as a technician has built a simple device which surveys an adjustable number of r.p.m. (see sketch below). Whenever a fan drops below that number an acoustic signal and/or a light calls for help. Since there are more than twenty fans in our Bruker CXP 200 we can perhaps hear some simple melody after proper selection of the acoustic signals.

Yours sincerely

Frank H. Köhler

(F. H. Köhler) (U. Scheer)

U. Scheer



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14 September 1987
(received 9/23/87)

Professor B. L. Shapiro,
966 Elsinore Court
Palo Alto, California 94303
UNITED STATES OF AMERICA

Generation of E.COSY Spectra from Interleaved

Multiple Quantum Filtered COSY Spectra

Dear Professor Shapiro,

One of the joys of working in Australia is the sea mail that arrives with ultimatums a week after something should have been completed, e.g. pink sheets. Hopefully the following will reinstate us in your good graces.

There has been some discussion in the newsletter recently about E.COSY type experiments, with the suggestion of the P.E. COSY experiment from Luciano Müller and a reminder from the Ernst group that E.COSY data can be collected in efficient ways. We have taken a somewhat different approach to these experiments. In particular, combining multiple quantum filtered COSY spectra of various filter orders with appropriate weighting will give an E.COSY spectrum (1,2),

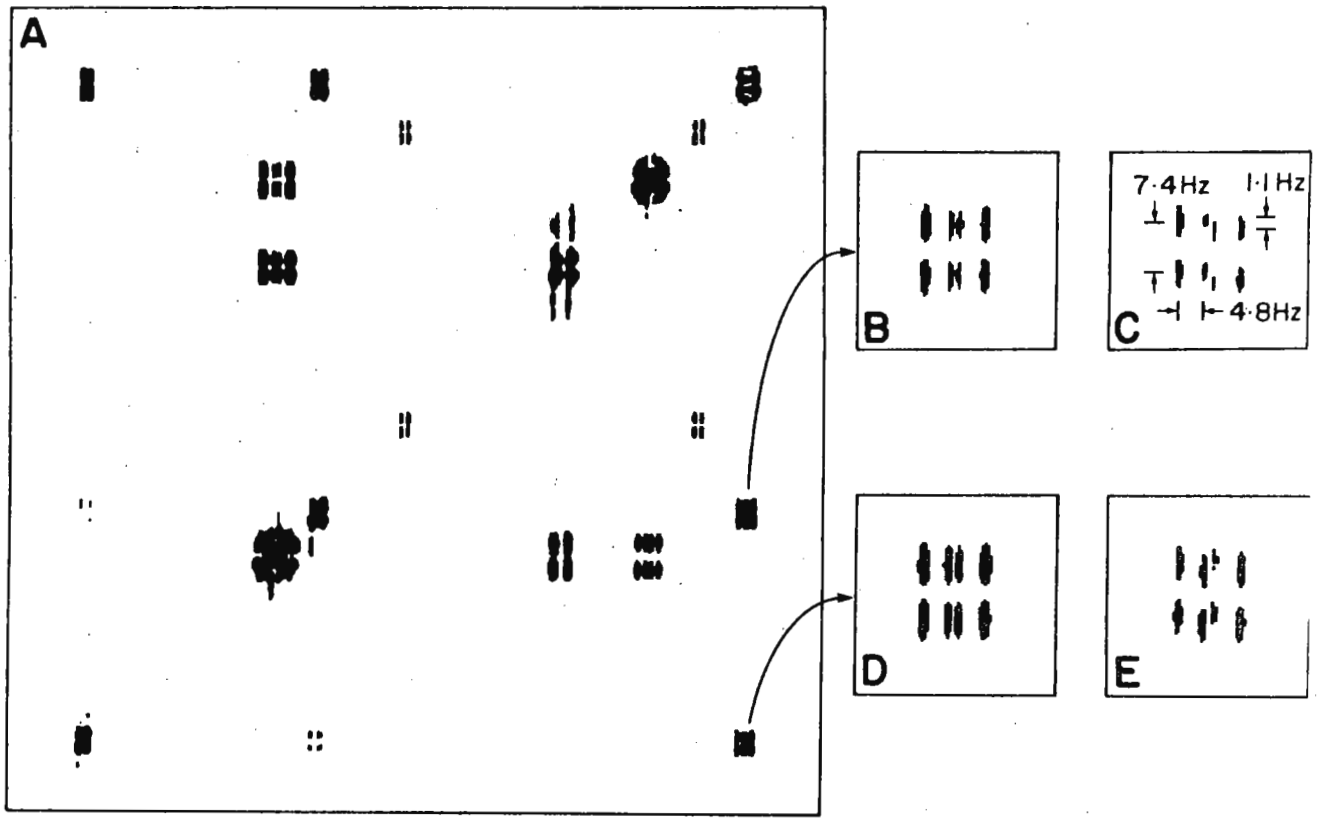
$$S^{E.COSY}(t_1,t_2) = \sum_{j=0}^{K} W_j S_j^{MQF}(t_1,t_2)$$

where the $S_j^{MQF}(t_1,t_2)$ are the multiple quantum filtered COSY data with filter orders (j) ranging from zero to the maximum possible quantum order (K) possible in the system (sample) and the W_j are the weighting factors. As the Ernst group pointed out in these pages, if spectra with filters of each different quantum order are acquired separately, this method of obtaining E.COSY spectra implies a considerable amount of experimental time. This is the reason for the development of phase cycles which will directly give an E.COSY spectrum (1,2).

In dealing with macromolecules, e.g. proteins, we have found that multiple quantum filtered COSY spectra with filter orders higher than two are often very helpful in sorting out resonance assignments. Recently we have developed an experiment which allows multiple quantum filtered COSY spectra of any filter order to be generated from a single data set (3).

This experiment has the advantage that every transient collected is used to generate filtered spectra of each quantum order, i.e. there is no penalty in sensitivity to collecting all filter orders simultaneously. Data storage and processing is more complex since a digital Fourier analysis with respect to the phase of the RF pulses must be performed (3).

With COSY spectra corresponding to the different filter orders available from a single experiment, it is a simple matter to take the above linear combination to obtain E.COSY spectra. Fig.1A shows a portion of a double quantum filtered COSY spectrum for a mixture of compounds containing AX, AMX, and AKMX spin systems. This spectrum was recorded, with relatively low resolution along t_1 (t_1,t_2 = 180, 4096 data points), using the interleaved method outlined previously (3). As can be seen in the multiplet pattern shown in Fig 1B, which is a cross peak from the AMX spin system, the small, passive couplings are obscured in the multiplet patterns for the double quantum filtered COSY spectrum. Using the same, interleaved data set, the E.COSY spectrum was then generated. The corresponding multiplet pattern (Fig. 1C) in the E.COSY spectrum clearly allows a small, passive coupling of 1.1 Hz to be extracted from the data. These same features are seen in other cross peak multiplets from the double quantum filtered COSY spectrum (Fig. 1D) and the E.COSY specturm (Fig.1E). We note that because of the low t_1 resolution of this experiment, the apparent active coupling is strongly distorted along ω_1 (J_{app} = 7 Hz, Fig. 1C) as compared to its actual value, which is reliably given along ω_2 in the present spectra (J = 4.8Hz, Fig. 1C). On the other hand, passive couplings as small as 1 HZ can be reliably measured in these spectra.



In cases where an E.COSY spectrum would alone be sufficient to completely analyze a spectrum, interleaved acquisition of multiple quantum filtered COSY spectra is probably overkill. However, in more complex spectra, where multiple quantum filtered COSY spectra of higher filter orders are helpful in spectral interpretation, the interleaved acquisition procedure allows an E.COSY spectrum to also be obtained purely for the price of a little extra data processing.

Barry Gray L.R. Brown

B.N. Gray L.R. Brown

1. C. Griesinger, O.W. Sørensen and R.R. Ernst, J. Amer. Chem. Soc. 107, 6394 (1985).
2. C. Griesinger, O.W. Sørensen and R.R. Ernst, J. Chem. Phys. 85, 6837 (1986).
3. R. Ramachandran, P. Darba and L.R. Brown, J. Magn. Reson. 73, 349 (1987).

P.S. NMR-88 Meeting. Thredbo, New South Wales, Australia. 14-18 February, 1988.

Newsletter readers may have spotted a short notice for the NMR-88 meeting in recent issues. This biennial meeting is the Australian NMR community's equivalent to the ENC or EENC, but of the older, more imtimate flavour, i.e. with ca. 150 participants. For the 1988 meeting, invited speakers include the following.

J.J.H. Ackerman (Washington), R. Bendall (Griffith), G. Bowden (New South Wales), C. Brevard (Bruker), P. Callaghan (Massey), D. Chaplin (ADFA), D. Doddrell (Queensland), D. Gadian (Royal College of Surgeons), L. Jackman (Penn. State), R. Kaptein (Utrecht), R. Lynden-Bell (Cambridge), S. Macura (Belgrade), M. Mehring (Stuttgart), G. Moad (CSIRO), R. Norton (New South Wales), S. Opella (Pennsylvania), J. Pope (New South Wales), B. Sanctuary (McGill), R. Shulman (Yale), O. Sørensen (E.T.H.), G. Wagner (Michigan), E. Williams (Varian), and M. Wilson (CSIRO).

We always have a fair number of overseas visitors and would be pleased to welcome others (see contact address on p. 1 of this issue). The meeting will be held at a ski resort in the Australian Alps (near Canberra), where it does not snow in February.

POST-DOCTORAL FELLOWSHIP: A position is available at the Lilly Research Laboratories for a post-doctoral scientist with experience in applying modern techniques of NMR spectroscopy to the study of complex carbohydrates; specific experience in glycoprotein studies is desirable. The NMR laboratory operates four superconducting spectrometers, ranging from 250 to 500 MHz; a second 500 MHz instrument will be ordered shortly. The post-doctoral fellow will receive an excellent stipend and full employee benefits; publication of research results will be encouraged. Interested scientists should send a curriculum vitae to Dr. Ann H. Hunt, Dept. MC525, Eli Lilly and Company, Indianapolis, IN 46285-1513.

Texas A&M University NMR Newsletter - Book Reviews

Book Review Editor:
William B. Smith, Texas Christian University, Fort Worth, Texas.

"Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes"

(Methods in Stereochemical Analysis, 8.)

by

John G. Verkade and **Louis D. Quin**, Eds.

VCH Publishers, Inc., 303 N.W. 12th Avenue, Deerfield Beach, Florida 33442-1705; (1-800-422-8824); 1987; 717 pages; $125.00.

Phosphorus-31 NMR spectroscopy is a vital experimental technique in many areas, spanning organic chemistry, coordination and organometallic compounds, and biochemistry. For this reason, and the fact that the last major review of the field [Crutchfield, M.M., Dungan, C.H., Letcher, J.H., Mark, V., and Van Wazer, J.R. in *Topics in Phosphorus Chemistry, Vol. 5*; Grayson, M. and Griffiths, E.J., Eds., Wiley-Interscience: New York, 1967] is now twenty years old, the new volume edited by Verkade and Quin is a very welcome and timely effort. Also, the coverage here is much broader than, and does not duplicate, that of another recent book [Gorenstein, D.G., Ed., *Phosphorus-31 NMR, Principles and Applications*, Academic Press: New York, 1984] which deals mainly with the important biological applications of ^{31}P NMR spectroscopy.

This book consists of twenty chapters, each written by a recognized expert in his respective field. More importantly, the editors have done an excellent job in the planning and organization of the total subject. Readers new to the area are first introduced (Chapters 1 and 2) to the simple measurement and general interpretation of ^{31}P chemical shifts. These chapters also serve as a good outline for the detailed material which follows.

The next several chapters (3-6) deal with experimental techniques (including 2D and solid state experiments) and theoretical considerations (both chemical shift and spin-spin coupling phenomena are well-explained). Chapters 7-13 cover, in a logically progressive manner, particular applications of ^{31}P NMR to the solution of structural, conformational, and mechanistic problems in organophosphorus chemistry.

The important concept of the stereospecificity of ^{31}P couplings to all of the NMR-active nuclei is especially well-treated in chapters 11-13. The last seven chapters are devoted to all varieties of coordination compounds of phosphorus: unidentate, polydentate, bridging, one- and two-coordinate phosphines, ylides, phospholes, and phosphoramides. Although a great many types of compounds are covered, one noticeable omission from the book is the subject of poly(organophosphazenes). Given the technological importance of these P-N polymers, and the utility of ^{31}P NMR in their characterization, a chapter on such materials and their cyclic analogs would seem to have been warranted.

Overall, however, this is an excellent book with well-connected chapters which are remarkably consistent in terms of their level of coverage, clarity of organization, and comprehensiveness. Unquestionably, this is a landmark volume, not only for the field of ^{31}P NMR spectroscopy, but also for phosphorus chemistry in general.

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349-22

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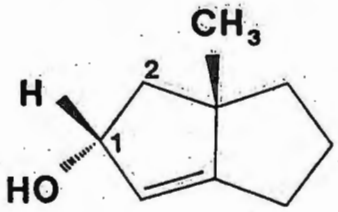
august 28, 1987
(received 9/9/87)

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

Dear Dr. Shapiro

Adventures with $^1H/^1H$ NOE Experiments

In order to determine the relative configuration of carbon C-1 in 1 we applied homonuclear 1D NOE experiments. By irradiation of the protons at C-1 at the OH-and the methyl group in subsequent experiments we could unambiguously solve the problem, since the explanation of the NOE effects detected for the two methylene protons at C-2 in these experiments was straightforward. More interesting was the fact, that by irradiation of the



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OH-proton a strong "negative NOE" could be detected for the methine proton at C-1 and vice versa. The extent of this effect (> 50%) is so large that it can hardly be attributed to a real negative NOE. This effect must therefore be explained by saturation transfer due to slow chemical exchange among these protons. The effect is absent in the corresonding epoxid.

Surprised by this - at least in the eyes of NMR-spectroscopists - unexpected process two questions arrised:

1. Which are the reasons for this unusual exchange ?
2. Why there is no isomerization at C-1 in the course of this process ?

The subsequent figure gives possible answers which would explain this phenomena

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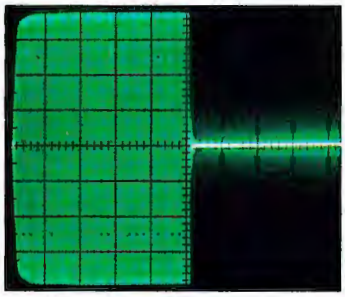
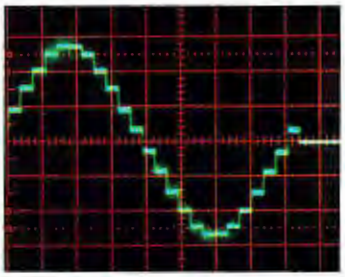
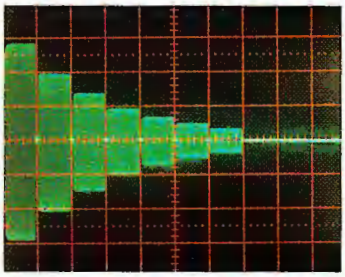
A 5μsec ^{1}H observe pulse. ▼





15° phase shift through 360°. ►



Shaped decoupler pulse. ►

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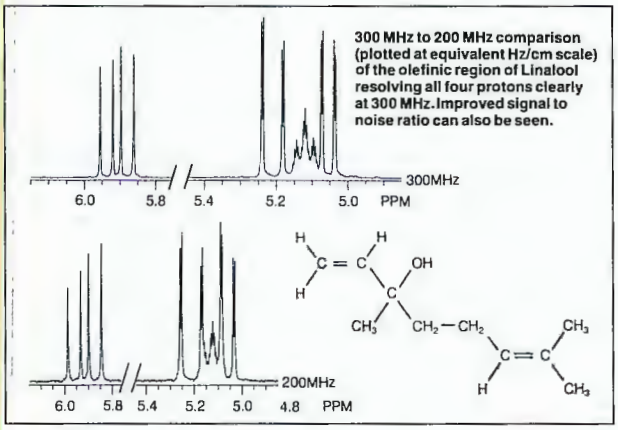

300 MHz to 200 MHz comparison (plotted at equivalent Hz/cm scale) of the olefinic region of Linalool resolving all four protons clearly at 300 MHz. Improved signal to noise ratio can also be seen.

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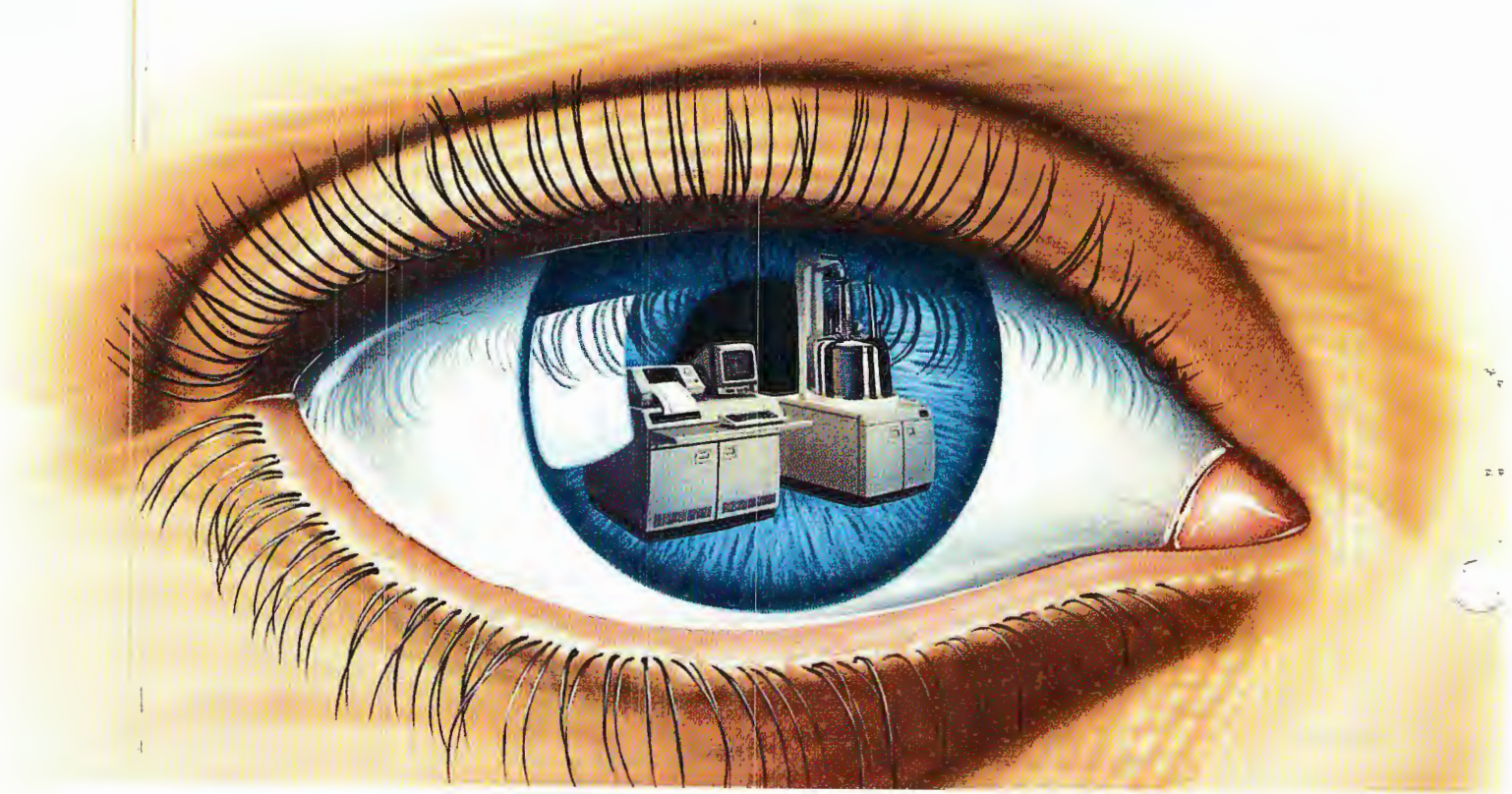
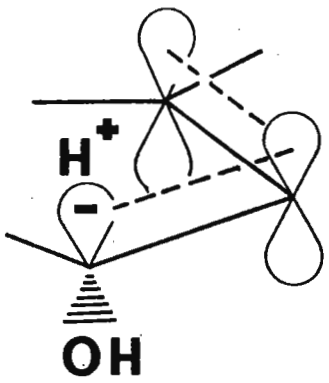
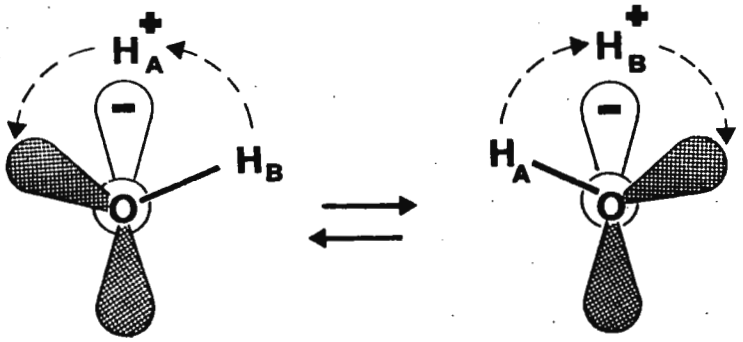


a



b



a) partial overlap of the sp^3-orbital at C-1 with the π-system of the double bond. The concomitant partial change of hybridization at the quaternary olefinic carbon ($sp^2 \rightarrow sp^3$) would probably reduce some strain inherent in this structure.

b) proton exchange mechanism without isomerization at C-1

Please do not hesitate to inform us about your doubts, corrections and better explanations.

Yours sincerely

Peter Bigler

SYRACUSE UNIVERSITY
NMR and DATA PROCESSING LABORATORY
GEORGE C. LEVY, DIRECTOR (315) 423-1021

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

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

26-Aug-1987 (received 9/1/87)

2D MAXIMUM ENTROPY SPECTRAL DECONVOLUTION

Dear Barry:

Spectroscopists who do high-resolution 2-D nmr on macromolecules are painfully aware of the problems that occur with broad overlapping peaks and sample-limited sensitivity. RNA is one of the most difficult systems since the proton NOESY has only the base-base and base-H1',H5 regions relatively free of overlap; the five other sugar protons resonating over a 1 ppm range. Even the base-H1',H5 region is complex for 20-mer size RNA. Figure 1 shows a portion of the base (purine H8, pyrimidine H6) to H1', pyrimidine H5 region of the 500 MHz NOESY spectrum of a 25-mer analog of the coat protein binding domain of R17 viral RNA. The molecule forms a hairpin loop under the conditions of our spectra. The large H5-H6 cross-peaks are most conspicuous, but all of the peaks are broad and overlap badly, making assignments via the base-H1' NOESY walk very difficult. The sample was 4mM in D_2O and the spectrum was acquired in about 48 hours with a 500 ms mixing time.

Anyone who has seen a computer enhanced satellite photo of a license plate taken from space is aware of possibilities in image enhancement. We have applied the same principles to the RNA spectrum. Figure 2 shows the same 128 x 128 spectral region enhanced by maximum entropy spectral deconvolution, with 10 Hz removed from the natural linewidth. The calculation required about half an hour of cpu time on a VAX 8650 (it would take less than one hour on a Sun-3 or perhaps 15 minutes on a Sun-4, all without array processor). The contrast between Figures 1 and 2 is impressive. We have not completed the analysis yet, but we now believe we can make a complete assignment of the base and H1' protons.

John Milligan and Olke Uhlenbeck at the University of Colorado prepared the RNA using T7 RNA polymerase; Feng Ni wrote the MEM processing routine and performed the image enhancement; Karl Bishop and Steve LaPlante are engaged in the experimentation and data analysis.

Sincerely,

Philip N. Borer
Associate Director
Research Associate Professor

George C. Levy
Professor and
Director

R17 VIRAL RNA
COAT PROTEIN BINDING SITE

^{12}U C^{13}

^{11}A A^{14}

^{10}G C^{15}

^{9}C G^{16}

^{8}A ^{7}G C^{17}

^{6}U A^{18}

^{5}C G^{19}

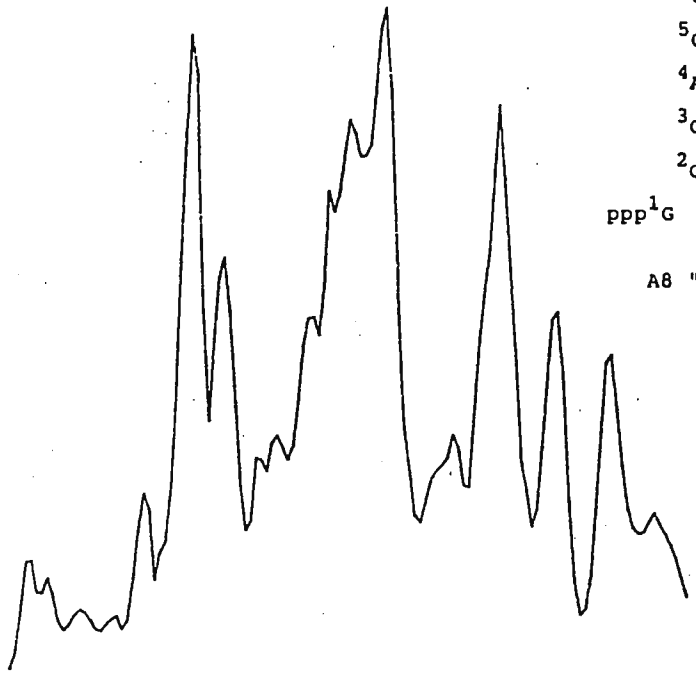
^{4}A U^{20}

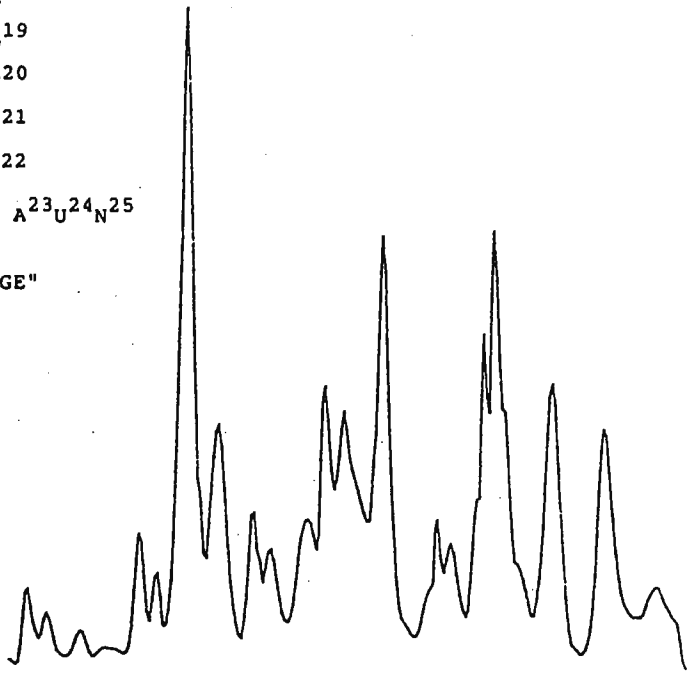
^{3}G C^{21}

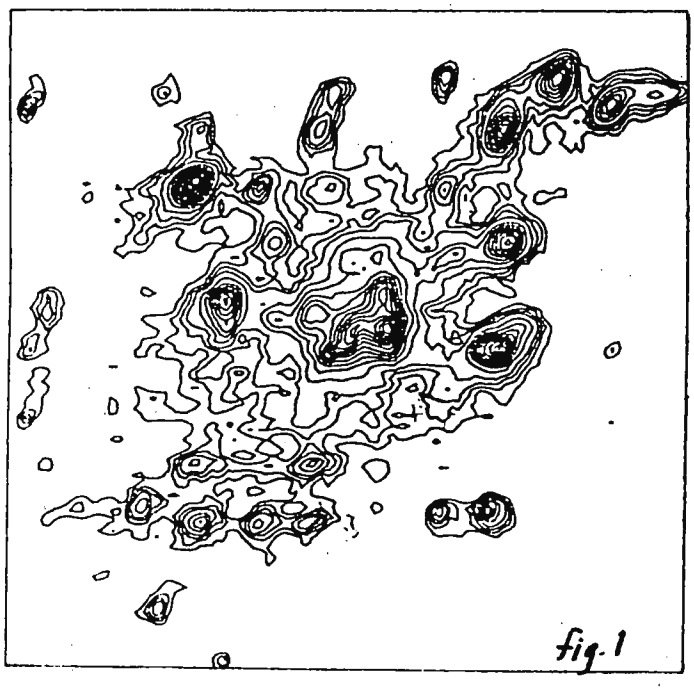
^{2}G U^{22}

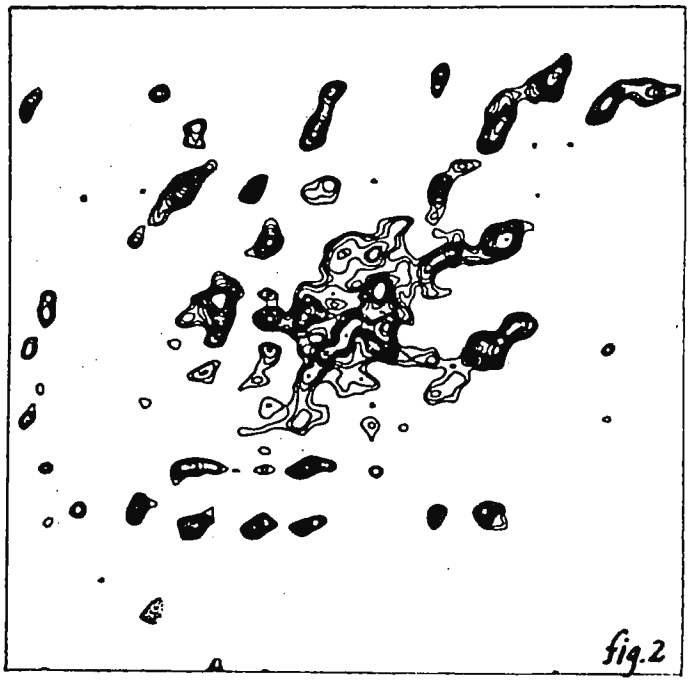
$ppp^{1}G$ $A^{23}U^{24}N^{25}$

A8 "BULGE"









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(BASE - H_1' REGION)

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DEPARTMENT OF CHEMISTRY BERKELEY, CALIFORNIA 94720

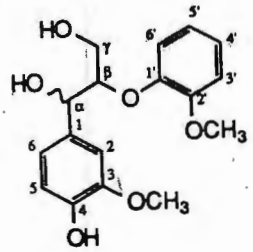
(received 8/29/87)

Professor B.L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303

Long-range C-H Correlations through Oxygen

Dear Professor Shapiro,

For many years there has been considerable confusion over the assignment of aromatic carbons, particularly the quaternary ones, in ^{13}C NMR spectra of lignin model compounds such as 1.



1

With all the excellent enhancements to the long-range C-H correlation experiment around these days, we would like to have shown you how one of these rapidly solved our problem.

We say "*would like to have*" - the truth is that the first wham-bam long range C-H correlation using the good old Bax and Morris sequence[1] with delay times chosen with almost total disregard to coupling constant,[2] worked so beautifully to give us unequivocal results we have a tough time justifying a more esoteric approach. We present it here because, while the ability to do it is no surprise, we are not aware of many examples of correlations between a carbon and a phenolic hydroxyl proton being so useful.

The figure shows the 2D long-range C-H correlation plot from compound erythro-1 (100 mg in $CDCl_3$, Bruker AC-200, program XHCORD.AU, delay times[1] $\Delta 1$ = 35 ms, $\Delta 2$ = 25 ms, 1K data points in F2, 256 zero-filled to 512 in F1, Gaussian apodization in both domains). The phenolic hydroxyl proton correlates strongly with C5 (114.3 ppm, 3-bond) and clearly with C3 (3-bond) and C4 (2-bond). One of these carbons (146.6 ppm) also correlates with methoxyl

protons and is therefore unambiguously assigned to C3. The remaining correlated peak must logically be C4. Correlating with the methoxyl protons is also a peak at 151.3 ppm. Clearly this must be C2'. By default, the remaining oxygenated aromatic carbon (146.9 ppm) must be C1'. Other correlations are also informative and aid the complete assignment.

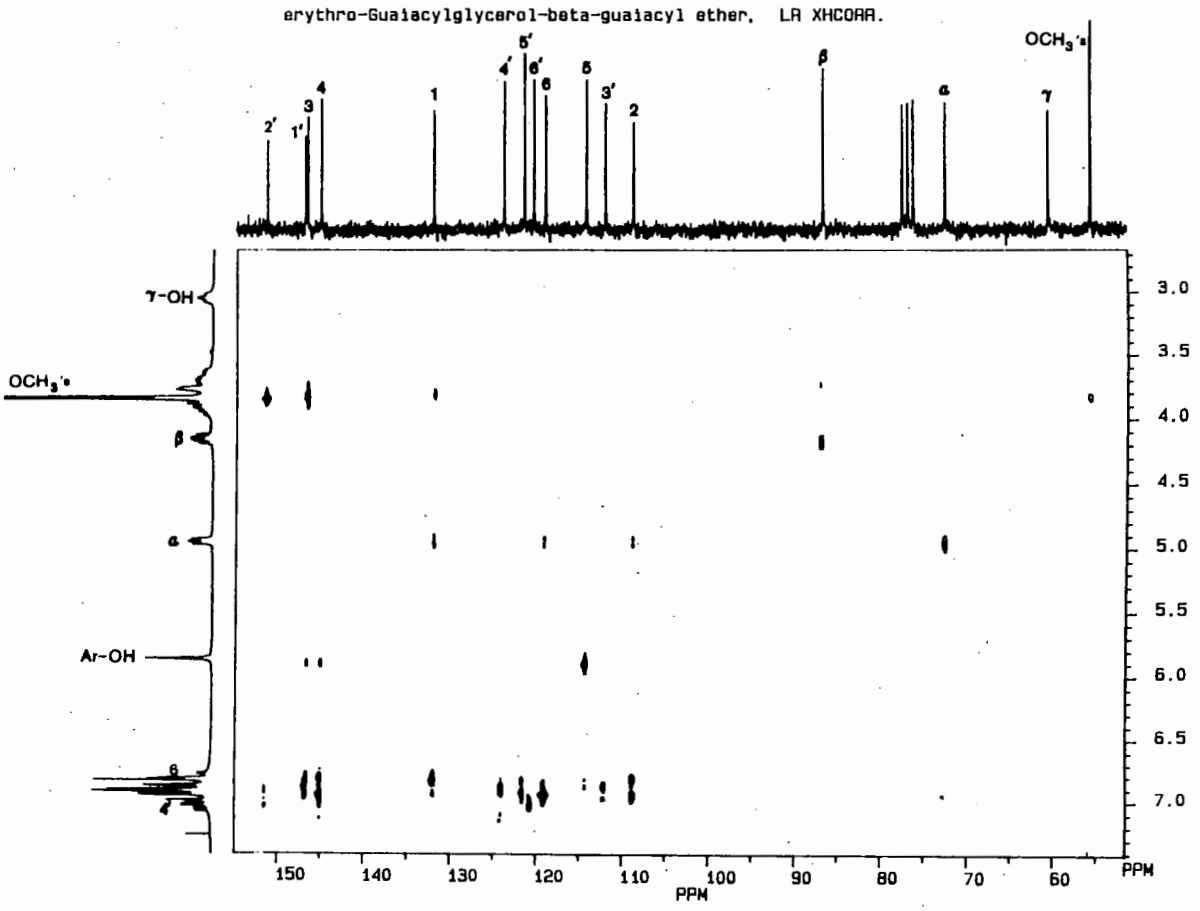
References:

1. A. Bax and G.A. Morris. J. Magnetic Resonance **42**, 501 (1981).
2. W.F. Reynolds *et. al.* Canadian J. Chem. **62**, 2421 (1984).

Yours sincerely,

John Ralph

(Please credit the account of Rudi Nunlist)



FACULTE DES SCIENCES
Université de Nantes - Dépt de Chimie

RÉSONANCE MAGNÉTIQUE NUCLÉAIRE
ET RÉACTIVITÉ CHIMIQUE
UA - CNRS N° 472

Nantes,
le 31 août 1987
(received 9/9/87)

Precision and Accuracy of SNIF-NMR

Dear Barry,

I apologize for being so late in "paying" my subscription to the TAMU-NMR Newsletter. Fortunately your ultimatum which expired at the end of June has been kindly reported to the end of August !

In our investigations of Site-specific Natural Isotope Fractionation we are faced with many problems associated with the precision and accuracy of quantitative deuterium NMR. In this respect it became necessary to compare deuterium/hydrogen ratios obtained in different laboratories equipped with different NMR spectrometers, and to report the results on the same scale. Moreover, since mass spectroscopists, who pioneered the field of natural abundance isotope ratios, use to report their results on the scale defined by the IAEA (1), it was also necessary to compare the data given by both techniques.

The precision is defined in terms of repeatability, r, (short period of time, same spectrometer and same operator) and of reproductibility, R, (long period of time, different spectrometer and/or operator) (2). A collaborative study was organized by the Community Bureau of References in Bruxelles and 16 different european laboratories were involved in the work. We have considered more specifically in Nantes the problem of short and long term repeatibility since we use to run periodically the same test samples since 1984. The confidence interval, defined for a probability of 95 %, on a given measurement is on the order of 0,25 % for site-specific isotope ratios D/H of about 120 ppm obtained with a Bruker AM 400 spectrometer and a specific $^{2}H\{^{1}H\}$ probe (Ø 10 or 15 mm OD) with a 19F field-frequency lock and an automatic sample changer. The repeatibility, r, defined according to the ISO norm (2) at a 95 % confidence level is equal to 0.8 % and the reproducibility, R, after elimination of outlyers, is on the order of 2-3 %. However it should be noted that the 16 laboratories concerned are equipped with very different system and probe configurations. If we compare the results given by spectrometers having comparable performances, the reproducibility R becomes on the order of 1 %.

The accuracy is usually defined as the closeness of agreement between the mean result over a large number of experiments and the true value which characterizes the quantity under study. Then the determination of the accuracy of SNIF-NMR involves a comparison with the results of an independent technique, and owing to the great dilution of deuterium in natural compounds we have choosen mass spectrometry. Since MS may also suffer from systematic deviations, the NMR-MS comparison could be considered as a self-consistency test for both techniques.

Two samples of water were used in this experiment. One sample of GISP (3) was provided by the IAEA in Vienna and submitted to a collaborative study in which 45 laboratories were engaged. Among them only one (Nantes) used NMR spectroscopy as a tool :

(1) (D/H)GISP	NMR (Nantes, 10 replications)	126,5 ppm
	MS (45 laboratories)	126,2 ppm

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Output: +3 to +10dBm: 50 ohm
Spurious Outputs: −75dBc

Phase Noise: −75dBc, (0.5Hz-15KHz)
Freq. St'd: Oven, TCXO, Ext.
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Switching: 5-20μs
Output: +3 to +13dBm: 50 ohm
Spurious Outputs: −75dB

Phase Noise: −63dBc, (0-15KHz)
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Spurious Outputs: −70dB

Phase Noise: −63dBc, (0-15KHz)
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Resolution: 0.1Hz-100KHz (opt.)
Switching: 5-20μs
Output: +3 to +13dBm: 50 ohm
Spurious Outputs: −70dB

Phase Noise: −63dBc, (0-15KHz)
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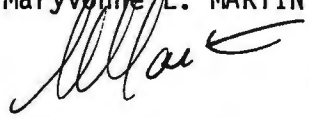
The second sample was Nantes tap water used as a secondary reference (NTW) and calibrated by NMR and MS in our laboratory.

(D/H)NTW	NMR (10 replications)	150,1 ppm
	MS (5 replications)	149,9 ppm

The results may be considered as being quite gratifying, but we should say that the accuracy is not so high when organic molecules are considered. However, it is not easy to assess which technique, from MS and NMR, gives the true value ! (4)

Sincerely,

Gérard J. MARTIN Maryvonne L. MARTIN



(1) Advisory Group Meeting on Stable Isotope Reference Samples IAEA, Vienna, September 1983
(2) ISO 5725-1981 Case Postale 56 (CH) 1211 Geneva
(3) Groenland Ice Sheet Precipitation
(4) The complete results and statistical considerations will be published soon

---

Position available

In the scope of a research program concerning the application of stable isotope methods in biotechnology and food processing performed in collaboration with Institutions of the EEC, we may apply for a one or two years grant.

This grant may concern :

a) - post graduate students (the preparation of French PhD can eventually be considered) - Grant : about 9000 FF per month.

b) - people having obtained a PhD or having a professionnal experience of at least 5 years in a research laboratory. The amount of the grant depends on the qualification.

Fields of interest

Application of stable isotope fractionation (H,C,N,O) at the natural abundance (NMR,MS) to the investigation of natural products (perfumes and aromas). NMR (Bruker AM 400) and MS (VG SIRA9) spectrometers as well as computing facilities will be available for this research.

Application

The application should be addressed to Gérard J. MARTIN, University of Nantes RMN-RC, 2 rue de la Houssinière, (F) 44072 NANTES CEDEX, with a detailed CV and at least one letter of recommendation.

EMORY UNIVERSITY
Department of Chemistry

1515 Pierce Drive
Atlanta, Georgia 30322
404/727-6585

Postdoctoral Positions Available:

Two postdoctoral positions are available in the Chemistry Department at Emory University applying high field NMR techniques to the study of biological molecules. Modern 2D NMR techniques will be emphasized, particularly 2D heteronuclear indirect detection and isotope directed methods. Systems under study include peptides, proteins and oligonucleotides. Facilities available for this work will be a modified NT-360, a GN-500, and a GN-600, the latter due in 1988. Familiarity with biomolecules and/or 2D NMR techiques is strongly preferred. Send CV and names of three references to either Dr. Luigi Marzilli or Dr. David Live, Department of Chemistry, Emory University, Atlanta, GA 30322.

Equipment Available:

An HFX-90 NMR spectrometer (CW) console and the associated 18 inch magnet are available. When last used (some time ago) the console worked and the magnet is in good condition. Contact David Live, Dept. of Chemistry, Emory University, Atlanta, GA 30322.

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PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

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

Position Available - NMR Instrumentation Specialist:

Dear Barry:

There is a position open in the Department of Chemistry for a person with experience in the maintenance, operation, and development of modern (200 MHz or greater) NMR spectrometers.

We are seeking an individual with at least a Bachelor's degree in a physical science or engineering discipline. This individual must have taken introductory Chemistry courses at some point in his/her career. A minimum of three years "hands-on" experience with superconducting NMR spectrometers is a requirement for the position. If an exceptionally well qualified and experienced candidate should apply, certain of the above educational requirements could be waived.

This individual will spend about one-half of his/her time engaged in relatively routine set-up and daily maintenance of various Departmental NMR spectrometers ranging in field strength from 200 to 600 MHz. The remainder of his/her time will be spent in special projects which are intended to expand the capabilities of the departmental NMR spectrometers for use by the faculty.

We will consider candidates with training in interpretive NMR methods with a strong interest and experience in NMR hardware and/or software development. We will equally consider candidates with training in the electronic, instrumental, and computer aspects of NMR spectroscopy. The successful candidate must possess basic skills at NMR spectral interpretation and sufficient chemical training to communicate with faculty and graduate students who are **not** NMR specialists.

The starting salary for the position will be competitive and commensurate with the successful candidate's demonstrated skills and qualifications. The appointment is a budgeted position within the Department of Chemistry. This individual will report to me for administrative purposes and overall technical direction. The position is classified as a Professional Staff appointment within the University. The benefit package is particularly attractive.

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Any interested person is encouraged to submit a resume to me, in complete confidence, at the letterhead address. Three professional references must be supplied in the resume.

If any reader of this letter should have specific questions about this appointment, please feel free to contact me at (317) 494-5230 by telephone.

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Sincerely Yours,

Robert E. Santini

Robert E. Santini
Director NMR Instrumentation
Department of Chemistry

UCSF DEPARTMENT OF RADIOLOGY

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Several openings for experienced In Vivo NMR spectroscopists. Requirements: Ph.D. in Chemistry, Physics, Electrical Engineering, or related fields and expertise in areas of NMR localization techniques and chemical shift imaging. Research focus: MRS studies of humans and animals, and design of new NMR methods. Successful applicants will develop independent research and seek funding to support this research. University of California is an Equal Opportunity/Affirmative Action employer. Women, minorities and handicapped individuals are encouraged to apply. Send C.V., description of proposed research, and names of 3 references to: Dr. M. Weiner, Magnetic Resonance Unit (11D), Veterans Administration Medical Center, 4150 Clement St., San Francisco, CA 94121.

349-36 University of Illinois at Urbana-Champaign

School of Chemical Sciences

505 South Mathews Avenue
Urbana, IL 61801

September 1, 1987
(received 9/8/87)

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

Dear Barry:

Title: Solid-State NMR Potpourri

Here are three, rather disparate, observations concerning multinuclear solid state NMR that we think may be of interest.

First, since it is common practice to set the "magic-angle" with a small amount of KBr in the sample, we felt that anyone using ^{23}Na MASS NMR would be interested in Figure 1. This is the ^{23}Na MASS NMR spectrum of reagent grade KBr (MCB Reagents, "Na content 0.02%"). The high frequency signal arises from NaBr. The low frequency signal is, we believe, due to Na occupying a K site in the KBr lattice. The spectrum is referenced to an aqueous 1M NaCl solution.

Secondly, for those lucky enough to possess isotopically enriched $^{29}SiO_2$, we include the spectrum shown in Figure 2. This is the ^{29}Si MASS NMR spectrum of 95.28% enriched $^{29}SiO_2$ obtained from Oak Ridge National Laboratories, and shows that at least two different silica phases are present. Roughly 60% of the material appears to be cristobalite, as indicated by the high frequency peak at δ = -108.88 ppm, while the lower frequency signals (δ = -110.10 and -111.59 ppm) occur in the region ascribed to tridymite.

Finally, in Figure 3 we show what we believe to be the first solid-state ^{73}Ge NMR spectrum of a non-metallic compound, obtained from a static sample of GeI_4 (2 grams). The spectrum required three hours to obtain, and is referred to neat $GeCl_4$. Incidentally, we couldn't see a signal from GeO_2, our compound of interest, even after an overnight run.

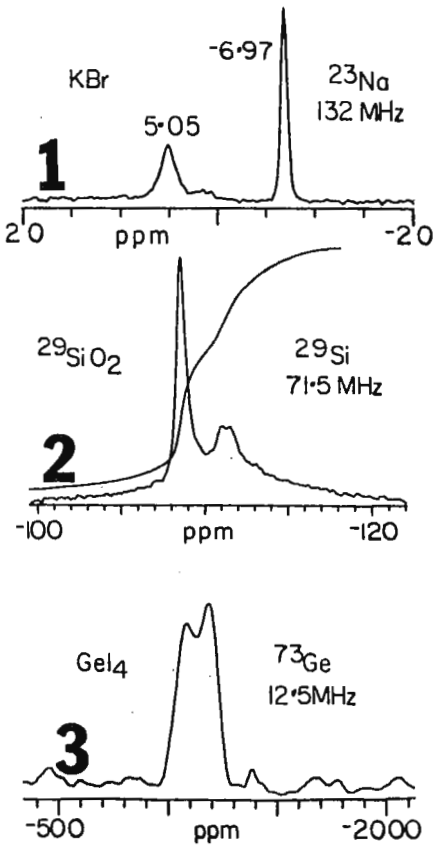
Yours sincerely,

C. T. G. Knight B. L. Phillips G. L. Turner

CTGK/BLP/GLT/kjm

Enclosures

Please credit this to the account of Eric Oldfield.



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MR PHYSICIST

The Department of Radiology of the University of Arkansas for Medical Sciences anticipates having a position for a physicist or similar person involving research in clinical magnetic resonance. The individual will be expected to apply MR imaging and spectroscopy to problems of a clinical nature. The Department currently has a GE Signa NMR imager with spectroscopy accessory. Some computer programming may be required. The opportunity also exists for working on the GE CSI-4.7/33 system and GN-300 WB spectrometers in the UAMS NMR laboratory. An M.S. or Ph.D. degree is required. Salary is commensurate with training and experience.

Interested individuals should send a resume and names of references to:

Richard A. Komoroski, Ph.D.
Director, NMR Laboratory
Department of Radiology
University of Arkansas for Medical Sciences
4301 West Markham
Little Rock, AR 72205

POSTDOCTORAL POSITION

A postdoctoral position is available in the NMR laboratory of the Department of Radiology and Pathology of the University of Arkansas for Medical Sciences. The candidate should have a Ph.D. in one of the basic sciences and some previous NMR experience.

The NMR laboratory currently consists of a General Electric CSI-4.7/33 NMR imaging/spectroscopy system and a GN-300WB with multinuclear capability for high resolution NMR of both solids and liquids. There is also liberal access to a GE Signa clinical MRI system with spectroscopy accessory. The laboratory currently has independent or collaborative projects in a number of areas, including imaging of metabolites, clinical MR spectroscopy of ^{31}P, $^{1}H$and, ^{19}F, ^{7}Li imaging and spectroscopy <u>in vivo</u>, and NMR imaging of elastomeric materials.

Interested individuals should send a resume and names of three references to:

Richard A. Komoroski, Ph.D.
Director, NMR Laboratory
Department of Radiology, Slot 596
University of Arkansas for Medical Sciences
4301 West Markham
Little Rock, AR 72205

SYRACUSE UNIVERSITY
NMR and DATA PROCESSING LABORATORY
GEORGE C. LEVY, DIRECTOR (315) 423-1021

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

September 18, 1987
(received 9/25/87)

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

Dear Dr. Shapiro:

We have been examining interactive enhancement algorithms from the field of image processing for applications in 2D spectroscopy. One class of these transforms generalizes diagonal symmetrization procedures previously proposed[1] . They differ in the fact that they base their discrimination between peaks and noise on the neighborhood of each point and its counterpart.

We propose to fold the matrix over the diagonal so that points I(m,n) and I(n,m) become neighbors. This results in an intercalation of points coming from above and below the folding axis, forming a hexagonal network (see Figure 1).

One technique applied to this folded data with interesting results is the morphological filter[2] (see Figure 2). This procedure makes use of erosion and dilation operators. In the erosion operation, each point in the original data is replaced by the minimum value over a neighborhood defined by a template. Dilation applies the same procedure, only the local maximum is used. These definitions apply to positive-definite spectra, but alternative definitions are possible. We have employed a combination of these filters in a process called opening, which is the result of an erosion followed by a dilation.

The shape of the template is of primary importance. If we use an isotropic template 1 point wide, the opening transform removes local maxima which are less than 3 points in diameter; therefore, this template eliminates narrow local maxima.

Because of the intercalating procedure, peaks and their symmetric partners will form a surface twice as large as that of either peak. By contrast, noise which has no symmetric correlation will be spread and weakened in the folded data set, and the opening process will reduce it, since it will not likely contain wide maxima.

If we consider the neighborhood of a given point in the folded spectrum, we observe that it contains the symmetric partner of this point too. Consequently, a template which takes only these two points into account gives the traditional symmetrization procedure.

The folding process allows the application of a background noise filtering method derived from a class of well known image processing tools. Note that while this technique only enhances the appearance of the spectrum, the result can be used as a mask for peak finding and extraction in the presence of heavy noise, for instance as a pre-processing step for automated spectral interpretation. The versatility of morphological filters, already widely used for the processing of numerous biochemical data sets[3], should provide other interesting feature extraction methods for NMR spectroscopy.

Best regards,

Pascale Sole
Image Processing Applications
NIH Resource for NMR and Data Processing
and CASE Center

Frank Delaglio
NMR2 Product Manager
New Methods Research, Inc.

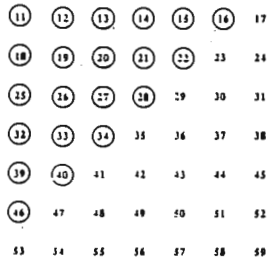
Figure 1 (a) 2D matrix; (b) The same matrix, with folding applied. The template defining neighbors for point 51 is outlined.

Figure 2 COSY spectra of fluorenthene with Gaussian noise added (σ=10% data maximum). (a) Original data plus noise. (b) Traditional symmetrization, replacing point and image with minimum. (c) Morphological filter. (d) Data with no noise added. ALL DATA PROCESSED AND PRESENTED BY NMR2; ALL CONTOUR PLOTS MADE WITH LEVELS EQUALLY SPACED STARTING AT 10% OF DATA MAXIMUM.

REFERENCES

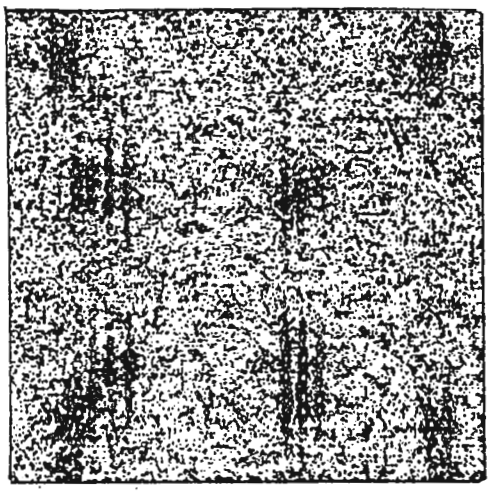
1. R. Baumann, G. Wider, R.R. Ernst, and K. Wuthrich, *J. Magn. Reson.* **44**, 407 (1981).
2. R.M. Haralick, S.R. Sternberg, and X. Zhuang, *IEEE Trans. on Pattern Analysis and Machine Intelligence*. **4**, 532 (1987).
3. M.M. Skolnick, *Computer Graphics, Vision, and Image Processing*. **35**, 306 (1986).

1a.



1b.

2a.



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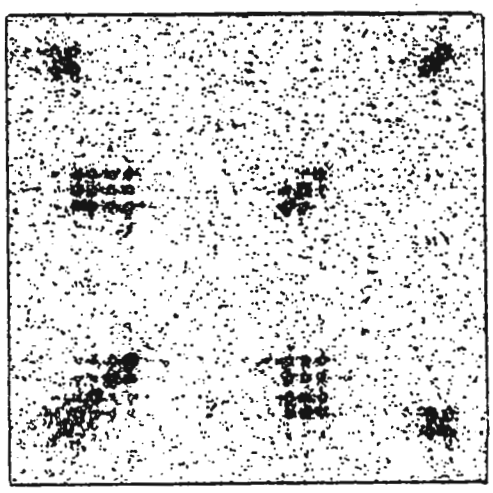
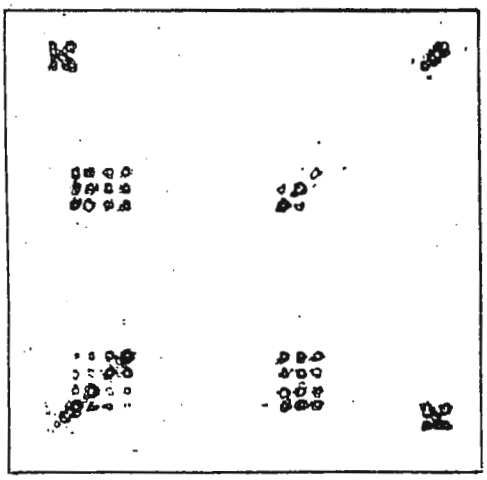
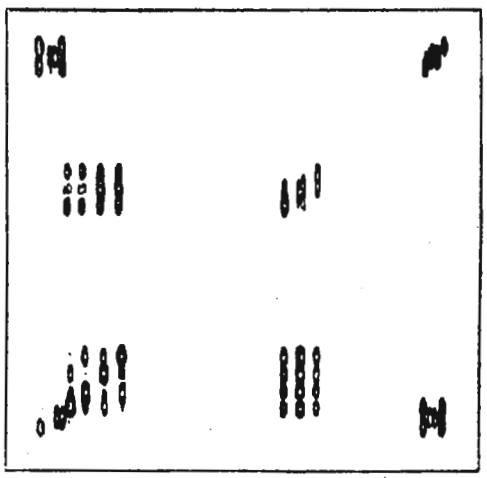


2c.



2d.



UNIVERSITY OF FLORIDA
GAINESVILLE, 32611

DEPARTMENT OF CHEMISTRY

September 17, 1987
(received 9/21/87)

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

Dear Barry:

I should like to call to the attention of your readers the magnetic resonance aspects of the program that has been arranged for the Southeastern Regional American Chemical Society Meeting in Orlando, November 4-6, 1987. Of special interest should be the symposium on Magnetic Resonance Imaging which will occupy a full day on Thursday, November 5. The meeting will be at the Sheraton Twin Towers Hotel, 5780 Major Boulevard, with a toll-free phone number outside Florida: 1-800-327-2110. Anyone wishing to attend should identify the "SERMACS" meeting when making reservations in order to obtain the special rate available to those who act with sufficient alacrity. Any questions about the program can be directed to me at 904-392-0520.

Yours sincerely,

Wallace

Wallace S. Brey
Professor of Chemistry

Wednesday Afternoon
Nuclear Magnetic Resonance
R. W. King, Presiding

1:10--113. Synthesis and NMR Analysis of Fentanyl Analogs. G. A. Brine, P.-T. Huang, D. K. Sawyer, K. G. Boldt, F. I. Carroll

1:30--114. Solid State and Solution ^{13}C NMR of Methadone Hydrochloride and Related Analgesics. C. G. Moreland, S. J. Sumner, F. I. Carroll, G. A. Brine, K. G. Boldt

1:50--115. ^{13}C-NMR Spectroscopy of Polymer-Bound Cholic Acid Derivatives. E. C. Blossey, W. T. Ford, M. Periyasamy, S. Mohanraj, R. G. Cannon

2:10--116. Multi-Quantum NMR Experiments Utilizing a Toroid Coil and Cell. B. Bebout, T. E. Glass, H. C. Dorn

2:30--117. NMR Relaxation Behavior of Small Molecules in Supercritical Fluids. L. Allen, T. E. Glass, H. C. Dorn

2:50--Break

3:10--118. Studies in Selenium-77 and Tellurium-125 Nuclear Magnetic Resonance. Substituent Effects and Polarizability. A. M. Boccanfuso, N. P. Luthra, R. B. Dunlap, J. D. Odom

3:30--119. NMR Studies of Al(III)/Acetate Complexes. K. R. Williams, W. S. Brey

3:50--120. Synthesis of Deuterated Radicals Suitable for DNP Studies. C. Tsiao, T. E. Glass, C. Wild, H. C. Dorn

4:10--121. Preparation and Characterization of Immobilized Radicals for Flow DNP NMR Studies. R. Gitti, T. E. Glass, H. C. Dorn

4:30--122. Flow ^{1}H NMR DNP Studies. L. Allen, T. E. Glass, J. Wang, H. C. Dorn

Thursday
Symposium on Magnetic Resonance Imaging
T. H. Mareci, Presiding

8:40--Introductory Remarks. W. S. Brey
8:45--206. Magnetic Resonance Imaging: Macroscopic, Microscopic and Spectroscopic. P. C. Lauterbur
9:35--207. NMR Imaging in Solids. J. B. Miller, A. N. Garroway
10:05--208. NMR Imaging of Oil Cores. W. A. Edelstein, P. B. Roemer, C. J. Hardy, H. J. Vinegar, P. N. Tutunjian
10:35--Break
10:55--209. Spectral-Spatial EPR Imaging. M. M. Maltempo, S. S. Eaton, G. R. Eaton
11:25--210. Electron Spin Resonance In-Vivo. L. J. Berliner

R. W. Briggs, Presiding

1:30--298. NMR Chemical Microscopy. L. D. Hall
2:10--299. Magnetic Resonance Microscopy. G. A. Johnson
2:40--300. Chemical-Shift Imaging of Dynamic Polymer-Solvent Systems. M. D. Cockman, T. H. Mareci, A. Rigamonti
3:05--Break
3:20--301. The Use of Magnetic Field Gradients in Magnetic Resonance Imaging. M. A. Brown
3:50--302. NMR Imaging and Spectroscopy Using Non Uniform RF Fields. D. L. Foxall, A. R. Rath, M. Garwood, K. Urgurbil
4:20--303. Computer-Optimizd Narrowband Pulse Shapes for Selective Spin Manipulation. J. B. Murdoch

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Contact: J. R. Shapley
Department of Chemistry
University of Illinois
452 NL, Box 20
505 S. Mathews
Urbana, IL 61801
(217) 333-0297

College of Arts and Sciences

UNIVERSITY OF MISSOURI-ROLLA

Department of Chemistry

142 Schrenk Hall
Rolla, Missouri 65401-0249
Telephone (314) 341-4420

(received 9/9/87)

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

Dear Barry:

First Annual **MISSOURI MAGNETIC RESONANCE SYMPOSIUM**

I would like to inform the midwestern TAMU readers of the first annual Missouri Magnetic Resonance Symposium and invite them to Rolla to participate in it. The symposium has been initiated by Tuck Wong, Dave Larsen and myself to promote the exchange of knowledge between researchers in the midwest, particularly Missouri and adjacent states. The first of the symposia will be held on the Rolla campus on Tuesday, November 17, 1987. The next two will be held in St. Louis and Columbia. It is hoped that academic, governmental and industrial scientists will make this a yearly event.

The tentative schedule for the symposium is attached. We have an excellent list of speakers. In addition, we plan to have a poster session. The posters may include either applications or advances in magnetic resonance. In other words we want posters from interested users of MR as well as the MR "jocks". We are particularly interested in using this medium for exchange of information between industry and academia.

The weather in southern Missouri is usually very nice in November. You could combine the trip with trout fishing, canoeing, cave exploring, or a weekend at Lake of the Ozarks. In any case, we hope to see you in November. If you need further details call or write.

Sincerely

Frank D. Blum
Associate Professor of Chemistry

an equal opportunity institution

-TENTATIVE SCHEDULE - (First Announcement)-

MISSOURI MAGNETIC RESONANCE SYMPOSIUM

Centennial Hall
University of Missouri-Rolla
Rolla, Missouri

Tuesday, November 17, 1987

8:50 a.m.	Welcoming Remarks
9:00 a.m.	**David Larsen** - University of Missouri-St. Louis "Phosphorus-31 and Deuterium NMR Studies of Membrane Phospholipids"
9:40 a.m.	**James Shoolery** - Varian Associates "Recent Advances in Solution NMR"
10:20 a.m.	Refreshment Break
10:40 a.m.	**Joel Miller** - Naval Research Laboratory "NMR Imaging of Solids"
11:20 a.m.	**Cecil Dybowski** - University of Delaware "Magnetic Resonance Studies of Heterogeneous Catalysis"
12:00 Noon	Lunch
12:30 p.m.	**Poster Session** (General Papers) Exhibits, Tours
2:30 p.m.	**Jacob Schaefer** - Washington University "Chain Motions in Glassy Polymers, Magic Angle Spinning Carbon-13 Analyses"
3:15 p.m.	To Be Announced
4:00 - 6:00 p.m.	Reception

For more information, please contact:

Frank D. Blum
Department of Chemistry
University of Missouri-Rolla
Rolla, MO 65401
(314)-341-4451 (x4420 if no ans.)

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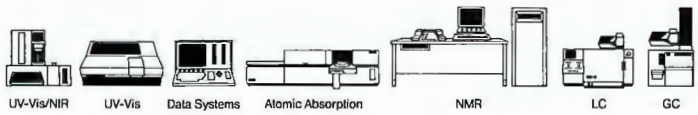

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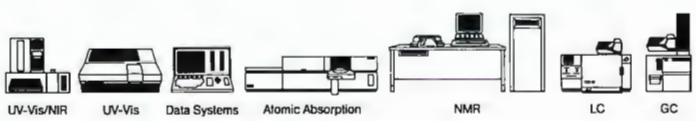

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University of Edinburgh

Department of Chemistry

West Mains Road, Edinburgh, EH9 3JJ Scotland.

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Our ref.: IHS/MAP

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

Telex 727442 UNIVED G
Telephone 031 - 667 1081
Ext. 3676

11th September 1987
(received 9/17/87)

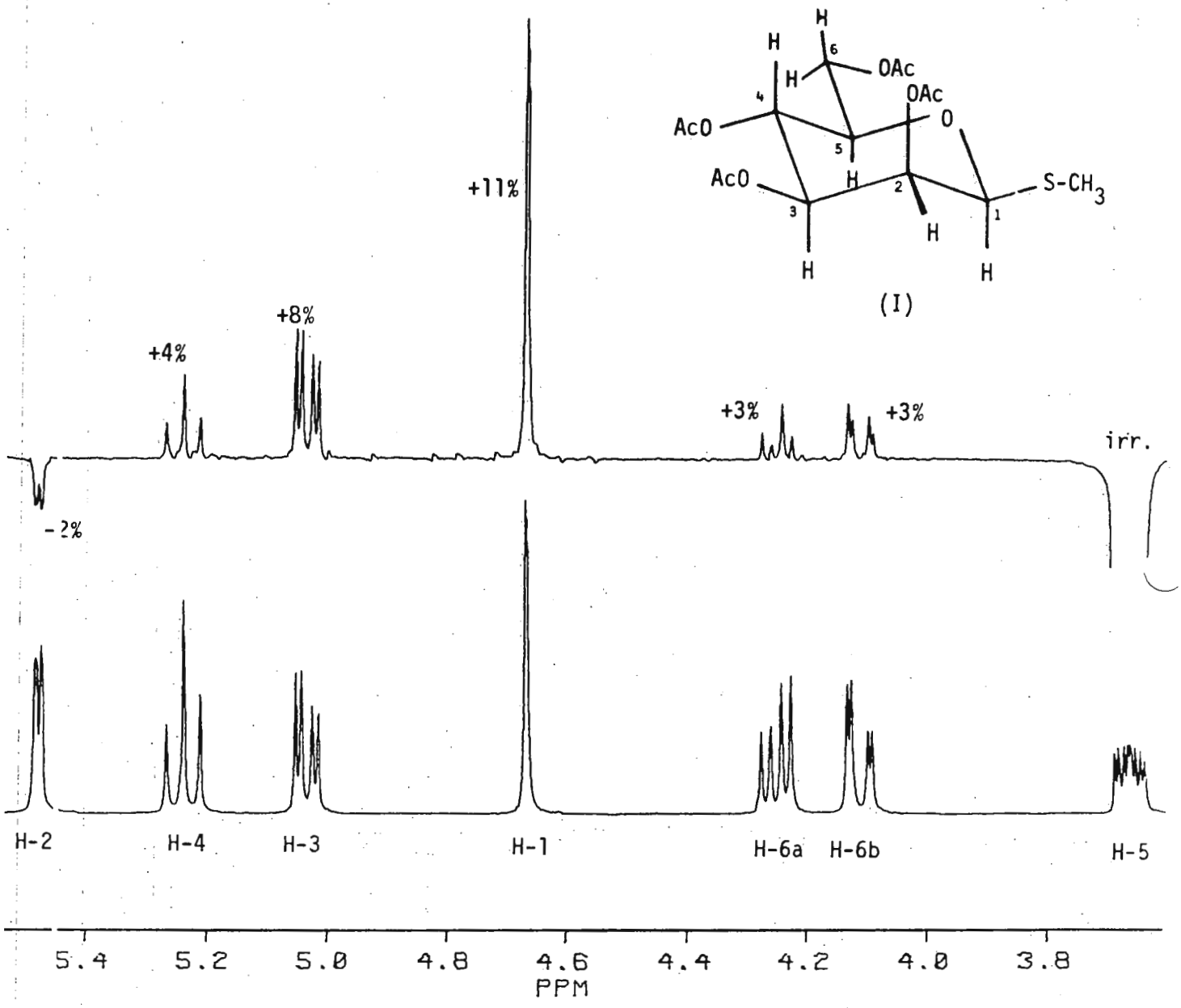
Dear Barry,

An "unexpected" proton NOE in monosaccharide derivatives

Distinction between α- and β-glycosides of mannose derivatives is not always clear cut on the size of the coupling between H-1 and H-2 particularly if only one anomer is available. A clear distinction is usually possible by NOE difference spectroscopy[1] since in the β-anomer the axial protons H-1, H-3 and H-5 are sufficiently close to each other (ca. 3Å) for irradiation of the resonance of any one of these to give significant enhancements of the resonances of the other two. This was observed for the thioglycoside tetraacetate I. In particular irradiation of H-5 using the multipoint technique[2] gave positive enhancements for H-1, H-3, H-6a and H-6b (see figure) as expected and a negative "three spin" enhancement for H-2 presumably transmitted via H-1 and/or H-3. The observation of a positive 4% enhancement for H-4 as well was surprising in view of the diaxial relation of H-4 and H-5, and thence their separation (ca. 4Å), no net enhancement for H-4 being obtained on irradiating H-3. However we are apt to forget that the size of the NOE is determined by the relative disposition of all nearby spins rather than simply the separation of the irradiated and observed spins[3] and also that "three spin" effects are negative only where the two most distant spins form an obtuse θ angle with the third. We believe that this "unexpected" enhancement occurs since both H-6a and H-6b both spend a significant part of their time within 3.5Å of both H-4 and H-5. In these situations the angle θ is always less than 70°. In such a situation a positive enhancement is likely. We felt that some other readers might not be aware that NOEs may be observed "between" diaxial protons in certain situations.

Yours sincerely,

Dr. I.H. Sadler



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1 J.K.M. Sanders and T.D. Mersh, Prog. Nucl. Magn. Reson. Spectrosc., 1982, 15, 353

2 M. Kinns and J.K.M. Sanders, J. Magn. Reson., 1984, 56, 518

3 J.H. Noggle and R.E. Schirmer, "The Nuclear Overhauser Effect", Academic Press, N.Y 1971, p57-95.

AIR PRODUCTS

18 September 1987
(received 9/20/87)

Prof. B. L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303

Fluorine-Decoupled ^{13}C NMR of Liquids

Dear Barry:

Research interests at Air Products have prompted us to develop fluorine-decoupled ^{13}C NMR techniques. Ability to obtain ^{19}F decoupled ^{13}C NMR spectra in a simple and routine manner can greatly simplify structure determination. Such capability is beyond the scope of most older commercial NMR spectrometers because of wide resonance frequency range exhibited by fluorine (typically 140 ppm in perfluorocarbons), and the magnitude of carbon-fluorine scalar coupling ($^1J_{CF}$ is usually about 300 Hz). At Air Products, we have implemented routine ^{19}F decoupled ^{13}C NMR techniques by utilizing high-power capabilities of a Doty CPMAS probe and a solids NMR spectrometer (Bruker CXP-200). Furthermore, we have experimentally compared the efficacy of various multiple-pulse, broadband decoupling techniques.

Hardware modifications involved were minor, requiring the acquisition of a frequency synthesizer and a ^{19}F decoupler pulse unit with 90° phase shifting capabilities. The Doty probe decoupler channel was pretuned as close to the ^{19}F resonance frequency as possible, providing a 10 microsecond 90° ^{19}F decoupler pulse with 100 watts of input power. O-ring endcaps for the Doty rotors were also obtained for sample spinning giving rotation frequencies of >50 Hz and linewidths of approximately 1.5 Hz.

Various multiple-pulse broadband decoupling pulse programs were implemented and tested on the Bruker CXP-200 NMR spectrometer. In addition to CW decoupling, square wave 180°-phase modulated decoupling with 100% duty cycle during acquisition was implemented utilizing either regular phase shifting intervals (henceforth referred to as SWD) or random intervals (RND). Furthermore, MLEV-4, WALTZ-4, and WALTZ-8 were also implemented. Higher analogues of these sequences (such as WALTZ-16 or MLEV-64) were not possible because of pulse programmer limitations.

Figure 1 demonstrates the quality of decoupling obtained by each of the broadband decoupling methods, utilizing 39 watts decoupling power which provides a 16 microsecond 90° decoupler pulse. The sample is neat (liquid) perfluoromethylcyclohexane with 300 Hz MAS. The most upfield and downfield carbon resonances (the perfluoromethyl carbon and the C-1 ring carbon) are most sensitive to decoupling efficiency since their attached fluorines show the greatest frequency offset from the decoupler frequency, equivalent to 11.3 kHz each

at our field strength. Note in Figure 1 that CW decoupling has failed completely, while the sequences based on simple 180° phase modulation (SWD and RND) provided only partial decoupling as indicated by the residual linewidth. Pulse sequences utilizing composite 180° pulses for phase modulation (WALTZ-4, WALTZ-8, and MLEV-4) were quite successful however, providing optimal decoupling over the entire fluorine shift range.

It should be noted that the hardware used is designed for proton decoupling, and the receiver preamp and probe are not perfectly tunable for ^{19}F resonance frequencies. One disadvantage observed with all the decoupling techniques is the appearance of glitches in the spectra, apparently arising from incomplete rejection of the ^{19}F RF in the ^{13}C observe channel electronics. These glitches are reduced as the number of scans is increased or the modulation timing is randomly shifted with respect to signal acquisition.

Plots of the frequency offsets for a given reduction in ^{13}C peak intensity versus decoupler field strength indicate that the relative decoupling efficiencies of the various techniques are

WALTZ-8 > WALTZ-4 > MLEV-4 > > SWD,RND > > CW

Table 1 summarizes the decoupler field strength required to completely decouple all fluorines within the 140 ppm (26.3 kHz) shift range typically observed for perfluorocarbons at our magnetic field strength (4.7T). Results in Table 1 should be able to be extrapolated to different field strengths for the WALTZ-8, WALTZ-4, and MLEV-4 results, since these techniques experimentally show a linear relationship between frequency range effectively decoupled and decoupler field strength. Such an extrapolation may serve as a guide to other spectroscopists, providing a prediction as to decoupler field strengths required using various techniques.

Currently, we are incorporating some of the fluorine decoupling techniques into a variety of ^{13}C applications, including polarization transfer experiments and 2D NMR techniques. One early example is shown in Figure 2, which may be called AFT (Attached Fluorine Test), the fluorine-decoupled analogue to the APT experiment.

In summary, utilization of a solids NMR spectrometer and high power decoupling probe optimized for proton decoupling provides effective ^{19}F decoupling for liquid samples when simple multiple pulse decoupling techniques are used. Further experimental details and results will be published at a future date.

Sincerely,

M. R. Seger
Corporate Research Services Dept.
Air Products and Chemicals, Inc.

H. J. Yue
Corporate Research Services Dept.
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Figure 1. Comparison of Decoupling Methods

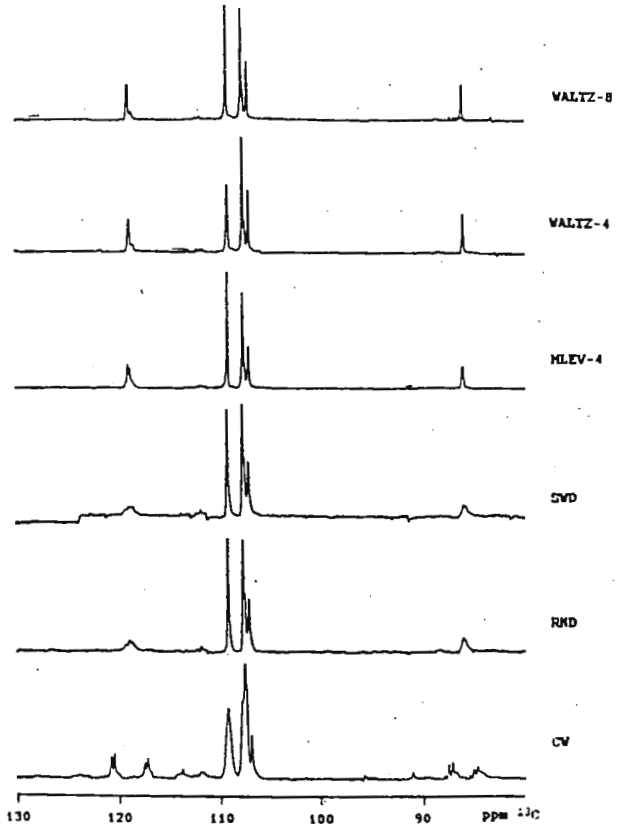

Figure 2. Attached Fluorine Test (AFT)

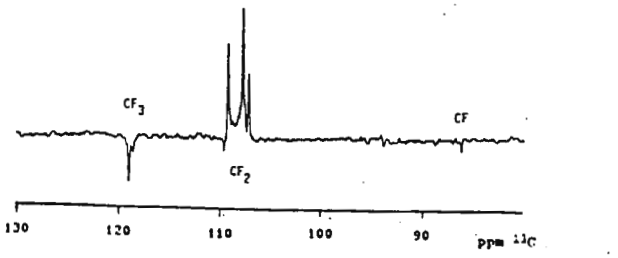

Table 1

Technique	188.2 MHz ^{19}F decoupler field strength required: for -1db	for -3d8
WALTZ-8	11.0 kHz	10.5 kHz
WALTZ-4	11.5 kHz	11.0 kHz
MLEV-4	12.5 kHz	12.0 kHz
SWD	~30 kHz	~20 kHz
RND	~35 kHz	~25 kHz
CW	>50 kHz	>50 kHz

The Ohio State University

Department of Chemistry
120 West 18th Avenue
Columbus, Ohio 43210
Phone 614-292-2251

September 2, 1987
(received 9/9/87)

Dr. B. L. Shapiro
966 Elsmore Court
Palo Alto, CA 94303

Dear Barry:

In response to the dreaded pink note we describe some recent NMR data obtained from ether solutions of 2-methylallyllithium.

Low temperature, 200° K proton NMR data for ether and THF solutions of allyllithium exhibit non-equivalent methylene hydrogens implying the species exist as ion pairs which contain conjugated allyl anions

Above 200° K, with increasing temperature the methylene resonances undergo signal averaging. This effect has been universally ascribed to fast rotation about the C(1,2) and C(2,3), bonds respectively. NMR line shape analysis yields experiment barriers to rotation in the region of 10 to 12 kcal/mole. In many of these experiments it was not possible to obtain well resolved low temperataure, < 200° K, NMR data due to "alleged" viscosity broadening and precipitation effects. In fact as the following results show this selective broadening actually comes from previously undetected dynamic effects.

Figure 1 shows the methylene proton NMR (500 MHz) of 2-methylallyllithium in diethylether-D_{10} at different temepratures down to 155° K. Notice how the CH_2 line splits into two by 205° K, as seen previously for similar systems, but on further cooling the left hand peak broadens and resolves into two resonances. The ^{13}C NMR of these $^{13}CH_2$ carbons is one sharp line at all temperatures down to 155° K.

These results are best interpreted as coming from two different 2-methylallyllithium aggregates containing conjugated allyl anions in each of which the syn and anti methylene hydrogens are magnetically non-equivalent, as indicated with vertical lines on Figure 1. We assign the 2.88 ppm resonance to the more associated aggregate since this peak increase in intensity relative to the others with increasing concentration of the solute. The system is subject to two dynamic processes whose rates have been extricated using our methods of NMR line-shape analysis; they are a very fast exchange of allyl moieties among aggregates, $\Delta H_e^{\ddagger}$ = 7.3 kcal $\Delta S_e^{\ddagger}$ = 4.3 eu, seen at the lowest temperature and the allyl bond rotation with $\Delta H_r^{\ddagger}$ = 9.6 kcal and $\Delta S_r^{\ddagger}$ = -4.3 eu. Clearly the exchange process is responsible for the unexplained selective line broadening seen by other workers, previously.

The entire Fraenkel group conveys their best wishes for your new (more civilized) site!

Yours sincerely,

Gideon Fraenkel
Professor

Randy Winchester
W. R. Winchester
Research Associate

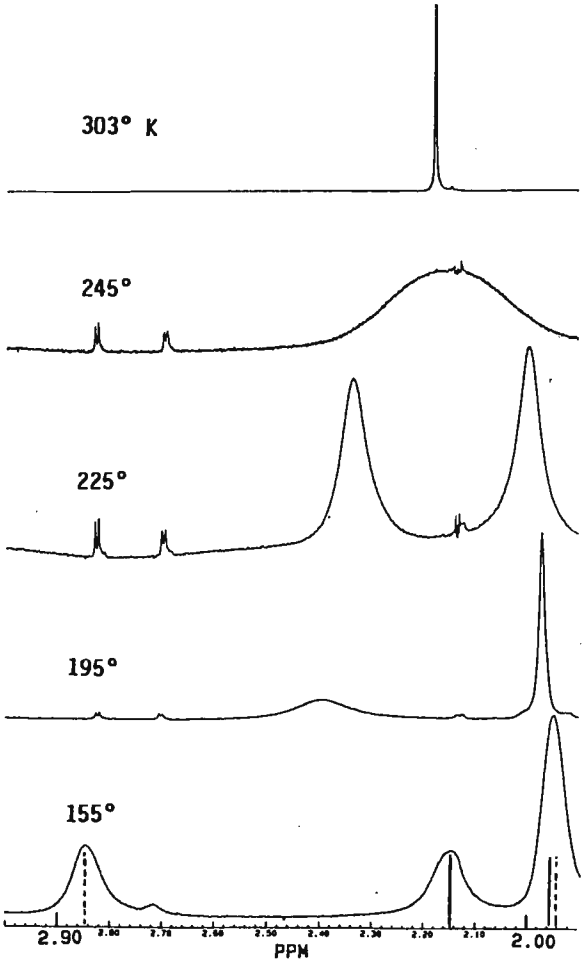

Figure 1
Proton NMR, 500 MHz, CH_2 region of 2-methylallyllithium, 0.05 M in diethylether-D_{10}, different temperatures.

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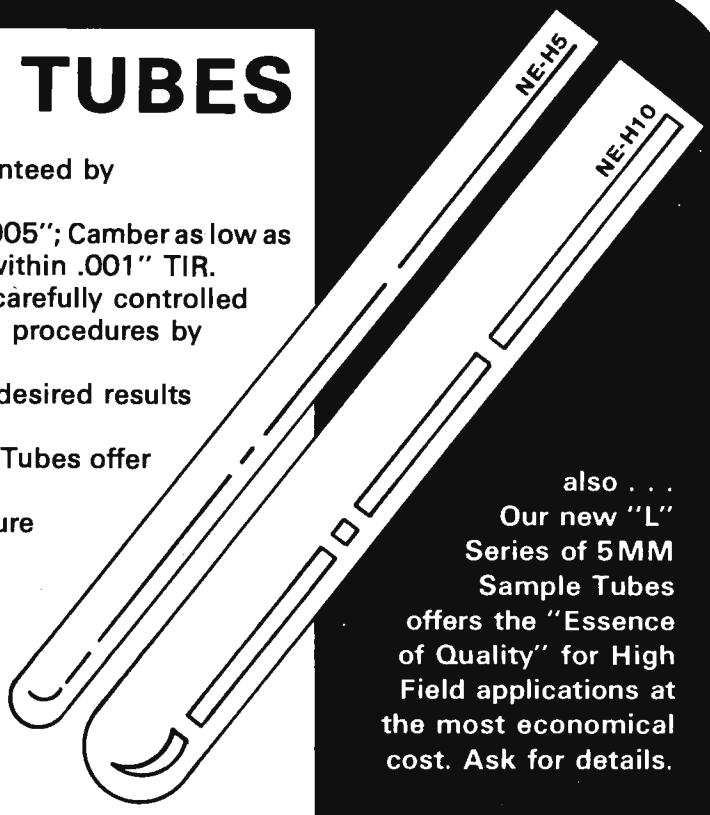

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Department of Chemistry

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

02 - 09 - 87
(received 9/7/87)

Dear Barry,

$^{7}Li^{+}$ Transport Through Phospholipid Membranes
Studied by Magnetisation transfer

Magnetisation transfer for the study of chemical exchange processes is most useful in the region where the exchange rates are similar to or somewhat slower than relaxation rates. This means the region just before linebroadening starts in the conventional dynamic nmr experiment.

Richard Briggs' group wrote in your June issue describing the application of magnetisation transfer to study $^{23}Na^{+}$ transport through phospholipid bilayers mediated by monensin. In their case the magnetisation transfer experiment offers no significant advantage over the line broadening technique. However, for the corresponding $^{7}Li^{+}$ transport, where exchange rates are slower, relaxation times longer and only very small dynamic line broadening effects are observed, magnetisation transfer is the method of choice. We have employed magnetisation transfer in the study of this exchange.

The experimental techniques are those described previously and involve growing phospholipid vesicles, adding a shift reagent outside the vesicle in order to observe separate signals from $^{7}Li^{+}$ inside and outside the vesicles. The pulse sequence that we employ is the 90-D1-90-τ-90-FID sequence described by Briggs and used in our earlier reported work.

The figure shows the lines from $^{7}Li^{+}$(in) in two typical experiments. Reciprocal lifetimes of intravesicular Li^{+} of 1.85 and 0.9E sec^{-1} are derived from a least squares fit. In suitable cases with more rapid exchange the intravesicular peak can be made to invert due to the exchange of magnetisation.

We conclude that magnetisation transfer can be employed in studies of membrane transport and that it is particulary useful in the region befcre conventional dynamic exchange sets in.

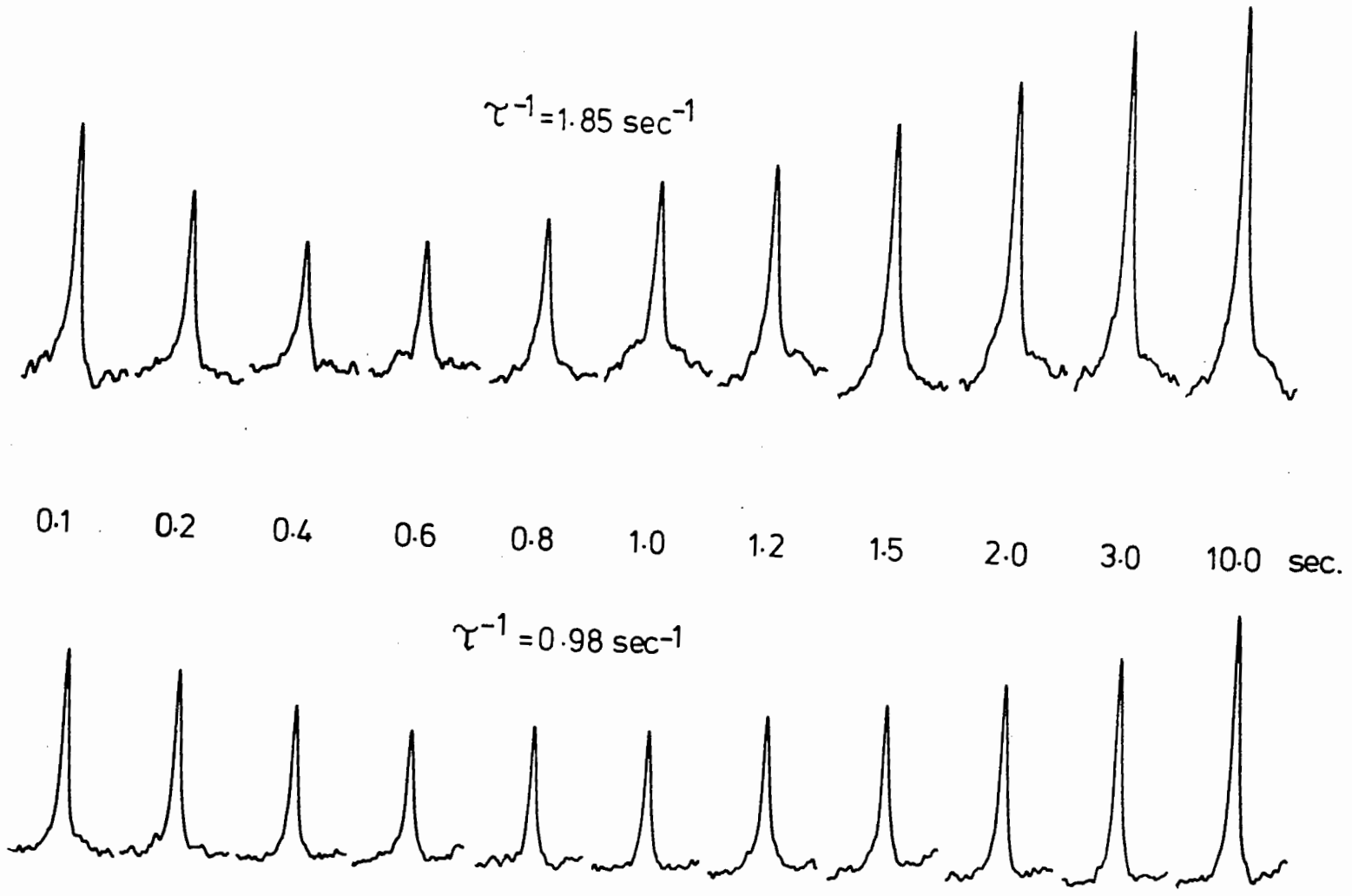
It was nice to see you again in Canterbury at the RSC nmr meeting.

Best wishes,

Frank

(Frank G. Riddell)

(S. Arumugam)


^{7}Li nmr
75 mM Li^+
τ^{-1}=1.85 sec^{-1}
Mon : PC
1 : 215
0.1
0.2
0.4
0.6
0.8
1.0
1.2
1.5
2.0
3.0
10.0
sec.
τ^{-1} = 0.98 sec^{-1}
1 : 431

DEPARTMENT OF THE NAVY
NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20375—5000

IN REPLY REFER TO:

6120-593:JBM:mbr
3 September 1987
(received 9/8/87)

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

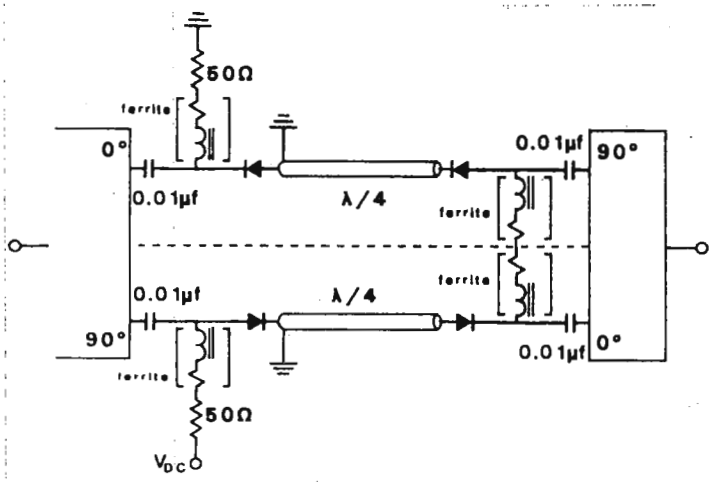
Constant Phase RF Attenuator and Coil Swapping

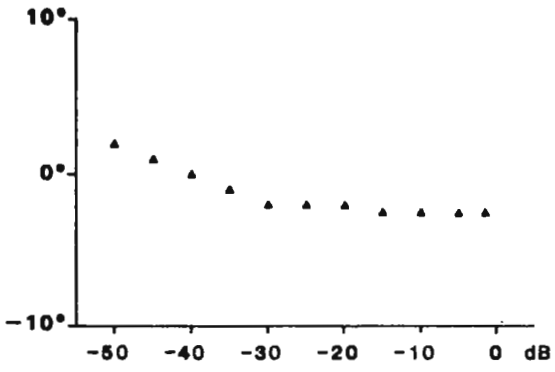
Dear Barry:

Recently, we had need for an electronically controlled rf attenuator with a range of about 50 dB. Further, the application required that the attenuator introduce very little phase shift of the rf. We had on hand a commercially available unit which met the first criterion but not the second. Because of time considerations we decided to build one ourselves rather than try to purchase one that fit our requirements. The design we used is shown in Fig. 1. The design is not new or original (see Microwave Diode Control Devices, by Robert V. Garver, Artech House, 1976) and it may be familiar to some readers but we found it to be quite simple and fast to set up.

The main component of the attenuator is the HP 5082/3081 PIN diode. The PIN diodes are matched to the transmission line via quadrature splitters. With a single PIN diode in each arm of the circuit, the bandwidth is determined by the splitters. We have opted to increase isolation at the expense of bandwidth by using two diodes separated by a quarter-wavelength cable in each arm. Series capacitors are places at the rf inputs and outputs to block the dc current and ferrites or tuned circuits are placed at the dc inputs and outputs to block rf current.

The two series diodes separated by a quarter-wavelength cable seem to introduce very little phase shift, less than ± 3°, between 0 and -50 dB attenuation provided the proper rf blocking circuits are used on the dc lines. At 50 MHz we used Ferroxcube VK200-09/3B ferrites. A plot of attenuation versus phase shift relative to an unattenuated reference is also shown in Fig. 1.





For sentimental more than programmatical reasons, we recently changed a coil on a Varian 12 inch 60 MHz magnet. We were vaguely aware of the special sling, table, and specialized tools which Varian has available for the coil change as well as the reported difficulty of the procedure. Still, we elected to jury-rig the tools and do the work ourselves. We had a used but good coil available from another magnet. The changeover went surprisingly smoothly; we had an NMR signal on the 'new' magnet two days after finding that the old coil had shorted.

To make the coil removal and installation very easy, we rotated the yoke by 90°. Ken McGrath made a wagon out of angle iron (Dexion), plywood, casters, and four eyebolts. Spare coil chocks, which normally ride on the yoke and support the coil, were bolted to the base of the wagon. The wagon was then positioned under the coil with four chains from the eyebolts on the wagon leading to a boom hoist. Fig. 2 shows Ron Siatkowski with the suspended coil and the wagon. The entire procedure is quite stable since the coil is always supported vertically.

It is true that this simplified procedure is presented about twenty years too late for most modern NMR spectroscopists; yet such exercises remind us of our professional roots.

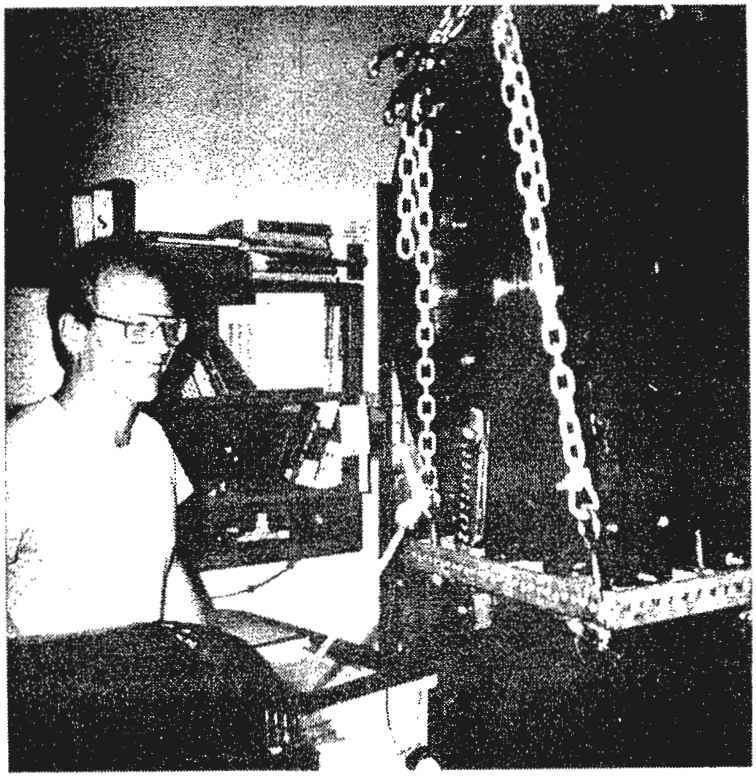
J. B. Miller

M. A. Doverspike

K. J. McGrath

A. N. Garroway
Code 6120
Chemistry Division

R. E. Siatkowski



University of Illinois
College of Medicine at Urbana-Champaign

Department of Medical Information Sciences
BIOMEDICAL MAGNETIC RESONANCE LABORATORY
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Urbana, Illinois 61801
(217) 244-0600

September 3, 1987
(received 9/8/87)

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

Dear Barry:

"Old ultrasimple and new

ultracomplex NMR imaging"

The recent (343-28) Newsletter contribution by Andy Evans prompts me to reveal the ultrasimple reconstruction algorithm actually used in the first NMR (zeugmatographic) imaging experiments. Four projections were measured by turning a 5mm sample tube through three 45° intervals in an A-60 with a linear homogeneity knob twisted as far as it would go from the correct setting. Each projection was then hand-digitized (plastic ruler and pencil, then a key punch). The 0° and 90° projections were measured at 20 positions, but the 45° and 135° ones were measured at 39 positions, separated by intervals $\sqrt{2}/2$ as large. Thus, each corresponded to rows of points in a square array, as seen from those angles. This trick made it possible to back-project without interpolation by distributing signal intensities uniformly over rows of sites. An iterative scheme was then used to urge the reconstructed image toward consistency with the experimental projections. Although I thought at the time that it was all my clever idea, a paper was eventually pointed out to me (Gordon and Herman, Comm. ACM 14, 759 (1971)) that revealed that I had reinvented iterative ART-type algorithms (although they did not use any special digitization tricks). A more recent general reference and text is Gabor Herman's "Image Reconstruction from Projections," Academic Press, New York, 1980.

The special form of ART that I devised is natural and easy to use for four projections (the first tests were done by hand, using mental arithmetic), but it has not, to my knowledge, ever been extended to more angles. An undergraduate in my lab started to work on the cases for six and eight angles many years ago, but gave it up to do something more interesting.

After that flashback: Forward to the future.

Our research programs are about to expand considerably with the acquisition of new equipment and laboratories. We invite inquiries from prospective visiting scientists, post-doctoral research associates, graduate students and technicians who may be interested in coming here. Projects underway in the Laboratory include:

Theory, techniques and apparatus for microscopic NMR imaging.
Applications of NMR imaging, microscopy and spectroscopy to developmental biology and neurobiology.
Theory, development, characterization and use of magnetic contrast agents and labels.
Techniques and applications of three-dimensional image display.
Applications of spectroscopic techniques to neurodevelopment, retinal physiology, ion transport in red cells and epithelia, cellular metabolism, muscle contraction and reproductive biology.
Development of methodology for combining fluorescence dynamics techniques with NMR spectroscopy.

The Laboratory has a multinuclear GE GN300 300/89mm vertical bore spectrometer (being equipped for microscopic imaging), and a VIS 4.7T/33cm spectroscopy and imaging system (Spectroscopy Imaging Systems Corporation, nee Varian Fremont) is about to be shipped. A field cycling Relaxometer, constructed at IBM Watson Research Laboratory, is ready for delivery and will be employed in a collaboration with Dr. Seymour Koenig, who holds an appointment as Adjunct Professor of Physics here.

Collaborative research programs are being pursued and developed with several local research groups and laboratories in the areas of:

Agronomy
Contrast agent development
Developmental biology
Fluorescence dynamics combined with NMR spectroscopy
Image display and processing
Ion transport
Liver disease and alcoholism
Metabolism
Muscle contraction
Neurobiology
Reproductive biology, and
Veterinary medicine.

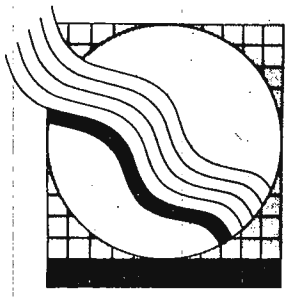
Additional information may be obtained from me at the address given above, or from:

Prof. M. Joan Dawson
University of Illinois
Dept. of Physiology & Biophysics
524 Burrill Hall
407 S. Goodwin Street
Urbana, IL 61801
(217) 244-1295

Sincerely yours,

Paul C. Lauterbur
Professor

PCL:dm
1401m



XIII International Conference
on Magnetic Resonance
in Biological Systems

Madison, Wisconsin (USA)
August 14–19, 1988

FIRST ANNOUNCEMENT

(PLEASE POST)

Scientific Program

The program will consist of lectures, symposia, workshops, and poster sessions.

A commercial exhibition is planned.

Location and Dates

The conference will be held from August 14 to 19, 1988, in the Memorial Union Meeting Facilities of the University of Wisconsin-Madison on the shore of Lake Mendota. Registration and welcoming reception at 7:00 pm, Sunday, August 14, 1988. Last session ends at 12:30 pm, Friday, August 19, 1988.

Language

The official language of the meeting will be English; no simultaneous translation facilities will be provided.

Accommodations and Registration

All meals will be included in the registration fee of $250 (US$).

The basic accommodation rate (5 nights, shared occupancy) will be $225 (US$).

Information

Prof. John L. Markley *or* Mr. Jim Shurts

Department of Biochemistry
University of Wisconsin
420 Henry Mall
Madison, Wisconsin 53706
U.S.A.

Telephone: (608) 263-9349
Telex: 26 54 52
Bitnet: markley@wiscmacc.bitnet
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Conference Co-chairmen

Chien Ho
Department of Biological Sciences
Carnegie-Mellon University
4400 Fifth Avenue
Pittsburgh, PA 15213

James S. Hyde
National Medical ESR Center
Medical College of Wisconsin
8701 Watertown Plank Road
Milwaukee, WI 53226

John L. Markley
Department of Biochemistry
University of Wisconsin-Madison
420 Henry Mall
Madison, WI 53706-1569

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Heinz Ruterjans, Frankfurt
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Pre-registration Form for Further Announcements

Please fill out and return this form (or a copy of it) to Mr. Jim Shurts.

Address *(Please type or print)*

Last name: _____

Title: _____ First name(s) _____

Affiliation: _____

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I am interested in the following workshop and symposium topics:

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Free radicals	☐	☐
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Protein structure-function	☐	☐
Carbohydrates	☐	☐
Cellular NMR	☐	☐
Chemical shift imaging	☐	☐
Post-acquisition processing of data	☐	☐
Heteronuclear 2D NMR	☐	☐
Iron-sulfur proteins	☐	☐
Contractile systems	☐	☐
Protein-lipid systems	☐	☐

	attend	present poster
Nucleic acids	☐	☐
Plant spectroscopy	☐	☐
Supramolecular structure	☐	☐
Fast imaging	☐	☐
Resonators/probes	☐	☐
3D structure from 2D NMR	☐	☐
Perfusion	☐	☐
Visual systems	☐	☐
Enzyme mechanisms	☐	☐
Photosynthesis	☐	☐
Metalloproteins	☐	☐
Spectroscopy of animals and man	☐	☐

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☐ Special dietary requirements

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06 September 1987
(received 9/14/87)

Prof. Bernard L. Shapiro
966 Elsinore Court
Palo Alto, California 94303

Dear Barry,

TITLE: COMPUTER-CONTROLLED SINGLE CRYSTAL PROBE FOR NICOLET 1280 SYSTEMS

To further our studies of molecular dynamics in solids, we have constructed a computer-controlled single crystal NMR probe for our 6 Tesla, 72 mm bore magnet system. As demonstrated in Figure 1, we now can measure principal frequencies and relaxation rates of individual tensors in compounds where overlapping polycrystalline lineshapes obscure such information.

Figure 2 shows the design of the probe head. The crystal is mounted in an alumina cube and cube holder in the normal manner. Repositioning the sample cube allows three orthogonal rotations of the crystal in the field to be made.[1] Our design employs a thin-walled glass tube, held between two clamps, which acts as a guide for the sample holder and insures the absence of goniometer wobble during rotations. Currently we are using a free-standing r.f. coil wound about the glass guide tubing. This construction allows easy replacement of coil and glass guide, assuring that the coil filling factor can be maximized for a crystal of arbitrary, ususally small, dimensions.

Two 45° miter gears connect the sample holder to a stepping motor at the base of the probe via a flexible shaft. Antibacklash gears were chosen to preserve the motor's 3% angular tolerance in stepping (i.e. ±0.054°). The motor control circuit, diagrammed in Figure 3, provides both manual and computer control of stepping. When under computer control, a single TTL level triggers the circuit to move the motor through the preset number of 1.8° steps. We generate the TTL level on one of the spare Nicolet BNC ports, SP8. The port goes high for a time D3 when the experiment program contains the line D3,G. A 1 µsec D3 is sufficient to trigger the circuit, although, due to motor inertia, the actual time required for stepping is on the order of milliseconds.

Alumina, glass, plexiglass, brass, and 303 stainless steel have acceptable mechanical and magnetic properties as probe materials. The stepping motor, however, must be removed as far as possible from the magnetic field. With sufficient motor isolation, both motor and probe perform well, freeing the spectroscopist during long single crystal experiments.

Sincerely,

S Sparks R. Tschudin Dennis Torchia

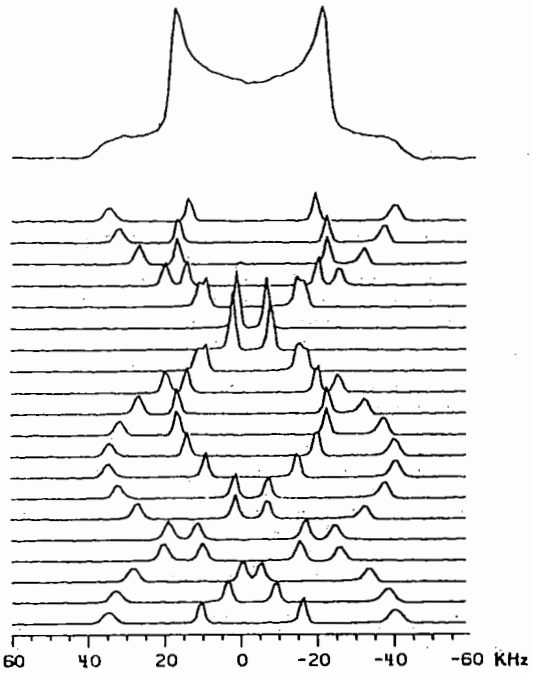
Steven Sparks Rolf Tschudin Dennis Torchia

Please credit this contribution to Dennis Torchia's subscription.

Reference

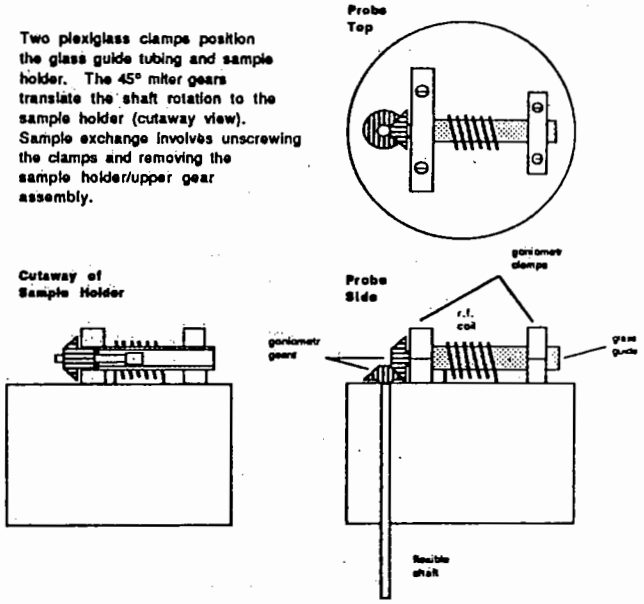
[1] U. Haeberlen, High Resolution NMR in Solids: Selective Averaging, Academic Press, 1976.

Figure 1. Deuterium Spectra of Single Crystal and Polycrystalline L-Alanine (methyl-d3)



The top trace is the lineshape of polycrystalline L-Ala-d3, 128 acquisitions on 57 mg of sample, 38 MHz, using a 0.20 s recycle time. The lower traces, of single crystal L-Ala-d3, were collected in 1.5 hours on a 4.6 mg crystal, 1024 acquisitions per spectrum, using a 0.25 s recycle time. Five motor steps, 9°, separate adjacent spectra. Only one of three orthogonal rotations of the sample is shown.

Figure 2. Single Crystal Probe Head Design



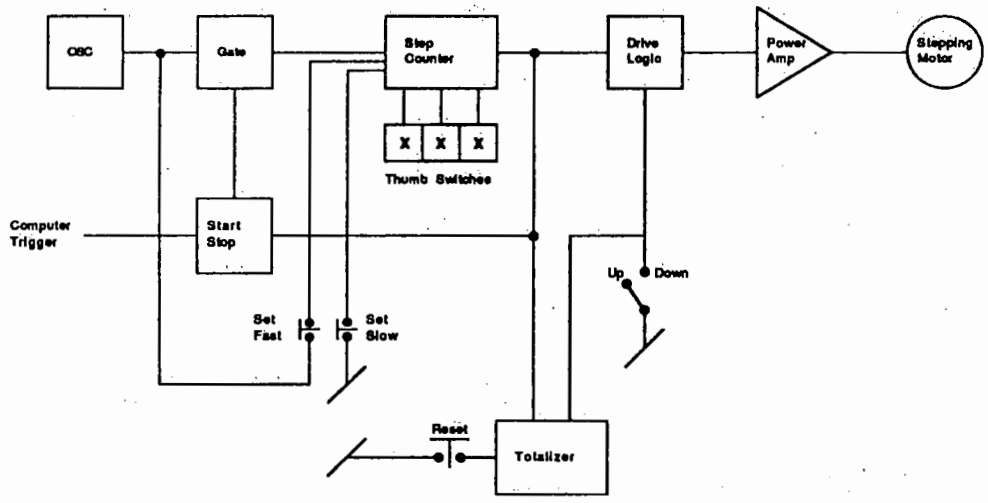


Figure 3. "Crystal Twister" Circuit Block Diagram

Manual fast (multiple) and slow (single) motor steps are controlled by button switches, as shown. Under computer control, a trigger pulse first loads the preset number of steps from the thumb switches into the counter, then gates the pulses on. At end of count, the pulses are gated off and the circuit readied for the next trigger. The up/down switch provides for clockwise and counter-clockwise motor stepping.

TEXAS A&M UNIVERSITY
NMR NEWSLETTER

No. 349
October 1987

Table of Contents, cont'd.

Positions Available . . . . . Komoroski, R. A. 38

Interactive Enhancement Algorithims for 2D Applications . . Sole, P. and Delaglio, F. 39

NMR at the November 1987 Southeastern Regional A.C.S. Meeting . . . Brey, W. S. 41

Equipment Available . . . . . Shapley, J. R. 42

First Annual Missouri Magnetic Resonance Symposium . . . . . Blum, F. D. 43

An "Unexpected" Proton NOE in Monosaccharide Derivatives . . . . Sadler, I. H. 47

Fluorine-Decoupled ^{13}C NMR of Liquids . . . . Seger, M. R. and Yue, H. J. 49

Site Exchange for Allyllithiums *(So RM's Do It, Too!)* . . Fraenkel, G. and Winchester, W. R. 52

$^{7}Li^{+}$ Transport Through Phospholipid Membranes Studied by Magnetisation Transfer . . . . . Riddell, F. G. and Arumugam, S. 54

Constant Phase RF Attenuator and Coil Swapping . . . . Miller, J. B., Doverspike, M. A., McGrath, K. J., Garroway, A. N., and Siatkowski, R. E. 56

Old Ultrasimple and New Ultracomplex NMR Imaging . . . . Lauterbur, P. C. 58

XIII International Conference on Magnetic Resonance in Biological Systems . . . . . Markley, J. L. and Shurts, J. 60

Computer-Controlled Single Crystal Probe for Nicolet 1280 Systems . . . . . Sparks, S., Tschudin, R., and Torchia, D. 62

* * * * * *

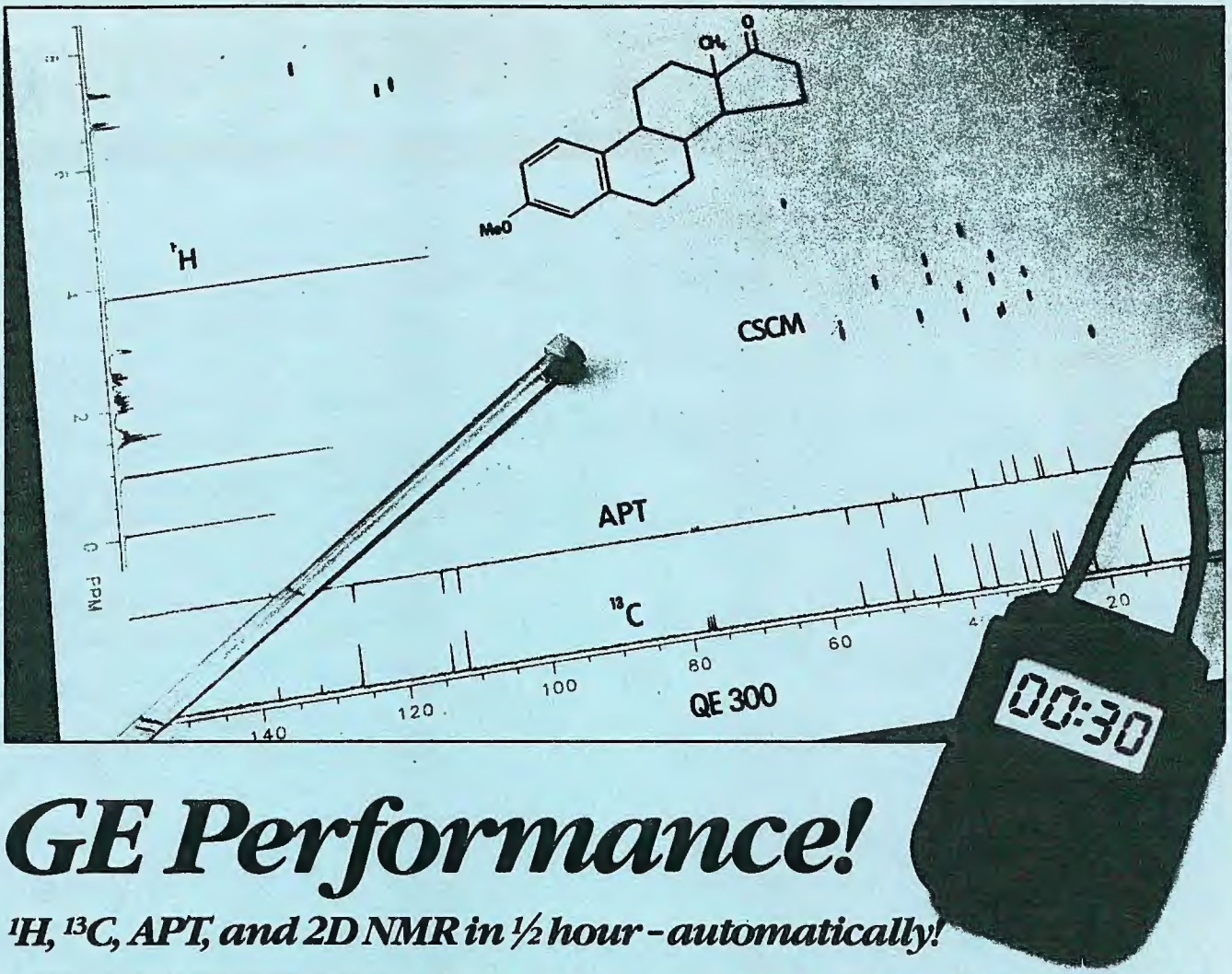
If you have paid for your 1987-88 Newsletter subscription, or have arranged for its payment, many thanks. If you have not arranged for payment of our invoice, please do so immediately, for the November Newsletter will be sent only to 'paid-up' subscribers. If you didn't receive an invoice, please telephone me without delay, to avoid being dropped from the mailing list: 415-493-5971.

* * * * * *

Concerning the physical format and nature of contributions to the Newsletter contents:

1. Contributions may not exceed three pages without prior approval.
2. All contributions must be formatted so as to leave a 1" (25.4 mm) margins on all four sides. This is especially important for foreign subscribers, whose paper is normally not the same size as that used in the U.S.A. and Canada.
3. Please provide titles for all topics of your contributions.
4. "Positions Available", "Equipment Available", and similar notices should be formatted so as to use the minimum vertical space. I believe that position available notices should rarely if ever need to exceed one-half of a page, and surely not more than one full page. This issue of the Newsletter is probably the last time I will allot space for this purpose in excess of these guidelines.

B.L.S.



GE Performance!

^{1}H, ^{13}C, APT, and 2D NMR in ½ hour – automatically!

The GE QE-300 does it all – faster than any other NMR spectrometer.

A ^{1}H spectrum, ^{13}C spectrum, an attached proton test (APT), and a ^{1}H-^{13}C chemical shift correlation map (CSCM). All these analyses can be performed in as little as ½ hour, on as little as 50 mg. of sample, for most organic compounds. And the QE-300 does them all – automatically.

With the NMR industry's most advanced automation.

This performance is made possible by the QE-300's automated software, hardware, and powerful MACRO programming capability.

Set-up starts with *Autolock*. Lock on as little as 10% $CDCl_3$ in a 5 mm tube.

Use *Compushim* for touching-up spinning shims or complete shimming with both spinning and non-spinning gradients using the lock signal or observe FID.

Autogain optimizes the receiver gain independently for sequential ^{1}H and ^{13}C acquisition.

After data acquisition, *Autophase* accurately phases ^{1}H and ^{13}C spectra.

And finally, the analysis is completed with *Autointegrate*.

All these routines can be called up from QE-300 MACROs. In fact, any QE-300 operation, including pulse programs, can be implemented via MACROs for automatic, unattended sample analysis.

And the most complete package of hardware accessories.

The QE-300 is available with the industry's most reliable, highest capacity (100 positions!) *Automatic Sample Changer*. Plus, you can add an array processor, a variety of hard disks, and switchable probes for even higher sample throughput and performance.

Structural elucidation simplified.

For many organic molecules, the four experiments presented above will be all you need to determine or confirm molecular structure. For more complex applications, GE/NMR offers an extensive ^{13}C library with outstanding search capability. This library contains data from over 10,000 compounds and is currently being expanded using a QE-300 in operation at the Aldrich Chemical Company.

High throughput and performance demonstrated.

Get all the facts on the GE/NMR QE-300. Better yet, arrange for a demonstration. Call the GE/NMR group at (415) 490-8310. Or write General Electric Company, NMR Instruments, 255 Fourier Avenue, Fremont, CA 94539.

GENERAL ELECTRIC

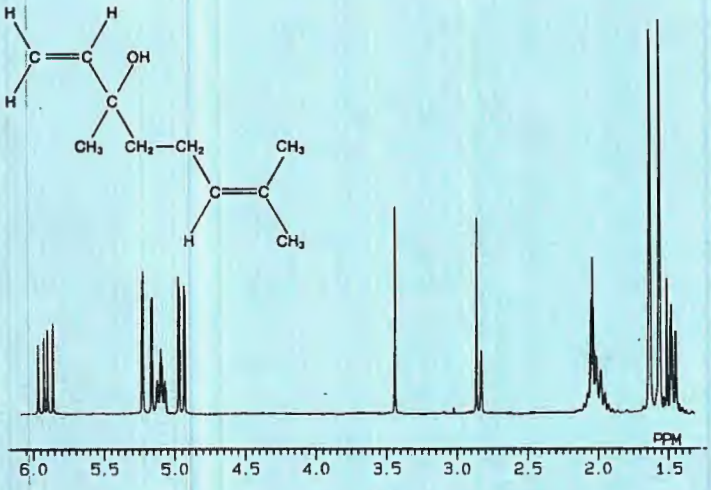
JEOL'S GX-FT NMR Systems

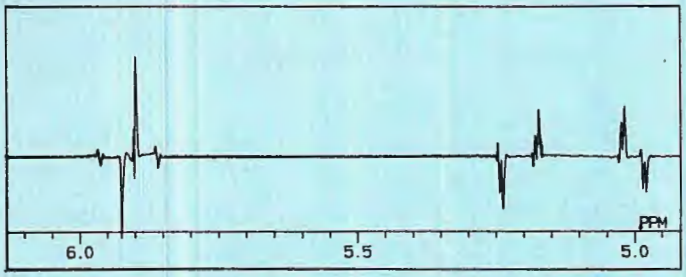
Subject: Automation

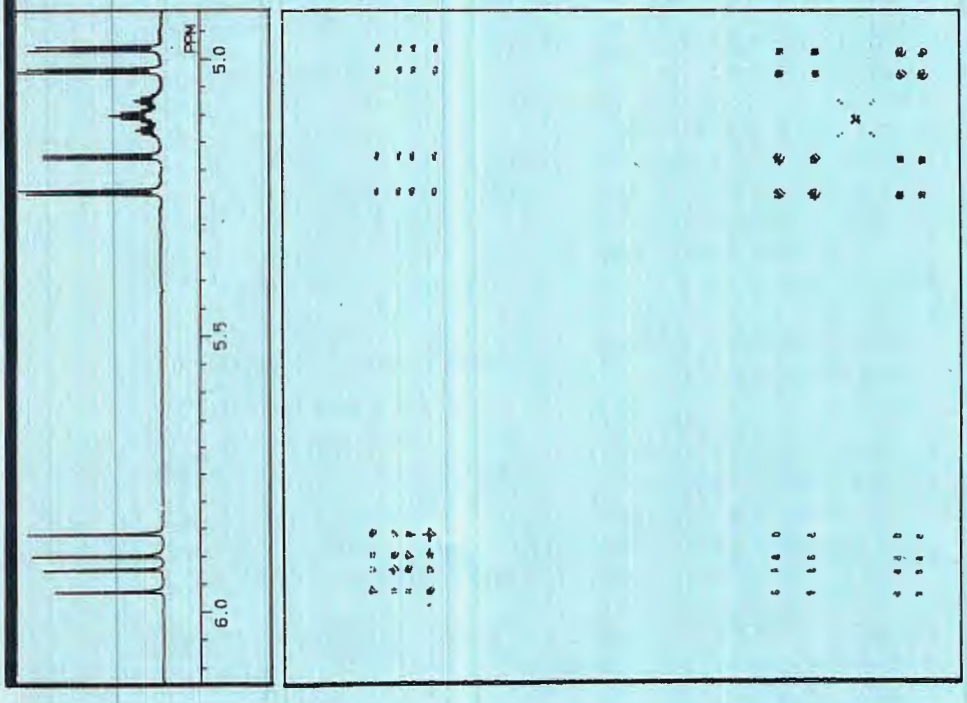
One of the more than 200 (and growing) automated routines available on the GX-Series; the data illustrates a Double Quantum Filter Phase Sensitive Cosy on the downfield section of Linalool run on a GX-270/WB (89mm) MHz spectrometer. From the moment you load the sample, spinning, lock, shimming, acquisition, transform, phase correction, and plotting are totally automated. Should you need something not already in our menu a few strokes on the keyboard will put it there.

So whether your requirements are for routine or research, the GX-FT NMR is an instrument that you should consider when evaluating FT-NMR Systems.

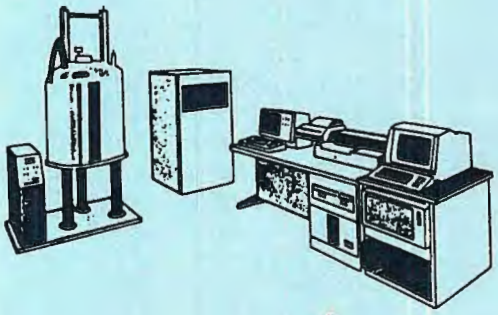
Linalool







The GX Series FT-NMR Spectrometer



For further information call:

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