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A monthly collection of informal private letters from laboratories involved with NMR spectroscopy. Information contained herein is solely for the use of the reader. Quotation of material from the Newsletter is *not* permitted, except by direct arrangement with the author of the letter, in which case the material quoted *must* be referred to as a "Private Communication". Results, findings, and opinions appearing in the Newsletter are solely the responsibility of the author(s). Reference to The NMR Newsletter or its previous names in the open literature is strictly forbidden.

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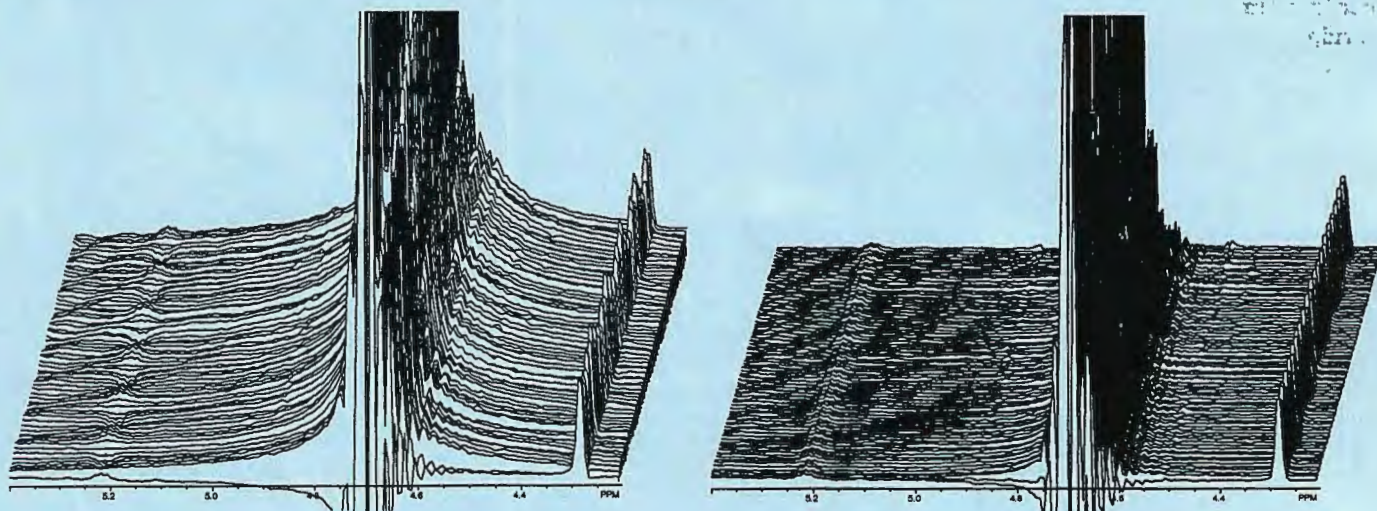
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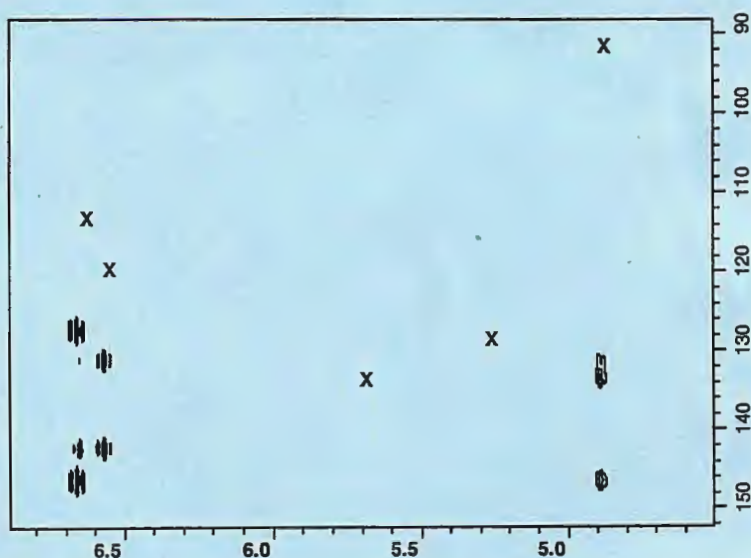
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NOESY spectrum before and after elimination of the dispersion component



3) **Compare 2D plots**—Display a mask from one spectrum (marked with X) overlaid on another contour plot.

Downfield portion of the HMBC spectrum of codeine with overlay of peaks from HMQC



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Gustaf H. Carlson School of
Chemistry and Biochemistry
950 Main Street
Worcester, MA 01610-1477

(508) 793-7116 Phone
(508) 793-8861 Fax
chemistry@clarku.edu
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Dr B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
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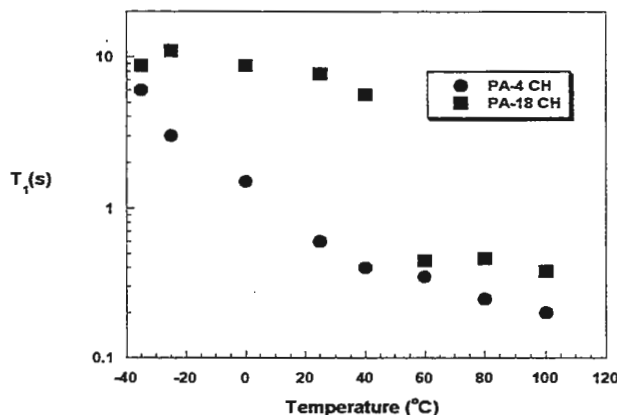
August 15, 01
(received 8/18/2001)

Comblike polymers as molecular switches

Dear Barry:

We have been using NMR to look at polymer materials which have dynamic transitions that can be exploited as molecular switches. An example is poly(octadecyl acrylate)(PA-18), in which the alkyl side chains form crystallites which have a melting point at 50°C. Abrupt changes in the permeability and other properties occur at this temperature making this material useful as a protective coating which suddenly becomes permeable at a certain temperature. An example would be as a seed coating which protects the seed when cold and then at 50° it becomes permeable to water and allows germination.

Solid state C-13 T₁'s provide a method for examining the details of the transition and the involvement of the polymer backbone. The T₁'s for the acrylate backbone carbon in PA-18 are shown and compared to PA-4 which does not have the long comblike sidechains. PA-4 exhibits normal behavior for a polymer above its glass transition whereas in PA-18 the backbone is constrained by the crystalline comb and suddenly released with an increase in the rate and/or amplitude of the segmental backbone motion. NMR can thus provide a detailed probe of both backbone and sidechain dynamics and their interrelation in solid polymers of this type.



Barry, the last issue of the newsletter certainly marks the end of an era in NMR, not much lasts for 43 years these days. Many of us have been contributors and readers for this same time and I am sure I speak for all in acknowledging your dedication and humor in providing this forum for the NMR community. My own involvement with you dates back to Preston Abs. which is more than a few years ago. It is also a coincidence that my own retirement is later this year.
My very best to you.

Paul.

Paul T. Inglefield.
(email: pinglefield@clarku.edu)

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ENABLING LIFE SCIENCE TOOLS
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(received 8/29/2001)

August 27, 2001

Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry,

On behalf of the Bruker BioSpin group, I would like to express our deepest appreciation for the valuable forum you provided to the NMR community for the past 43 years.

We thank you for all your time and efforts in maintaining the NMR Newsletter and most important for your generous heart. Your vision made a difference and benefited many spectroscopists.

Sincerely,

The Bruker BioSpin Staff

Towards Protein Structure Without Assignment

To solve the structure of a protein in solution using NMR, it is widely held that assignment of the resonances is an essential first step, following data acquisition. Resonance assignment allows assignment of NOEs to particular pairs of nuclei and thus a list of distance constraints may be compiled for use in structure calculations. More recently, measurement of residual dipolar couplings and hydrogen bonds provide alternative or additional sources of structural information, but the assignment step remains. Some appear to consider it a beneficial, character-building, even cathartic exercise.

This does not have to be. Several authors, frustrated at having to repeat the assignment procedure yet again, recognised that NOEs may be interpreted as distance between unconnected and unassigned hydrogen atoms and that the distance information is sufficient to position the atoms correctly with respect to each other in space¹⁻⁴. This transform into real space totally avoids assignment and requires building of the covalent structure into the cloud of protons, in a manner reminiscent of fitting the model into electron density practised by X-ray crystallographers. Resonance overlap has proved a major obstacle to the practical implementation of this approach⁵.

It is now common to label proteins with ¹³C and ¹⁵N, and a set of heteronuclear scalar coupling experiments are routinely used to assign the ¹H, ¹³C and ¹⁵N resonances of the molecule. But these may also be used in a radically different manner. Simply by interpreting each cross-peak in these experiments as a distance, sufficient information may be gathered to reconstruct the unfolded skeleton of the protein. Thus, a cross-peak at 117 ppm and 8.2 ppm in the ¹⁵N-¹H HSQC spectrum is interpreted as a distance of 1.02 Å between two atoms, N₁₁₇ and H_{8.2}. The cross-peak from these frequencies to 55.4 ppm in the HNCA experiment yields distances of 1.46 and 2.23 Å between N₁₁₇ and C_{55.4} and H_{8.2} and C_{55.4}, respectively, and so on.

The atoms of the unfolded skeleton carry their chemical shifts, so inspection of the 'structure' allows assignment at this stage, if the spectroscopist so wishes. It may be that the three-dimensional structure has been solved previously by X-ray crystallography, or that a good homology-based model is available. The skeleton may be forced onto the template to yield both the assignment and a model structure that allows detailed interpretation of relaxation data or protein-protein interactions. But the inclusion of data from additional NMR experiments may yield the three-dimensional structure of the protein, still without a single nucleus being formally assigned to an atom in the covalent structure. Hydrogen bonding information will serve to define elements of secondary structure. residual dipolar couplings may be used to produce the three-dimensional fold and NOEs may be used to produce a 'full' structure. The resultant structure is full in the sense that it contains all observed nuclei, but it would require refinement by inclusion of all atoms in the side-chains, and imposition of correct covalent geometry and chirality.

The validity of the concept has been demonstrated using synthetic data generated for ubiquitin (paper submitted). The application to experimental data presents a number of practical problems but is well under way. An analogous approach may be envisaged for solid state NMR data on polypeptides.

R. Andrew Atkinson
andrew@esbs.u-strasbg.fr
 NMR group, UPR 9004
 ESBS, 67400 Illkirch, FRANCE

Vladimir Saudek
vladimir@incyte.com
 Incyte Genomics,
 Cambridge, CB2 1FF, UK

¹Malliavin, T.E., Rouh, A., Delsuc, M.A. and Lallemand, J.-Y. (1992) *C. R. Acad. Sci. Paris II*, **315**, 653-659.

²Oshiro, C.M and Kuntz, I.D. (1993) *Biopolymers*, **33**, 107-115.

³Kraulis, P. (1994) *J. Mol. Biol.*, **243**, 696-718.

⁴Atkinson, R.A. and Saudek, V. (1996) In *Dynamics and the Problem of Recognition in Biological Macromolecules* (Eds., Jardetzky, O. and Lefèvre, J.-F.), Plenum Press: New York, pp. 49-55.

⁵Atkinson, R.A. and Saudek, V. (1997) *J. Chem. Soc., Faraday Trans.*, **93**, 3319-3323.

Laboratorium für Physikalische Chemie
Prof. Dr. R. R. Ernst

Zürich, August 24, 2001
(received 8/20/2001)

2515

Postadresse:

Laboratorium für Physikalische Chemie
ETH Hönggerberg HCI, CH-8093 Zürich
Switzerland

Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Durchwahl-Nr. 01 / 632 43 68
Telefonzentrale 01 / 632 11 11
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An Invaluable Communication Channel is Lost

Dear Barry,

We all will miss the blue bostiched Newsletter which monthly came to our desk, reminding us that we are part of a world-wide friendly group of NMR lovers. It gave us inspiration and it demanded from us contributions of which we did not want to be ashamed afterwards.

Dear Barry, you did a heroic and enormously valuable mission, fertilizing the friendly interaction among NMR enthousiasts. For me, the emergence of the MELONMR Newsletter in October 1958 pretty much coincided with the beginning of my own adventures in NMR. The MELLONMR, the TAMU, and the NMR Newsletters remained companions and a source of inspiration ever since then. My own career ended three years ago, but the blue Newsletter helped me to remain informed about a field which I still love, although I have nothing to contribute anymore.

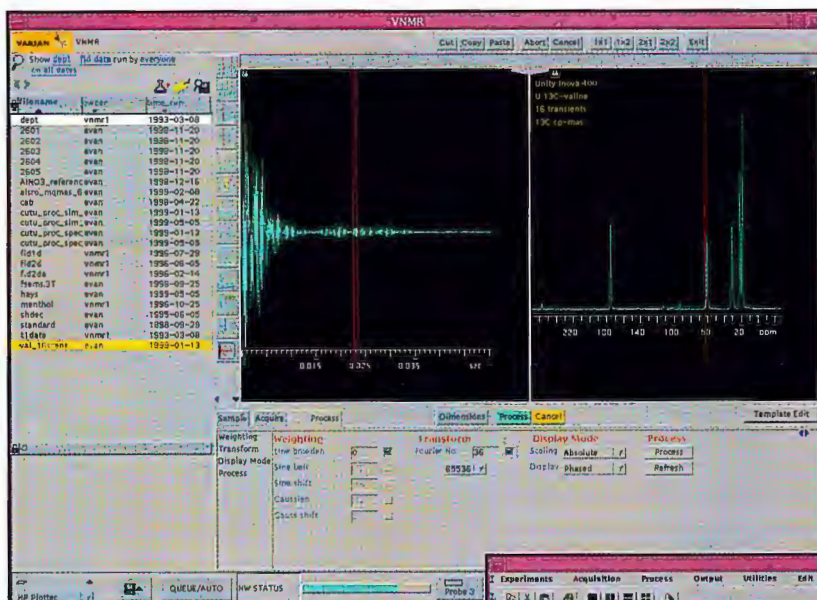
What you, dear Barry, together with Axel Bothner-By have started 43 years ago ("This is No.1 of a proposed monthly letter designed to expedite the exchange of information and ideas among laboratories engaged in research on the application of N-M-R to problems in organic chemistry.") will remain an invaluable document of NMR history. Perhaps, it is now time to abandon the strict forbidding law of 'no reference to The NMR Newsletter or its previous names in the open literature'. It would be a shame if this rich source of historical information would remain closed for ever to future generations.

Dear Barry, you will certainly be remembered and admired for many of your great scientific achievements. But our respect and our gratefulness for your enormous contribution to the NMR community by providing this unique channel of communication are on a different level of appreciation. I hope that you have enjoyed your activities as much as we appreciated the results,

(reproduced through the courtesy of Dr. Uwe Oehler,
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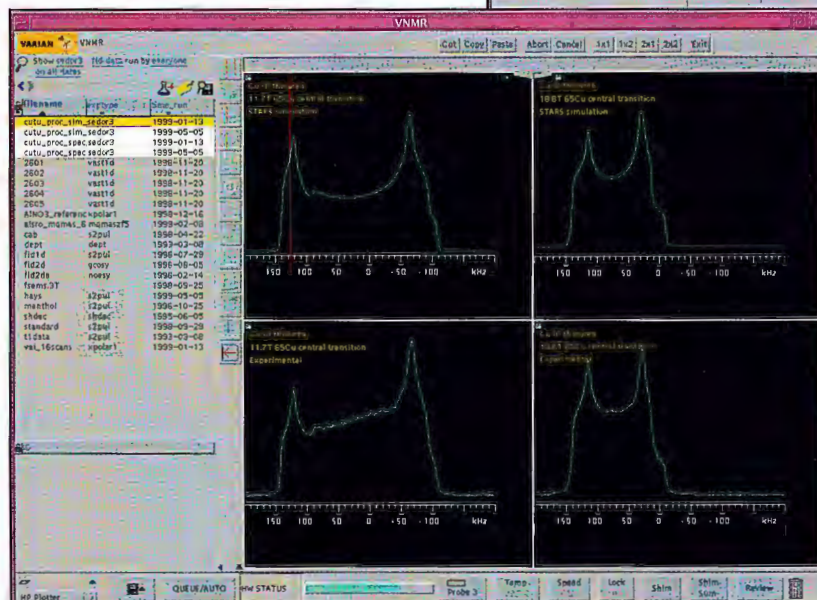


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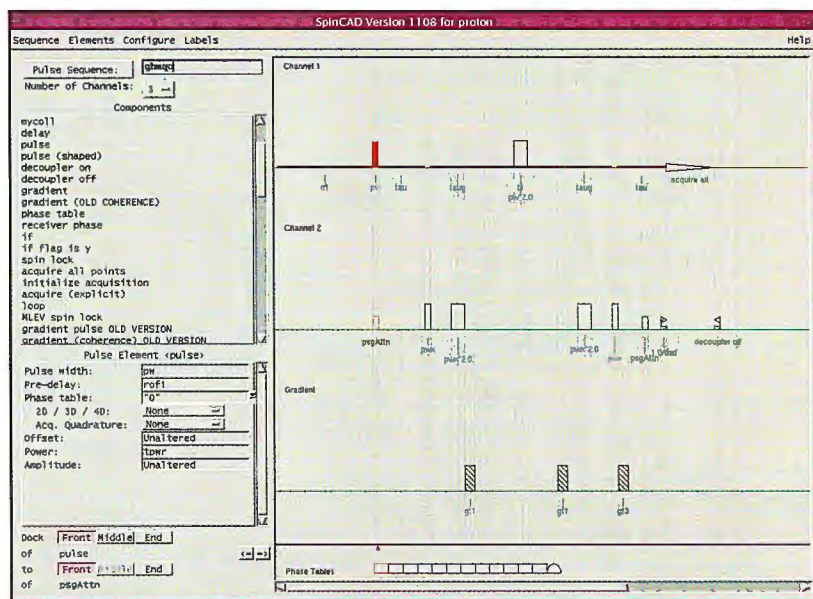


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Dr. B. Shapiro,
The NMR Newsletter
966 Elsinore Court,
Palo Alto, CA, 94303-3410

August 27 2001

(received 8/27/2001)

The last newsletter, and xenon in strange places

Dear Barry,

I was somewhat saddened to read in the August issue of the Newsletter that you felt the time had come to retire this valuable collection of letters. I must admit as I watched the number of contributions drop in recent months, I had wondered whether you would reach this conclusion. Perhaps the internet has won, however I will miss the Newsletter as a valuable source of information both on current research in a wide variety of labs and NMR-related news from conferences to jobs to vendor-horn-blowing, and for subtle amusement from cartoons to epistles from Ray Freeman and Alex Pines. Having been a keen contributor for close to 10 years now, and from 3 countries, I did not want to let the opportunity pass me to wish you well in true retirement, and to get one last page in describing NMR of xenon in strange places (or xenon NMR in strange places, depending on your view of my letter-head above!)

We have been in the time-consuming process of bringing on-line a larger-scale xenon gas polarizer situated in the lab of Prof. David Cory at MIT, where it is placed beside a 4.7 T horizontal imaging system. As I have come to learn, all things involved in construction of apparatus for this process is time consuming, however we can now unveil our first one-dimensional image of laser-polarized xenon in something useful (Fig. 1), acquired by our new grad student, Ruopeng Wang. The sample is a synthetic rock, we believe made of pure calcite or some similar material. It is shaped in a standard Haessler core size, being a cylinder roughly 1 inch in diameter by 1.5 inches long. These cores are placed in a machined teflon cell designed to hold such rocks cores for high-pressure liquid-flow experiments. As such, the design makes them perfect for evacuating the rock sample of air and then flowing in laser-polarized xenon. The gas flows directly from the laser-polarization cell outside the magnet room into the cell via teflon tubing, and is able to penetrate so far into the rock by virtue of a vacuum pump being applied at the far end of the rock. The two initial spikes in xenon signal result from the inflow into the teflon cell, and the machined diffuser plate hard against the rock sample, which spreads the initial flow across the rock surface. The actual rock sample begins at ~ -8 mm on the horizontal scale, and extends to $\sim +30$ mm. The depolarization effect of the crystal surfaces on the laser-polarized xenon is clearly visible, giving an exponential decay to the shape of the profile. With improvements in gas flow control and polarization, we will be able to observe xenon ingress into the rock as a function time, measure the relaxation times as a function of position, and possibly provide a rapid determination of core permeability. The image was acquired with 4 scans using a non-slice-selective hard-pulse spin echo sequence across a field of view of 100mm, using approx. 7 G/cm imaging gradients.

My old standard of thermally polarized xenon time-dependent diffusion experiments $D(t)$ have also been continuing whenever long periods for signal averaging were available. In trying to track down all non-theoretical behavior of the gas phase time-dependent diffusion coefficient, I had become concerned with data in packs of large glass beads (4 - 2 mm) that initially followed theoretical behavior, then started to decrease more rapidly than expected. Given the phenomenon disappears with smaller beads, I suspected finite size effects, and so repeated experiments on the same 4 mm beads used in earlier work, but now in a cell ~ 3 times larger volume. The results are in Fig 2, contrasting xenon $D(t)$ data from a small and large cell - and it is clear the data from the large cell now follows the expected theoretical behaviour out to maximum

observable diffusion distances. So I guess this is yet another pro or con of gas-diffusion NMR. The effect appears to kick in when the same size is within an order of magnitude of the bead diameter. Only gas-phase diffusion allows us to measure meaningful $D(t)$ data in samples with such large characteristic lengths that the bead diameter may approach any physically feasible sample size.

The $D(t)$ data is in a paper being prepared for J Mag Res, while the rock profiles are the start of a new project in this area, which will be reported later in media other than this one.

Thanks for all the effort with the NMR Newsletter, and best wishes for the post-NMR days,

(insert electronic signature!)

Ross Mair

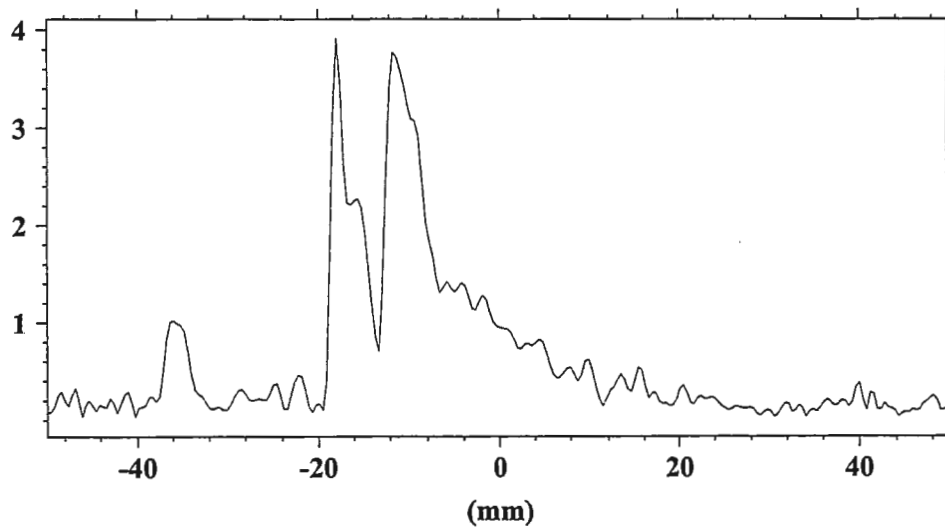


Fig. 1: 1D profile of laser-polarized xenon gas being pumped through a synthetic rock sample. The two initial spikes are free gas entering the sample chamber. The rock is located between -8 and +30 mm. Acquired at 4.7 T using hard-pulse spin echo sequence, TE ~ 3ms, read-out gradient ~ 7 G/cm.

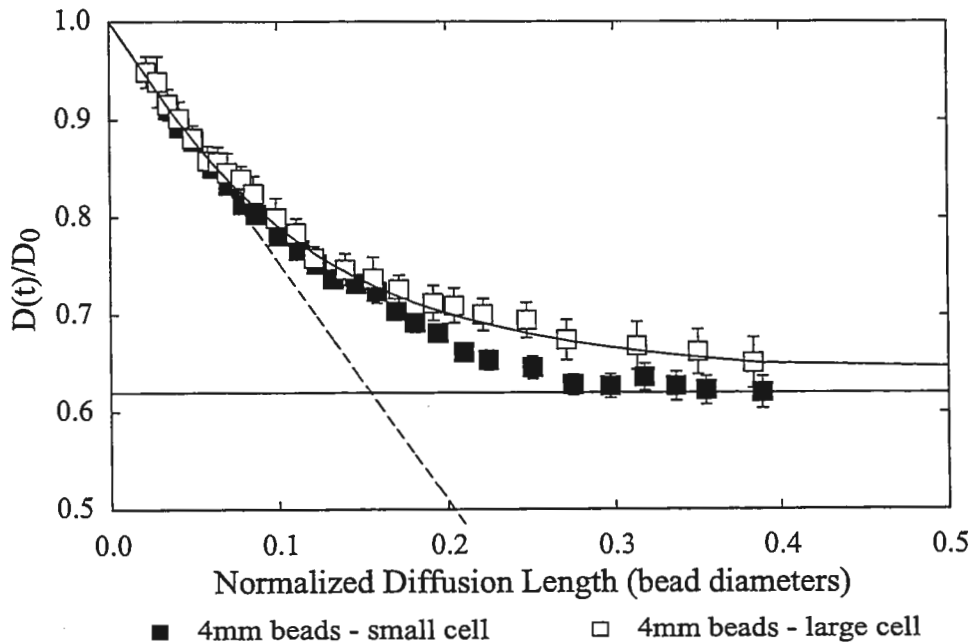


Fig. 2: Plot of normalized time-dependent xenon diffusion coefficient vs diffusion distance (related to PGSE diffusion time Δ). Dashed and solid lines show short and long time asymptotic behavior, curved line is the expected intermediate behavior. When data is acquired in a small cell (~ 4 cm) the $D(t)$ data clearly deviates from expected values in intermediate times. Such an effect is not seen in the larger cell (~ 9 cm).

Prof. Dr. Stefan Berger

Tel: +49 341 97 36101

Institut für Analytische Chemie Fax: +49 341 97 11833 oder 97 36115

Linnéstraße 3,

e-mail: stberger@rz.uni-leipzig.de

04103 Leipzig

Prof. Dr. B. L. Shapiro
 The NMR Newsletter
 966 Elsinore Court
 Palo Alto, CAL. 94303
 USA



Final Contribution # 38

Dear Barry,

Leipzig, 20.08.01

(received 8/31/2001)

To every thing there is a season, and a time to every purpose under the heaven¹. Having submitted continuously over the last 27 years to your newsletter I regret its decline very much.

We have recently continued our studies on solvation² by the means of intermolecular NOE's. As a farewell contribution we present in Figure 1a the NOE spectrum of the 14mer peptide bombesin in water. Nearly all protons of the peptide respond to the selective excitation of the water signal. After adding 30% trifluoroethanol (TFE) the peptide is changing its conformation and the same experiment allows only 4 protons to still feel the water as shown in Figure 1b. Wish we could tell your readers more in another issue!

With all our best regards and many thanks for your long lasting editorship!

Dr. Dolores Diaz

S. Berger

¹ Ecclesiastes 3.1.

² D. Diaz, S. Berger, *Magn. Reson. Chem.* **39**, 369-373 (2001).

Figure 1a: Selective NOE from water to bombesin in water

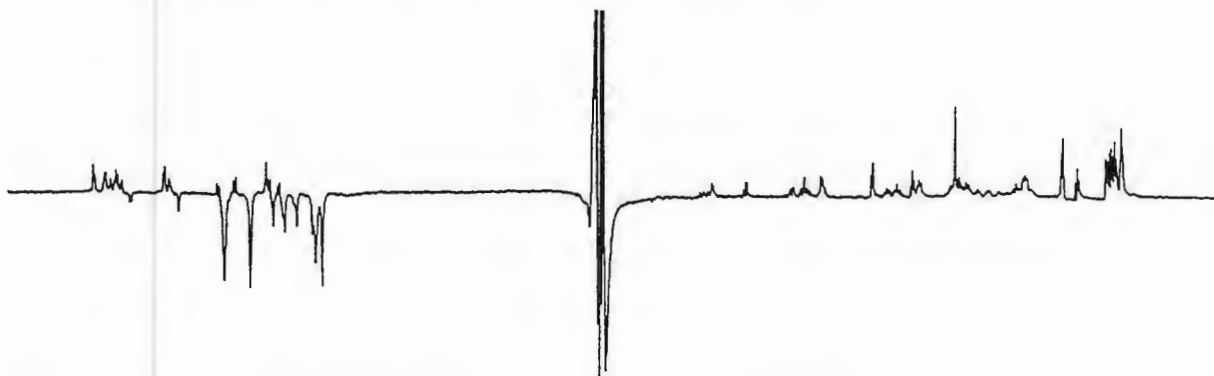
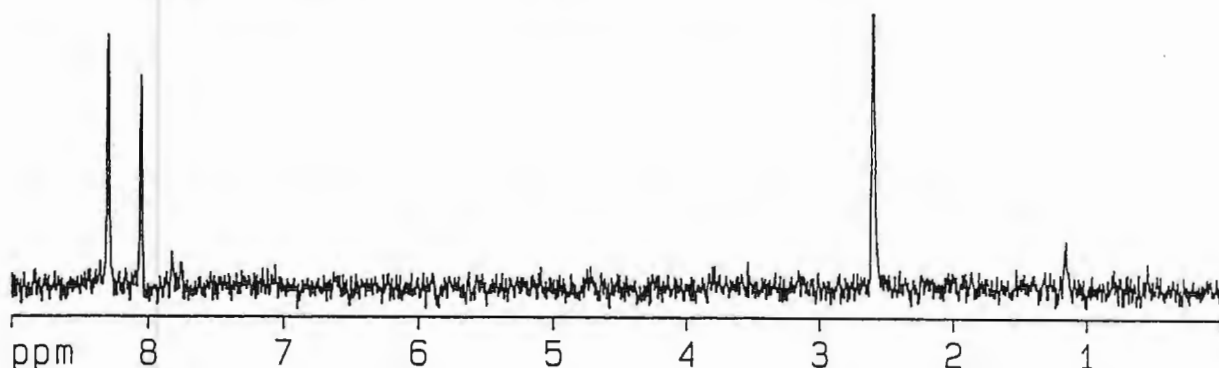


Figure 1b: Selective NOE from water to bombesin in water/TFE



FORTHCOMING NMR MEETINGS

EMBO Practical Course: Structure Determination of Biological Macromolecules by Solution NMR, EMBL, Meyerhofstr. 1, D-69117 Heidelberg, Germany, **September 12-19, 2001**; Email: nilges@EMBL-Heidelberg.de; sattler@EMBL-Heidelberg.de; <http://www.embl-heidelberg.de/nmr/sattler/embo>.

EMBO Workshop on NMR and Molecular Recognition, Ravello, Italy, **October 3-7, 2001**; Contact: Dr. T. Tancredi: ttancredi@icmib.na.cnr.it, or Dr. P. Amodeo: pamodeo@icmib.na.cnr.it. Information: <http://www3.icmib.na.cnr.it/ravello2001>.

43rd ENC (Experimental NMR Conference), Asilomar Conference Center, Pacific Grove, CA, **April 14-19, 2002**. Contact: ENC: 505-989-4573; 505-989-1073 fax; enc@enc-conference.org; <http://www.enc-conference.org>; See Newsletter **515**, 26.

ISMRM (International Society for Magnetic Resonance in Medicine), 10th Scientific Meeting and Exhibition, Honolulu, Hawai'i, **May 18 - 24, 2002**; Contact: ISMRM, 2118 Milvia St., Suite 201, Berkeley, CA 94704; Fax: 1+510-841-2340; <http://www.ismrn.org>.

XXth International Conference on Magnetic Resonance in Biological Systems, Toronto, Ont., **August 25-30, 2002**. For further information check www.uso.ca/chem/icmrbs/, or contact: mgordon@julian.uwo.ca.

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Thank you to Barry Shapiro and The NMR Newsletter for their 43 years of technical contributions to the NMR community. Cambridge Isotope Laboratories, Inc. has appreciated the important role of The NMR Newsletter in providing a forum for the informal exchange of technical ideas and NMR techniques.



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KISS Isn't Always Better!

Bernard L. Shapiro, Ph.D.
Editor, The NMR Newsletter
961 Elsinore Court
Palo Alto, CA 94303

(received 8/31/2001)

Dear Barry,

The old adage, KISS - Keep It Simple Stupid, isn't always better in terms of getting the NMR correlations that you're looking for. The HMBC/GHMBC pulse sequence, employing only five pulses, is one of the simplest heteronuclear 2D NMR experiments and works extremely well in most applications. However, for long-range ^1H - ^{15}N 2D NMR at natural abundance, that isn't always the case. For quite some time we've been investigating accordion-optimized long-range heteronuclear shift correlation experiments. These experiments, in contrast to the simple HMBC pulse sequence, are relatively complex. Our explorations began with the ACCORD-HMBC experiment of Stefan Berger^{1,2} and have progressed through various iterations.³⁻⁵ In one communication published early last year in *Magnetic Resonance in Chemistry*, we did some comparison work on GHMBC vs. ACCORD-HMBC vs. IMPEACH-MBC for the acquisition of long-range ^1H - ^{15}N 2D data at natural abundance.⁶ More recently, we've been exploring the utilization of cryogenic NMR probes for the very rapid acquisition of long-range ^1H - ^{15}N 2D NMR data at natural abundance.⁷

One of the problems plaguing investigators wanting to use long-range ^1H - ^{15}N 2D in their structural studies is the question of optimizing the long-range delays to observe all couplings in the long-range spectrum.⁸ As demonstrated previously, using GHMBC experiments with a single optimization can lead to either missing some responses or having them visible albeit with weak relative response intensity. In contrast, when using an accordion-optimized experiment, while the overall signal-to-noise ratio may be somewhat lower than a GHMBC experiment acquired in the same total time, the relative signal intensities in the data set will tend to be more uniform.⁶ It is also quite probable that all possible long-range correlations will be observed in the accordion-optimized experiment.

Using the greatly enhanced sensitivity of a cryogenic NMR probe to facilitate quick comparison studies with a 2 mg sample of the antibiotic eperezolid, we've examined a series of GHMBC (no low-pass J-filter) spectra with various optima (4, 6, and 8 Hz) vs. a single CIGAR-HMBC experiment (2-6 optimization of the accordion delay). These data show some rather interesting results in the time span from a mid-morning coffee break to lunch!

Shown in Figure 1, are the results from the the 4, 6, and 8 Hz optimized GHMBC and a 2-6 Hz optimized CIGAR-HMBC spectra. Each of the four spectra were recorded using a 2 mg sample of the antibiotic eperezolid in 24 min (ni = 40; nt = 16). As will be quickly noted, the 8 Hz data show only one of the possible three-bond correlations from the H2' and H6' phenyl protons to the oxazolidinone N3 nitrogen resonance (98.0 ppm). The intensity of the response observed in the 8 Hz experiment increases slightly in the 6 Hz optimized experiment with the other three-bond

correlation also beginning to give a response. Finally, in the 4 Hz optimized GHMBC experiment both of the three-bond correlations from the phenyl resonances are observed to the oxazolidinone N3 resonance. The 2-6 Hz optimized CIGAR-HMBC spectrum ($J_{\text{scaleU}} = J_{\text{scaleD}} = 0$) shows both of these correlations with intensity comparable to the 4 Hz GHMBC experiment, without any prior knowledge of the actual long-range $^2J_{\text{NH}}$ coupling constant and none of the iterative reoptimization done with the GHMBC experiment to get to this point. It should also be noted that the four-bond correlation from the H2' phenyl proton to the N1" piperazine nitrogen resonance is also observed with appreciable response intensity in the 2-6 Hz CIGAR-HMBC data.

Full 2-6 and 2-10 Hz optimized CIGAR-HMBC spectra are shown in Figure 2. As noted above, the 2-6 Hz optimized data were recorded in 24 min; the 2-10 Hz optimized data were recorded with 96 increments of the evolution time in approximately 1 hr. The spectra are plotted as close to the noise floor as possible for presentation purposes. The traces showing the correlations from the three phenyl protons to the N3 oxazolidinone nitrogen (98.0 ppm) from the 2-6 and 2-10 Hz optimized spectra and the proton reference spectrum are shown in Figure 3. Correlations from both of the anisochronous oxazolidinone 4-methylene protons to the oxazolidinone N3 nitrogen resonance are observed as well as a relatively weak correlation from the H5' phenyl proton to the oxazolidinone N3 resonance.

Long-range ^1H - ^{15}N 2D NMR experiments at natural abundance now represents an area of increasing research interest. The use of an accordion-optimized long-range experiment such as CIGAR-HMBC, in conjunction with a cryogenic gradient inverse NMR probe makes experimental access to these data a very facile undertaking with a few milligrams of compound. With somewhat longer but still very manageable acquisition times, *e.g.* overnight, long-range ^1H - ^{15}N can be acquired on quantities as small as 0.5 μmole of material.

Sincerely,



Ron Crouch
Varian



Gary Martin
Pharmacia



Chad Hadden
Pharmacia



Dave Russell
Pharmacia

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1. R. Wagner and S. Berger, *Magn. Reson. Chem.*, **36**, S44 (1998).
2. G.E. Martin, C.E. Hadden, and R.C. Crouch, *Magn. Reson. Chem.*, **37**, 527 (1999).
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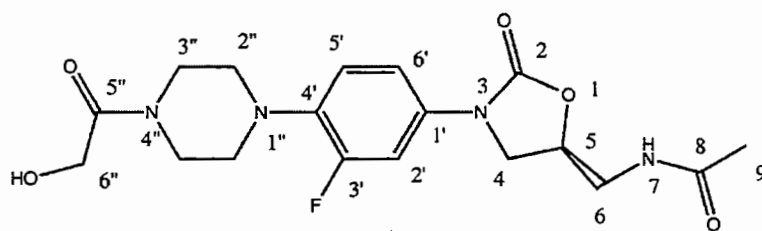
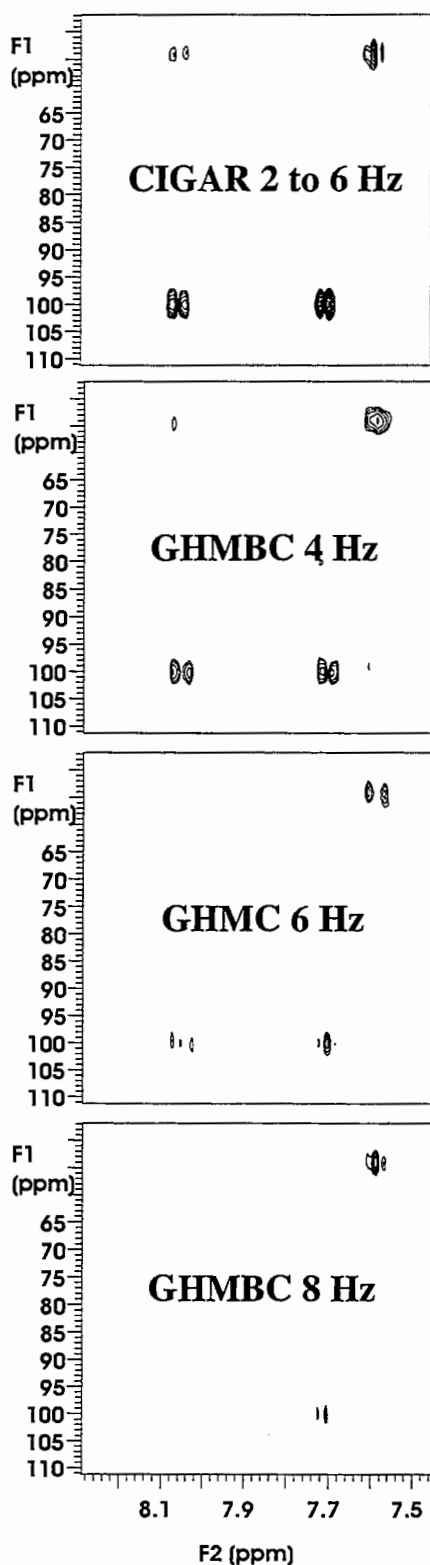


Figure 1. Series of long-range ^1H - ^{15}N 2D NMR spectra of a 2 mg sample of the antibiotic eperezolid dissolved in 150 μL of d_3 -acetonitrile in a 3 mm NMR tube (Wilmad). Data were acquired using a Varian INOVA 500 MHz four channel spectrometer equipped with a Varian Cryo-Q 5 mm gradient inverse triple resonance cryogenic NMR probe. Standard GHMBC and CIGAR-HMBC⁴ pulse sequences were used from the Varian pulse sequence library. All four experiments were performed using 40 increments of the evolution period; 1024 points were acquired in t_2 . The data were sinebell processed to a final data matrix of 1024 x 2048 points. Acquisition time for each experiment was approximately 24 minutes. The region containing the correlations for the aromatic proton resonances of eperezolid is shown in the four panels plotted to the left. The upfield resonance shown is the N1'' piperazine nitrogen resonance; the downfield resonance corresponds to the oxazolidinone N3 nitrogen resonance. As shown in the 8 Hz optimized only one weak correlation is observed to N3. In the 6 and 4 Hz optimized GHMBC data, response intensity progressively improves. Also, in the 4 Hz optimized experiment, a second long-range correlation to the N1'' resonance is also weakly observed. In comparison, in the 2-6 Hz optimized CIGAR-HMBC spectrum shown in the top panel, all four correlations are observed with good response intensity.

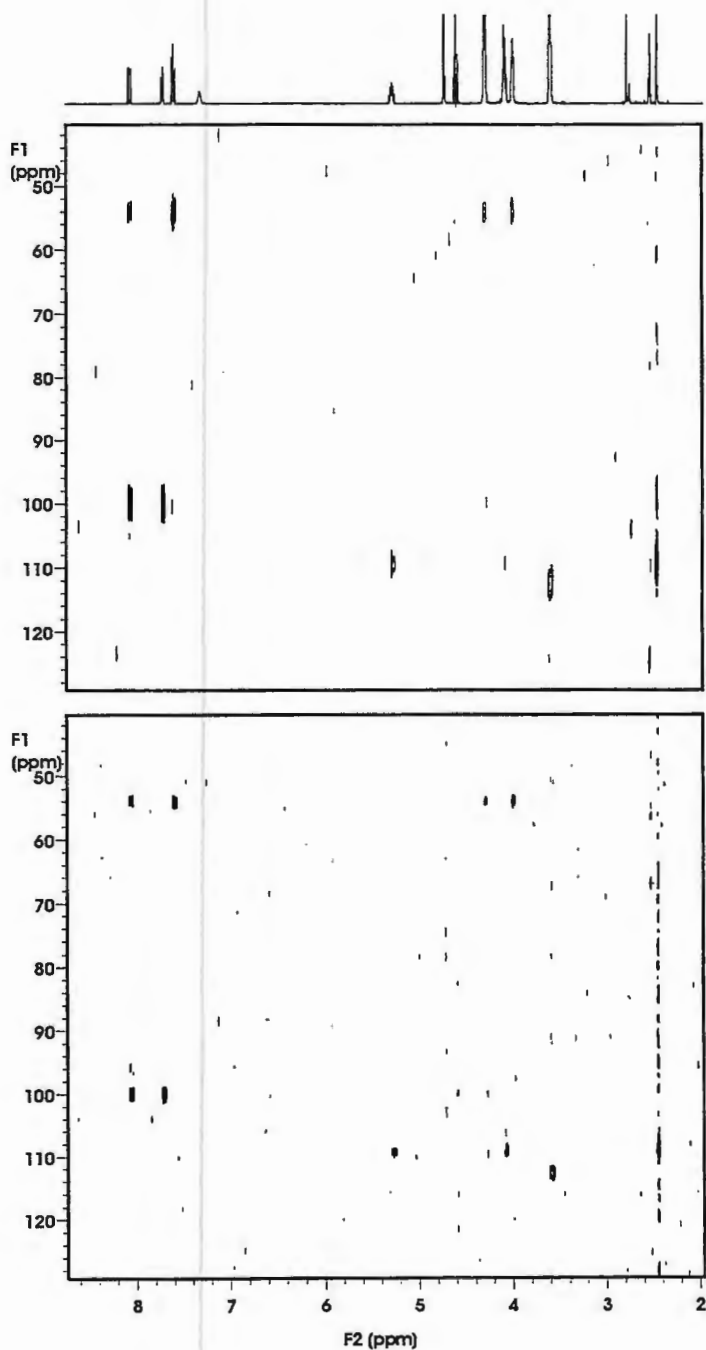


Figure 2. Full CIGAR-HMBC spectra of a 2 mg sample of eperezolid optimized for 2-6 (bottom panel) and 2-10 Hz (top panel). The data for the bottom panel were acquired using 40 increments of the evolution time in 24 min; the data shown in the top panel were acquired in just under 1 hr using 96 increments of the evolution time. Both spectra were processed using sinebell multiplication and zero filling to yield a final data matrix of 1024 x 2048 points. Numerous previously unobserved long-range correlations are observed in these spectra.

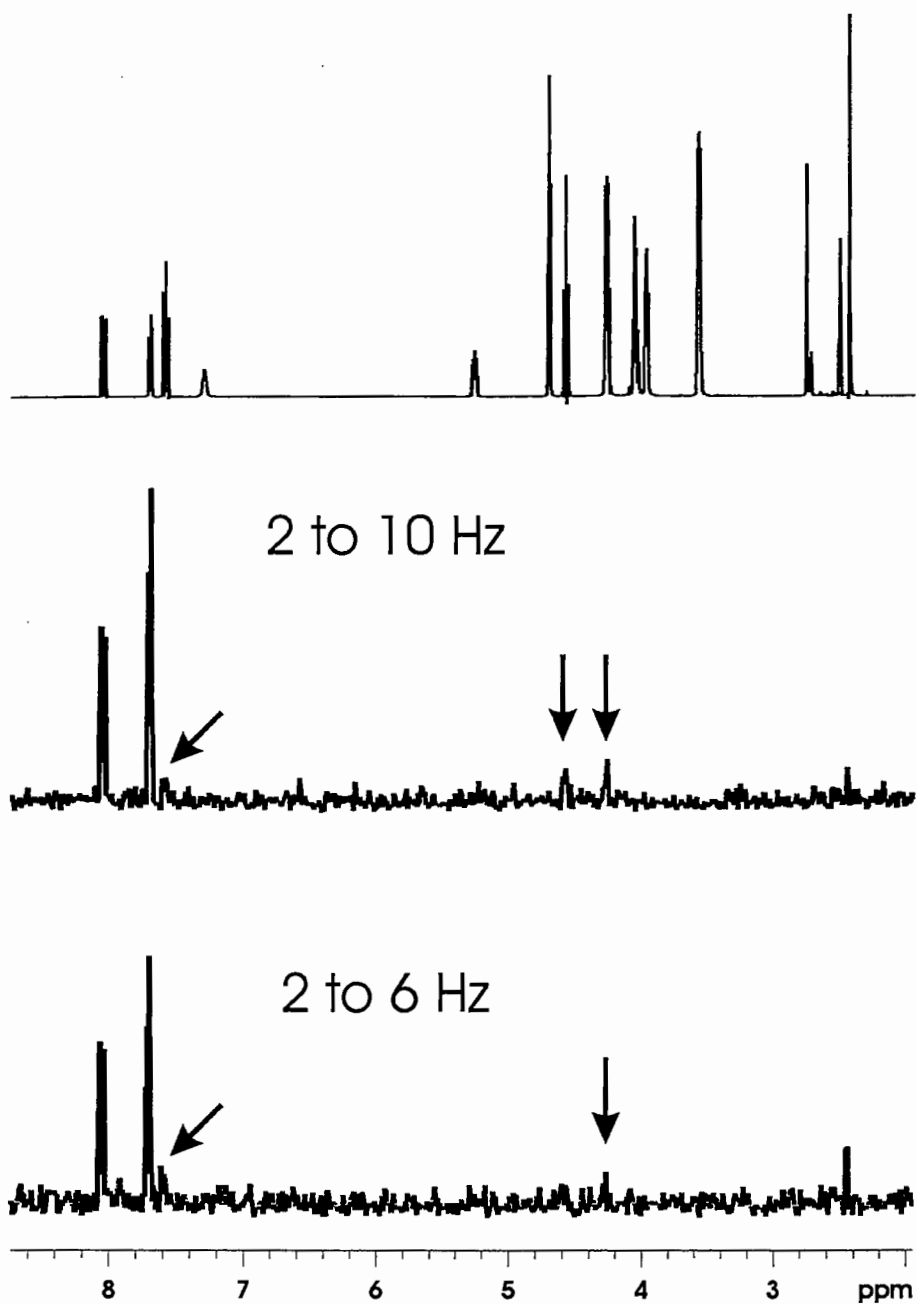


Figure 3. Stack plot showing the ^1H reference spectrum of eperezolid (top) and the slice from the 2-10 and 2-6 Hz optimized CIGAR-HMBC spectra (middle and bottom respectively) extracted from the 2D spectra shown in Figure 2 at the nitrogen chemical shift of the N3 oxazolidinone nitrogen resonance. The two weak correlations denoted by arrows in the figure correspond to a previously unobserved four-bond long-range correlation from the H5' phenyl proton to the N3 oxazolidinone nitrogen resonance. These correlations are below the threshold of the contour plots shown in Figure 2. In the 2-10 Hz trace, the correlations at approx. 4.3 and 4.6 ppm correspond to long-range correlations from the anisotropic H4 oxazolidinone methylene protons.

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For further information or submission of resumes, please contact

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New Mexico Tech
Socorro, NM 87801
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08/08/01



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"T"-purge valve

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Dr. Shapiro,

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Frank B. Contratto
406 Sans Souci Drive
Aurora, Illinois 60506

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

Ethylbenzene at 30 MHz

August 11, 2001
(received 8/12/2001)

Dear Dr. Shapiro,

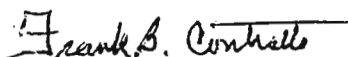
The first NMR spectrum, ^1H NMR of ethanol observed by Arnold, Dharmatti, and Packard in 1951, credited with showing the analytical promise of NMR was acquired on an NMR spectrometer operating at 32.4 MHz. And since the first commercial NMR spectrometer was a 30 MHz instrument, I thought the last issue of The NMR Newsletter should include a 30 MHz ^1H spectrum.

The enclosed ^1H spectrum of ethylbenzene was acquired on a 30 MHz spectrometer located in my garage. Air conditioning for this location is provided by raising and lowering the garage door, so while the environmental conditions of the garage is probably not as good as the laboratory environment available to Arnold, Dharmatti, and Packard, I am sure this spectrum was acquired in a much shorter period of time and with considerably less effort.

We are going to miss the NMR community contact provided by the Newsletter.

Thank you for 43 years of great service.

Best regards,

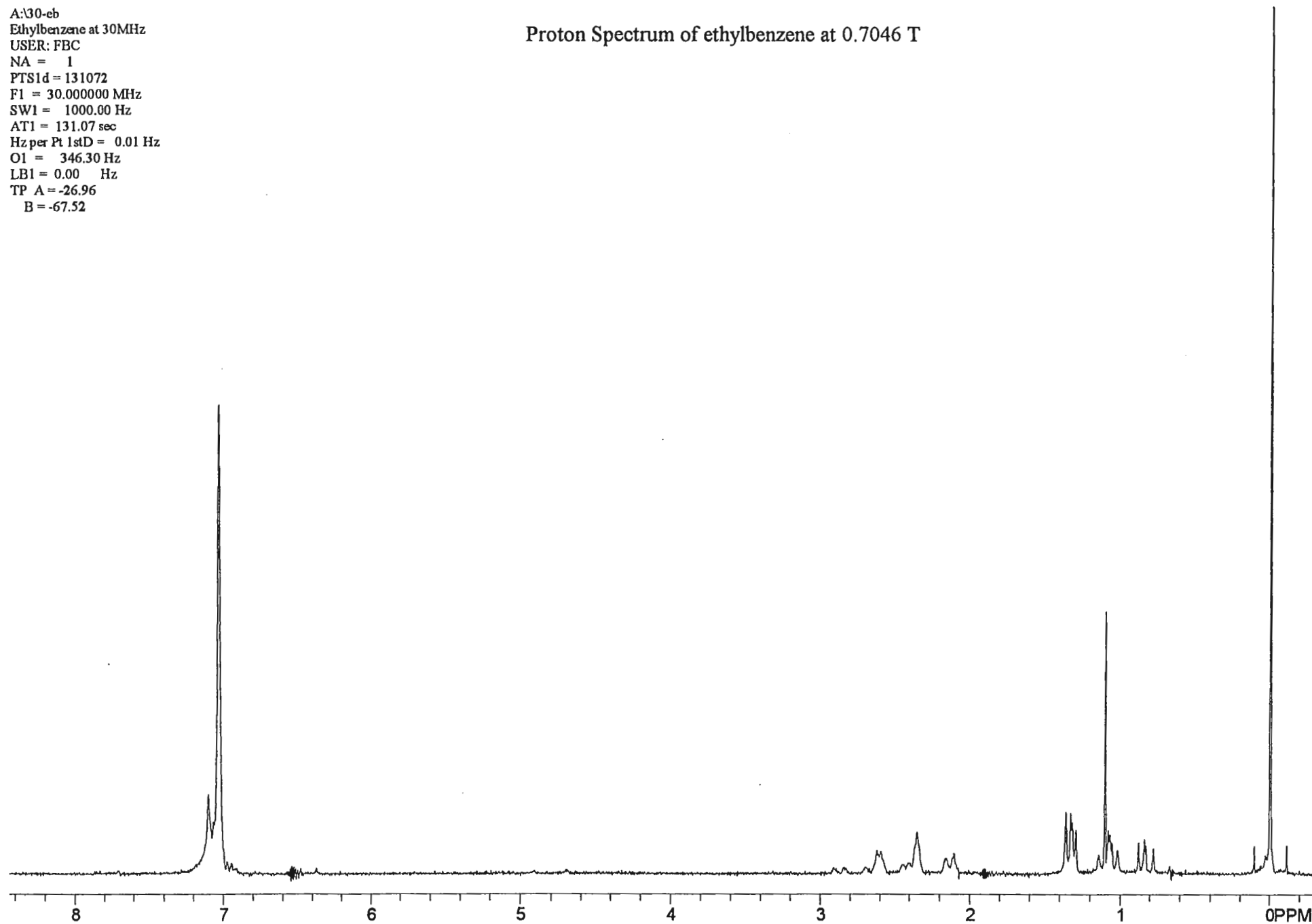


Frank B. Contratto

A:\30-eb
Ethylbenzene at 30MHz
USER: FBC
NA = 1
PTS1d = 131072
F1 = 30.000000 MHz
SW1 = 1000.00 Hz
AT1 = 131.07 sec
Hz per Pt 1stD = 0.01 Hz
O1 = 346.30 Hz
LB1 = 0.00 Hz
TP A = -26.96
B = -67.52

Proton Spectrum of ethylbenzene at 0.7046 T

516-26





Dr. B.L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 9403-3410

August 25, 2001
(received 8/29/2001)

Double-Resonance High-Power Decoupling

Dear Barry,

The number of publications concerning triple-resonance experiments in solid-state NMR has considerably increased during the last few years. While testing new pulse sequences, we have recently performed experiments involving aluminum, phosphorus and proton. Results show that the HETCOR-MQMAS sequence offers the means to correlate phosphorus and aluminum nuclei in a two-dimensional experiment, with an isotropic dimension for the quadrupolar nucleus obtained through triple-quantum excitation (for more information, see Fernandez et al., submitted). The correlation is obtained by cross-polarization (CP), which transfers the magnetization from the aluminum to the phosphorus. Figure 1-a is the result of a CP/MAS sequence with aluminum decoupling, applied during the acquisition of the free induction decay, on an aluminophosphate sample (AlPO₄-14). This material has 4 crystallographically different phosphorus sites even though the spectrum can resolve only 3 of them. In addition to the decoupling procedure applied on the aluminum channel, we applied a strong decoupling power (ca. 100kHz) on the proton channel (see figure 1-b). The spectrum obtained clearly demonstrates that a double decoupling enables a better resolution than that recently reported by Fyfe et al. (Solid-State NMR 9(1997) 97-106). Consequently, triple resonance probes need sometimes to undergo double-resonance high-power decoupling during acquisition in order to obtain optimum resolution. To further observe the potential of this approach, we decided to investigate if in the same sample, a similar effect would be visible when applying decoupling after cross-polarizing from proton to phosphorus. The results are showed in figure 2-a and 2-b. With high-power (100kHz) proton decoupling only, the resolution is rather poor at least for the 2 phosphorus sites at -19 ppm. However, by further applying the aluminum decoupling, we were able to clearly distinguish the 2 phosphorus sites present in that region. Ongoing work in our Bruker application laboratory is further demonstrating the beneficial use of triple resonance sequences for the study of solid samples.

Sincerely Yours,

Christian Brevard Laurent Delevoye High Resolution NMR Application Lab

Christian *LD* *TIP* *Boudouneau* *D. Assémat*

Barry: we are quite close
to the 1000 Hz. Remember
Stirling! *C-oh, yes! Je me souviens.*

Figure 1. CP/MAS $^{27}\text{Al} \rightarrow ^{31}\text{P}$ with ^{27}Al CW decoupling

- a. top : without ^1H CW decoupling
b. bottom : with ^1H CW decoupling

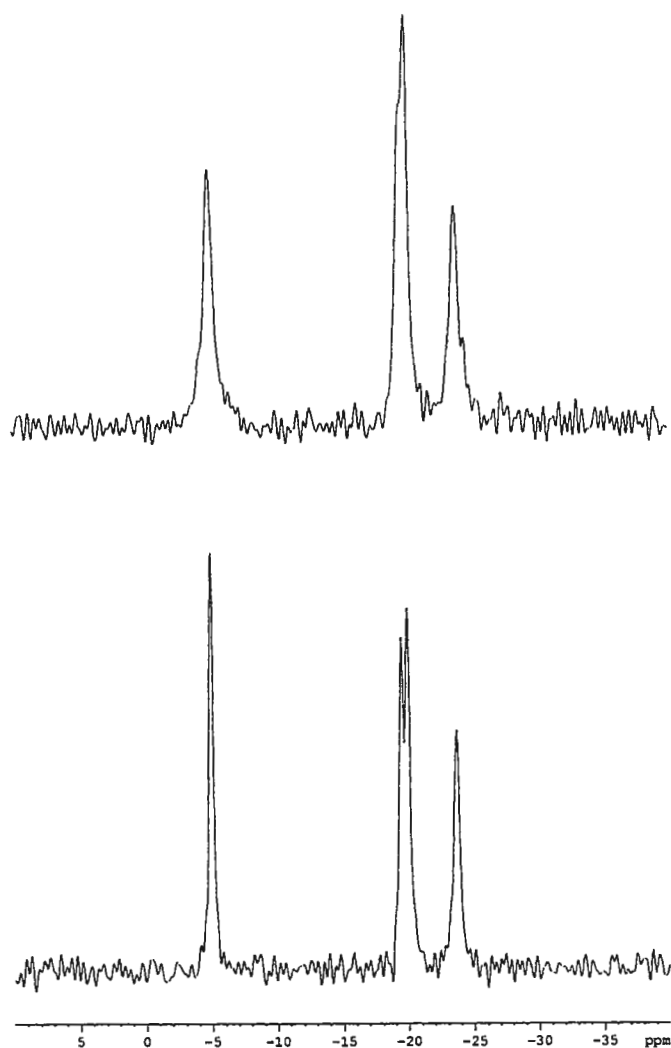
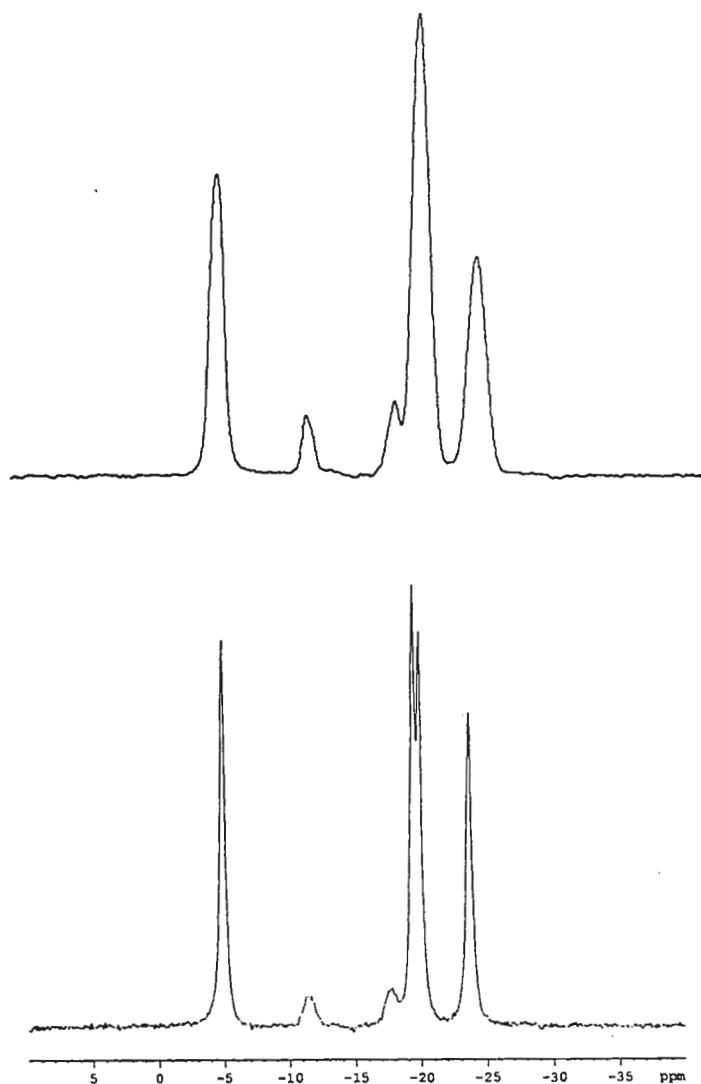


Figure 2. CP/MAS $^1\text{H} \rightarrow ^{31}\text{P}$ with ^1H CW decoupling

- a. top : without ^{27}Al CW decoupling
b. bottom : with ^{27}Al CW decoupling



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3 mm	327-PP-8	400	8 in	0.012"	0.0010"	0.0010"	10.45	+100	9.40
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5 mm	507-PP-8	360	8 in	0.015"	0.0020"	0.0010"	8.30	+100	7.20
5 mm	506-PP-7	100	7 in	0.015"	0.0020"	0.0020"	5.85	+100	5.10
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5 mm	WG-5MM-ECON-7*	60	7 in	0.015"	0.003"	0.003"	1.49	+100	1.30	
5 mm	WG-5MM-ECON-8*	60	8 in	0.015"	0.003"	0.003"	1.75	+100	1.58	
							(1 pk=100 ea)	1-4 pks	5-9 pks	10 pks
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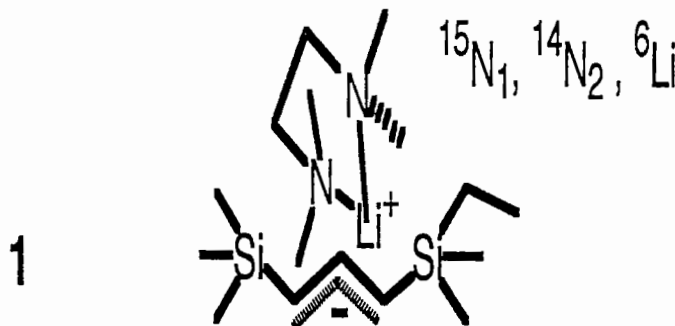
August 31, 2001
(received 8/31/2001)

Department of Chemistry
The Ohio State University
100 W. 18th Avenue
Columbus, OH 43210, USA
Voice: 614-292-4210
Fax: 614-292-1685

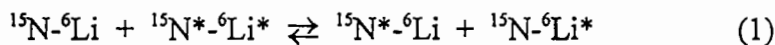
Dynamics of N-Li Exchange of an Allylic Lithium Compound Complexed to a Diamine.

Dear Barry:

Not long ago ion-pair structure was an amorphous concept. Ion-pairs were not believed to have favored structures. The fact that they do was shown by Pochapsky's elegant NMR experiments and some of the low temperature NMR data we collected for ion-paired organolithium compounds. We have also found that ion-pairs undergo several modes of fast reorganization processes at equilibrium, one of which is bimolecular N-Li bond exchange (the N is part of the coordinated ligand). We have now monitored the dynamics of this process by means of suitable isotope enrichment, see **1**.



At 180 K ^6Li NMR of **1** in diethylether- d_{10} consists of an equal doublet, separation 3.5 Hz, which is due to the ^{15}N - ^6Li coupling constant. As would be expected the ^{15}N NMR, under the same conditions is a 1:1:1 triplet, same splitting as for ^6Li NMR. This shows that the tetramethylethylenediamine, TMEDA, is bidentately coordinated to ^6Li . With increasing temperature above 180 K these multiplets progressively average to single lines at their respective centers. Lithium-6 quadrupole induced relaxation is much too slow to average the ^6Li - ^{15}N coupling constant. The effect can only be due to intermolecular N-Li exchange. As far as ^{15}N and ^6Li NMR of **1** is concerned one can simulate the system as pseudospecies "N-Li". NMR lineshapes were calculated taking bimolecular N-Li exchange see into account, as proposed in (1).



Comparison of observed with calculated line shapes gave the pseudo first order rate constants for the exchange process. The activation parameters for ΔH^\ddagger and ΔS^\ddagger are, respectively, 7 kcal.mol⁻¹ and -19 eu.

Also, due to the chiral structure of **1** ^{13}C NMR of its gem silyl methyls at 180 K consists of an equal doublet. With increasing temperature this doublet progressively averages to a single line by 260 K. Such behavior can only be due to fast overall inversion brought about by the transfer of lithium coordinated tetramethylethylenediamine between faces of the pi anion. Line shape analysis of the collapsing doublet reveals that inversion comes with ΔH^\ddagger and ΔS^\ddagger of, respectively, 7 kcal.mol⁻¹ and -19 eu.

It is interesting that bimolecular N-Li exchange and inversion have essentially the same Eyring parameters. It implies that a common mechanism is responsible for both processes. We have ideas about the mechanism. You will not read about it in the Newsletter because the Newsletter is closing down. Watch your copies of J.Am.Chem.Soc.

The Newsletter has been an important, almost defining influence on the progress of NMR worldwide. Most of the new developments surfaced in the Newsletter and its predecessors. It kept us together and it kept us honest. I think it will be missed. Barry has presided so wonderfully and with such good humor.

All best wishes, Barry.

Yours sincerely,

Gideon Fraenkel
Newman Professor of Chemistry

Hua Liu
Research Associate

GF/kv

Positions Available.

Postdoctoral Positions in NMR Spectroscopy and Bio-inspired Nanotechnology

We are currently seeking postdoctoral fellows for research positions in the area of solution-state NMR spectroscopy at New York University, Department of Chemistry, College of Arts and Sciences, and, the Department of Biochemistry, School of Medicine, located in New York City, USA. The candidates should be recent Ph.D. graduates (1999-2001) with research expertise in solution or solid-state multidimensional NMR spectroscopy of proteins and polypeptides.

Our research centers on high-field NMR structural determination of protein sequences which have application to nanostructured materials. Our current instrumentation includes a UNITY-500 z-axis triple resonance equipped PFG spectrometer, which will be upgraded to either an INOVA or Bruker AVANCE system within the next 12 months. In addition, the New York State Structural Biology Center, slated to open in 2002, will provide us with access to 800 MHz and higher field spectrometers for solution and solid-state experiments.

These NSF, ARO funded positions are for 2 years, with the possibility of a third year, and the salaries are negotiable based upon experience and qualifications. The start date is January 1, 2002, but can be negotiable. Interested candidates should forward their CV (plain text format ONLY) and the names and contact information of three references to Professor John S. Evans at jse@dave-edmunds.dental.nyu.edu.

Deadline for receipt of application is October 1, 2001. Applicants will be requested to send hardcopy materials after their initial contact. New York University is an equal opportunity employer.

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Albuquerque, NM 87185-1407(received 8/15/2001)
08/15/2001

Barry,

We will truly miss the NMR Newsletter! We appreciate all your hard work over the years.

MAS Air Line Modification: Bruker to Doty Conversion

A Doty XC4 triple resonance MAS probe was part of the package for the Bruker Avance 600 spectrometer recently installed in our laboratory. In an attempt to simplify the probe setup, reduce the number of MAS air lines, and utilize the Bruker MAS controller we have made the modification to the MAS air line connections described below. The modification simply consists of a short section that directly connects the existing quick connects on the Bruker MAS air lines (European) to the Snap-tite Inc. fitting provided with the Doty MAS probe. The modification required the machining of only one nylon screw-in bushing, while the remainder of the pieces were obtained from either Swagelok, Bruker or Doty or the quick connects available from Bruker. Fig. 1 shows the exploded view of the air line modification, while Fig. 2 shows the completed setup attached to the MAS probe. This modification now allows the Bruker MAS lines to be used for the drive and bearing control of the Doty probe. Depending on your configuration, the Bruker bearing pressure sense line may also need to be included in the modification of the bearing air MAS line. Additional details, including a CAD drawing of the nylon bushing, will also be available on our lab web site in the near future.
(http://www.sandia.gov/materials/sciences/nmr_lab).

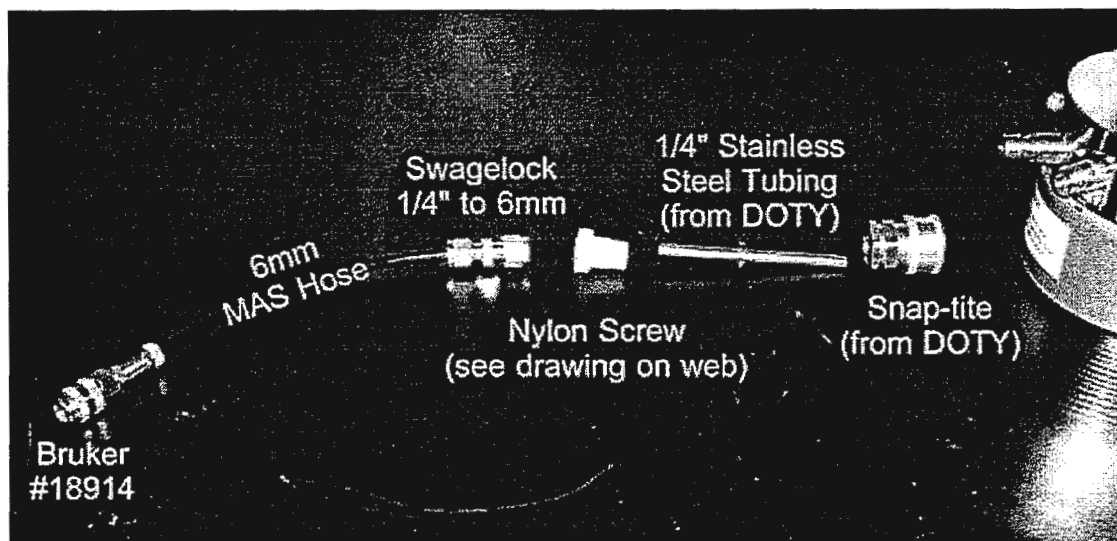


Figure 1: Exploded view of the Bruker to DOTY MAS conversion. The Bruker quick connect (#18914) directly attaches to the existing MAS bearing and drive lines.

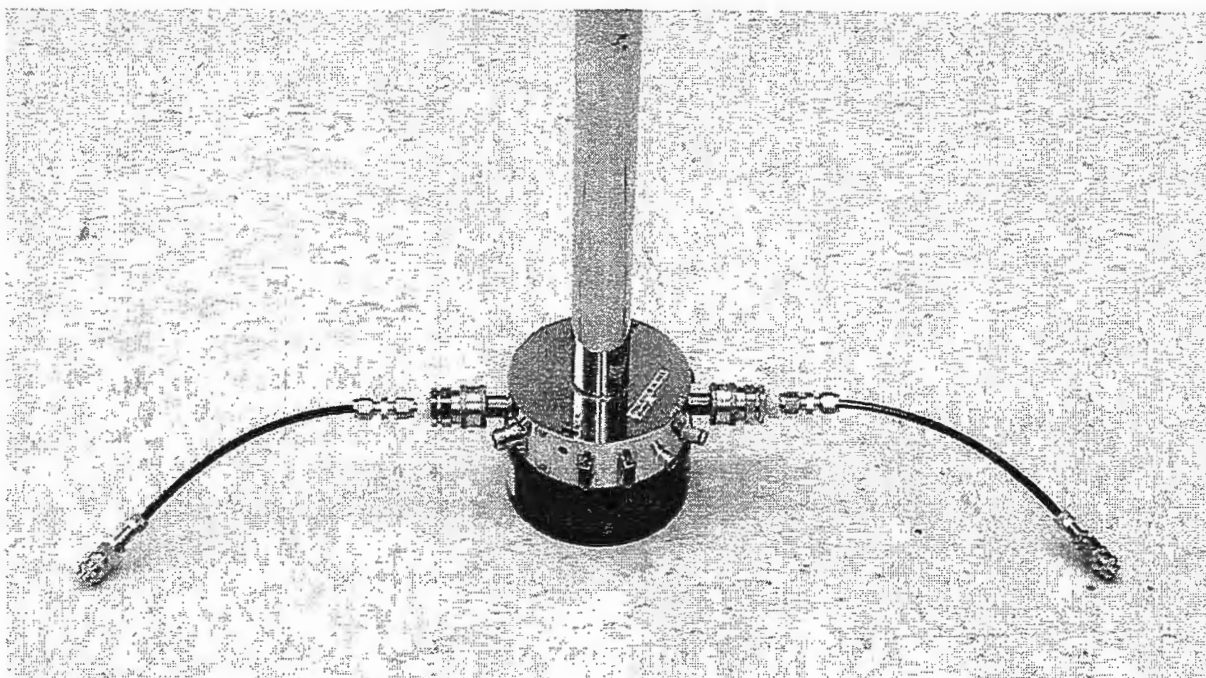


Figure 2: The final assembly showing the bearing and drive line modifications on the Doty triple resonance MAS probe. An additional bearing pressure sense connection may be required for correct functioning of the Bruker MAS controller depending on your configuration. Manual control of the bearing and drive pressure via the MAS controller is required for the Doty probes as the pressures ranges for stable spinning are different than those encountered for the Bruker MAS probes.

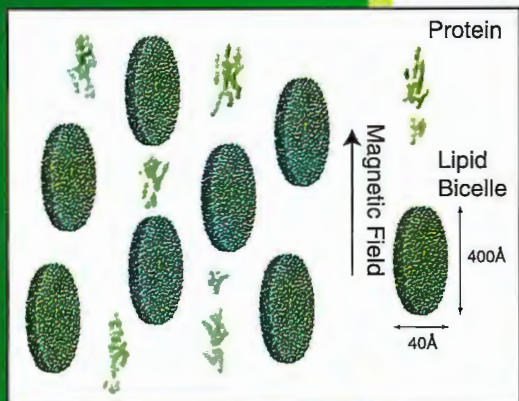
Todd M. Alam

Nick Frame

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Determination of Water Soluble Protein Structure



Tjandra & Bax¹ recently developed a new nuclear magnetic resonance (NMR) technique that gently aligns protein molecules in a bath of liquid crystals, allowing researchers to determine how each bond between neighboring atoms is oriented with respect to the rest of the molecule. By compiling all such orientations between atoms, a precise map of the protein can be derived. In aqueous solution, just above room temperature, the lipids switch from a gel to a Liquid Crystal (LC) phase, where they form disc-shaped particles, often referred to as bicelles², with diameters of several hundred angstroms and thicknesses of ~40Å. The lipids are diamagnetic, and, as a result, the bicelles orient with their normal orthogonal to the magnetic field. However, the lifetimes and temperature ranges of orientation for these samples are critically dependent on sample composition and experimental conditions. Losonczi & Prestegard³ demonstrated that doping dilute bicelle solutions with small amounts of charged amphiphiles substantially improves the stability and degree of alignment, as well as extends the temperature range of orientation for these systems.

1. Tjandra, N. and Bax, A. (1997). Direct measurement of distances and angles in biomolecules by NMR in a dilute liquid crystalline medium. *Science* 278:1111-3.
2. Sanders, C.R. II and Schwonek, J.P. (1992). Characterization of magnetically orientable bilayers in mixtures of dihexanoylphosphatidylcholine and dimyristoylphosphatidylcholine by solid-state NMR. *Biochemistry* 31:37,8898-905.
3. Losonczi, J.A. and Prestegard, J.H. (1998). Improved dilute bicelle solutions for high-resolution NMR of biological macromolecules. *J Biomol NMR* 12:447-51.

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Bicelle Preparation

Buffer:

An effective and convenient method for preparing bicelles makes use of a buffer solution containing 10mM phosphate buffer, pH 6.6, 0.15 mM sodium azide, 93% H₂O (HPLC-grade), 7% D₂O (99.9%). Below, this solution will simply be referred to as buffer.

Bicelle Formation:

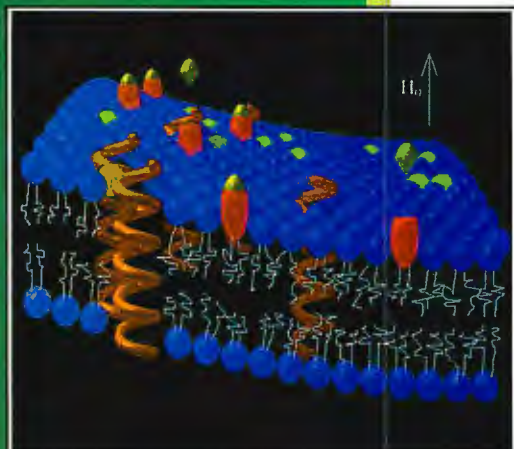
DMPC/DHPC stock solutions containing a total of 15% w/v (150mg lipid/ml) are prepared as follows: Add buffer to the lyophilized lipid mixture - 50mg lipid mixture/280µg buffer or 200mg lipid mixture/1130µg buffer. Let the mixtures hydrate at room temperature (18-22°C) for several hours.

Lipid mixtures with a "q" of 2.8 - 3.0, the hydration is complete in 2 - 3 hours. Lipid mixtures with a "q" of 3.25 - 3.5 require 24 hours for complete hydration. Accelerated hydration (one hour) may be effected by heating any mixture to 40°C for 10 minutes and cycling to 18°C twice, then briefly vortexing.

Protein-Bicelle Mix: Two volumes of protein solution are added to one volume of bicelle solution.

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Magnetic Alignment of Biological Membranes



Blue, green, and red stylized molecules represent DMPC, DMPG, and DMPE-DTPA, respectively, and yellow represents the Yb³⁺ ion DHPC, which is believed to be sequestered in curvature defect regions, is not shown in this figure.

We thank Biophysical Journal for permission to use this graphic.

A phospholipid chelate complexed with ytterbium (DMPE-DTPA:Yb³⁺) is shown to be readily incorporated into a model membrane system, which may then be aligned in a magnetic field such that the average bilayer normal lies along the field. This so-called positively ordered smectic phase, whose lipids consist of less than 1% DMPE-DTPA:Yb³⁺, is ideally suited to structural studies of membrane proteins by solid-state NMR, low-angle diffraction, and spectroscopic techniques that require oriented samples. The chelate, 1,2-dimyristoyl-sn-glycero-3-phospho-ethanolamine diethylenetriaminepentaacetic acid, which strongly binds the lanthanide ions and serves to orient the membrane in a magnetic field, prevents direct lanthanide-protein interactions and significantly reduces paramagnetic shifts and line broadening. Similar low-spin lanthanide chelates may have applications in field-ordered solution NMR studies of water-soluble proteins and in the design of new magnetically aligned liquid crystalline phases¹.

The addition of lanthanides (Tm³⁺, Yb³⁺, Er³⁺, or Eu³⁺) to a solution of long-chain phospholipids such as DMPC and short-chain phospholipids such as DHPC is known to result in a bilayer phase in which the average bilayer normal aligns parallel to an applied magnetic field. Lanthanide-doped bilayers have enormous potential for the study of membrane proteins by solid-state NMR, low-angle diffraction, and a variety of optical spectroscopic techniques².

The equimolar complex, consisting of the lipid-like, amphiphilic chelating agent DTPA-18 and Tm³⁺, is shown by deuterium NMR to be useful in aligning bicelle-like model membranes, consisting of DMPC and DHPC. As shown previously, in the absence of chelate, the lanthanide ions bind loosely with the lipid phosphate groups and confer the membrane with a sufficient positive magnetic anisotropy to result in parallel alignment. Two conclusions could be drawn from this study: 1. The addition of Tm³⁺ to the bicelle system is consistent with a conformational change in the surface associated peptide, and this effect is shown to be reversed by addition of the chelate, and 2. The paramagnetic shifts are shown to be significantly reduced by addition of chelate³.

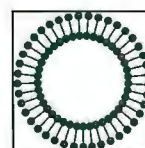
1. Prosser, R.S., et al. (1998). Novel chelate-induced magnetic alignment of biological membranes. *Biophys J* 75:2163-9.
2. Prosser, R.S., et al. (1998). Solid-state NMR studies of magnetically aligned phospholipid membranes: taming lanthanides for membrane protein studies. *Biochem Cell Biol* 76:443-51.
3. Prosser, R.S., et al. (1999). Lanthanide chelates as bilayer alignment tools in NMR studies of membrane-associated peptides. *J Magn Reson* 141:256-60.

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DEPARTMENT OF CHEMISTRY

(received 8/20/2001)

August 15, 2001

Dear Barry:

I can only imagine the travail you went through in the decision to bring the Newsletter to an end. However, the times they are a changing. NMR is now a mature discipline where new developments have come with increasing slowness. I have Newsletters back to #45 (a few missing issues only) if someone is interested they can have them for the cost of the shipping. I'll be away from my desk in the UK until the first week in September.

The data on the accompanying page are GIAO calculations on the ring carbon chemical shifts for a series of $\text{Cr}(\text{CO})_3$ complexes of benzene, the benzyl cation, the benzyl anion, and the cumyl cation. I have been interested in seeing how well ab initio calculations can model such structures. The chemical shifts were done at the BPW91/6-311G**//MP2/6-31G* level. My impression is that the geometries are quite good. Life is too short to do them with a larger basis set. Optimizations ran to many days on a large 600 MHz workstation. The benzene complex is actually in a state of fluxional motion. The experimental value of the chemical shift for the ring carbons is 93.5 ppm. The averaged value for these is computed as 89.6 ppm. Some of the values for the cumyl cation complex are less satisfactory. I won't engage in the arm waving necessary to rationalize this.

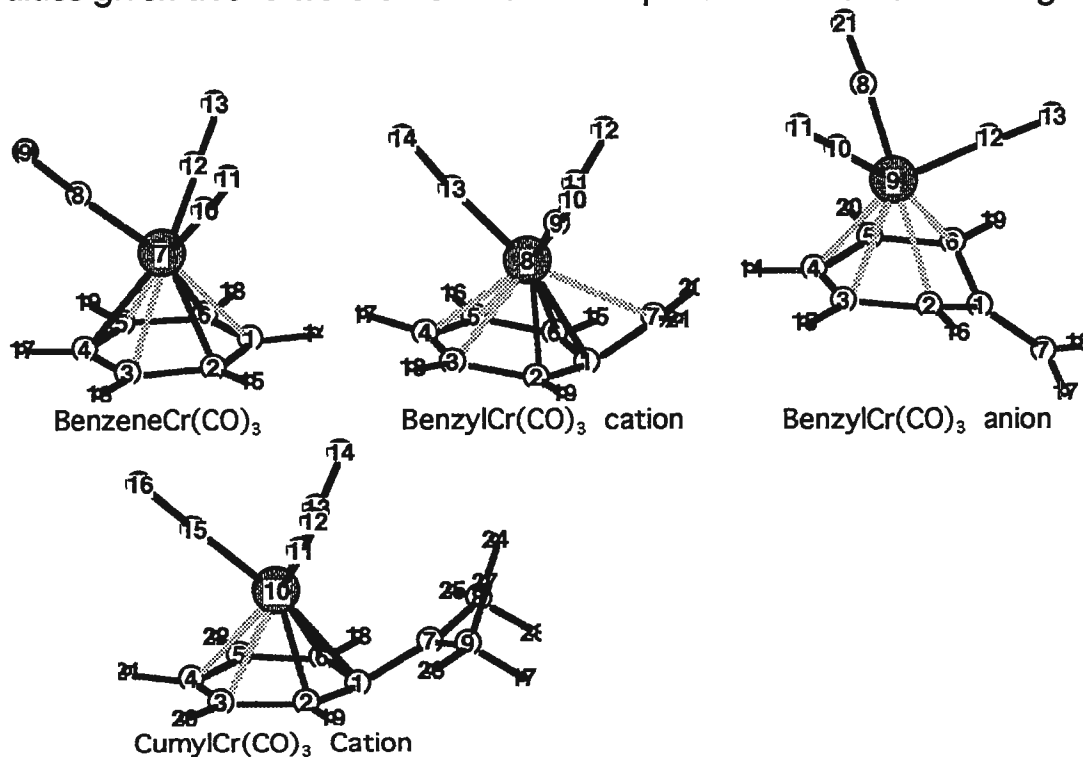
As you and Lee sail off over the western horizon, I can but wish you both the best for the many years of service-both personal and via the Newsletter.

Regards,
Bill

GIAO Carbon-13 Chemical Shifts for the $\text{Cr}(\text{CO})_3$ Complexes in This Study

	1	2	3	4	5	6	7
Benzene $\text{Cr}(\text{CO})_3$	95.4	83.8	95.4	83.4	95.4	83.4	-
Benzyl cation	142.1	153.4	136.6	165.8	136.6	153.4	200.5
Benzyl $\text{Cr}(\text{CO})_3(+)$	110.3	110.8	96.8	100.3	96.8	110.8	95.5
Cumyl(+)	137.7	138.2	133.8	156.6	133.8	138.2	246.7
Lit. values ^a	140.0	142.4	133.3	155.9	133.3	142.7	254.3
Cumyl $\text{Cr}(\text{CO})_3(+)$	98.6	101.1	97.3	102.2	97.3	101.1	178.9 ^b
Lit. value ^a	101.7	99.5	109 ^c	96.7	109 ^c	99.5	170.9 ^b

a. Olah, G.A., Yu, S.H. *J. Org. Chem.* 1976, 41, 1694, CDCl_3 plus magic acid at -30° . Referenced to external TMS. b. The external methyls are exp.^a 24.7; cal'd 23.8 ppm. c. There is a typographical error in ref. A. Table 1 there show the chemical shifts for C3 and C5 as 120.7 ppm. The spectrum for this complex (Figure 1) shows no lines in this region. The values given above were taken from an expanded version of their Figure 1.





CENTRO DE INVESTIGACION Y DE ESTUDIOS AVANZADOS DEL I.P.N.

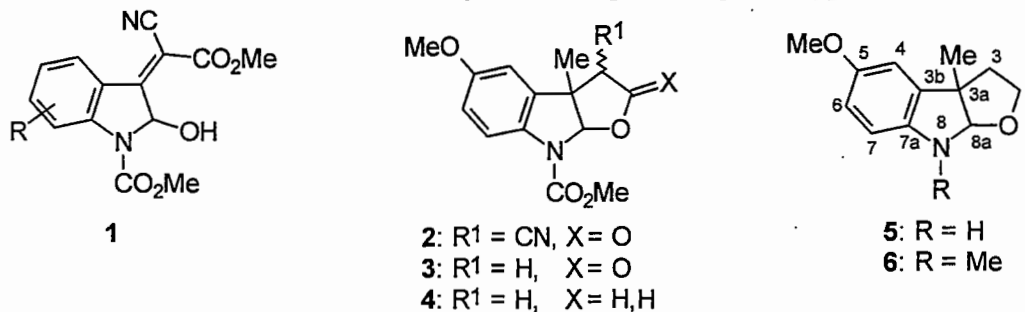
August 6, 2001
(received 8/15/2001)

Dr. Bernard L. Shapiro
Editor/Publisher
The NMR Newsletter
966 Elsinore Ct.
Palo Alto, CA 94303 USA

Conformational Analysis of N(8)-Carbomethoxylated Furo[2,3-*b*]indoles

Dear Dr. Shapiro:

In the middle 1990s, we discovered that Grignard addition to **1** followed by ring closure gave highly functionalized furoindoles, as **2**, in good yields.¹ This reaction is interesting because **2** represents a class of advanced intermediates for the total synthesis of physostigmine type indole alkaloids.²



The N(8)-carbomethoxylated compounds **2-4** showed very broad H-7 and N(8)-CO₂Me proton signals in the ¹H NMR spectra at room temperature, as well as very broad N(8)-CO₂Me, C-7a, C-3b and C-3a carbon signals in the ¹³C NMR spectra. Hindered rotation about the N(8)-CO₂Me single bond in these compounds appeared to be responsible for such broad signals, because at higher temperatures (80 °C in DMSO-*d*₆) the rotation barrier was exceeded and sharp signals in both the ¹H (Figure) and the ¹³C NMR spectra were obtained. As expected, the NMR spectra of the corresponding N(8)-H or N(8)-Me substituted tricyclic compounds **5** or **6** showed no such abnormal behavior and were clearly resolved at room temperature in CDCl₃ or CD₂Cl₂.

The conformational analysis of **4** was derived from the measurements of vicinal ³J₂₋₃ and ⁴J coupling constants, computed simulated spectra, detection of specific NOE contacts, and structural simulation (MMX, ab initio and DFT). In solution, the C-ring in **4** was blocked in an enveloped ²E conformation with tetrahydrofuran ring pucker of C2-exo.

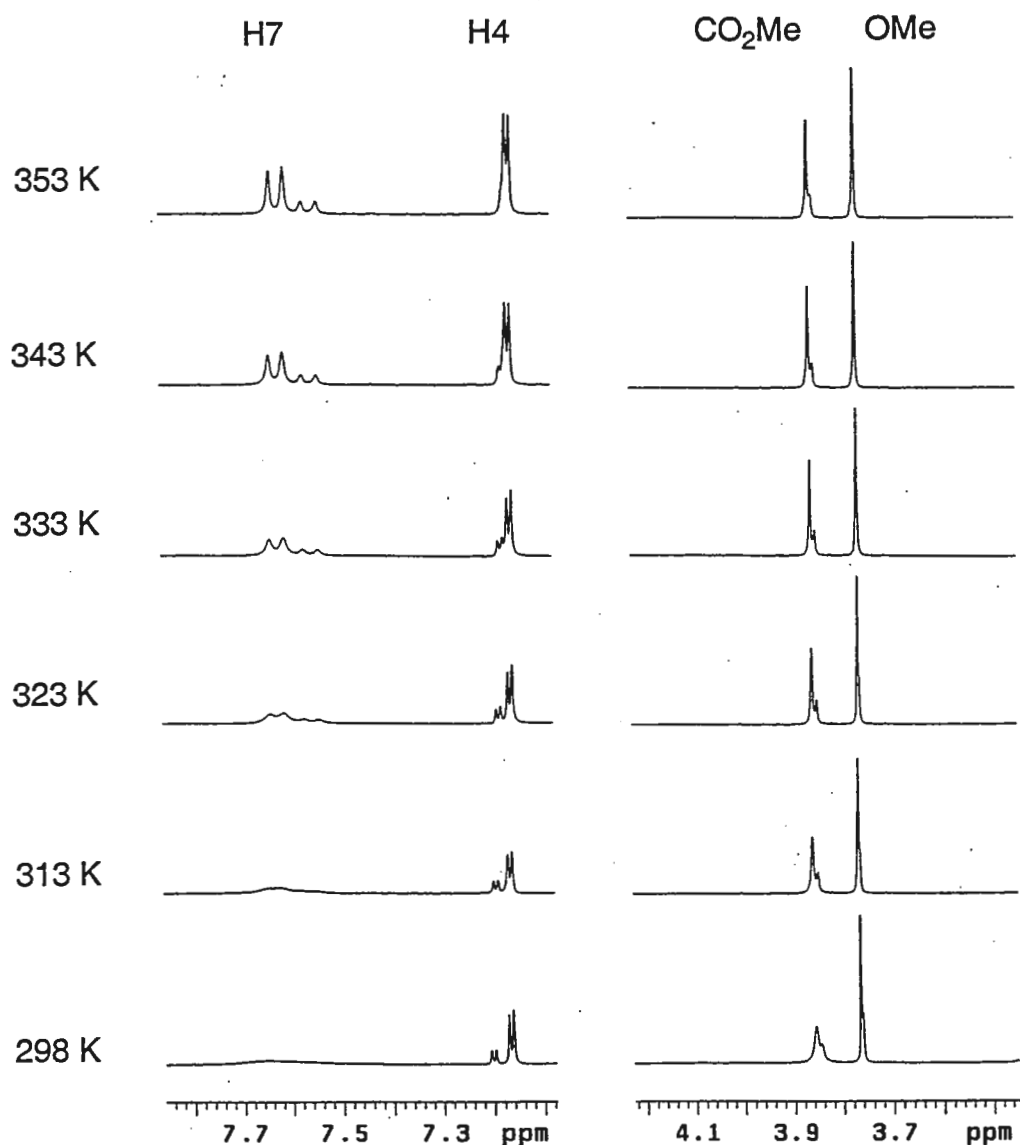


Figure. 300 MHz ¹H NMR spectra (DMSO- *d*₆) of the H-7 (left) and N(8)-CO₂Me (right) regions of C(3)-CN endo-exo epimeric mixture of **2**.

1. Morales-Ríos, M.S.; García-Martínez, C.; Bucio, M.A.; Joseph-Nathan, P. *Monatsh. Chem.*, **1996**, *127*, 691.
2. Morales-Ríos, M.S.; Suárez-Castillo, O.R.; Trujillo-Serrato, J.J.; Joseph-Nathan, P. *J. Org. Chem.* **2001**, *66*, 1186.

Sincerely yours,

Martha S. Morales-Ríos

Norma F. Santos-Sánchez

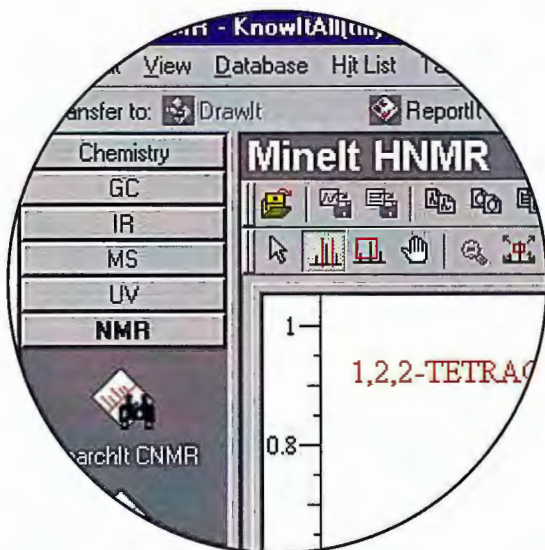
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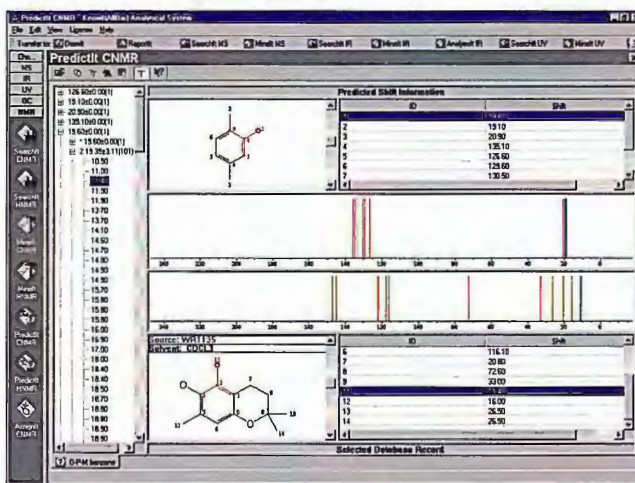


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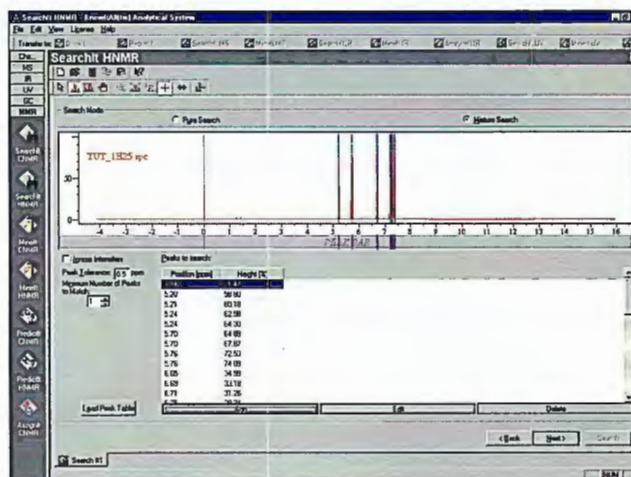
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Dr. B. L. Shapiro
The NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303-3410

August 15, 2001
(received 8/20/2001)

What is Your NMR Breathing?

Dear Barry,

In the September 2000 volume of the NMR Newsletter we read an article by Peter Stilbs with great interest (Tracking Down Strange B_0 Artifacts in PGSE-NMR Experiments). In it, he discussed an oscillation instability of the NMR that was directly linked to the regeneration cycle of their Balston air dryer. Their solution was to add a length of PVC piping to the outlet of the air dryer. This additional buffer volume greatly reduced the modulation observed on the NMR. The focus of this letter is to address what we believe to be the underlying cause for these instabilities. It is commonly thought that the addition of some type of extra volume, either in the form of a ballast tank or large diameter tubing, reduces instabilities by smoothing out pressure fluctuations caused by the dryer recycle. If significant, the pressure fluctuations would affect the position of the sample and the temperature stability, which could both lead to lock oscillations. We would suggest that variation in the pressure actually plays a smaller role and that a change in the composition of the air is the major source for these lock oscillations.

When AK was a graduate student in the lab of Dallas Rabenstein at the University of California, Riverside we took delivery of an Inova console that came with an FTS air cooler that required that the dew point be -60°C or better. Since the house air was significantly wetter than this, a Balston model 64-20 air dryer was also purchased and installed. Naively, (and fortunately for this letter) we did not initially install a ballast tank after the air dryer. Once the spectrometer was up to field, the installation engineer put in the lineshape sample and began to shim. It quickly became apparent that the lock level was dropping about 30% approximately 20 seconds after the air dryer cycled from one chamber to another. It would then recover slowly over the period of a couple of minutes. We initially thought that it might be due to a combination of the high humidity of our house air and an inlet air pressure that was just below the dryer specs. The other possibility that came to mind was sample movement due to pressure fluctuations. To troubleshoot, in place of the house air, a compressed air tank was attached to the inlet side of the dryer. Unfortunately, this still led to the temporary drop in the lock and pointed to pressure fluctuations. Much to our surprise, attaching a compressed nitrogen tank to the air dryer inlet resulted in a reasonably steady lock level. After some thinking, we surmised that the zeolite desiccant in the dryer is preferentially adsorbing either N_2 or O_2 , so after the recycle the emerging gas is enriched in O_2 or N_2 (respectively). Since O_2 is paramagnetic, its depletion or enrichment would temporarily change the susceptibility surrounding the sample and result in a drop in the lock level. A similar effect can be observed if N_2 is used for the VT gas and air is used for the spin/cooling/bearing. Poor mixing of these gases will modulate the susceptibility.

This theory is supported in the text book *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, by D. W. Breck (Wiley-Interscience, 1974). Therein lie many examples of zeolites that

exhibit a substantial difference in adsorption isotherms of N_2 vs O_2 . Previous literature indicated that the ratio of N_2 and O_2 can be determined using laser Raman spectroscopy.^{1,2} We performed these experiments at various time intervals by capturing the gas at the NMR by flushing out and sealing an NMR tube (Table 1). The air dryer was attached to the compressed house air for these experiments. Additionally two control samples were run 1) Regular atmospheric air to establish a baseline O_2/N_2 ratio and to assure optimum instrument performance, and 2) 100 % nitrogen to verify that the sample tubes could be flushed fully. No correction was performed to compensate for differing intrinsic scattering powers of the two gases. This data gives a clear picture that a plug of air substantially enriched in O_2 emerged from the dryer after the tower recycle and remained so for quite some time. Clearly, the performance of any NMR spectrometer would be compromised by such a variation in the composition of the incoming air.

The solution was no different than if the cause was solely due to pressure fluctuations, the addition of a ballast tank after the air dryer and prior to the NMR spectrometer. The tank consisted of a retrofitted 5' compressed gas tank that had an inlet with a tube that went to the bottom of the tank, and an outlet at the top of the tank. This was sufficient to thoroughly mix the emerging dryer gas, which allowed for the use of the compressed house air, and resulted in a rock steady lock level.

Table 1: Raman Spectroscopy Results

O_2/N_2 peak integral ratios	Calculated % O_2	Time Interval or Sample
0.28	22	Air
0.00	0	N_2
0.24	19	15 sec before tower switch
0.23	19	10 sec after tower switch (ATS)
0.52	34	20 sec ATS
0.54	36	20 sec ATS
0.33	25	30 sec ATS
0.35	26	40 sec ATS
0.33	25	50 sec ATS

Regards,



Andreas Kaerner, Ph. D.
Lilly Research Labs
Eli Lilly & Company
Indianapolis, IN 46825



Dan Borchardt, Ph. D.
Department of Chemistry
University of California
Riverside, CA 92521

References:

1. W. H. Weber, M. Zanini-Fisher, and M. J. Pelletier, *Applied Spec.* **51**, 123-129 (1997).
2. L. P. Powell and A. Campion, *Anal. Chem.* **58**, 2350-2352 (1986).

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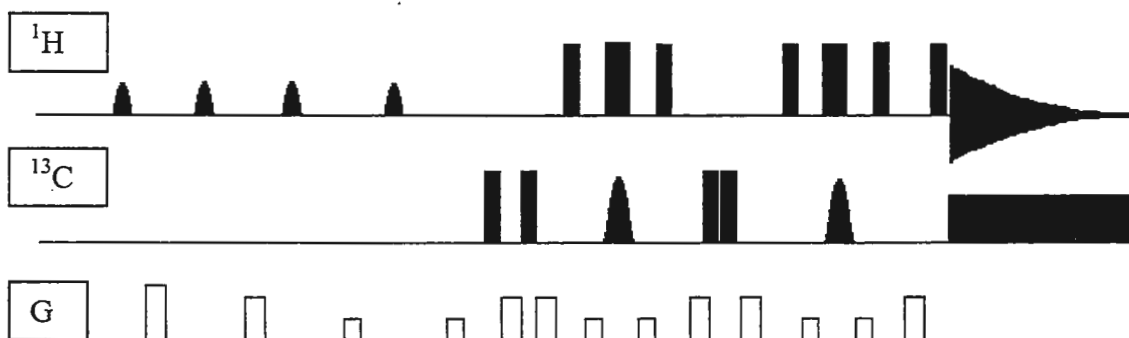
August 1, 2001
(received 8/8/2001)

Dear Barry,

Title: Optimizing HSQC signal to noise in LC-NMR

We've been attempting to optimize signal to noise in HSQC for LC-NMR on our 500MHz system. It's well known that replacing the 180 degree carbon hard pulses with adiabatic pulses can significantly improve the quality of HX correlation data at high fields.^{1,2} We were curious as to whether this would hold true for intermediate fields as well. We have found that the sequence below with adiabatic pulses does indeed produce a significant improvement in signal to noise. The sequence is an HSQC from the Varian "ProteinPack" modified to include WET solvent suppression.² (Figure 1.)

Figure 1.



Below are shown two wet-HSQC spectra of a sample of the LC standard methyl 4-hydroxybenzoate in $\text{CH}_3\text{CN}/\text{D}_2\text{O}$. The first spectrum is a standard HSQC modified to include WET solvent suppression instead of presat.(Figure 2) The second spectrum is the similarly modified HSQC from "ProteinPack" which uses STUD pulses for inversion.¹

As one can see from the spectra the cross peak at 128ppm is significantly attenuated in the standard spectrum whereas it has full intensity in the spectrum with adiabatic pulses. This is even more apparent from slices taken through the proton chemical shift.(Figure 3) In this case the ^{13}C 180 degree pulse was 28 μs and the ^{13}C signal is approximately 8.7KHz away from the transmitter. At this offset the effect of incomplete excitation is clearly apparent. This is predictable since a Bloch simulation of the resulting pulse indicates incomplete inversion at this offset.(Figure 4). Use of the adiabatic sequence therefore produces a significant improvement in the signal to noise of the aromatic region of the spectrum.

Please credit this submission to Chris Roe's DuPont account.

Figure 2.

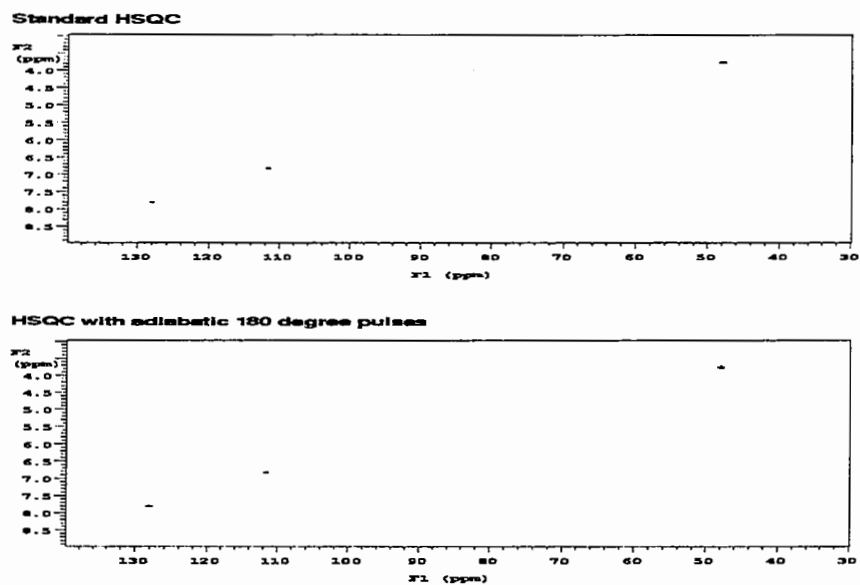
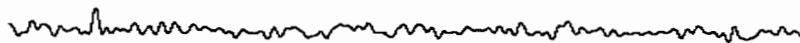


Figure 3.

Standard HSQC



HSQC with adiabatic 180 degree pulses

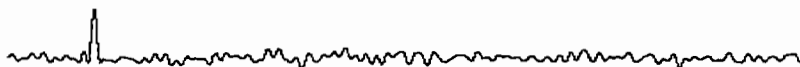
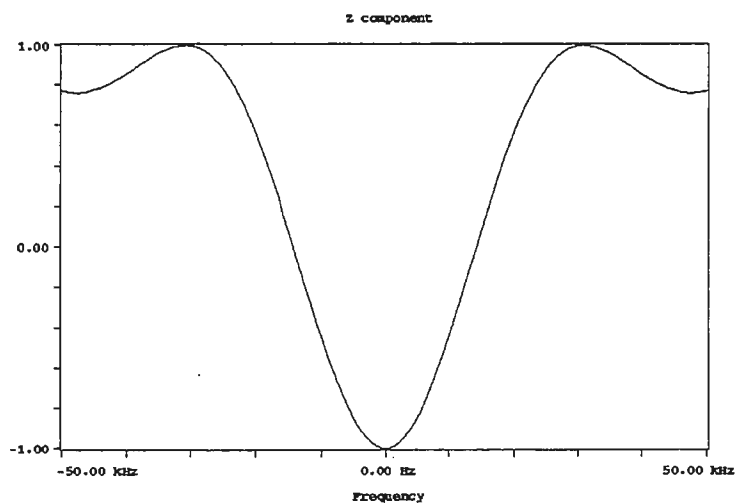


Figure 4. Inversion profile calculated for a $28\mu\text{s}$ 180 degree pulse.



1. Bendall, MR; J. Magn. Reson. A., 116, 45-58 (1995)
2. Zweckstetter, M., and Holak, T.A., J. Biomol. NMR, 15(4): 331-334 (1999)
3. Smallcombe, S., et. al., J. Magn. Res., 117, 295-303 (1995)

Steve Cheatham
Steve Cheatham
DuPont Crop Protection

Igor Goljer
Igor Goljer
Varian NMR Applications

The NMR Newsletter - Book Reviews

Book Review Editor: István Pelczer, Dept. of Chemistry, Princeton University, Princeton, NJ 08544

"Solid-State NMR Spectroscopy of Inorganic Materials"

Edited by

John J. Fitzgerald

Oxford University Press, ACS Symposium Series 717, 1999.
ISBN 0-8412-3602-X; \$125.00 (hardcover); <http://www.oup-usa.org>

Solid-State NMR Spectroscopy of Inorganic Materials describes recent advances in solid-state NMR methods as applied to modern inorganic materials such as metal oxides, catalysts, zeolites, glasses, ceramics, semiconductors, ion conductors, superconductors, and composites. The book is dedicated exclusively to inorganic systems, and is the outcome of the successful symposium on this topic held at the National ACS Meeting, in Orlando, Florida, in 1996.

The introductory chapter 1 (Fitzgerald and DePaul) makes a comprehensive examination of the various solid-state techniques in use for inorganic materials, and is followed by thirteen additional chapters, in 405 pages overall. All but chapter 1 (with 409 references for its own) refer to about 40 references. The book has a Subject Index in its final 17 pages.

The section on *NMR of Metal Oxide Systems* comprises chapters 2 through 5. In chapter 2, Medek and co-workers detail the theoretical framework of MQMAS, discuss some of the pulse sequence aspects, and present various MQMAS spectra of ^{23}Na and ^{59}Co . In chapter 3, Reimer and Adler exploit the use of ^{17}O NMR (relaxation and chemical shifts) to carry out conductivity measurements of complex oxides, such as CeO_2 doped with Y_2O_3 , whereas Pan (in chapter 4) applies ^{31}P - ^{19}F REDOR to study the F^- distribution in apatites. Chapter 5 (Fitzgerald) reviews the literature on ^{27}Al and ^{17}O CP/MAS and MQMAS applied to the determination of the chemical nature of bulk and surface of alumina, and its relation to catalytic activity. In addition, satellite transition spectroscopy (SATRAS) is mentioned as a valuable experiment to extract NMR parameters from quadrupolar nuclei (C_Q , 0 and $^*\text{iso}$). Fitzgerald also refers to ^1H -CRAMPS, which has contributed significantly to the understanding of alumina's surface chemistry.

The next section on *Solid-State NMR of Amorphous Glasses and Gels* is divided into chapters 6 through 8. Chapter 6 (Wenslow and co-workers) investigates sodium phosphate glasses, and discusses some important aspects of cross polarization from $^{23}\text{Na} \rightarrow ^{31}\text{P}$. It comments on 2D correlation experiments via DAS/CP combination. In Chapter 7 Zwanziger, Youngman, and Braun employ ^{11}B DAS NMR to make chemical assignments to various structural units from potassium borate glasses. This section ends with the contribution of Klemperer and Richard, who employ ^{17}O MAS NMR to study the phase changes in lead zirconium titanates.

Chapters 9 through 12 compose the section: *NMR Studies of Silica-Containing Materials*. Engelhardt investigates structural changes in sodalites with various guest molecules by means of ^{29}Si MAS. Molecular sieves and their structural changes are the subject of chapter 10 (Fyfe and co-workers). In this chapter, it can be seen how ^{29}Si MAS provides the number of T-sites in zeolites, and how the spectrum changes upon adsorption of organic guests, which can thus be associated to symmetry change. Cross-polarization and REDOR further demonstrate their usefulness on the determination of molecular sieve/sorbate complexes' three-dimensional structures. In chapter 11 Shore and co-workers examine the theoretical aspects of the dynamics of the $^{23}\text{Na} \rightarrow ^{29}\text{Si}$ and $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ CP transfers in minerals that do not contain hydrogen. The results demonstrate the appreciable S/N enhancement in the ^{29}Si spectrum of crystalline albite upon $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ CP. In chapter 12, Maciel discusses various applications of ^{29}Si NMR, including the monitoring of silylation reactions on silica surfaces.

In the last section, *NMR Studies of Inorganic Nitrogen-Containing Solids*, Yesinowski and Hill present the application of wide-line ^{14}N NMR to diverse nitrogen-containing solids. They discuss a new approach of mechanical rotation of the sample around the main magnetic field axis as a means to improve ^{14}N S/N. The chapter also focuses on *hole-burning* experiments, which provides the dynamics of $\text{N}_4(\text{CH}_2)_6$. Smith, in the last chapter, employs ^{29}Si MAS NMR to determine the phase composition of commercial silicon nitrides (Si_3N_4) and discusses the ^{27}Al NMR to investigate the impurities in aluminum nitride based ceramics. The author further exemplifies on how ^{29}Si and ^{15}N are used to characterize metal silicon nitrides.

Solid-State NMR Spectroscopy of Inorganic Materials is a collection of research reports in the field of inorganic materials. It is quite comprehensive, covering all features of this extremely important branch of materials science. The book reflects the state-of-the-art of solid-state NMR in 1996, and it is certainly a precious source of information for chemists, chemical engineers, and physicists.

(received 8/26/2001)

Carlos R. N. Pacheco
Department of Chemistry
Princeton University
Princeton, NJ
08544-1009

cpacheco@Princeton.edu

Dear Barry,

Presenting a book review as a letter is unusual, but there is a special reason for it. Having the last issue of The NMR Newsletter is a sad moment in a way, but I'd rather take this opportunity to celebrate the history and accomplishments of this periodical in various incarnations over the decades under your caring editorship. I found the following book to be just the right subject to do so, both for its quality and for the theme, which overarches almost the whole history of NMR structural studies, just as your Newsletter does. Please find my review below.

With my warmest regards,

István.

(received 8/26/2001)

The NMR Newsletter - Book Reviews

Book Review Editor: István Pelczer, Dept. of Chemistry, Princeton University, Princeton, NJ 08544

"The Nuclear Overhauser Effect in Structural and Conformational Analysis" (2nd ed.)

by

David Neuhaus and Michael P. Williamson

Wiley-VCH, New York, 2000; ISBN 0-471-24675-1, \$125.00, <http://www.wiley.com>

Can a reviewer be "speechless"?! This is certainly a paradox, but I found it quite difficult to praise the second edition of this book of David Neuhaus and Mike Williamson (and James Keeler, as kind of a 'ghost writer', see the Preface) at the true level of its quality. The first edition from ten years before was an exceptional work already, only it was presented right at the time when new, important applications of this phenomenon were just about to take off and develop rapidly, such as extensive structural and dynamics studies of isotope-labeled large biomolecules, interactions with water, kinetics of ligand binding, extensive use of pulsed field gradients, etc. The new edition includes these applications, and the rich section of selected applications has also been extended and re-written significantly, including many new relevant cases.

The second edition has grown to the size of 656 pages, extended with contents, prefaces for both the second and the first edition, warm acknowledgments, four pages of a quite useful list of symbols, abbreviations, and units, a short but historically very informative introduction, appendices on equations for enhancement involving groups of equivalent spins, and quantum mechanics and transition probabilities, respectively, as well as an Index of nine pages.

The book is cleanly divided into three parts: theory, experimental, and applications. Obviously the first part needed the least upgrade, discussing general background, the steady-state NOE for two spins, that in more extended rigid multispin systems (chapters 1, 2, and 3) and complications from spin-spin couplings (chapter 6). Chapters 4 and 5 in this section, which deal with issues of kinetics of NOE and transient effects, carry the most "added value", discussing biomolecular aspects much more extensively than in the former edition. It is especially visible in chapter 5, which also has a short overview now of intermolecular NOE/exchange processes, which involve water.

The second part on experimental issues has received a significant face-lift. In chapter 7 the beauty of gradient applications is the most important news; it is almost unbelievable knowing (remembering) the sensitivity limits of the first incarnations of 1D NOE difference experiments, how sensitive and artifact-free this method can be using excitation sculpting and careful

optimization. Smart methods developed for network editing, both homo- and heteronuclear, are now available for blocking spin-diffusion, and/or simplifying multispin effects in general, as this is now added to the material presented in chapter 8. This chapter also presents one of the most comprehensive and best overview of experimental and data processing details for two-dimensional NMR, apart from those few reviews and book chapters specifically dedicated to this subject. Chapter 9 is now extended significantly by more information on heteronuclear NOE, and X-filtered/separated NOE experiments, including 2-4 dimensional applications, and discusses more various ROESY methods in detail.

The third section presents a long list of selected applications. Chapters 10 and 11 are about small molecules, and is changed only a little. However, these examples cover many typical scenarios, and present useful strategies to solve them. It is pleasing to realize reading these pages that a higher field is not necessarily the most important ingredient in this process, rather knowing your system and finding the most efficient method.

There is a brand new chapter next, which discusses calculating structures of biopolymers, which is a very useful and thoughtful addition to this book. It is not restricted to how NOE can be used for this purpose, but assesses other possible input parameters, presents and compares the most widely used protocols, and advises on quality control, too. The following chapter 13 is about NOE-based structural studies of major classes of biopolymers, such as proteins (including solid-state study of ^{13}C -labeled spider silk!), polynucleotides, such as DNA and RNA, oligosaccharides, and various complexes.

NMR keeps developing fast (pleasing to see), and new techniques and applications are being presented by the day. I've missed some discussion of Claudio Dalvit's excellent works on hydration and solvent solute interactions. Also, just a short time later, perhaps somewhat more would have been written about the use of residual dipolar couplings, ligand-target interactions, and hydration using gradient-based methods, and through-hydrogen-bond scalar couplings would have made it to the list of explicit restraints for biomolecular structure calculations, for example. But every manuscript has a final deadline for cutoff, even the best ones.

The book is easy to read and the figures are well done. It is not by accident, that Overhauser's name is mentioned most often in the scientific literature – as Geoffrey Bodenhusen disclosed at ENC few years ago, when introducing Overhauser himself as the honored speaker. I do believe that everyone in the community of NMR spectroscopists, but even in a much wider circle of chemists, physicists, and all who are dealing with molecular structure and dynamics, would benefit a lot of having access to this outstanding book. It also has an exceptional educational value both for students and educators, as it is written clearly and elegantly, and presents both theory and plenty of great practical and/or illustrative applications. The authors predict in the Preface that no third edition will be published; and it will probably be not justified for a long time – apart from, perhaps, reprintings... And if you'd happen to have both editions – keep them both; one for the lab, the other as a home copy.

So long,

István Pelczer
Department of Chemistry
Princeton University
ipelczer@princeton.edu

Some Glances Backward.

The following pages contain gleanings from past Newsletters that, for one reason or another, I found interesting. Some are fragments of Newsletter contributions, some are in my opinion amusing, some are landmark contributions, and some are, perhaps, a bit of all these. This page also has a non-Newsletter item from the estimable John Wertz. From a present-day perspective, a review of all of NMR and ESR is amazing, but he was careful to publish this review before the countless applications of NMR occurred.

I did not set out to emphasize 1973 - it just worked out that way. The selection criteria were somewhat hazy, and admittedly subjective (Gold is where you find it.). The difficulty was to keep the whole collection to what I hope is a reasonable length. There was no attempt to sacrifice other factors for balance or breadth, and I hope that readers who find their own or their favorites names missing will understand. The last page of the 1990 contribution is somewhat poetic and philosophical (*i.e.*, I agree with it.).

BLS

Quotation from the 1955 review

"Nuclear and Electron Spin Magnetic Resonance"

by

John E. Wertz

(Chem. Rev. 55, 829-953 (1955))

III. CHEMICAL SHIELDING

"At a time when physicists were busy comparing magnetogyric ratios of various nuclei and expressing these to seven or more significant figures, several disquieting papers appeared (147, 312, 443). It was reported that in compounds of phosphorus, nitrogen, and fluorine the resonant frequency for a particular nucleus depended on the compound in which it was present. This effect was called the "chemical shift," because physicists could think of no stronger term of damnation for an effect which was making insignificant several digits in their nuclear moment data."

MELLON INSTITUTE

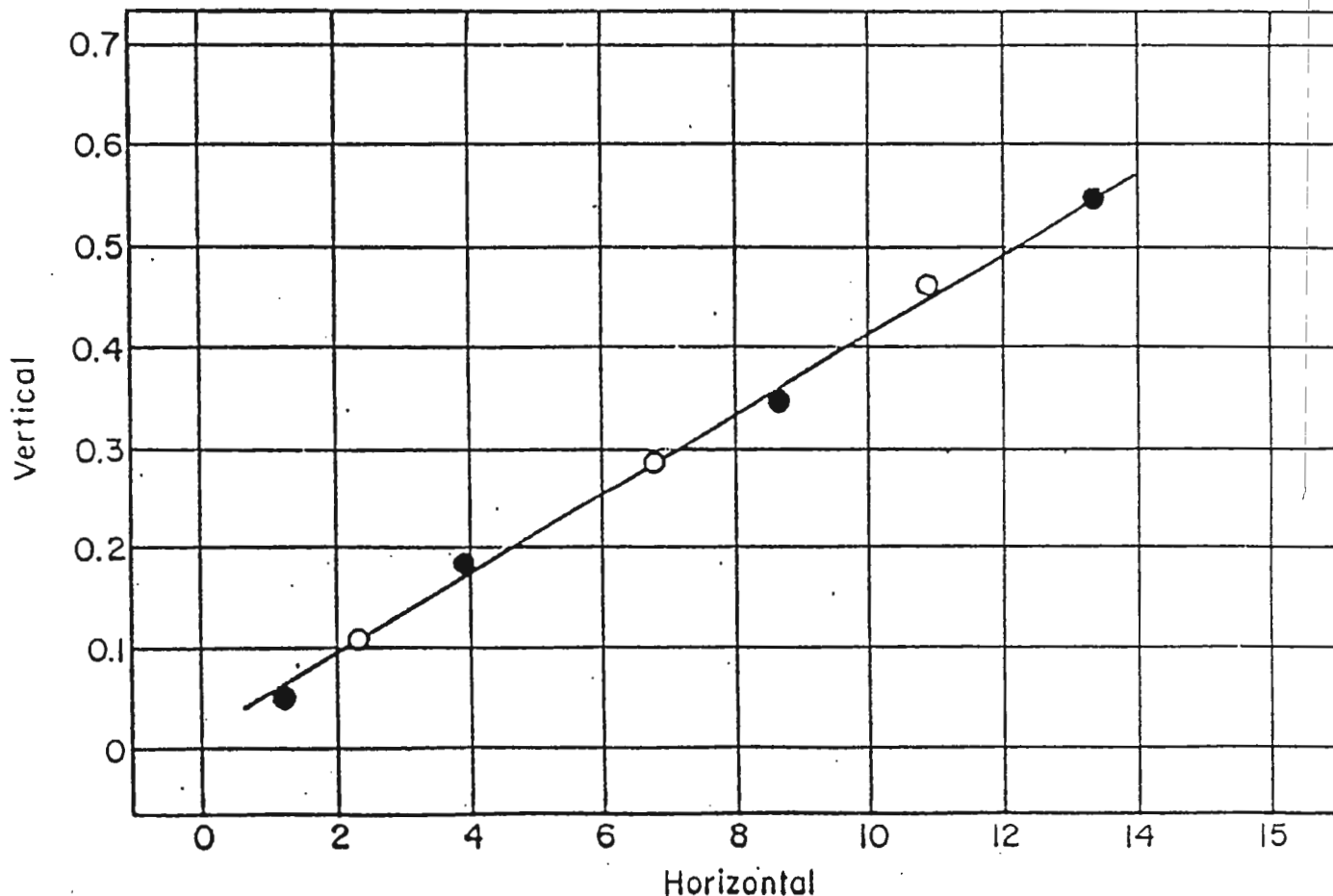
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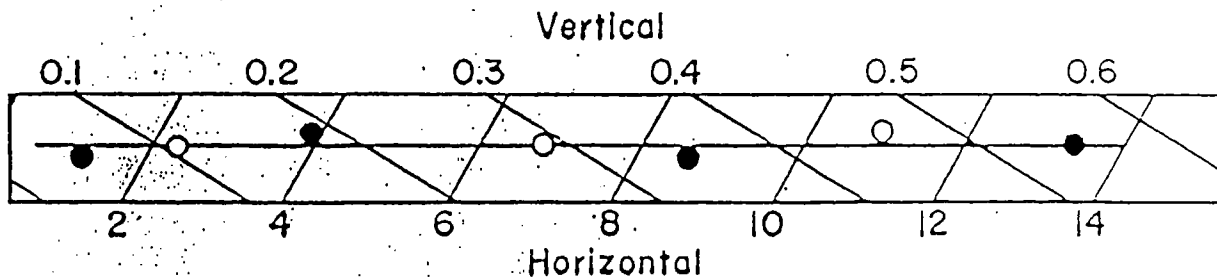
ON BREVITY

Appeals for brevity have been occupying increasing amounts of space in this organ of late, and the views of editors of most real scientific journals on this subject are well known to most of us. Proximity and double spacing are rightly condemned, but the wisdom of the common tendency to go even further and to suppress the actual spectra which are the foundations of spectroscopic papers may be doubted. By a well-known psychological process, frustration with this state of affairs led to the formulation of the following plan to distribute excessive brevity more evenly.

Although we all recognize that the ultimate goal of most true scientific investigations is a neat linear plot, there seems to be no reason why such plots should occupy the inordinate space required by the traditional format. Consider the figure below.



In its conventional form, it takes up about six vertical inches. The same plot, without any reduction in scale but with all unnecessary area removed, may be presented as shown below.



Less than one-third the area is required, and no information has been sacrificed. Some of the space saved by this simple stratagem could be devoted to spectra, to the benefit of all concerned.

Paul C. Lauterbur

Monthly
Ecumenical
Letters
Laboratories
Of
N - M - R

(October 1958)

Illinois
Institute of
Technology
N - M - R
Newsletter

(March 1964)

Texas
A &
M
University
N - M - R
Newsletter

(August 1968)

TEXAS A&M UNIVERSITY

NMR
NEWSLETTER

(January 1995)



THE
NMR
NEWSLETTER

(February 1995)

17 July 1967

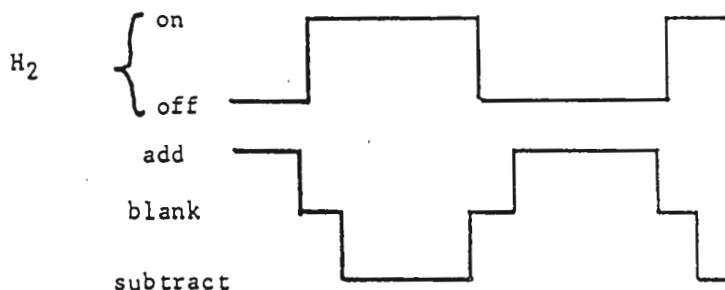
varian/611 hansen way/palo alto/california 94303/u.s.a./415/326-4000

Professor B. L. Shapiro
Department of Chemistry
Stanford University
California, 94305

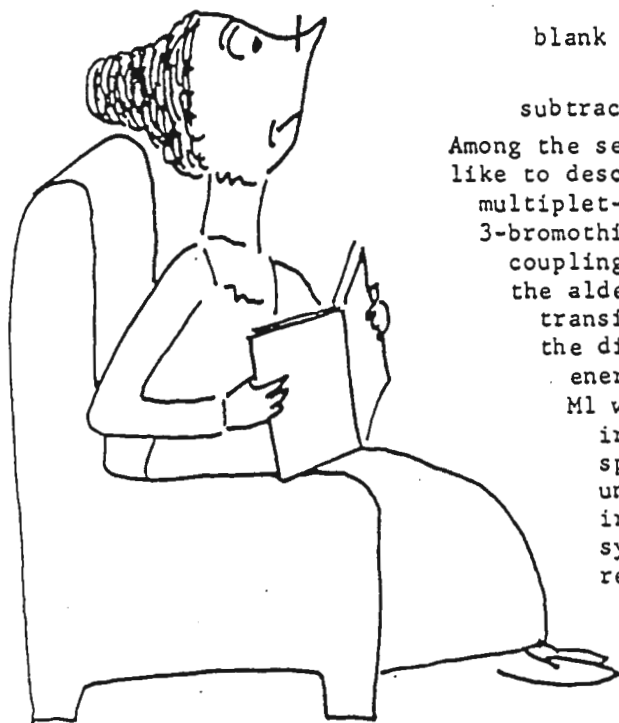
Decomposition of Unresolved Multiplets

Dear Barry,

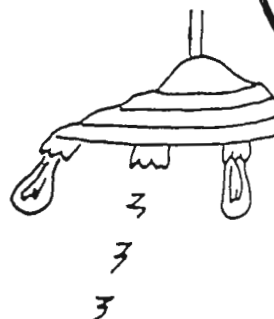
For some time we have been interested in the problem of generating "differential" double resonance spectra, where all resonances are cancelled except for those perturbed by the irradiation. Experimentally this entails pulse modulation of H_2 at a very low frequency, and inversion of the signal in synchronism with the pulses, either in a conventional lock-in detector or through the "add" and "subtract" functions of a time averaging computer. Although this proved to be straightforward for heteronuclear double resonance¹, our first attempts at proton-proton work could only be described in terms of a phenomenon first reported by Thurber's grandmother², i.e. "modulation was leaking out all over the molecule." Every transition appeared to be directly connected to every other. We feel this was due to the rapid transients induced in the internal lock field-frequency loop as H_2 was switched, displacing all the spectral lines. It can be cured by introducing a short blanking period during which both the "add" and "subtract" functions are inhibited:



Among the several possible applications we would like to describe the decomposition of an unresolved multiplet--a 0.05 Hz doublet in the spectrum of 3-bromothiophene-2-aldehyde due to long-range coupling between the proton at position 4 and the aldehyde proton. This doublet consists of transitions X1 and X2, distinguishable by the different ways in which they fit into the energy level diagram; X1 is connected to M1 while X2 is connected to M3. Thus weak irradiation of line M1 causes X1 to split into a doublet but leaves X2 unaffected. Pulse modulation of the irradiating field on M1, followed by synchronous detection of the signal results in a response with a central



Electricity was leaking all over the house.



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Yours sincerely,

Ray

My Freeman

Chem. Phys. 4

Thurber, Mv L

Varian Postdoctor

STATE UNIVERSITY OF NEW YORK
AT STONY BROOK

DEPARTMENT OF CHEMISTRY

STONY BROOK, N.Y. 11790

AIR MAIL

March 26, 1973

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

Dear Barry:

Title: NMR Zeugmatography

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Magnetic resonance is peculiar, if you stop to think about it. Other forms of spectroscopy are associated with image-forming techniques. From radio astronomy through radar, optical pyrometers, eyes, ultra-violet microscopy, X-ray radiography and scintigraphy, as well as acoustic and particle spectroscopies, the interactions responsible for spectra are also used to make pictures. But who ever heard of an NMR picture?

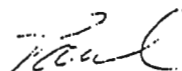
A pointless parallel, you may say. A moment's reflection reveals that the wavelength of 60 MHz radiation, for example, is about 5 meters, and who but a geologist or an astrophysicist would be interested in pictures of something with 5 meter resolution? Besides, how are you going to maintain a 1.4T field over that volume? That last comment, however, contains the key to a solution to our heretofore unformulated problem. For magnetic resonance is also distinguished from other forms of spectroscopy in a more fundamental way. It depends upon the presence of two fields, and that fact makes the usual Abbe resolution criterion irrelevant. If the magnetic field is inhomogeneous within an object, the Larmor condition will be satisfied for a given frequency only within certain surfaces of constant field, restricting the interaction between the object and the radiation field to regions that may be very small compared with the wavelength.

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It is now obvious that it should be possible to use NMR to make pictures of things - only the details remain to be worked out. Several methods appear to be possible, including one that requires only a standard NMR spectrometer (an A-60, for example) and a pencil and paper. The example shown below was obtained by slightly less primitive techniques, involving

It is not possible, of course, to do more than just touch upon these matters here or to discuss techniques, algorithms, or applications. Even those curious about the title of this TAMUNRN contribution will have to await the first paper (in NATURE) or write for a preprint. Just a hint on pronunciation, though. It is ZEU as in ZEUS (ZOOS).

Yours truly,



Paul C. Lauterbur
Professor of Chemistry

PCL/sb

December 12, 1973

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

"NEW UNITS FOR CHEMICAL SHIFTS"

Dear Barry:

Recently one of my colleagues submitted a paper to a Journal which shall remain unnamed to protect the innocent. The paper was accepted with the requirement that the nmr chemical shift data be reported in micro grames/gram vice ppm since the journal in question did not permit the use of ppm. Lest you think I am "putting you on" a copy of the galley proofs is attached below.

Sincerely,



Michael L. Maddox, Ph.D.
Institute of Organic Chemistry

MLM:lo

EG V-19

EG V-19

→ Plant(Feb) 11395 11-20-11B p.6 11-12 3758 (1) Gal.4X—
NMR Spectra. ¹H NMR (*d*₆-dimethylsulfoxide) 3.7 to 4.2
μg/g (m, 4, C₃H, C₁H, and C₂H₂), 4.57 (dd, 1, J_{2,3} ≈ 5 Hz,
C₂H), 5.90 (d, 1, C₁H, J_{1,2} = 5.5 Hz), 7.24 (broad s, 2, NH₂),
8.13, 8.36 (s, 1, C₂H and C₃H). The ³¹P NMR spectra of both
samples showed a chemical shift of 580 μg/g upfield from phos-
phoric acid. The coupling constant J_{PF} was 934 Hz in both cases.
This value is within the range observed for other fluorophosphate
derivatives (8). The spectra were measured under conditions of
noise modulated proton decoupling and no further attempt was
made to measure the J_{PH} values.

**SCHWEIZERISCHE ARMEE - ARMÉE SUISSE - ESERCITO SVIZZERO**

Ort und Datum - Lieu et date - Luogo e data:

STAB ODER EINHEIT:

ÉTAT-MAJOR OU UNITÉ:

STATO MAGGIORE O UNITÀ:

March 11, 1973

N°

Professor B. Shapiro
Department of Chemistry
Texas A + M University
College Station, Texas

Dear Barry:

Don't be afraid, I did not become a professional as the heading of this letter may suggest. But even here in military service, one is not exempted from your blue reminders! Unfortunately, I am not allowed to disclose to you against whom we are preparing our next war, So let me tell you something about my real interests. Actually, it is hard to remember anything intelligent in this unpleasant atmosphere.

Relation between Absorption and Dispersion Mode Signal in Fourier
Spectroscopy

It is generally claimed that absorption and dispersion mode spectra of linear time-independent systems are connected by a Hilbert transformation or by the Kramers-Kronig relations. This is not necessarily true for Fourier spectra obtained by a digital Fourier transformation.

NMR

NEWSLETTER

No. 384
September 1990

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A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is *not* permitted, except by direct arrangement with the author of the letter, and the material quoted *must* be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

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University of Illinois

College of Medicine at Urbana-Champaign

Department of Medical Information Sciences
 BIOMEDICAL MAGNETIC RESONANCE LABORATORY
 1307 West Park Street
 Urbana, Illinois 61801
 Phone: (217) 244-0600
 Fax: (217) 244-1330
 Email: bmrl@bmrl.med.uiuc.edu

August 16, 1990

Dr. James N. Shoolery
 Varian Associates

Dear Jim,

Archibald MacLeish had a blind spot. For him, science was dead dry birds in dusty cases, theories that proved beauty false. He never knew how close it is to poetry. Nevertheless, with apologies to him, and with bracketed substitutions, let me appropriate his "Poetical Remains" as

[SCIENTIFICAL] REMAINS

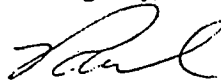
What will our reputations be?
 Whole things? Constructions
 Resisting time (that sea!)
 With the rock's persistent luck?

I doubt it. We leave behind
 An anthological rubble:
 Mind mingled with mind,
 Odd and even coupled.

But [science] thrives that way.
 Out of the tumbled coral
 One exquisite spray,
 Ivory, tipped with ore.

All of us who have lived through the classical, medieval and modern ages of NMR can look back and recognize the skillful poets among us, those whose styles and imaginations transcended categories and doubts and wove distinctive voices and meters into our communal epic. Others will, on this occasion, recall almost forgotten rhymes and schemes, or lost drafts and crossings-out, or serendipitous alliterations. Let me just celebrate the skill with which you helped to blend the lines of those who wrote for money, those who wrote for fame, and those who wrote for truth. Like all of the best ones, you loved it for the beauty in it.

Nostalgically,



Paul Lauterbur

THE
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B. L. Shapiro, Publisher
 The NMR Newsletter
 966 Elsinore Court
 Palo Alto, CA 94303-3410

650-493-5971
 650-493-1348 Fax
 shapiro@nmrnewsletter.com
 http://www.nmrnewsletter.com

Epilogue

The year 1958 was a long time ago, and the world was very different. Not only my world (pre-marriage, pre-children, pre-grandchildren) and the NMR world (pre-A60, and no one dreamt of 900MHz spectrometers), but the world in general. Let me indicate some persons and events of 1958:

The 1958 world leaders included Eisenhower, Macmillan, Diefenbaker, Ben-Gurion, Coty, Khrushchev, and Adenauer. Hula hoops and the laser were invented. We were innocent of such cultural aberrations as rock and rap. The first commercial jet airplanes began flying (A very early jet traveler was Varian's Emery Rogers, who described a jet landing as a controlled crash.). The John Birch Society was founded. E. Taylor opined that "Sex is dead." Britain's Frederick Sanger won the chemistry Nobel Prize.

The US Open was won by Tommy Bolt, the Masters by Arnold Palmer, and the British Open by Peter Thomson. The baseball Giants moved to San Francisco, and the Dodgers to L.A. The NY Yankees won the World Series. The Baltimore Colts won the NFL, and the Grey Cup was won by the Winnipeg Blue Bombers – using 2-point PAT's.

In 1958, I moved from Cambridge, Mass., to Pittsburgh, Penn., courtesy of Aksel Bothner-By's offering me my first real paying job at Mellon Institute, where we had just taken delivery of one of the first HR-60's east of the Rockies. At Mellon I met Lee Williams In October, Aksel and I started "MELLONMR" (see page 55), beginning the 43-year run of consecutive monthly publication.

It has been a wonderful 43 years – the sheer joy of seeing NMR evolve, the superb scientists and other people involved, the important friends. I have been multiply blessed. It would be quite impossible to thank individually all of those friends and colleagues and other Newsletter supporters without whom the Newsletter would not have lasted. The Newsletter's Sponsors and Advertisers have been models of loyalty and generosity, and for this I am most profoundly grateful.

In the last several weeks I have been very pleased and proud to have received many warm expressions of friendship and good wishes from subscribers, sponsors, advertisers, and others. It eases the stress of change to non-Newsletter life to read the good wishes which appear in this last Newsletter or which have been communicated privately to Lee and myself. "Thank you so much" is hardly adequate to convey our feelings.

Les jeux sont faits. Rien ne va plus.

Barry
 010902,



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FAX: 978-486-4495

Dear Barry:

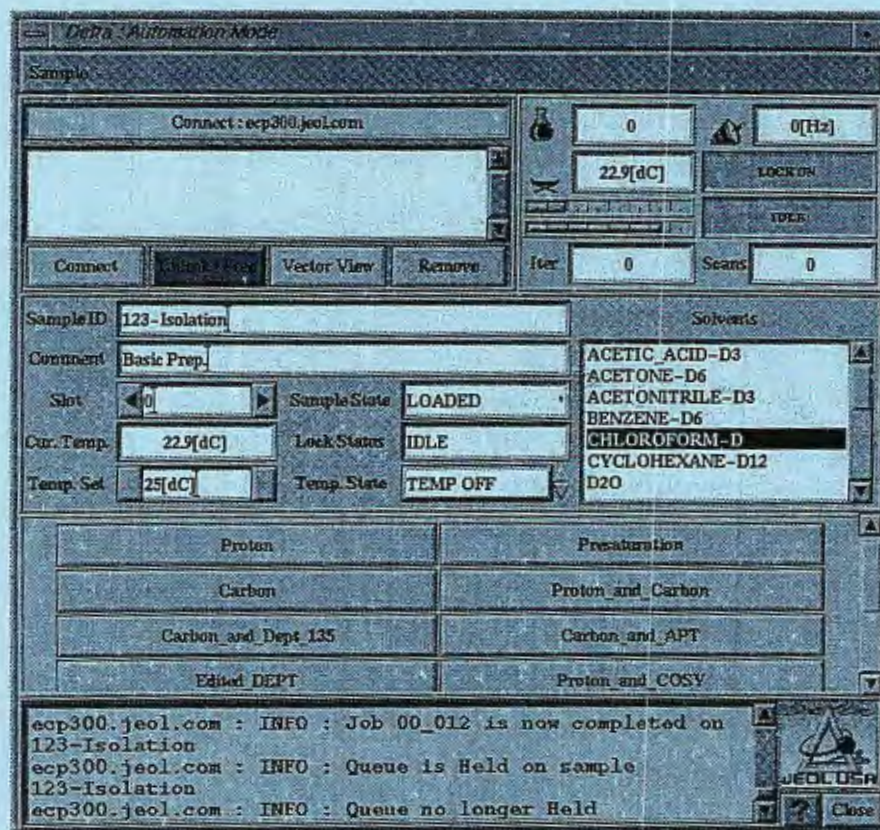
A final ad would not be appropriate at this juncture. We are very sorry to see the NMR Newsletter go. After 43 years I suppose, you have earned a respite. While PTS has been active in the NMR area only 25 years, we know that your contribution to science and industry in this field are immeasurable. Our relationship with you has always been a pleasure. So, we would like to add our voice to those who say:

Thank you Barry for a job well done. We hope you will enjoy retirement.

All the best,

Diane, George and all of us at PTS

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