TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 427

April 1994

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FORTHCOMING NMR MEETINGS

Gordon Conference on Magnetic Resonance in Biology and Medicine, New England College, Henniker, NH, **July 17 - 22, 1994**; Contact: Dr. Carlyle B. Storm, Director, Gordon Research Conferences, Gordon Research Center; Univ. of Rhode Island, Kingston, RI 02881-0801; Tel. (401) 783-4011 or -3372; Fax: (401) 783-7644.

8th International Symposium on Molecular Recognition and Inclusion, Ottawa, Ontario, Canada, **July 31 - August 5, 1994**; Contact: H. Morin-Dumais, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, ON K1A 0R6, Canada; (613) 993-1212; Fax: (613) 954-5242 See TAMU NMR Newsletter 427, 38

Solid-State NMR Symposium, 36th Rocky Mountain Conference on Analytical Spectroscopy, Denver, CO, **July 31 - August 5, 1994**; Contact: R. E. Botto, Chemistry Divn., Argonne Natl. Lab., Argonne, IL 60439; (708) 522-3524; Fax: (708) 252-92882 See TAMU NMR Newsletter 424, 46.

2nd Meeting, Society of Magnetic Resonance, San Francisco, California, **August 6 - 12, 1994**; Contact: SMR Berkeley Office, 1918 University Ave., Suite 3C, Berkeley, CA 94704; Tel. (510) 841-1899; Fax: (510) 841-2340.

Gordon Conference on Order/Disorder in Solids, New London, New Hampshire, **August 7 - 12, 1994**; Contact: Prof. M. A. White, Dept. of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3; Tel. (902) 484-3894; Fax: (902) 494-1310. See TAMU NMR Newsletter 421, 44.

XVIth International Conference on Magnetic Resonance in Biological Systems, Veldhoven, The Netherlands, **August 14 - 19, 1994**; Organizing Committee: M. J. A. de Bie, C. W. Hilbers, R. Kaptein; Contact: Secretariat XVIth ICMRBS, Bijvoet Center for Biolmolecular Research, Padualaan 8, NL-3584 CH Utrecht, The Netherlands; Tel. +31 30 53 2652/2184/3801; Fax: +31 30 53 7623/54 0980.

Ampere Summer School on Magnetic Resonance with Spatial Resolution, Eichstätt, Bavaria, Germany, **September 2 - 8, 1994**; Contact: L. D. Hall or B. Blümich - See TAMU NMR Newsletter 426, 56.

FACSS XXI (21st Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, St. Louis, Missouri, **October 2 - 7, 1994**; Contact: FACSS National Office, 198 Thomas Johnson Drive, Suite S-2, Frederick, MD 21702-4317; Phone: (301) 846-4797.

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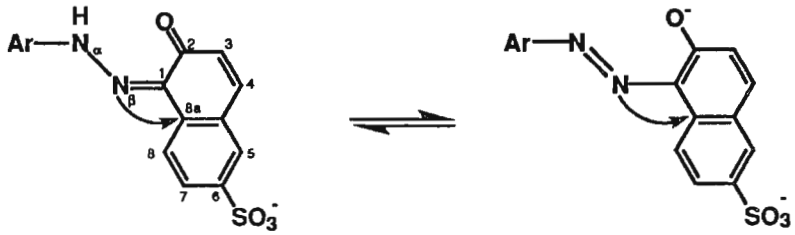
March 5, 1994
(received 3/11/94)

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

Azo-Hydrazone/Acid-Base Equilibria in Yellow No. 6 Revisited

Dear Barry,

Yellow No. 6 (Y6) exists in different "forms" over the pH range 7-14. It occurs almost exclusively as a hydrazone (**1**) at pH 7 and predominantly in the azo form (**2**) at pH 14. Approximately equal concentrations of these two species are present at pH 12. Their ^{13}C nmr



1 **2**

spectra exhibit considerable line broadening (with a maximum at pH 12) and shifting with pH of most resonances arising from these two forms.

These dynamic effects were initially believed to be due to either slow tautomeric interconversion of **1** and the conjugate-acid of **2** or a combination of *syn-anti* hydrazone interconversion (predominantly at pH values below 12) and *trans*-azo rotational isomerism (principally at pH values above 12). However, 2-bond N_β-C_{8a} couplings range from 8.6 Hz at pH 7 to 3 Hz at pH 14. If signal broadening were due solely to the appearance of higher-energy isomers, *viz. anti*-hydrazone and *trans*-azo species, then the observed $N_\beta C_{8a}$ coupling constants should decrease from either 8.6 or 3 Hz as the hydrazone-azo equilibrium point (pH 12) is approached from either pH extreme. In addition, we now have a fairly accurate value for the pK_a of the hydrazone-NH of **1**, and it is *ca.* 12. Moreover, the estimated pK_a of the conjugate-acid of **2** is considerably lower than we originally thought. It now appears that sufficient quantities of the latter "azo tautomer" cannot exist above pH 12.5 to give rise to the dynamic NMR effects found over this pH range, *i.e.* 0.5-2 units above the pK_a. The observed line broadening can most plausibly be ascribed to an acid-base equilibrium between **1** and **2** which involves relatively slow proton transfer between a nitrogen acid (the hydrazone-NH of **1**) and water.

Sincerely,

Saleh A.Turujman E.P. Mazzola

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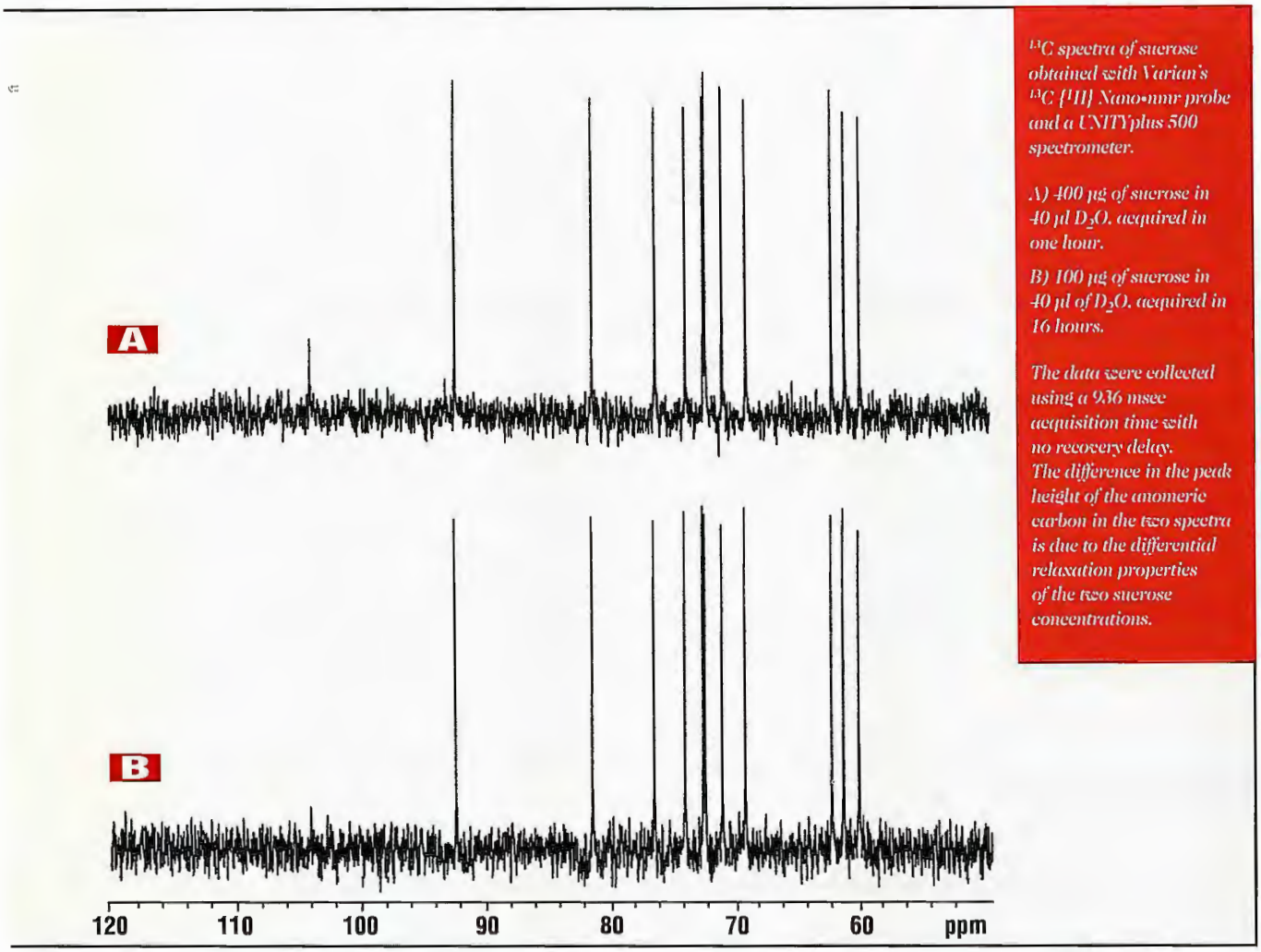

^{13}C spectra of sucrose obtained with Varian's ^{13}C {^{1}H} Nano•nmr probe and a UNITYplus 500 spectrometer.

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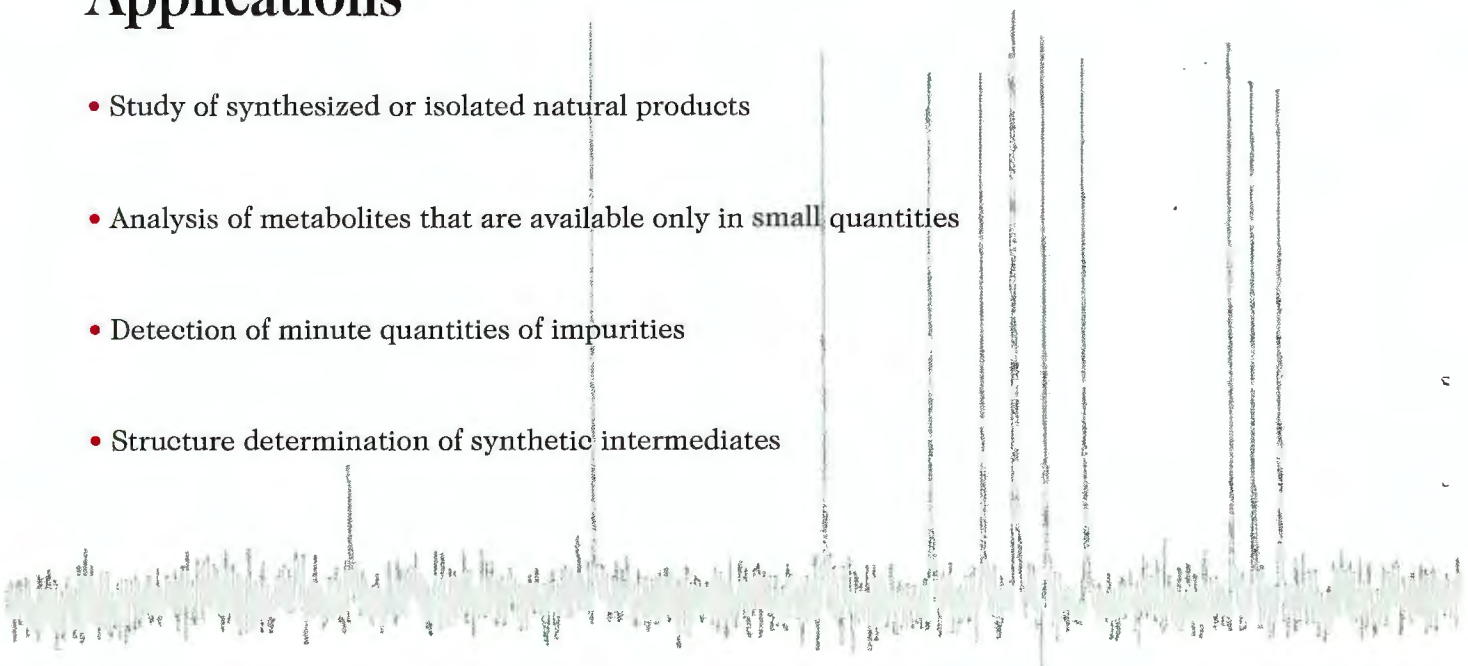

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February 28, 1994
(received 3/4/94)

Dr. Barry Shapiro
TAMU NMR Newsletter
966 Elsinor Court
Palo Alto, CA 94303

Estimating Parameters With Bayesian Probability Theory: II

Dear Barry:

Some of us at Monsanto (Norm Hoffman, John Kotyk, Joel Garbow and Jan Gard) together with Joe Ackerman and Larry Bretthorst (Washington University, Chemistry Department) have developed a robust software package to estimate parameters from one-dimensional spectra. We employ Bayesian probability theory, BPT, to model the free-induction decay[1]. When the highest probability model has been found, the number of resonances present and the frequency, amplitude, and decay rate of each resonance can be placed into a table and analysis/assignment can begin. Each parameter estimate is represented by a probability density function so its uncertainty is directly available. For convenience and tradition's sake only, we also compute a free-induction decay from the parameters which can be Fourier transformed to obtain a conventional spectrum.

The modeled data shown in Fig. 1 are from a 125 MHz carbon spectrum of lupeol. Lupeol is a thirty carbon plant triterpene. This particular sample was quite old and at least one decomposition product is evident in the conventional discrete Fourier transform spectrum (Fig. 2). The BPT analysis found sixty-six resonances in this free-induction decay (including the solvent). The analysis took less than one hour using an IBM RS6000/580 workstation. It is worth mentioning a noise spike (Fig.2) was not identified as a resonance even though it is much larger than the smallest NMR signal. Such a signal is a non-decaying sinusoid and its phase is uncorrelated to the NMR signals. BPT analysis was able to exclude the spike. The low signal-to-noise impurity peaks are rigorously identified as well. In our experience BPT is very useful to analyze complex mixtures and low signal-to-noise data.

Sincerely,

William C. Hutton
Science Fellow

1. G.L Bretthorst et al *J. Magn.Reson.* **79**, 369, 1988.

Fig. 1

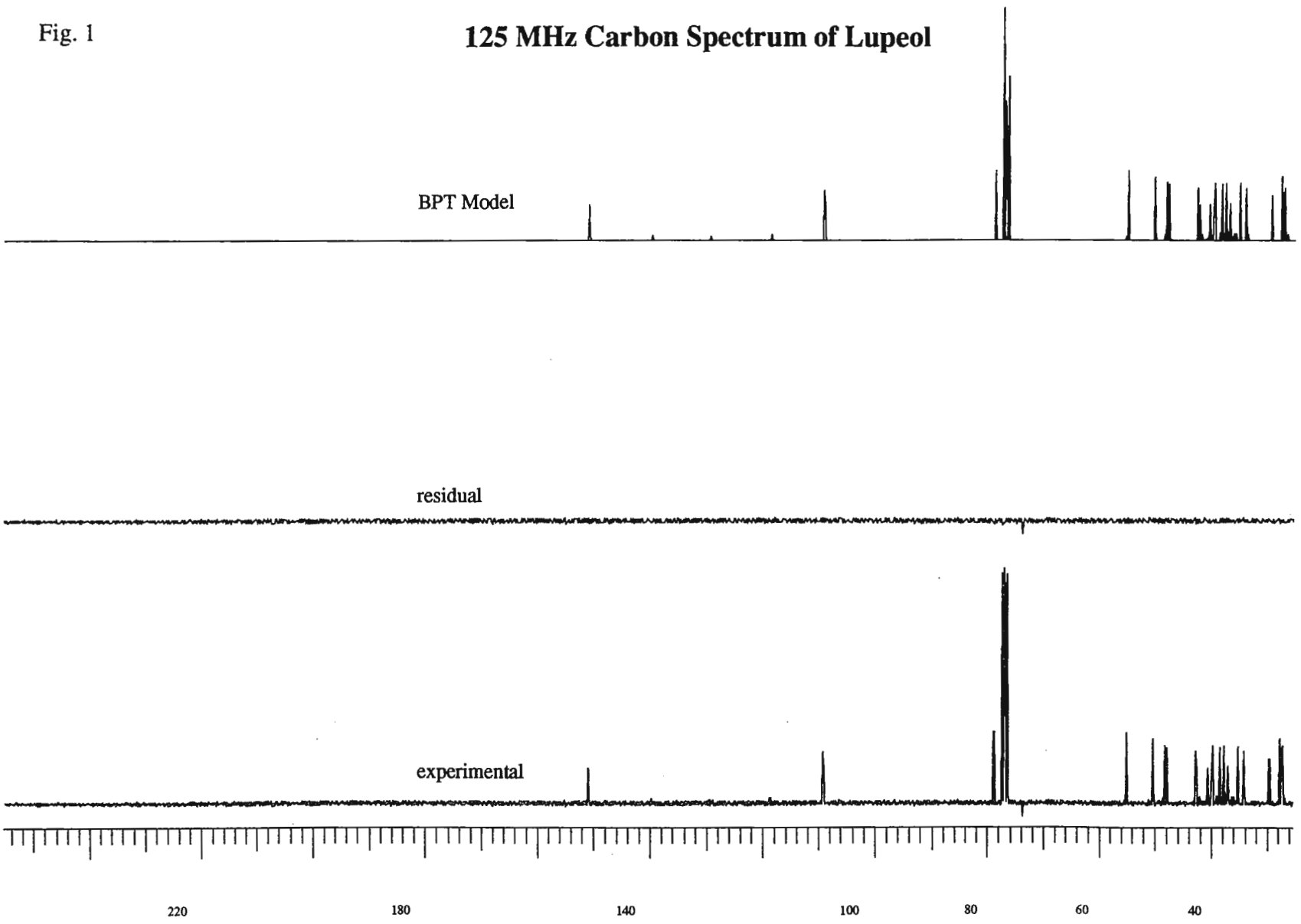
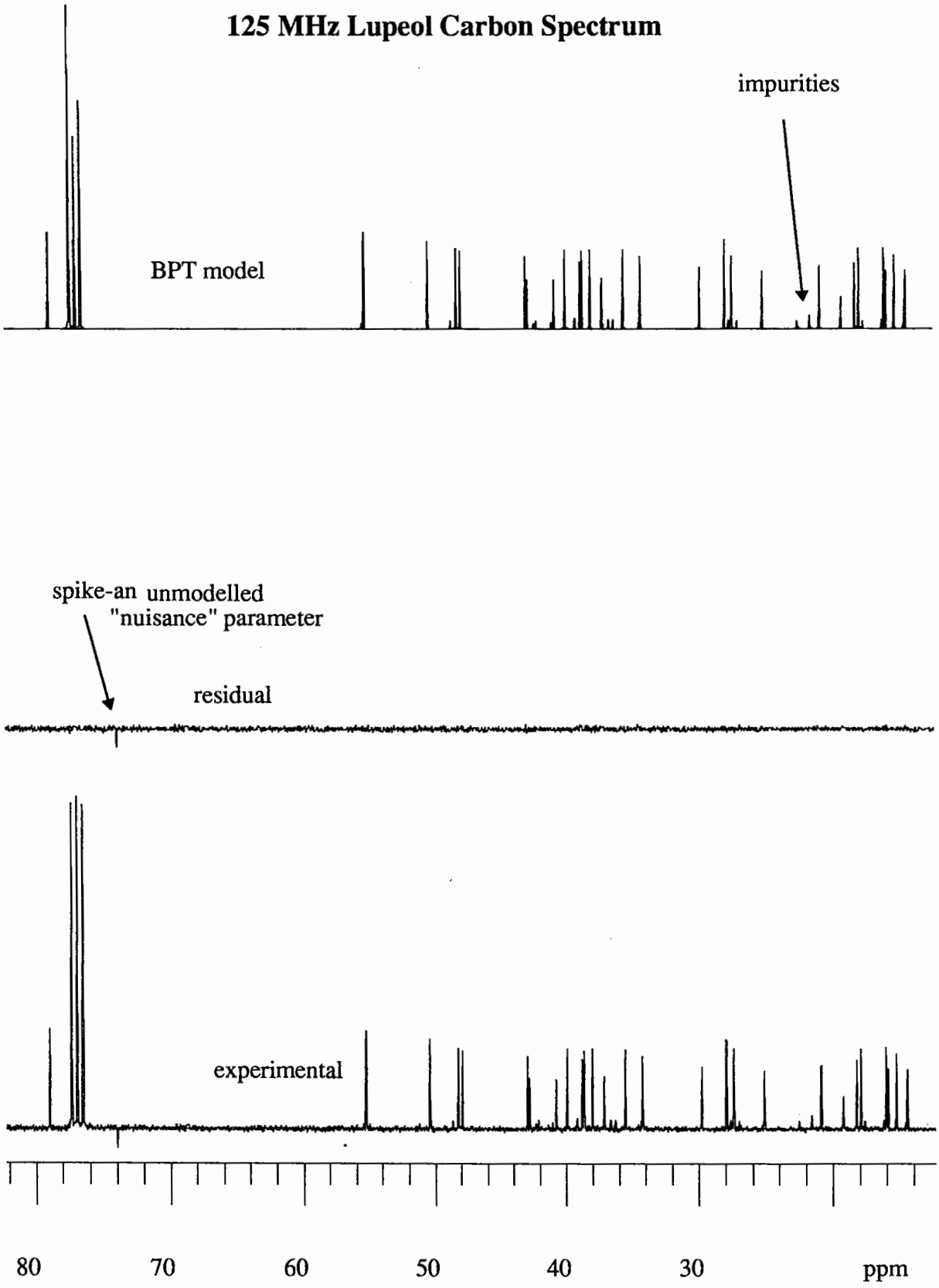

125 MHz Carbon Spectrum of Lupeol
BPT Model
residual
experimental
220
180
140
100
80
60
40

Fig. 2


125 MHz Lupeol Carbon Spectrum
impurities
BPT model
spike-an unmodelled
"nuisance" parameter
residual
experimental
80
70
60
50
40
30
ppm

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Flemming M. Poulsen

January 31, 1994
(received 3/19/94)

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

COMPUTER PROGRAMS FOR DATA PROCESSING AND ASSIGNMENT: PRONTO/3D AND MNMR.

Dear Dr. Shapiro

Pronto/3D was originally developed for the complex analysis of heteronuclear multidimensional protein studies, and it is still in this field the program has its strongholds. Pronto/3D has been used in our laboratory to assign NMR spectra of more than eight protein structures. It is a program that assists the user all the way through the steps of peak picking, sequential assignment, side chain assignment, and the NOE assignment. The program can analyze data of all the known types of 2D, 3D, and 4D homo- and heteronuclear (^{1}H, ^{13}C, ^{15}N) spectra. By a carefully designed database system it helps the user keeping all the spectral information readily available in an easy to view, read, and write status. When the user has completed the assignments the program can produce input to several structure calculation programs. Assignments get easier, more reliable and much faster. Every step of the analysis is performed on the computer and viewed on the screen. It is a definitive improvement and good alternative to the "pencil/paper method". So anyone having a good MIPS processor UNIX workstation can use Pronto/3D for their assignment work and get quickly on to the important part of their science: the structures and the function of the molecules they are working on.

Pronto/3D is not only for proteins. It has been very pleasing to see that our colleagues in the department studying glycoconjugates, glycopeptides and oligosaccharides have had great successes using the program. Therefore we are confident that Pronto/3D can be used for assignments of any molecule you may be studying, DNAs, RNAs, oligo- and oligodeoxy-nucleotides, steroids, and the natural products.

MNMR is the other program that we have developed. This is for multidimensional data processing, phasing, baseline corrections, window functions etcetera. MNMR is used to generate data for Pronto/3D. However, Pronto can read data processed by the processing software of most NMR-machine vendors as well as processing software of a number of software companies.

We have shared our program with colleagues in other laboratories, and it has been reassuring to see that the program can also be used by others than just us, the developers. So, we get the impression that the program is indeed very user friendly, and therefore, we would like to make the programs available to a larger group of scientists, whom we hope might benefit from using the programs.

THE TWO SOFTWARE PACKAGES PRONTO/3D AND MNMR CAN BE OBTAINED FREE OF CHARGE, HOWEVER, REQUESTS SHOULD BE ACCOMPANIED BY A CHECK OF 100.- US$ TO COVER HANDLING EXPENSES.

Yours sincerely

Flemming M. Poulsen

Mogens Kjær*)

Gamle Carlsberg Vej 10,
DK-2500 Valby, Denmark.

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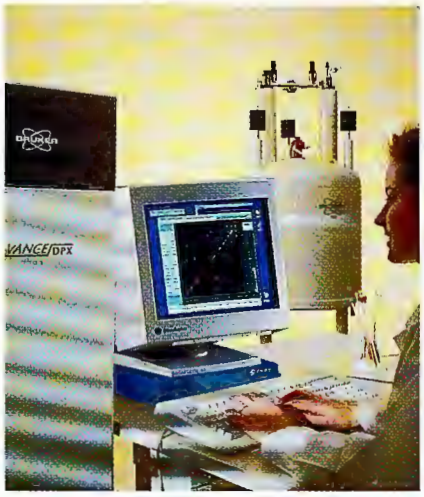

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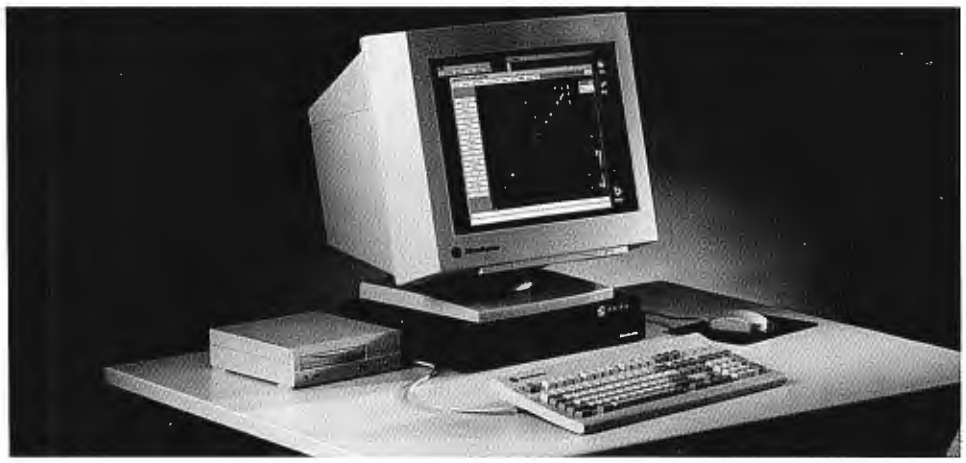

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PETROLEUM RECOVERY INSTITUTE

High Temperature Multiphase Analysis of Semicrystalline Polymers by Single Point Imaging

Dear Barry,

Feb 14, 1994
(received 2/22/94)

Thanks for the 'Reminder'. In this note we summarize some of the recent developments in the acquisition and analysis of semicrystalline polymer MRI (polyethylene and polypropylene) using our Bruker Biospex 24/30 imaging system, our home-built variable temperature apparatus, and the single point imaging technique.

The combination of these methods has significant implications for imaging of relevant industrial materials under conditions previously not feasible. Furthermore, there may be relevant applications in characterizing the spatial distribution effects related to processing conditions, optimization of process parameters, degradation/aging; residual stress/ induced stress; oxidation, effect of density distributions, and the effect of thermal history on product performance.

Many problems arise in these experiments. The T_2's are very short (about 5 μs to 2ms) even at high temperatures, and the polymers in question can contain up to (at least) six distinct phases (based on NMR relaxation time measurements and morphological considerations). All of these phases may change in nature, amount, and/or distribution for a given thermal history. Repeating an experiment on a sample in no way guarantees that the composition is the same unless careful precautions in sample preparation are taken.

In the SPI experiment we collect a number of images at systematically longer detection times to effectively map out the free induction decay. (The same data can be collected for a bulk sample via a benchtop NMR such as the Bruker NMS120, which has been done and which, for comparable temperatures, yields the same relaxation time decays.) The raw 32 bit image series is then downloaded from the Biospec to a personal computer (a 486DX66 in this case) via an Ethernet link. Programs written in-house (called 'Map' and 'Insight') then perform a pixel by pixel data analysis in which nothing is assumed about the form of the relaxation decay; several models are available to choose from. We usually obtain a two-component or three-component decay curve yielding the corresponding mass fractions of the components in question and their respective T_2^* values. We can then calculate histograms (Figure 1), contour maps, or 2D surface maps (shown in Figure 2).

Data representations such as these would be invaluable in visualizing the effects of distributions of relaxation times (and related physical and mechanical properties) for a wide variety of important processing and product problems. For example, we have completed a preliminary study of the effects of stress in bursting polyethylene pipes on the distributions of T_2^*s. Stress maps can now be generated for semicrystalline polymers characterized by T_2^*s of < 200 μs (as previously demonstrated on rubbers with T_2^*s > several ms).

These data illustrate that semicrystalline polymer imaging is quite feasible and that optimum data analyses will require off line processing capabilities such as those provided by our personal computer based data analysis.

Sincerely,

David E.Axelson Dave

Ken Green Ken

Doug Fisher

Petroleum Recovery Institute
3512 - 33 Street N.W., Calgary, Alberta, Canada
T2L 2A6

Telephone: (403) 282 - 1211 Fax: (403) 289 - 1988

Figure 1

Histogram of T_2^* values for polypropylene sample heated to approximately 150°C. Crystalline and non-crystalline components have been separated. The NCC data are shown here.

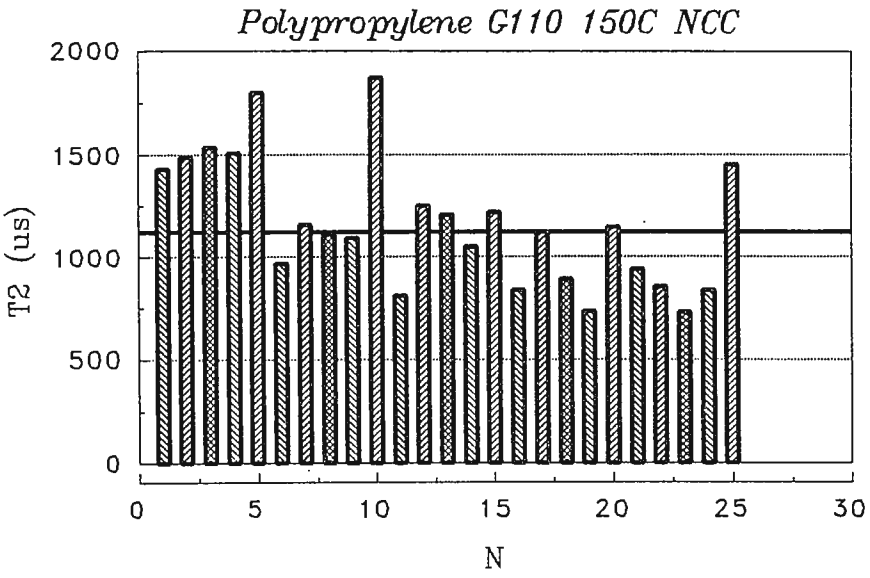
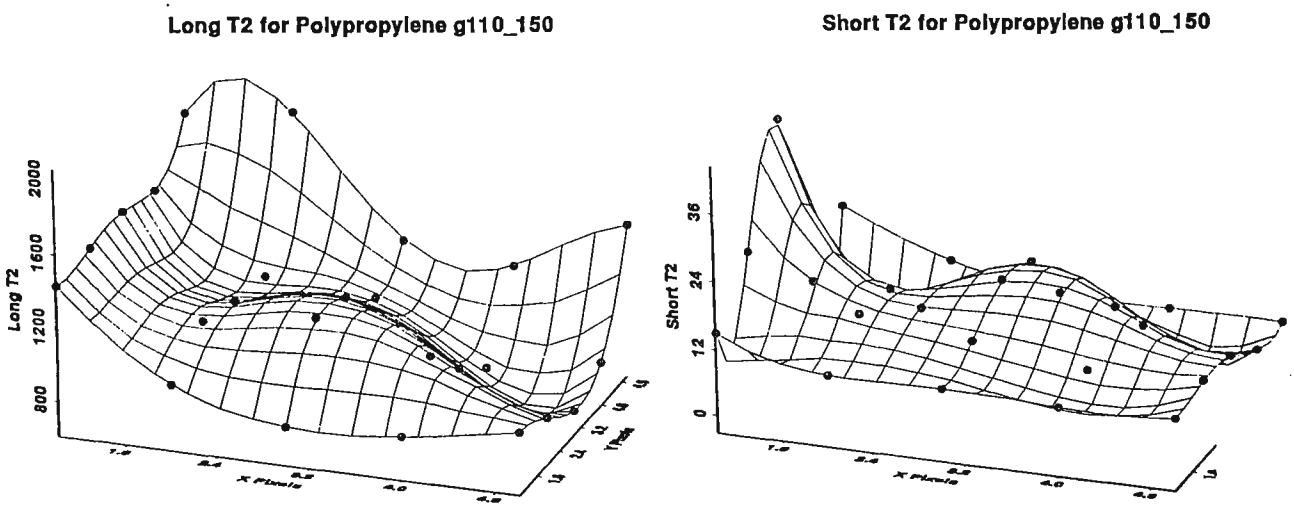


Figure 2

2D surface plot of crystalline component T_2^*'s and non-crystalline component T_2^*'s as a function of pixel location in a polypropylene sample heated to approximately 150°C. Data were collected before equilibrium was attained so that the sample is partially melted at the time at which data were collected (leading to a thermal gradient and a distribution of relaxation times).



UNIVERSITÀ DEGLI STUDI DI MILANO

Dipartimento di Scienze Molecolari Agroalimentari

DISMA Via Celoria, 2 I-20133 Milano Tel. 02-2663662 /2365029 /2362721

Milano, February 9, 1994
(received 2/26/94)

Dr. B.L. SHAPIRO
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

TERTIARY STRUCTURE OF ENDOTHELIN-1 IN WATER

Dear Barry,

we have recently determined the tertiary structure of endothelin-1 (ET-1) in water. The full paper will be published in J. Chem. Soc. Perkin 2. ET-1 is a 21-aminoacid peptide with an extremely potent vasoconstrictive activity. It is involved as local factor in the regulation of the cardiovascular system, but the mechanism of action of ET-1 is still unclear.

Up to now, the reported structural results have been obtained only from experimental data in DMSO or in media containing organic solvents and the proposed structures differ significantly with each other.

We derived the tertiary structure in pure water by using ^{1}H NOESY, COSY and TOCSY experiments at different pHs (3.5, 6.3 and 7.1) and temperatures (5°-25°C) and constrained molecular dynamics calculations.

As the primary structure was known, the sequential assignment of neighbouring amino acid spin systems resulted relatively easy. About 250 inter- and intra-residue NOE correlations were analyzed for each spectrum. The sequential NH-NH, αH-NH and ßH-NH were observed for nearly all residues. Stereospecific assignments were also performed for the valine methyls and for the ß protons of the methylene groups.

Variable temperature experiments from 6mg/ml down to 0.2 mg/ml did not show shift variation for the non-exchangeable aromatic protons. In addition, the correlation time value of 2 ns (obtained by some NOE interactions) gave, through the Debye-Stokes-Einstein equation, an average molecular volume which is consistent with solvated monomeric species.

The secondary structure of α-helix for the segment 9-16 was proved by the observation of strong (i,i+3) αH-ßH and αH-NH NOE interactions, supported also by the presence of some (i,i+4) αH-NH and by the absence of any (i,i+2) NOEs. The N-terminal and significantly the C-terminal segment, which is determinant for the binding with the receptor and for its activation, are also well defined by many long-range NOE interactions, involving residues 17-21 and the core of the molecule (residues 9-14). This indicates that the C-terminal of the peptide preferentially folds back, toward the α-helical segment, in close proximity to the pro-R methyl group of Val^{12}.

The tertiary structure of ET-1 was derived by a Simulated Annealing procedure. 170 interprotonic distances and 7 dihedral angles (obtained by the volumes of the NOE cross-peaks and by the αH-NH coupling constant values respectively) were used as constraints in the calculations. The last minimization yielded 11 structures (fig. 1) which satisfied all the interproton distances within 0.3 Å.

It appears from Fig. 1 that the conformation of both N- and C-terminals are well defined and that the side-chains also display ordered

structures, adopting a compact form, with the indole ring of Trp^{21} in close proximity to Val^{12}.

This leads to some packing of the aromatic rings of Tyr^{13}, Phe^{14} and Trp^{21} (see Fig. 2), thus allowing hydrophobic interactions, which should stabilize the folded conformations. The side chains of Leu^{17} and Ile^{19} are close to the aromatic rings of Tyr^{13} and Phe^{14}, thus concurring with Trp^{21} to create a small cavity, which contains the alkyl groups of 17, 19 and 20 residues. In such a way, they become protected from the polar solvent, as indicated also by the slow exchange with D_2O of the amidic protons of isoleucine 19 and 20, which proves the poor accessibility of water in this part of the molecule.

Sincerely yours

Rosanna Mondelli

Cys^{1}-Ser^{2}-Cys^{3}-Ser^{4}-Ser^{5}-Leu^{6}-Met^{7}-Asp^{8}-Lys^{9}-$Glu^{10}$$Cys^{11}$-$Val^{12}$-$Tyr^{13}$-$Phe^{14}$-$Cys^{15}$-$His^{16}$-$Leu^{17}$-$Asp^{18}$-$Ile^{19}$-$Ile^{20}$-$Trp^{21}$

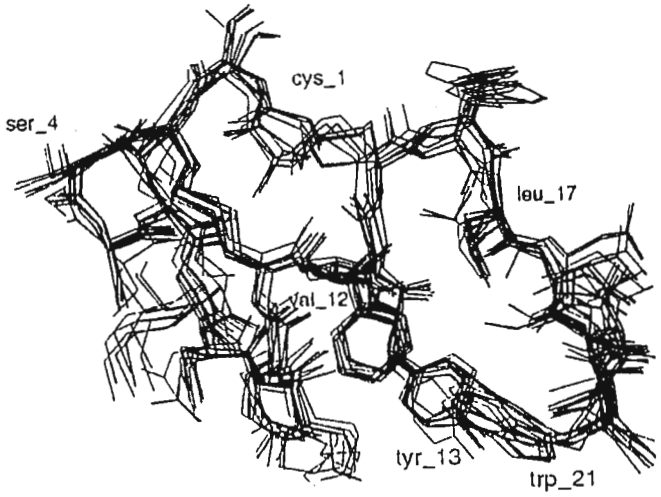


Fig. 1

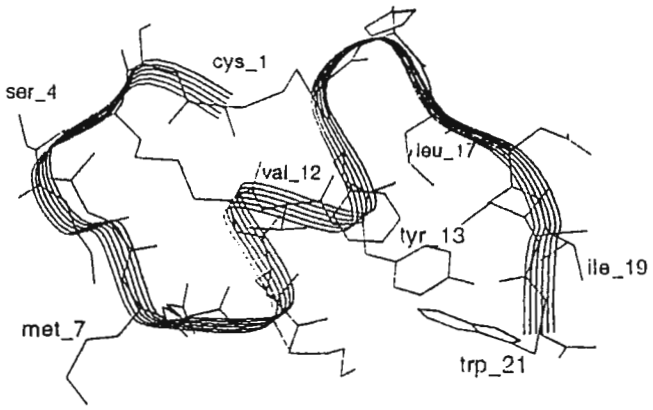


Fig. 2

Tertiary structure of endothelin-1 in pure water at neutral pH.

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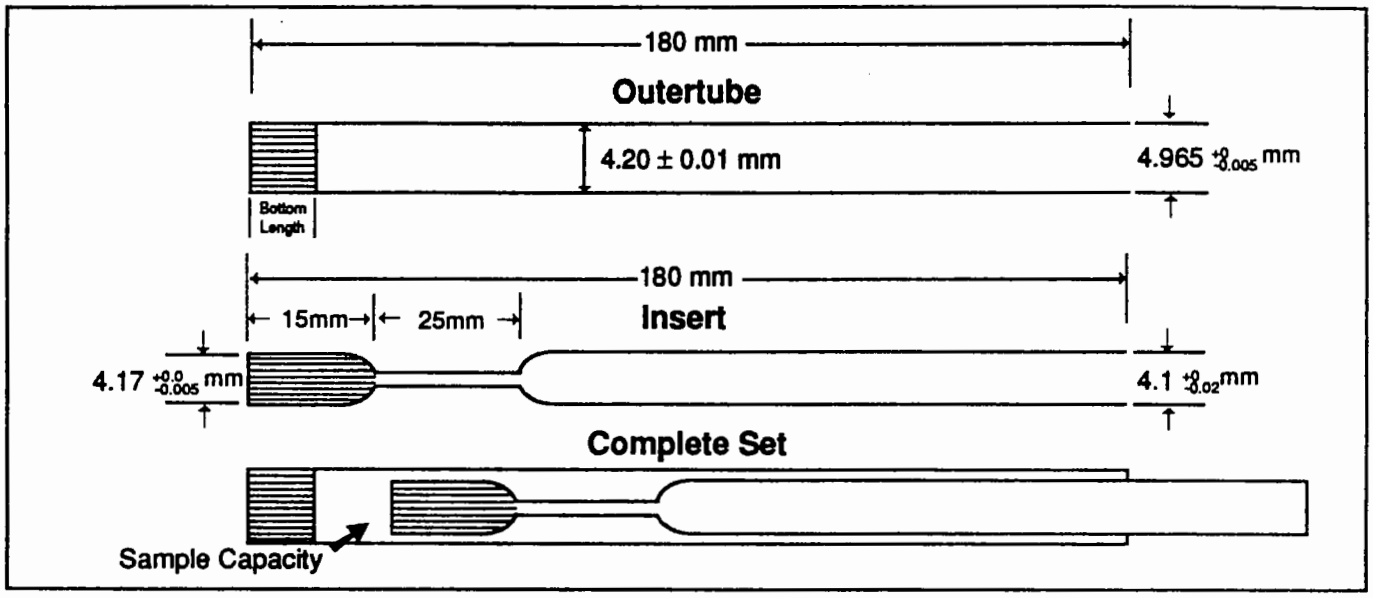

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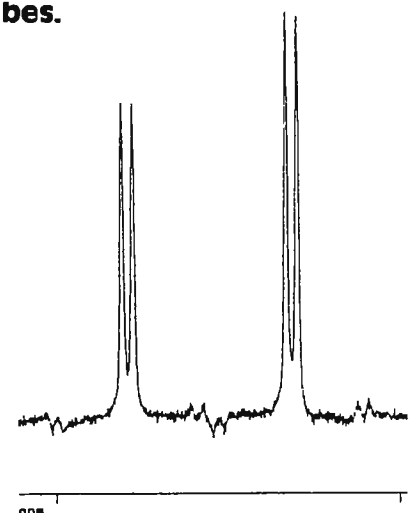
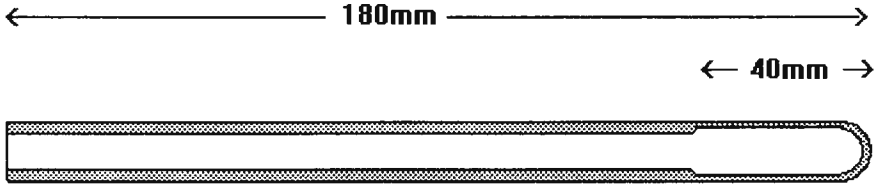


Fig.1a Fig.1b

The spectra of 20mm sucrose in D_2O were obtained with a single scan without apodization prior to Fourier transformation on a Bruker AMX-600 spectrometer at 298 K. By using Shigemi high quality 5mm standard tube (Fig.1a) and the Shigemi highly sensitive thin wall 5mm tube (Fig.1b), the spectra confirms a sensitivity enhancement of about 10%.



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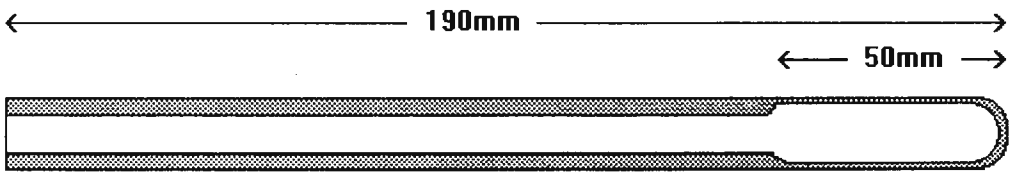

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6th March 1994
(received 3/14/94)

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

Patience Rewarded

Dear Barry,

Some 36 years ago I was co-author of a paper[1] in which the pinacol, formed by electrolytic reduction of 7-oxocholesteryl acetate, was described. At that time the pinacol was assigned the unsymmetrical structure (1), which has link which is α with respect to one steroid nucleus, and β with respect to the other. This assignment was based on the rather tenuous evidence of the formation of a monoepoxide pointing to differences in reactivity of the two double bonds, and the fact that it was impossible to make molecular models of the two symmetrical structures.

In 1958 only the fortunate few had access to nmr instrumentation (mostly 60 MHz proton machines) and we were not among them; hence the unsymmetrical structure has only just been confirmed. The ^{13}C nmr spectrum of the pinacol shows 57 peaks out of the expected 58 leaving no doubt that structure (1) is correct. Full analyses of the 1D and 2D proton and carbon spectra are being undertaken with a view to finding the conformation of the compound.

The pinacol has an unusually low melting point (150°) for a bis-steroid, and indeed it decomposes at this temperature to give an equimolar mixture of 7-oxocholesteryl acetate (2) and 7-oxocholestanyl acetate (3). When thermal decomposition experiments were performed on the pinacol, and on the analogue in which the hydroxyl hydrogens had been replaced by deuterium atoms, comparison of the ^{13}C nmr spectra of the products revealed that the resonances at δ= 46.11 and 46.73 ppm, ascribed to C-5 and C-6 in 7-oxocholestanyl acetate, were absent in the deuterated material. This shows that the two deuterium atoms are transferred to atoms 5 and 6 in the half of the structure which becomes the saturated steroid system. Whether this process is stereospecific still remains to be seen.

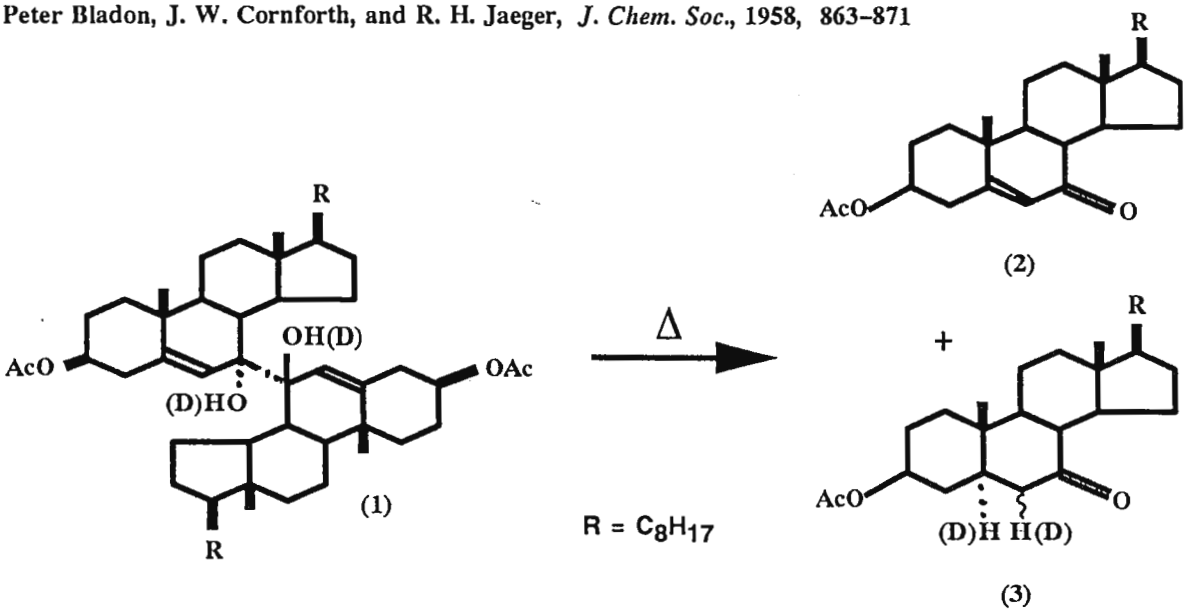
Best wishes,

Yours sincerely

Peter Bladon.

Peter Bladon

(1) Peter Bladon, J. W. Cornforth, and R. H. Jaeger, *J. Chem. Soc.*, 1958, 863-871



DEPARTMENT OF MEDICAL PHYSICS AND BIO-ENGINEERING
University College London Hospitals and University College London
1st floor, Shropshire House, 11-20 Capper Street, London WC1E 6JA

From: Ernest B. Cady (Director Bloomsbury Centre for MRS; President European Society MR in Neuro-paediatrics)
Tel 071-387-9300 x 8448/8227
FAX 071-380-9577
11/2/94 (received 2/22/94)

Sir,

In Oleg Jardetzky's review (TAMU Newsletter No.423, p37) of "In Vivo Magnetic Resonance Spectroscopy, Vols I, II, and III" (Springer; 1992) he criticises me for concluding that "*in-vivo* MRS techniques are now available that can provide realistic estimates of absolute concentrations." He is certainly correct that MRS is unable to measure intracellular metabolite concentrations. However, I do not claim that MRS can do this! I make it clear that absolute concentrations estimated by MRS are for bulk-tissue ie. in mmol/kg wet weight or mmol/l. Of course, these quantities are of less value than actual concentrations at the point of reaction. However, Dr Jardetzky ignores the fact that *in-vivo* MRS can estimate non-invasively for example cerebral concentrations of phosphocreatine (PCr), inorganic phosphate (Pi), nucleotide triphosphates etc. Surely some credit must be attributed to MRS for this achievement - particularly when estimates can be made in *in-situ* tissues often inaccessible to other techniques. Many researchers have found it useful to apply destructive methods, eg. freeze blowing, in order to measure concentrations. However, these techniques also often provide only bulk-tissue concentrations and can be susceptible to artefact. Hence, *in-vivo* MRS can, in certain instances, be at least as useful as more conventional competitors. Dr Jardetzky also claims that "... to calculate a true concentration... one would have to know the size of the compartment in which it *(a metabolite)* is distributed. We have no way of measuring that in a heterogeneous tissue." However, recent results from ^{1}H spectroscopy indicate that it is possible to differentiate between tissue and CSF volumes on the basis of the multi-exponential spin-spin relaxation of brain water. Dr Jardetzky is wrong! Concentration estimates do have clinical utility. For example, in ^{31}P studies of neonatal brain following severe birth asphyxia, the early abnormalities (eg. low [PCr]/[Pi]) often disappear after a week or so and abnormalities are only revealed by reduced absolute concentrations (presumably due to irreversible tissue loss).

Dr Jardetzky would have been better advised to train his guns on the large random and systematic errors of MRS concentration estimates. Currently there is a tendency amongst some researchers to assume that absolute quantitation will be a panacea for various MRS shortcomings. At its worst this may lead to giving less weight to the information provided by more immediately estimated quantities eg. peak-area ratios and T_1 and T_2 values. Because of their smaller associated errors, these indices may often prove more sensitive to abnormality than absolute concentrations. In many circumstances it may be more fruitful to focus efforts on improving both spectrum quality and analysis techniques. Although of utility in certain applications, unless the associated errors are reduced, the absolute concentrations estimated by MRS may eventually prove less useful than many researchers currently think.

Yours Sincerely,
Ernest B. Cady

E. B Cady

STANFORD MAGNETIC RESONANCE LABORATORY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305-5055

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

(415) 723-6153
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March 3, 1994
(received 3/5/94)

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

Dear Barry,

It is very reassuring to see that even before paying his dues to the *in-vivo* MRS party line (*MRS is great, anyone who questions it is wrong!*), Dr. Cady actually proceeds to agree point-by-point with everything I have said or implied.

The quantity which Dr. Cady defines, and which MRS *can* measure, has been known to biochemists for generations under the name "tissue content" -- in mg/kg wet weight or mg/l of (*heterogeneous*) tissue. It is a quantity very distinct from concentration in the usual chemist's definition -- as mg/l of a *homogeneous* solvent. Concentration as defined by the chemist appears in the law of mass action, optical, kinetic and thermodynamic laws. Tissue content is a rough measure that obeys no physical law and does not lend itself to either quantitative treatments or to an unequivocal interpretation. It is therefore quite improperly called a concentration, especially not an "absolute."

The point is not as trivial as it sounds. To wit: the fat content of cirrhotic mouse livers determined by chemical assay first increases and then dramatically decreases with time. Histology shows the reason for the decrease to be a progressive replacement of liver tissue by fibrous tissue. The fat content per liver cell continues to increase. Without histology, which MRS spectroscopists rarely get, the interpretation of changes in tissue content can lead to completely wrong biological conclusions. Dr. Cady, who attributes (I think correctly, but without evidence) the reduced "absolute ^{31}P concentrations" in hypoxic neonatal brains to irreversible tissue loss makes the same point. Not to be forgotten, however, is that if one does make the proper measurements to distinguish between tissue loss and a true concentration drop, one has in fact made a complete diagnosis to which the ^{31}P observations contribute little. MRS is an assay of total quantity, the signal reflects the sum of all nuclei. To disentangle the sum requires information MRS cannot provide. If we have to use invasive measurements to interpret a noninvasive measurement, the charm of noninvasiveness wears very thin very quickly.

My reason for taking Dr. Cady and others to task for creating false impressions by misusing the term concentration is that over the years I have had to referee scores of MRS papers in which the "MRS experts" built elaborate, but obviously wrong, theories about metabolic changes in disease on the basis of changes in tissue content assessed by MRS. Unclean terminology leads to unclean thinking.

I can only concur with Dr. Cady's closing statement that tissue content "estimated by MRS may eventually prove less useful than many researchers currently think." Calling it "absolute concentration" can prove positively harmful to our understanding of biology.

Yours sincerely,

Oleg

Oleg Jardetzky

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

March 11, 1994
(received 3/16/94)

Dear Dr. Shapiro,

Title: Squeezing 40% more C-13 S:N from a VXR-400

SEARLE

Our Varian NMR spectrometers require 0.7 ml of solvent in order to achieve the resolution and line-shape performance required for Fourier transformed data that have signals very close to each other and data with a high dynamic range. Thus for Proton data this performance is essential. The wide chemical shift range and the limited dynamic range of Carbon-13 spectra, however, are not as demanding. Typically, the critical element in Carbon-13 NMR spectroscopy is sensitivity.

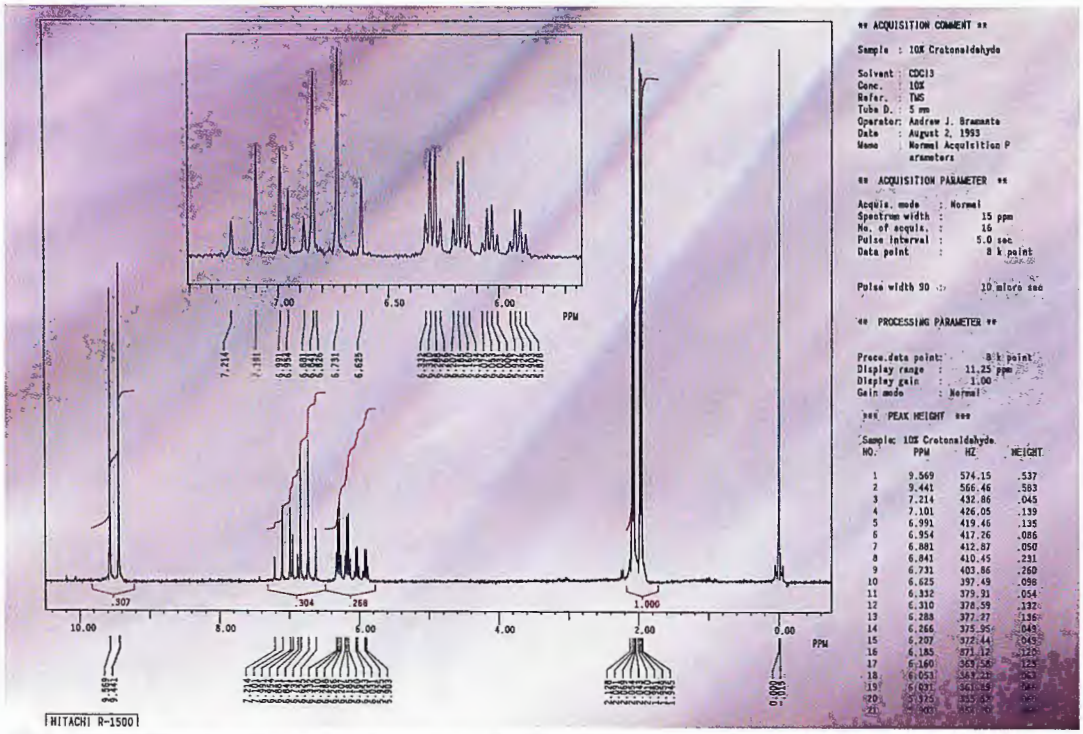
Recently, I have experimented by violating the 0.7 ml rule to see if an increase in Carbon-13 sensitivity could be achieved for limited sample quantity samples. The "bottom-line" is that a 40% increase in signal-to-noise can be realized by using only 0.5 ml of solvent. This 40% increase in S:N will reduce the NMR experimental time by a factor of two for signal-averaged data. This S:N increase matches that offered by a 'micro-probe' and also provides the same sensitivity as our VXR-500 when 0.7 ml of solvent is used.

I have found no performance trade-offs resulting from using 0.5 ml solutions for Carbon-13 NMR spectroscopy. Only z1,z2, and z3 shims were adjusted when changing from 0.7 ml to 0.5 ml solutions. A substantial change in z2 was required (z2 coarse changes were not required) and only moderate changes in the z1 and z3 shim currents. The sample must, of course, be positioned symmetrically about the probe's detection coil center-line.

Regards,

Robert W. Dykstra

P.S. Even more recently (yesterday) I tried a "SHIGEMI PST-001" sample tube on our AMX-500. Compared to a "Wilmad 535pp" a 15.8% S:N increase was realized for a constant concentration Proton sample. This may help in our quest for more C-13 S:N.



This R-1500 FT-NMR spectrum of crotonaldehyde represents a 16 pulse acquisition; each pulse was 10 µsec with a pulse interval of 5 seconds.

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IF YES, PLEASE LIST MANUFACTURER AND MODEL: _____

APPLICATION(S): _____

ARE YOU CONSIDERING AN NMR SPECTROMETER FOR PURCHASE? YES ❑ NO ❑

IF YES, AT WHAT FIELD STRENGTH? _____

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HAVE YOU DISCUSSED YOUR APPLICATION(S) WITH A HITACHI REPRESENTATIVE?
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March 1, 1994
(received 3/8/94)

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

CALCULATING ENTROPIES OF ACTIVATION IN CHEMICAL EXCHANGE

Dear Barry,

We have been having a lot of fun learning more about chemical exchange and NMR. In particular, what people want to know are the thermodynamics of the barrier. Linear regression is usually used to extract the activation parameters from an Eyring plot. As well as giving values for the slope and intercept of the line, most linear regression calculations will give errors for these parameters, and these errors are sometimes quoted in the literature. Particularly for entropies of activation, which involve a considerable extrapolation of the data, the errors are crucial in understanding whether values are significant or not. However, the calculated errors must be interpreted carefully, since many software packages do not emphasize the possibility of correlations of the errors. The intercept will have an error associated with it. The error in the slope, which is needed for the extrapolation, will also contribute significantly to the uncertainty in the intercept. In other words, quoting the variance of the intercept is of little use unless the covariance is also included.

The solution to this problem is to move the value of the zero of the independent variable (1/T in this case) so that the covariance vanishes. The covariance between the slope and intercept is proportional to the sum of the x values (in this case, the sum of the values of 1/T). If the average of the values of 1/T is used as the origin about which to do the regression, the errors are uncorrelated. The slope is always the same, but the intercept has been changed by shifting the data. It is then possible to estimate the error of the intercept with the line running through the true 1/T=0 point. The error in the slope dominates this, so the error in the intercept is approximately the error in the slope times the average of the 1/T values.

The statistical details are as follows. Many models of scientific data assume a linear relation - that is the measurement at some independent variable x_i gives a result y_i given by the following equation.

$$y_i = m\,x_i + b$$

If there are N such measurements, then if the measurements have equal variances, then the values of the slope and intercept that best fit the data are given by to following equations.

$$m = \frac{N\,S_{xy} - S_x\,S_y}{\Delta}$$

$$b = \frac{S_{xx}\,S_y - S_x\,S_{xy}}{\Delta}$$

where S_x is the sum of the x values, S_y, S_{xx}, S_{xy} are defined analogously and

$$\Delta = N S_{xx} - S_x^2$$

First the variance about the regression, S_R, is calculated.

$$S_R = \frac{\sum_{i=1}^{N} (y_i - m x_i - b)^2}{N-2}$$

$$var\ (m) = S_R \frac{N}{\Delta} \qquad var\ (b) = S_R \frac{S_{xx}}{\Delta}$$

$$covar\ (m,b) = -S_R \frac{S_x}{\Delta}$$

The variances of m and b, and the covariance between them are as above. If the x values are chosen so that S_x=0, the covariance vanishes, and the variance of any value y_k read off the regression line at a value x_k is given by the following equation.

$$var\ (y_k) = x_k^2\ var\ (m) + var\ (b)$$

$$= S_R \left(\frac{N x_k^2}{\Delta} + \frac{S_{xx}}{\Delta} \right)$$

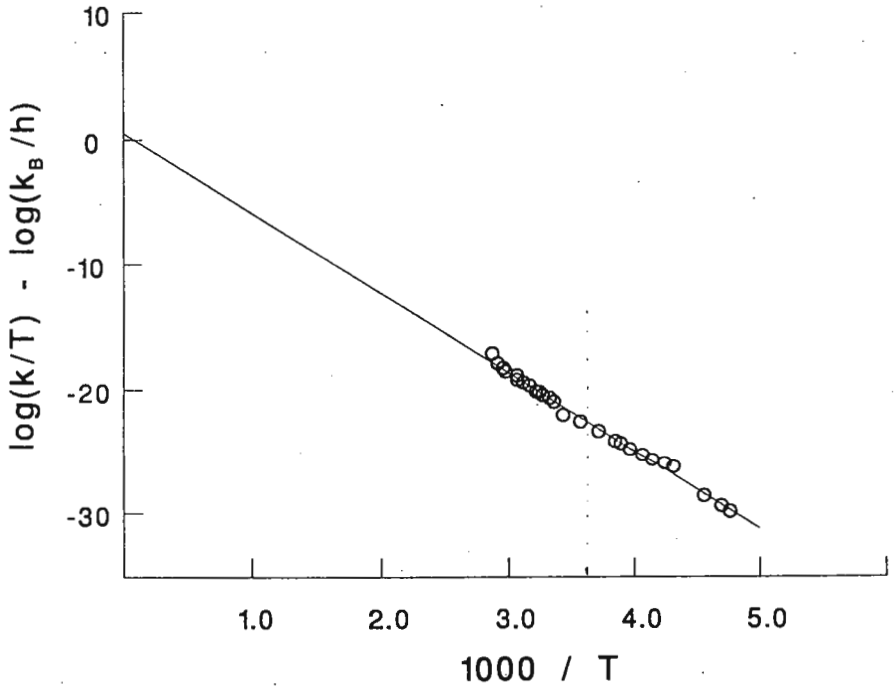
Note that x_k is measured from the value x=0, which is the average of all the x values (since S_x was assumed to be zero).

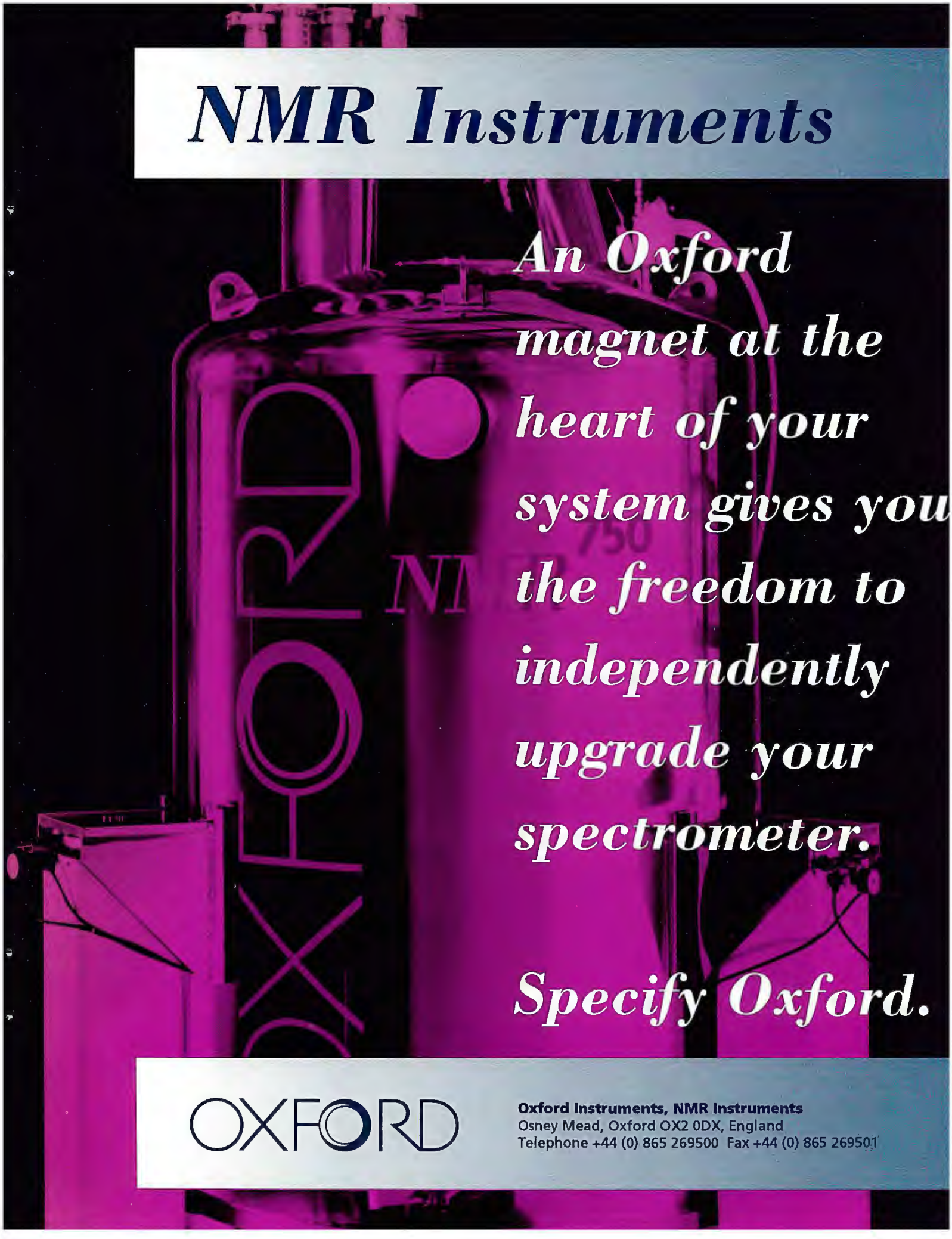
For the data on the exchange in N-acetylpyrrole in figure 1 below, the average value of 1000/T is 3.62, indicated by the vertical dotted line. The intercept with this line is -22.53 +/- 0.094, and the slope is -6.37 +/- 0.037. Therefore the error in the true intercept is $[\ (0.037*3.62)^2 + (0.094)^2\ ]^{1/2} = 0.16$. In this case, the small value of the error in the slope (<1%) means that the extrapolation to 1/T=0 is not too bad. In other cases, the errors can be much worse!

See you in Asilomar.

Alex D. Bain

Greg J. Duns

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2515

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Professor B.L. Shapiro
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U S A

Zürich, February 28, 1994
(received 3/5/94)

CONSERVATION LAWS IN POLARIZATION TRANSFER ?

Dear Barry,

Advanced NMR techniques heavily depend on the transfer of polarization and of coherence. In particular two–dimensional spectroscopy and the enhancement of sensitivity of low–γ nuclei rely on transfer processes. On a first glance, one might take it for granted that the quantity that is transfered is conserved. Thus, in a heteronuclear polarization experiment, the amount of polarization that leaves the I spins should arrive at the S spins, unless an irreversible loss mechanism, such as relaxation, is involved.

The actual facts are different. Even in the course of a fully reversible process, polarization may increase or decrease, and there are no universal conservation laws in polarization transfer. Of course there are other conserved quantities in a unitary and reversible transfer process. For example, the entropy of the system remains invariant, or the eigenvalues of the density matrix do not change, except for their arrangement (1). But the polarization and the magnetization do not belong to the conserved quantities. That magnetization cannot be a conserved quantity becomes evident when taking into account its dependence on the numerical values of the gyromagnetic ratio γ.

The (non)–conservation laws in polarization transfer have recently been discussed in some detail in "Absence of Conservation Laws and the Reciprocity Relation in Polarization–Transfer Experiments" by Shanmin Zhang, Ping Xu, Ole W. Sørensen, and Richard R. Ernst, which is in press in Concepts in Magnetic Resonance. It was found that an increase in polarization is usually associated with a transfer from a smaller to a larger spin group, e.g. from ^{13}C to the three protons in a $^{13}CH_3$ group, or from a spin $I=^1/_2$ to a spin $S>^1/_2$. For a transfer in the opposite direction, naturally a decrease of polarization must be expected.

The increase or decrease of polarization is simply associated with the importance that the matrix elements of the polarization operators $F_z = \sum_{k=1}^{N} I_{kz}$ and $G_z = \sum_{l=1}^{M} S_{lz}$ play in the calculation of the polarization P_I and P_S,

$$P_I = \mathrm{Tr}\{F_z\,\sigma\}\ , \qquad P_S = \mathrm{Tr}\{G_z\sigma\}\ .$$

The numerical values of the matrix elements of F_z and G_z depend on the spin system and its spin quantum numbers. On the other hand, quantities that depend exclusively on the density operator σ, such as the spin entropy, may obey conservation laws under unitary transformations. Considerations of this type are important when discussing heteronuclear polarization transfer in liquids and in solid phase.

Best regards.

Sincerely yours,

Richard R. Ernst

(1) O.W. Sørensen, Prog. NMR Spectrosc. **21**, 503 (1989);
O.W. Sørensen, J. Magn. Reson. **86**, 435 (1990).

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Pulse width	10 ms	20 ms
Duty cycle	Up to 10%	Up to 10%
Amplitude droop	5% to 10 ms typ.	5% to 20 ms typ.
Harmonics	Second: – 25 dBc max. Third: – 12 dBc max. to 30 MHz – 25 dBc max. above 30 MHz	
Phase change/output power	10° to rated power, typ.	
Phase error overpulse	4° to 20 ms duration, typ.	
Output noise (blanked)	< 10 dB over thermal	
Blanking delay	< 1 μ s on/off, TTL signal	
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Indicators, front panel	1. AC power on 2. CW mode 3. Overheat	4. Overdrive 5. Over pulse width	6. Over duty cycle 7. LCD peak power meter
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AC line voltage	208/230 VAC, 10%, 1Ø, 47-63 Hz		

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AC power requirements	1400 VA	700 VA
Size (HWL, inches)	8.75 x 19 x 24	8.75 x 19 x 24
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(AMPX00HV) 02/94

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Dr. Bernard L. Shapiro
TAMU NMR Newsletter
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March 04, 1994
(received 3/17/94)

Peak/Integral Lists from a Bruker to a LaserJet III

Dear Dr. Shapiro:

Happy new year! Listed below is an automation and a Pascal program to generate peak/integral lists on a LaserJet III printer (other printers should work similarly with possible variations in the escape codes). The automation program works in conjunction with the automation menu/automatic sample changer on our AC-300. Serial-serial connections between the ASPECT and printer were used with pinouts that are identical to those used with the 7550 plotter.

;PRPP.AU
Standard 1-D processing program with peak picking printout on a LaserJet III printer. This program works with the automation on our AC-300.

1 WAIT	wait until the file FID.n exists on disk
2 RE @	;read FID.n
3 EM1	;window multiplication if EM wanted
4 GM1	;if GM wanted
5 FT	;fourier transformation
6 APK	;automatic phase correction
7 ABS INT1	;polynomial baseline correction and integral rest
8 SRE1	;automatic scaling: set TMS to 0 ppm and
	;suppress TMS peak and solvent peak for plot scaling
NOPL	;no plot if scans completed < NS
9 SFN INT1	**;second file name needed for PPID command**
10 PPID INTEGRAL	**;ASCII file written to disk as INTEGRAL.001**
11 PASC PRINT	**;Pascal program to send file to LaserJet**
12 PXB1 INT1	;plot spectrum and integral
13 NP1	;next page
14 PP1	;peak picking if defined in dialogue
15 WR PROJH1	
16 EXIT	

```
(*PROGRAM WRITTEN ON ASPECT-3000*)
(*TO PRINT INTEGRAL FILE TO*)
(*LASER PRINTER AT A PITCH OF 16.5*)
(*COMPILED USING COMPLINK*)
(*REFER TO LASERJET MANUAL FOR*)
(*ESC SEQUENCES*)

PROGRAM PRINT;
CONST
 FNAME     = 'INTEGRAL.001';
 COUNTER   = 50;
VAR
 ANQ       : TEXT;
 INFILE    : TEXT;
 A,B,C,D,E,F : STRING;
 COUNT     : INTEGER;
BEGIN
(*SET ANQ TO CHANNEL B NO PARITY*)
 BEGIN REWRITE(ANQ,'=BO:P');
(*LEFT MARGIN OFFSET 15 COLUMNS*)
WRITE(ANQ,CHR(27));
        WRITE(ANQ,CHR(38));
         WRITE(ANQ,CHR(97));
          WRITE(ANQ,CHR(49));
           WRITE(ANQ,CHR(53));
            WRITE(ANQ,CHR(76));
      WRITE(ANQ,CHR(27));
(*COMPRESSED PITCH 16.5 - 16.7*)
       WRITE(ANQ,CHR(38));
        WRITE(ANQ,CHR(107));
          WRITE(ANQ,CHR(50));
           WRITE(ANQ,CHR(83));
         WRITELN(ANQ,'Beginning of integral
file');
(*INTEGRAL.001 AS INFILE*)
        RESET(INFILE,FNAME);
         FOR COUNT :=1 TO COUNTER DO
          BEGIN
           WHILE NOT EOF (INFILE) DO
          BEGIN
         READLN(INFILE,A,B,C,D,E,F);
        WRITE(ANQ,A,B,C,D,E,F);
 (*CARRIAGE RETURN*)
       WRITE(ANQ,CHR(13));
       END;
     REPEAT UNTIL EOF (INFILE)
    END;
    END;
     WRITE(ANQ,CHR(10));   (*LINEFEED*)
      WRITE(ANQ,CHR(10)); (*LINEFEED*)
       WRITELN(ANQ,'End of integral file');
 (*EJECT PAGE*)
         WRITE(ANQ,CHR(27));
          WRITE(ANQ,CHR(38));
           WRITE(ANQ,CHR(108));
            WRITE(ANQ,CHR(48));
             WRITE(ANQ,CHR(72))
 (*RESET PRINTER*)
                  WRITE(ANQ,CHR(27));
                   WRITE(ANQ,CHR(69));
                    CLOSE(ANQ,INFILE);
END.
```

Hope this contribution takes me off your "ultimatum" list . See you at the ENC.

Yours sincerely

Ashok Krishnaswami

MICROSAMPLE PROTON PROBES

BRUKER

In the past various attempts have been made in the NMR industry to design probes for milli-, micro- and even high nanogram amounts of sample. However, these probes typically suffered from a number of drawbacks which rendered them not very useful in practice: some designs use solenoidal coils which make it impossible to load/eject the sample at the top of the magnet; instead the probe has to be removed from the magnet to change a sample. Moreover, these probe designs are primarily useful for 1H-only coils, but cannot be readily built as broadband inverse or inverse triple-resonance probes. Typically, lineshapes for older microsample probes were not satisfactory for biological NMR experiments which require water suppression.

BRUKER INTRODUCES a new and unique series of 2.5 mm proton probes for microsample applications.

Our user friendly design offers:

- **sample insertion and ejection without probe removal**
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- **excellent lineshape, water-suppression and sensitivity**
- **sample volumes of 80 - 100 microliters**
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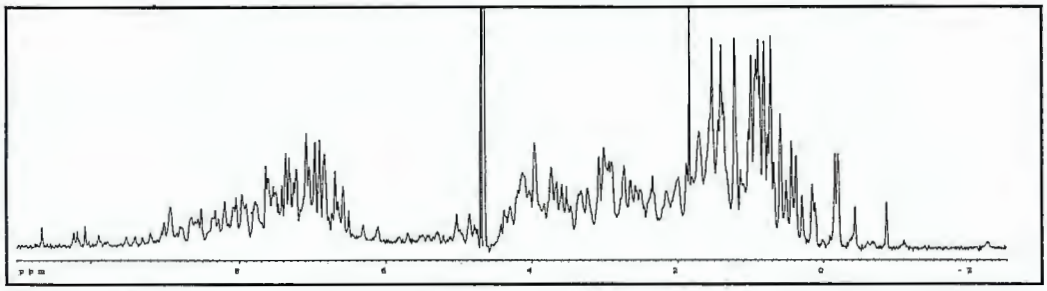
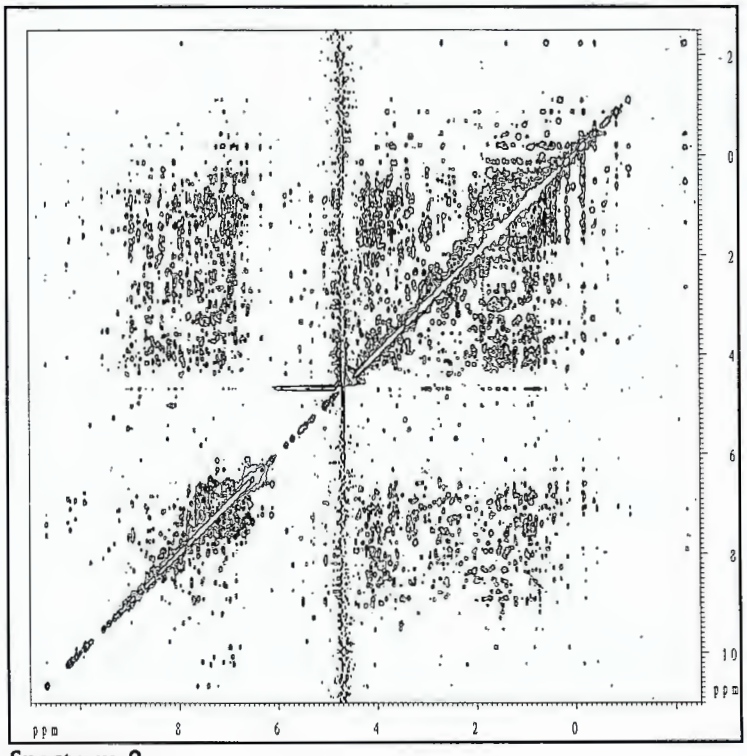


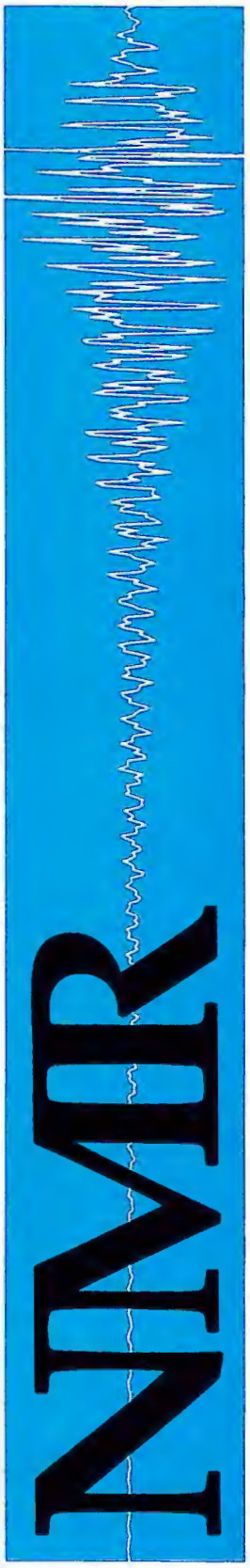
Spectrum 1



Spectrum 2

Spectrum 1: 64 scans of 1 milligram of lysozyme in 0.1 milliliter of 90% H_2O / 10% D_2O. The first increment of a NOESY experiment demonstrates the excellent lineshape and water-suppression capability.

Spectrum 2: 2D NOESY with 150 msec mixing time at 12 1/4 hours acquisition time.



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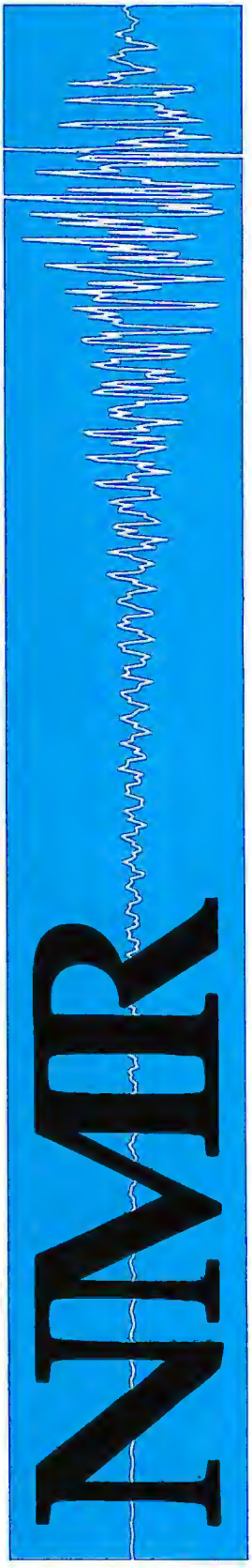


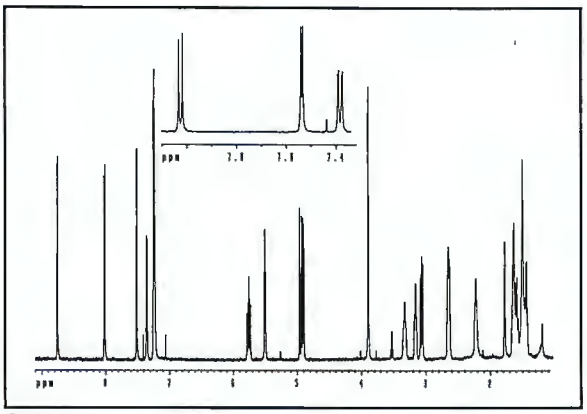
Spectrum 3: A 10 minute acquisition on 10 micrograms of quinine in $CDCL_3$. Note the excellent resolution for the aromatic peaks in the inset.

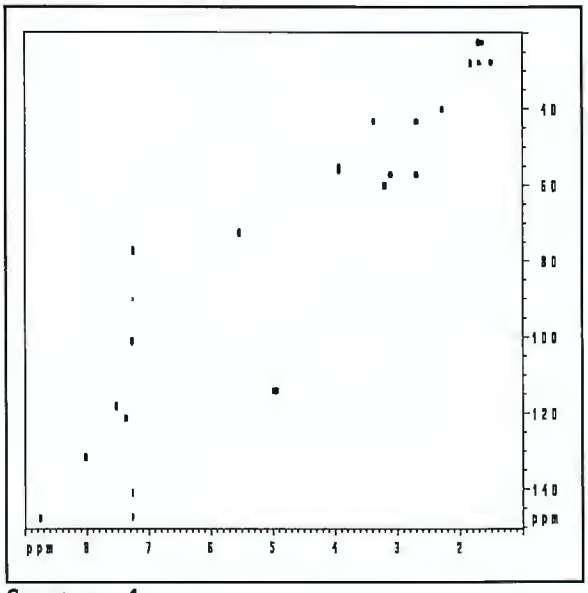
Spectrum 4: 2D HMQC at 12 hours. Same sample as spectrum 3.

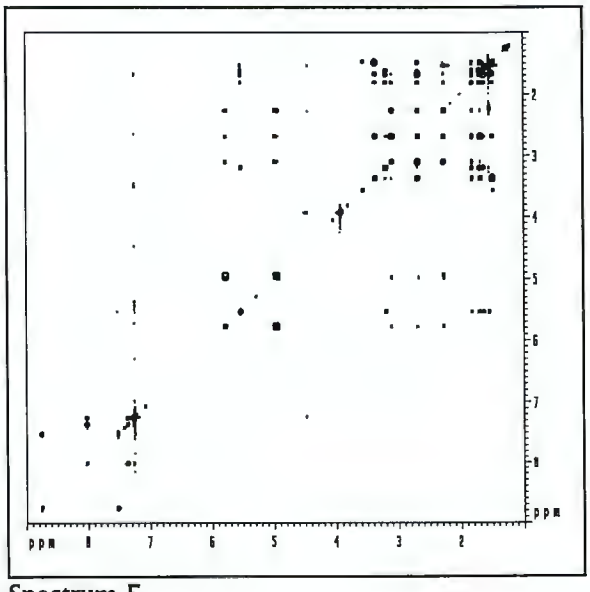
Spectrum 5: A 2D TOCSY with 3 hour acquisition time, same sample.

Experimental details:
All spectra shown here were acquired on an **AMX 600** equipped with the high-dynamic range **SE 451™** receiver, which is essential for measuring small sample amounts with good sensitivity. A **BOSS2™** (Bruker Orthogonal Shim System) was used for optimal lineshape, and the probe was a 2.5 mm inverse triple-resonance probe [$^{1}H\{^{13}C,^{15}N\}$]. All spectra were acquired non-spinning, and 90° pulse widths were <5 microseconds for ^{1}H, <12 microseconds for ^{13}C, and <40 microseconds for ^{15}N.

This novel generation of Bruker 2.5 mm proton probes ideally complement the standard 5 mm and 8 mm probes (for solubility-limited cases) in biological NMR applications.


Spectrum 3


Spectrum 4


Spectrum 5

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March 14, 1994
(received 3/19/94)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
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Documenting Pulse Programs

Dear Barry:

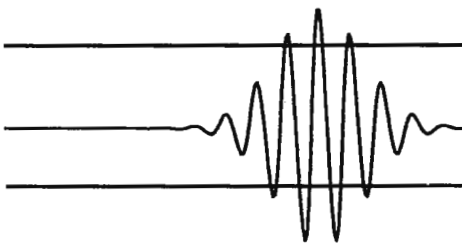
Readers of this august journal may find useful the PiCTeX macro package for the LaTeX typesetting system in precision documenting of pulse programs and other graphics which require precise positioning of graphical features. Habitual TeXies[a] and others with a penchant for self abuse ("if you've got plenty of time, do it by computer") will find it a natural way of including such graphics in their documents. The logo at the bottom, and the several examples in this letter are all created with Michael Wichura's PiCTeX, which is available from the TeX Users Group, P. O. Box 9506, Providence, RI 02940, and probably also from some of the vendors distributing commercial versions of TeX.

The advantage of PiCTeX, as opposed to many common PC and Mac drawing tools, is that all graphic elements are placed by specifying Cartesian coordinates in the LaTeX source file, which allows features to be represented in the appropriate scales and relationships, and to show functions which are numerically accurate. We have a Fortran program which generates ASCII coordinates for FID wiggles, etc., in a format readily accepted by PiCTeX. The disadvantage is that there is a fair amount of code involved in generating the finished products you see here, but it's easily reusable when altering existing graphics or creating new ones. I'll be happy to distribute examples, including ones which demonstrate inclusion of PostScript files (images, etc.) by email. Our style file also includes macros for many of the common NMR isotope designations, some chemical formulae, other goodies, and many of the standard NIH grant application forms as well (though you'll have to change the P. I. name if you want to have a chance of getting funded).

Best regards,

Jerome L. Ackerman Jerry

[a] TeXies are hacker-like creatures who spend long late hours peering into CRT's attempting to get their textbook-quality documents looking *just right* by trying to coerce TeX to do the ostensibly obvious but actually impossible.



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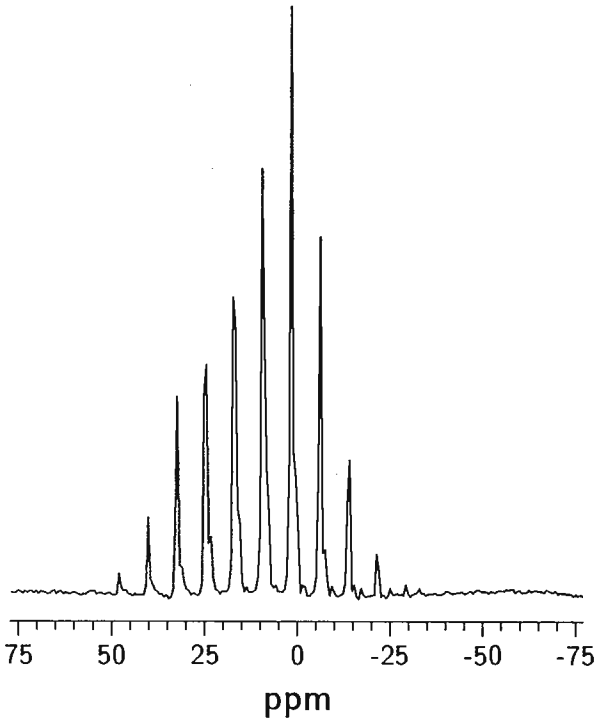
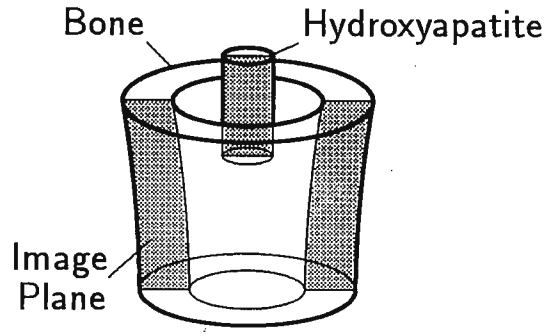
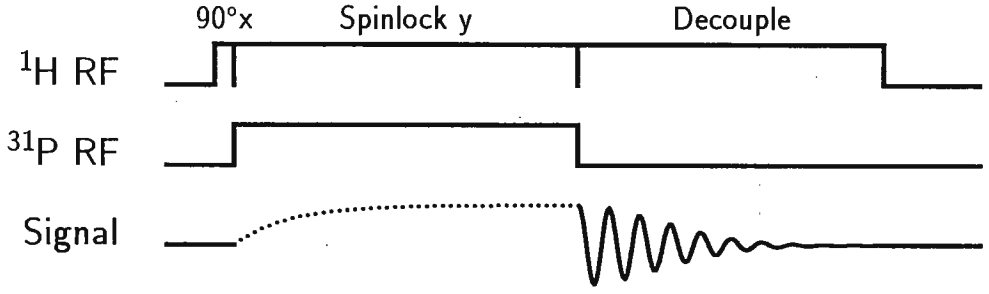
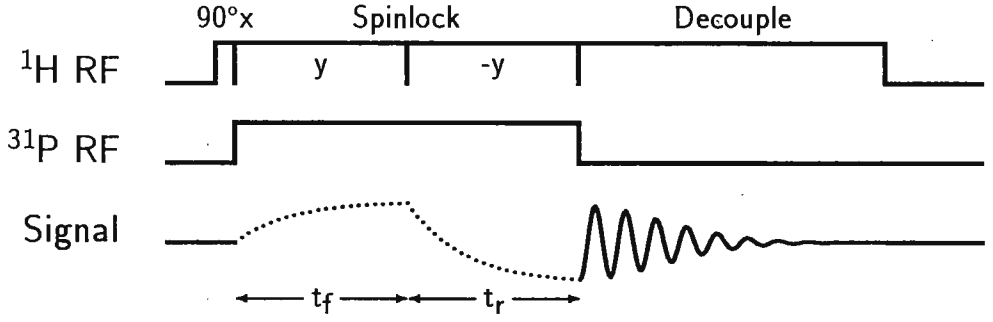




Conventional Cross Polarization



Differential Cross Polarization



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

21 March 1994
(received 3/26/94)

2D J-resolved NMR spectra of crystallographically equivalent nuclei under VAS conditions

Dear Barry,

A couple of years ago we noticed that ^{31}P CP/MAS NMR spectra of $M(PR_3)_2(NO_3)_2$ [M = Cd or Hg and R = C_6H_5] exhibited spinning frequency-dependent lineshapes.[1,2] The two phosphorus nuclei in each of these compounds are related by a C_2-axis; therefore, they have identical isotropic ^{31}P chemical shifts and are said to be crystallographically equivalent. However, the orientations of their respective phosphorus shielding tensors are not coincident; thus, they are magnetically nonequivalent. At 4.70 T, only a single sharp ^{31}P NMR peak was observed provided that the frequency of magic angle spinning, ω_R, exceeded 3 kHz. At slower spinning frequencies four peaks were observed. The relative positions and intensities of the four peaks varied with the MAS frequency. We have referred to these spectra as unusual AB spectra since ^2J(P,P) is given by splittings between alternate peaks in the four peak pattern in contrast to the situation in solution NMR studies. In order to extract J from the MAS spectra of two crystallographically equivalent nuclei, they must be dipolar coupled to one another and for a significant fraction of the spin-pairs their instantaneous chemical shift differences (in Hz) must be comparable to ω_R. A general description of such systems using average Hamiltonian theory is given elsewhere.[2]

Recently, we have examined ^{31}P NMR spectra of mercury complexes under conditions of rapid variable-angle spinning (VAS). When the sample is spun rapidly about an axis off the magic angle, one observes rather complex lineshapes which exhibit fine structure due to indirect ^{31}P-^{31}P spin-spin coupling or J-coupling. Note that both the anisotropic chemical shielding and the direct dipolar interactions are scaled by VAS; however, the isotropic J-coupling constant is invariant to sample spinning. Of course it is not essential that the two crystallographically equivalent nuclei be dipolar coupled in order to determine J under VAS conditions. Furthermore, we have found that the analysis can be simplified by acquiring 2D J-resolved ^{31}P NMR spectra with VAS at two angles other than the magic angle. Two such spectra of $Hg(PPh_3)_2(NO_3)_2$ are shown in Fig.1. Extensions of these studies are presently under way in our laboratory.

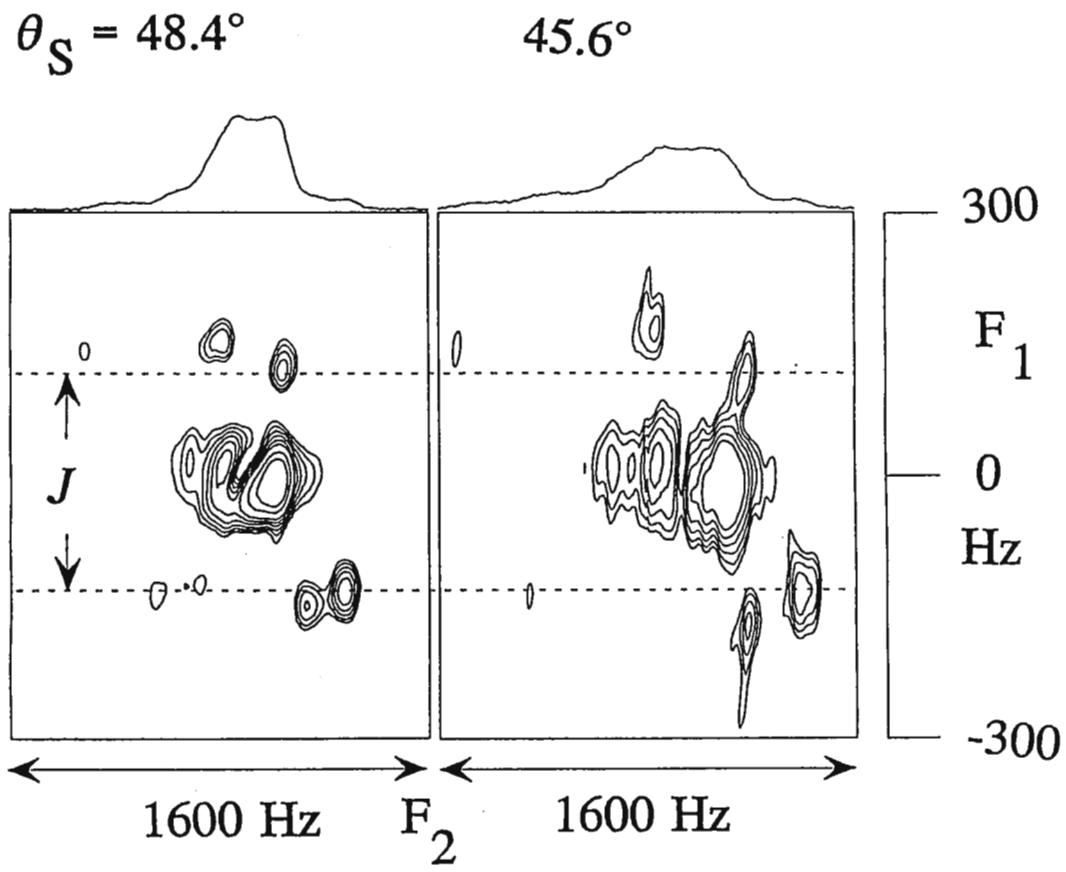
Yours sincerely,

Rod Gang Wu

Roderick E. Wasylishen Gang Wu

References: 1. K. Eichele, G. Wu and R.E. Wasylishen, *J. Magn. Reson.*, **A101**, 156 (1993).
2. G. Wu and R.E. Wasylishen, *J. Chem. Phys.*, **98**, 6138 (1993).

Fig. 1. 2D VAS ^{31}P *J*-resolved NMR spectra of $Hg(PPh_3)_2(NO_3)_2$ at 4.70 T. θ_S is the angle between the spinning axis and the applied magnetic field. In this case $^2J(^{31}P,^{31}P) = 250 \pm 10$ Hz.



FORTHCOMING NMR MEETINGS, *Continued from page 1.*

Symposium on "NMR as a Structural Tool for Macromolecules: Current Status and Future Directions, Indianapolis, IN, **October 30 - November 1, 1994**; Contact: Ms. Padmini Nallana, Coordinator, NMR Symposium, Dept. of Physics, Indiana University Purdue University Indianapolis, 402 N. Blackford St., Indianapolis, IN 46202-3273; Tel. (317) 278-1263; E-mail: PADMINI@INDYVAX.IUPUI.EDU; Fax: (3172) 274-2393. See TAMU NMR Newsletter 425, 31.

36th ENC (Experimental NMR Conference), Boston, MA, **March 26 - 30, 1995**; Contact: ENC, 815 Don Gaspar, Santa Fe, NM 87501; (505) 989-4573; Fax: (505) 989-1073

12th International Meeting on NMR Spectroscopy, Sponsored by the Royal Society of Chemistry, Manchester, England, **July 2 - 7, 1995** [sic]; Contact: Dr. J. F. Gibson or Ms. G. B. Howlett - See TAMU NMR Newsletter 415, 5; Phone: (44-71) 437-8656; Fax: (44-71) 437-8883.

ISMAR 1995, Sydney, NSW, Australia, **July 16-21, 1995**; Contact: Dr. Les. Field, Dept. of Organic Chemistry, Univ. of Sydney, Sydney, NSW 2006, Australia. Phone: +61-2-692-2060; Fax: +61-2-692-3329; Email: ismar-95@biochem.su.oz.au Also, see TAMU NMR Newsletter 419, 26.

Additional listings of meetings, etc., are invited.

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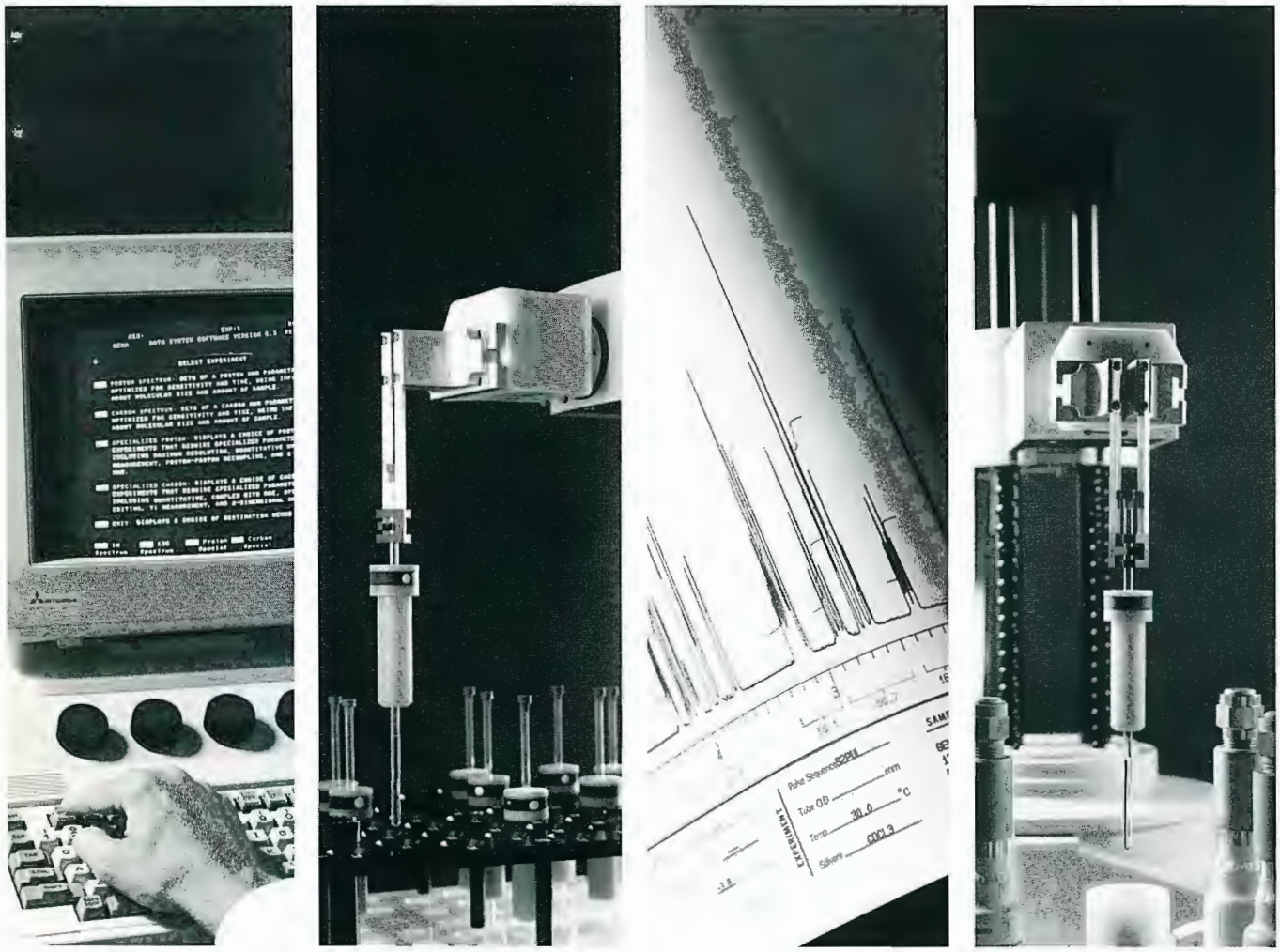

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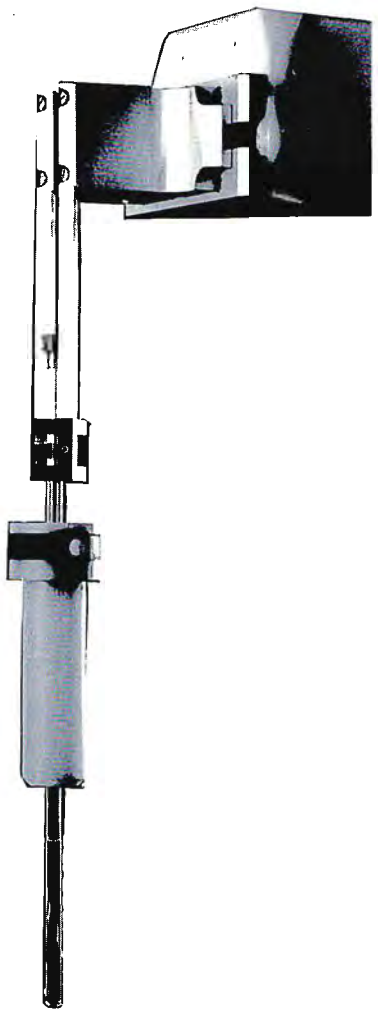

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February 25, 1994
(received 2/28/94)
To:
Dr. B. L. Shapiro
Editor/Publisher,
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Dear Barry:

"Unusual Chemical Shifts of Arg^{52} Cucurbita maxima Trypsin Inhibitor - V"

Protein structure and design studies have now assumed a particularly important role in biology. In keeping with this, our department has recently established a high field NMR facility for macromolecules. This facility is involved with all aspects of structure determination and molecular modeling investigations. We have started a number of NMR studies of peptides and proteins. A new Cucurbita maxima trypsin inhibitor, CMTI-V, isolated and characterized in our laboratory, has 68 amino acid residues including a single disulfide bridge. It belongs to the potato-I inhibitor family.[1] We have been interested in studying the solution structure and conformational properties of this protein inhibitor of trypsin and blood coagulation factor, $FactorXII_a$, by NMR spectroscopy. These studies, using various homo and heteronuclear two dimensional NMR techniques at 500 and 600 MHz, have led us to completely assign the backbone and side chain protons of CMTI-V.

This protein has six arginine residues at positions 26, 47, 50, 52, 58, and 66. A striking feature of the ^1H NMR spectra of CMTI-V is the highly shielded large chemical shift nonequivalence ($\sim$0.5ppm) of the diastereotopic β and γ-protons of Arg^{52} residue in contrast to those of the other five Arg residues (Table 1). Furthermore, the side chain NH_2 protons of this residue only was observed at 10.09 ppm in ^2H_2O solution, whereas for the other arginine residues, they were not observed. Interestingly, Arg^{52} was found to be part of a short strand of parallel β-sheet involving residues Val^{51}-$Ileu^{53}$, which are antiparallel with Thr^{43}-Phe^{46}, and parallel with Arg^{66}-Gly^{68}. These NMR observations suggest that the side chain of Arg^{52} residue is highly ordered, perhaps due to the fact that the side chain hydrogens of this residue are buried and closely packed, coming as they are, from the central strand of the parallel β-sheet in the molecule.

Table 1: ^{1}H Chemical Shifts of Side Chain Hydrogens of Arginine Residues in CMTI-V at 30°C, pH 5.39.

Arginine Residue Position	β-Hydrogens (ppm)	γ-Hydrogens (ppm)
26	1.98	1.72
47	1.82	1.43, 1.46
50	1.76, 2.12	1.49, 1.57
52	1.06, 1.50	0.57, 1.03
58	2.08	1.65, 1.75
66	2.07, 2.15	1.84, 1.89

Sincerely,

(O. Prakash) (Y. Gong) (J. Kao) (R. Krishnamoorthi)

1. R. Krishnamoorthi, Y. Gong and M. Richardson, FEBS Lett. 273, 163(1990).

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INDIAN INSTITUTE OF SCIENCE
BANGALORE-560 012 INDIA

March 4, 1994
(received 3/17/94)

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

2D in 5 minutes with imaging probe

Dear Barry,

We have been fascinated with lots of gradient experiments appearing in literature, but have yet to buy a gradient probe for our 4 year old AMX-400. We do have a micro imaging probe which has no lock channel. Since the supercon magnet is quite stable we tried a quick experiment with this probe. The shimming was done directly on the FID. We may add that we have a wide bore magnet (89mm) and shimming on this is not easy without lock. The result of a ge-2q-cosy[1] (figure 1) i.e. gradient enhanced double quantum filtered COSY on a hexapeptide (Boc-Cys-Val-Aib-Ala-Leu-Cys-NHMe) 10mM in DMSO-d_6 is shown in figure 2. 256 t_1 values, with single scan per t_1, were recorded in approx. 5 minutes. Rectangular, uncompensated gradient pulses of 2 millisecond duration were used with the gradient values of 5 and 15 gauss/cm. This symmetrized, absolute value spectrum is free of all the singlets (Aib NH, Aib and Boc methyls, the solvent and the absorbed water). The quality of the 2D as well as the 1D spectra (not projections) are comparable to normal spectra recorded with regular ge-probes, that we have seen in the literature and on the back of TAMU Newsletters. This spectrum contains sufficient details to allow complete assignments of the hexapeptide.

S----------S

This spectrum seems to indicate that we need not buy a gradient probe. Do you agree?

Please credit this contribution to the account of Professor C.L. Khetrapal.

Sincerely,

G.A. Naganagowda S. Raghothama K.V. Ramanathan Anil Kumar

1. Ralph E. Hurd, J. Mag. Res. 87, 422-428 (1990).

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Telephone : 3344411 Extn. 2536. Telegram : 'SCIENCE' Telex : 0845-8349 IISC IN. Telefax : 91-80-3341683

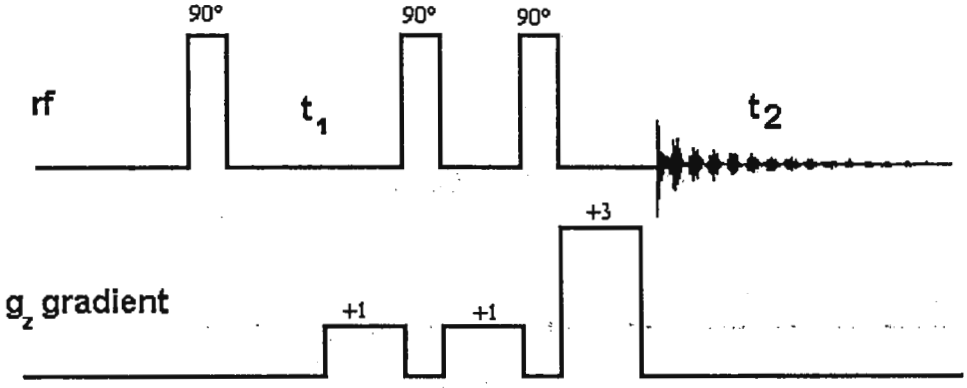

figure 1

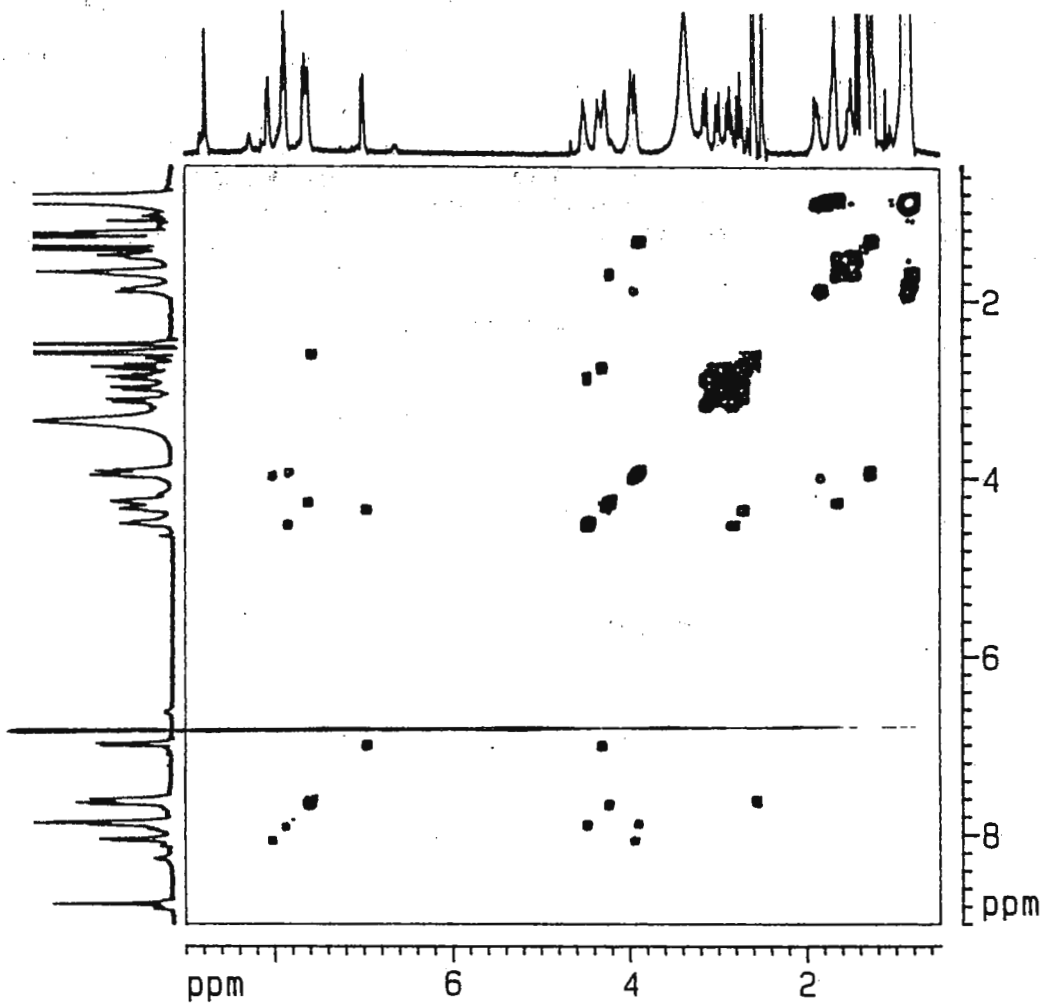

figure 2

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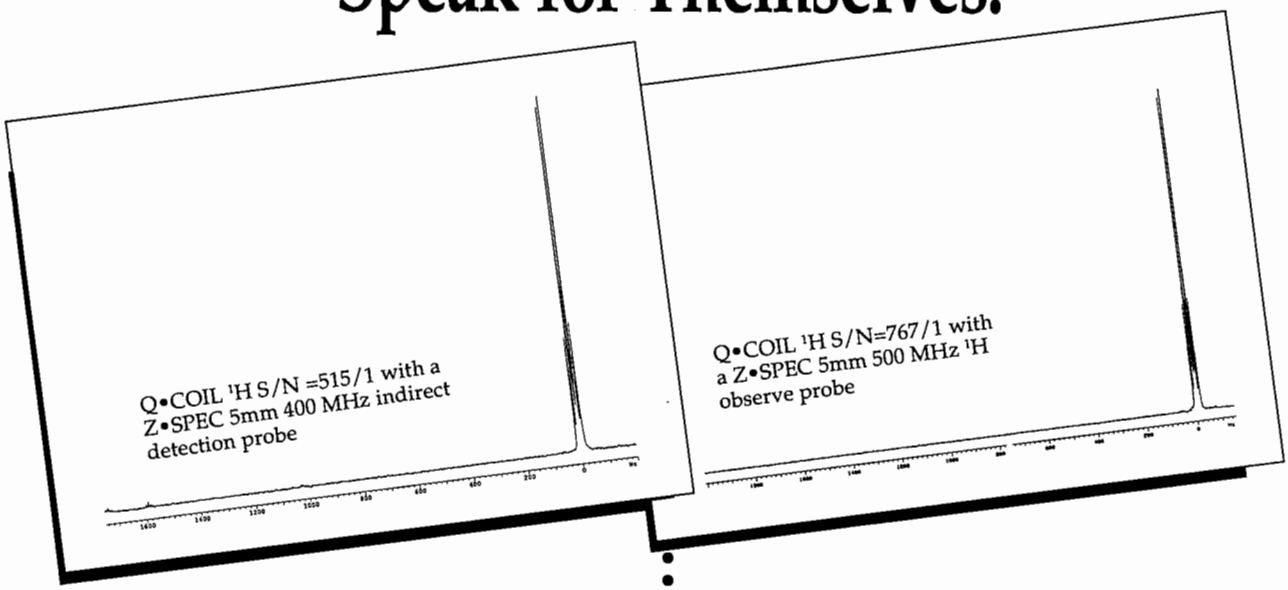

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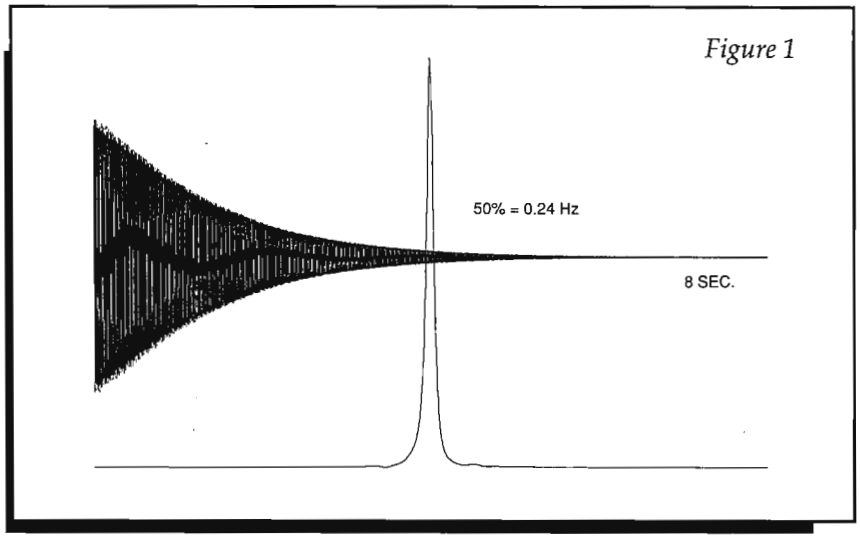

Figure 1: ^{1}H line shape determination on 1% $CHCl_3$ for Z•SPEC H 500-5 probe at 500 MHz. Resolution = 0.24 Hz.

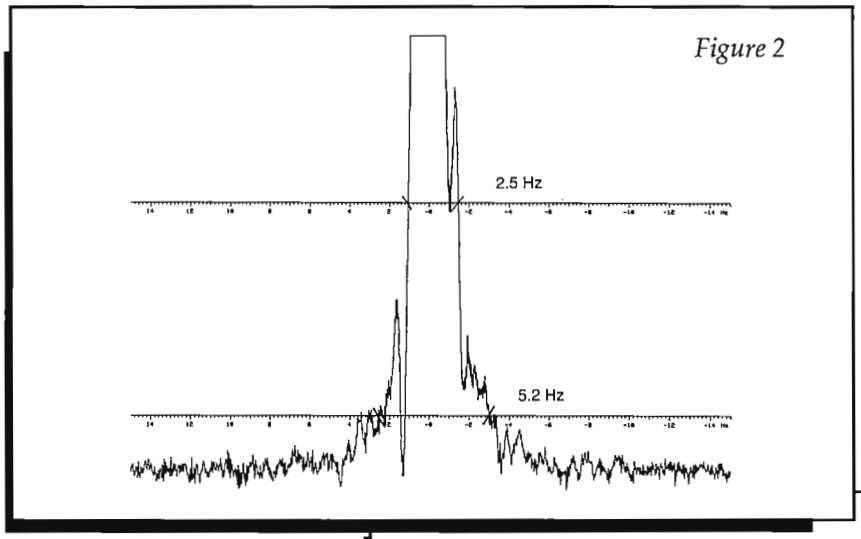

Figure 2: ^{1}H line shape determination on 1% $CHCl_3$ for Z•SPEC H 500-5 probe at 500 MHz, 2.5 Hz at 0.55% and 5.2 Hz at 0.11%.

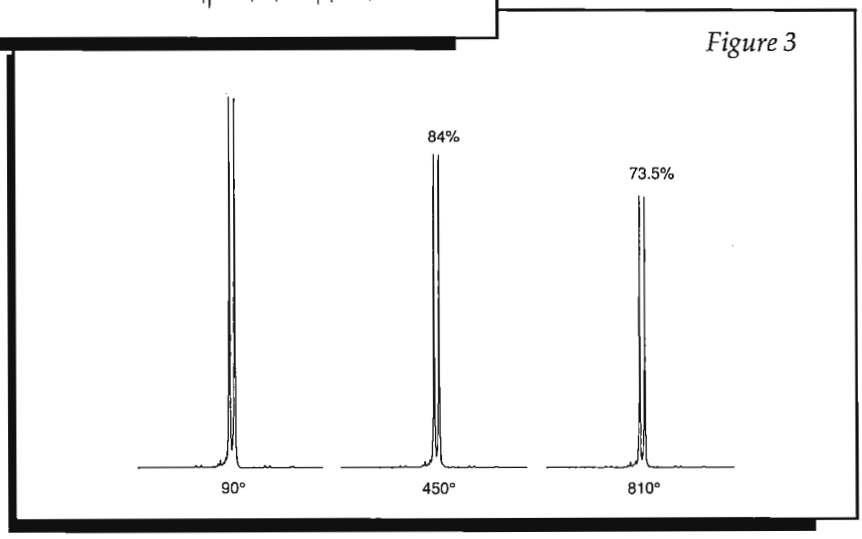

Figure 3: ^{1}H RF homogeneity determination for Z•SPEC ID 500-5 probe at 500 MHz, 84% at 450° and 73.5% at 810°.

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Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303
Thu Mar 17 1994 (received 3/19/94)

Jeffrey A. Reimer, Associate Professor
DEPARTMENT OF CHEMICAL ENGINEERING
BERKELEY, CALIFORNIA 94720-9989
FAX: (510) 642-4778
REIMER@GARNET.BERKELEY.EDU
510-642-8011

Dear Barry:

After several years of experience with equipment from Tecmag I am now in a position to provide some recommendations to the NMR community regarding their products. To place these recommendations in context, your readers should know that I have three Tecmag products: two Libra and one Aries NMR data stations. These data stations are interfaced to home-built *rf* gate and phase shift networks; NMR interferograms are digitized with the analog-to-digital converters provided by the Libra and Aries units. All three are interfaced to Macintosh computers using Tecmag's MacNMR software. We have about nine years of total time working with all three units.

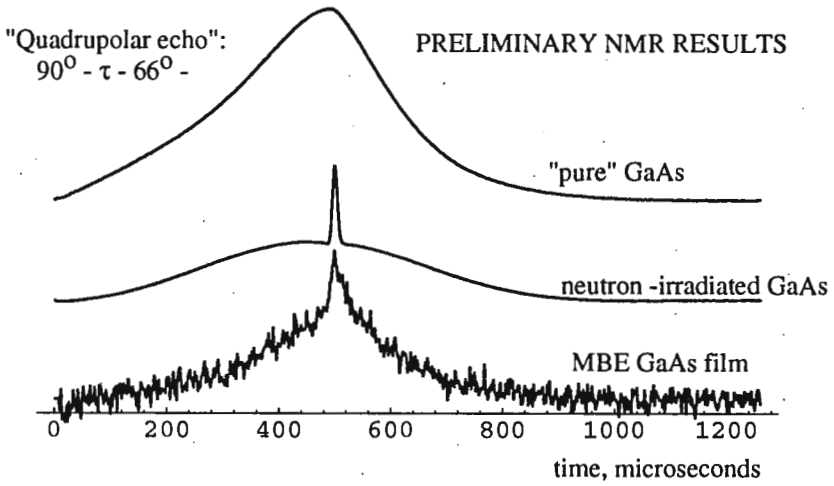
It is worth noting that many of the experiments conducted with our Tecmag-equipped instruments are rather straightforward, including appropriately phase-cycled inversion recovery T_1 measurements, spin-echo measurements, and CP-MASS experiments of various types, etc. On rare occasions we try something more challenging from the pulse programming perspective, such as two-dimensional carbon-13 spin diffusion experiments or homonuclear multiple pulse decoupling and multiple quantum experiments. Furthermore, you should know that as a faculty member in chemical engineering one of the goals of my graduate education program is training in NMR fundamentals, including equipment design, maintenance, and operation; in this context a fully enclosed "spectrometer-in-a-box" commercial instrument is a poor teaching aid.

In my opinion Tecmag ranks with ENI and PTS for equipment that is reliable, well thought out, and well supported by the company. Tecmag has been responsible in accepting purchase orders, delivering (gasp!) ahead of schedule, providing technical support, and chasing down difficult problems. In some cases Tecmag has provided hardware *gratis* while they chased down possible problems in the original equipment. In all cases they have been responsive to our needs.

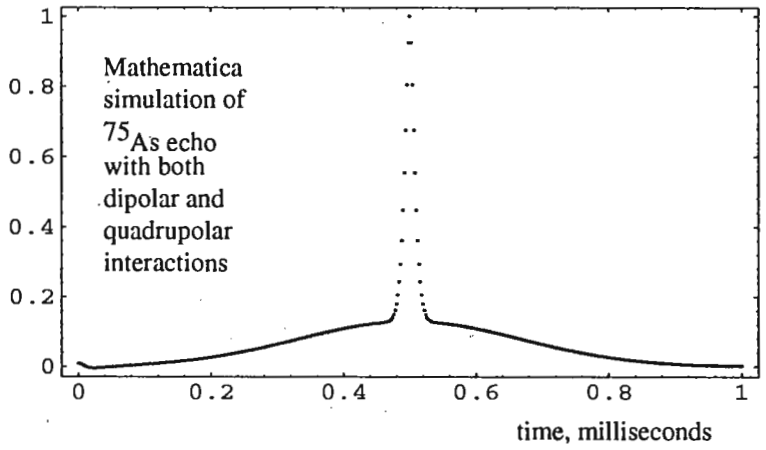
The hardware itself has exhibited few design flaws. Recognition of the 10 Mhz external clock input, in our case provided by PTS synthesizers, is problematic. In some cases special filters were required, in other cases amplification, and sometimes serendipity seems the best solution. Once the clock is recognized and the rf input connection is stabilized, however, you can count on years of continuous operation with no interruptions. The MacNMR software is straightforward; graduate students and postdocs with little or no NMR experience can program simple pulse sequences within a few minutes of playing at the computer. NMR data analysis, such as FFT, plotting, phasing, baseline corrections, etc., are implemented as well as I have seen on any low-end commercial NMR instrument.

What distinguishes the Tecmag equipment from others, however, is the choice of the Macintosh as the platform for instrument control, data acquisition and analysis. In much of my research considerable effort is paid to analysis of lineshapes and relaxation data, analysis that will never be a part of commercial instrument software. Hence for my group productivity is intimately connected to the ease of data export and analysis by other software. The example below demonstrates this issue.

Postdoctoral fellow Joachim Krueger is studying defects in thin films of GaAs using ^{75}As NMR data. The data shown below are (real) time interferograms obtained from various GaAs samples using a quadrupolar echo pulse sequence:



These data may be compared to density matrix calculations of the type found on page 242 (equation 36) of the text by Abragham. In our case the time evolution of the spin system was calculated with a Mathematica program running on the Macintosh computer; as shown below.



Data exported directly from MacNMR may be compared with the Mathematica calculations in order to extract fundamental physical parameters. Indeed, the preparation of this letter, including import of data, text editing, dawing or plotting, use of Mathematica, etc., can all be done on the Macintosh platform without the assistance of Central Computing Services or computer specialists.

My research group has successfully enjoyed the NMR data <-> Macintosh connection for some years. The combination of the two has made my group, I believe, more productive and affords the best possible educational environment for my students. If the goal of your work is results with minimal obfuscation by UNIX nerds, 24 bit word lengths, FORTRAN vs. PASCAL vs. C+++++ programming, etc., then the Tecmag <-> Macintosh connection is for you.

Regardless of your computer preferences, however, Tecmag equipment has served me well for several years. Should you be in the market for a low-cost NMR data station, or indeed a complete NMR instrument, I would give Tecmag a call.

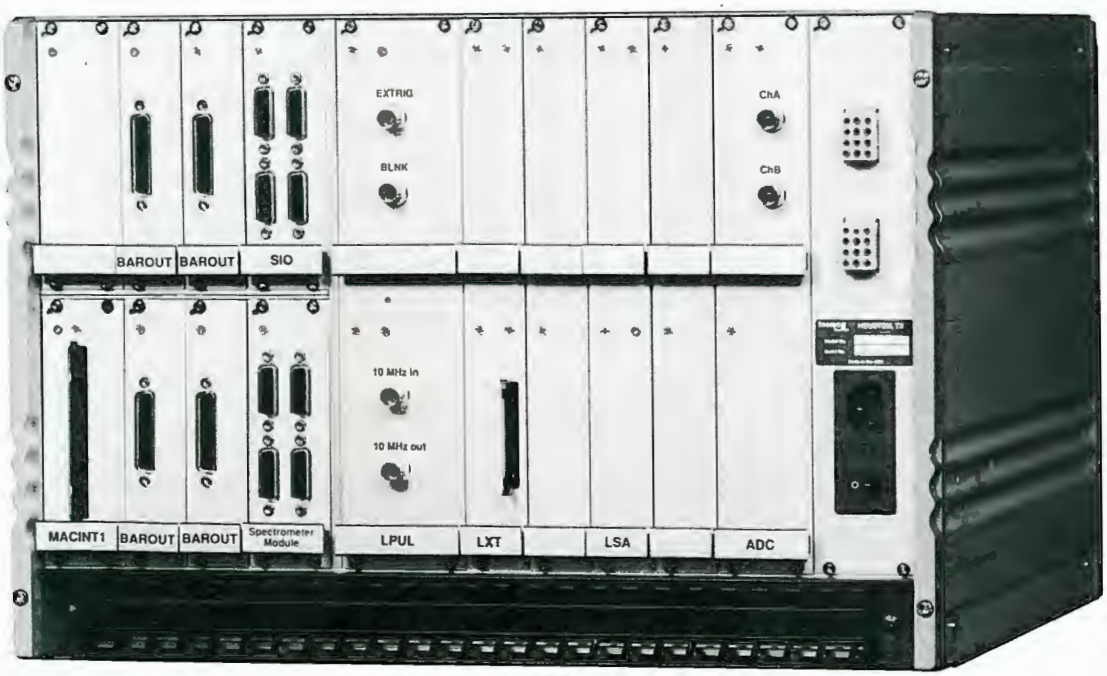
And in case you are wondering, I did not receive any special discounts, offerings, or other gratuities from Tecmag. Indeed, the company is completely unaware of this letter and will likely be quite surprised to see it in this Newsletter.

Please credit this contribution to the Raychem account.

Sincerely,

LIBRA

NMR Data Acquisition System



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Signal Averager: LSA

Although digitizer boards from other manufacturers are available for the Macintosh II, the LIBRA signal averager is the only one which allows signal averaging. The signal averager is capable of acquiring data at a rate of up to 100 ns per complex point (2 channels), depending upon the speed of the Analog-to-Digital Converter. The LSA has 128 k x 32 bits of memory. The LSA comes in different versions:

the - **S12**: 12-bit, 2.0 µs/complex point (500 kHz bandwidth).
the - **S16**: 16-bit, 3.5 µs/complex point (285 kHz bandwidth).
the - **F12**: 12-bit, 1.0 µs/complex point (1 MHz bandwidth).
the - **FTR**: 12-bit 5 MHz (10 MHz option) Transient Recorder with 8k x 16 bit memory.
the - **LTRI**: transient Recorder interface for Nicolet Explorer or Biomation Units.

For other versions, please contact the factory.

Slow IO Interface Board: SIO

The Slow Input-Output Interface Board controls all non real time operations such as setting the spectrometer frequency, decoupler frequency, Bessel and/or Butterworth filter settings, the VT controller, etc. A 12-bit general purpose register is also provided. This register is used by the Spectrometer Module to control various spectrometer functions.

Spectrometer Module

Combined with the SIO board, the Spectrometer Module emulates all output lines of a commercial spectrometer (Bruker, Chemagnetics, GE/Nicolet, Jeol and Varian). These modules minimize interfacing problems.

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UNIVERSITY

New York State Center for Advanced Technology
Biotechnology Program

130 Biotechnology Building
Ithaca, NY 14853-2703 USA

Telephone: 607 255-2300
Facsimile: 607 255-2428

March 16, 1994 (received 3/21/94)

Dr. B. Shapiro,
TAMU Newsletter
966 Elsinore Court
Palo Alto, CA
94303

Code Resource for MacNMR

Dear Barry,

We recently upgraded the pulse programmer and computer acquisition/data processing system of our home-built solid-state deuterium spectrometer. The old Nicolet console was replaced with a Libra station from Tecmag and a Macintosh Quadra 700 running Tecmag's MacNMR software. The upgrade to the new system was remarkably simple, and the new software is generally quite friendly.

Because the maximum digitization rate of the Libra station with 12 bit sampling is 1MHz, solid state spectra exhibit noticeable distortion effects if the sampling is not begun at the quadrupolar echo peak. To address this issue, we wrote software to shift our data set by a fraction of a sample dwell time. Not wanting to give up the comfortable interface and functionality of the MacNMR software, the Fractional Left Shift (FLS) software was written as a code resource. This left shift may then be performed simply by choosing a menu item within MacNMR. The command appears as any native MacNMR command. The new software is set up in a similar fashion to MacNMR's 'phase' command. There is one interactive version, which allows the user to set a left shift or have the program automatically scan for the echo peak, in addition to a non-interactive version which simply applies the last selected shift to the current data set.

Below is shown the deuterium spectrum of perdeuterated poly(methyl methacrylate). The solid line shows distortions which may arise if the acquisition is not begun exactly at the echo peak. The time difference between the echo peak and the acquisition start is 1.3 μs. We artificially set this difference 250% larger than the worst case possible to emphasize the distortion for pedagogical purposes. The dashed line is a simulated spectrum, while the broken line is the same spectrum as the first, with a left shift of 1.3 μs applied to it before Fourier transformation.

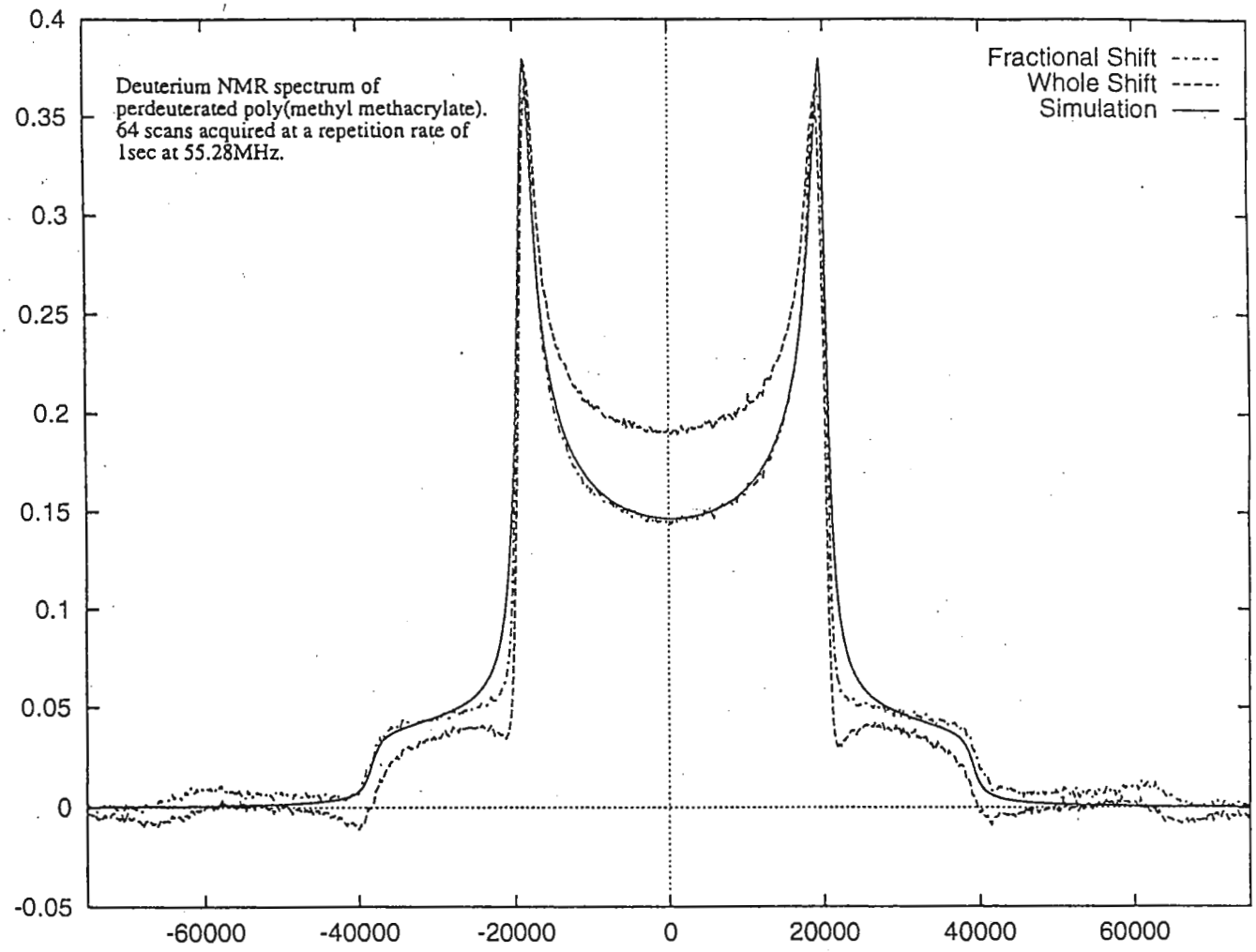
The code is available; contact Carl Michal, 153 Biotechnology Building, Cornell University, Ithaca, NY 14850; (607) 254-4853; cm10@cornell.edu.

Please credit this contribution to Aidan Harrison's account. This work was supported in part by an NSERC post-graduate scholarship (CM) and NSF MCB 9303870 (L.W. Jelinski).

Sincerely,

Carl Michal

Carl A. Michal



• • • • • POSITION SOUGHT • • • • •

I am seeking a PhD level NMR Spectroscopist opening. Over 5 years experience, including post-doc, in the analysis of small molecules, polypeptides, product formulations, and polymers using 1D, 2D, and multinuclear methods (Bruker, Varian, and Nicolet). Additional experience in coordinating projects, close NMR user group and client interactions, developing and monitoring NMR lab protocols, automation, developing analytical strategies, and organic synthesis. Willing to relocate. Please contact:

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6256 Longleaf Pine Rd
Sykesville, MD 21784
410-381-3846 (office)
410-549-2826 (home)

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

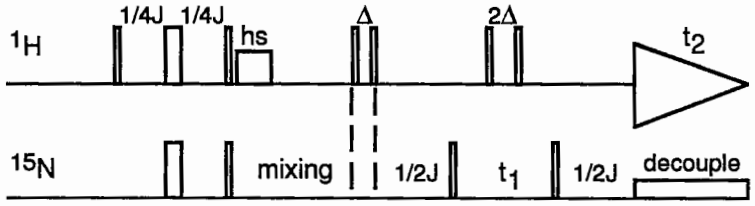
March 17, 1994
(received 3/18/94)

Measurement of amide hydrogen exchange rates in an unstructured peptide

Dear Dr. Shapiro:

Amide hydrogen exchange rates in proteins provide information on dynamics and stability of proteins. Hydrogen exchange has also been established as a powerful method to characterize intermediate species in protein folding. The degree of protection of a given amide proton from exchange is commonly expressed by the so-called protection factor, defined as ($k_{intrinsic}$ / $k_{experimental}$), where $k_{intrinsic}$ is the exchange rate of the amide proton in an unstructured state. Thus the determination of $k_{intrinsic}$ is essential to obtain a protection factor. $k_{intrinsic}$ depends on the local amino acid sequence and can be predicted by the use of factors determined with dipeptides by Englander and coworkers (1). We aimed to directly measure $k_{intrinsic}$ of longer peptides at neutral pH, where exchange rates are too fast to be measured by conventional H–D exchange methods.

We used a recently proposed method, MEXICO (2), which was originally designed for detecting fast exchanging amides in ^{13}C and ^{15}N-labeled proteins/peptides. We applied this experiment to a uniformly ^{15}N-labeled 12-residue peptide (LSMSEEDLLNAK) at neutral pH (manuscript in preparation). No evidence for secondary structure formation was found. Since NOEs are very small for a peptide of this size at the magnetic field strength used (300 MHz), the measured exchange rates have minimal contribution from NOE, thus justifying the use of the MEXICO experiment. The jump-return HMQC experiment (3) was used for the detection of amide protons to avoid reducing the water magnetization. By this method, a wide range of fast amide exchange rates can be easily determined. Except for residues near N- and C-termini, exchange rates are to a large extent in agreement with predicted values. This simple method can be easily applied to measure accurate exchange rates in short peptides with rapidly exchanging protons.



Sincerely yours,

Shohei Koide
Wolfgang Jahnke
Peter E. Wright

(1) Bai et al. *Proteins 17*, 75 (2) Gemmecker et al, *JACS 115*, 11620 (3) Roy et al. *Biochemistry 23*, 4395.

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(415) 493-5971 - *Please call only between 8:00 am and 10:00 pm, Pacific Coast time.*

Deadline Dates

No. 429 (June)	20 May 1994
No. 430 (July)	24 June 1994
No. 431 (August)	22 July 1994
No. 432 (September)	26 August 1994

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