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Newsletter

No. 226

July, 1977

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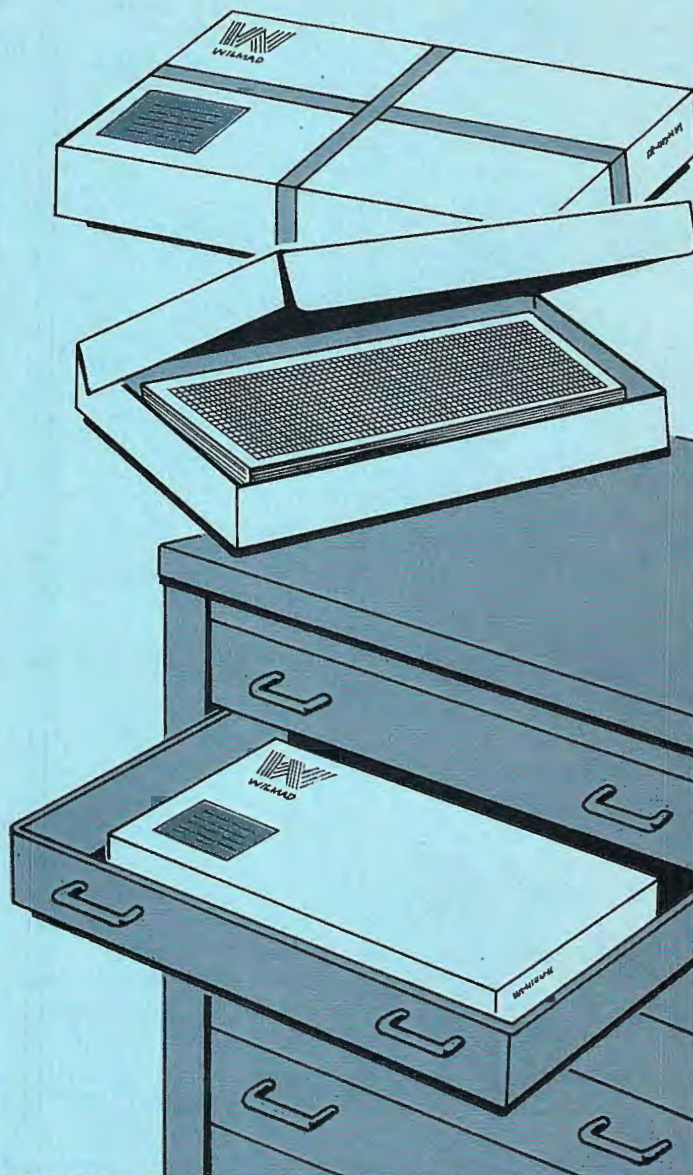
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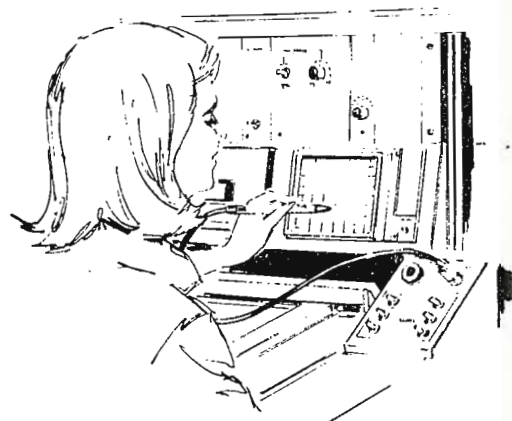
All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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DEPARTMENT OF CHEMISTRY

Sterling Chemistry Laboratory

225 Prospect Street

June 17, 1977

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

Dear Barry:

Dynamic range limitations of FT NMR instrumentation are a serious problem for researchers working with dilute solutions in solvents with substantial resonances of their own. For example, mM protein samples prepared by dialysis against a D₂O buffer frequently give a residual HDO resonance several thousand times the intensity of a protein peak of interest. A spectrometer's ability to deal with signals of large dynamic range is often limited by the number of bits in the ADC or word of the associated computer. Under these circumstances the limitation can be reduced by electronically filtering the unwanted peak from the signal at the input to the data processing system. To test the feasibility of this approach we have added a solvent filter network along with a system for single channel quadrature detection to a Bruker HX270 spectrometer having a BNC-12 Nicolet computer.

In theory the observation frequency is set to correspond to the unwanted resonance so that the phase detected spectral peak occurs at zero frequency, in the center of the quadrature spectrum. Each FID, real and imaginary, will then have the general shape of an exponential decay with a time constant T_2^* . The response of a simple RC high pass filter to a normalized exponential input with an initial voltage K across the capacitor is given by

$$S_{out} = \frac{T_2^*(1-K) + K RC}{T_2^* - RC} e^{-t/RC} - \frac{RC}{T_2^* - RC} e^{-t/T_2^*} \quad [1]$$

Assuming $T_2^* \gg RC$ we have,

$$S_{out} = (1-K) e^{-t/RC} + \frac{K RC}{T_2^*} e^{-t/RC} - \frac{RC}{T_2^*} e^{-t/T_2^*} \quad [2]$$

The first term of eq. [2] represents the transient response of the filter to the step rise of the exponential at time $t=0$ and can be eliminated by initializing the voltage across the capacitor to the initial value of the exponential ($K=1$). The remaining two terms are attenuated by a significant factor,

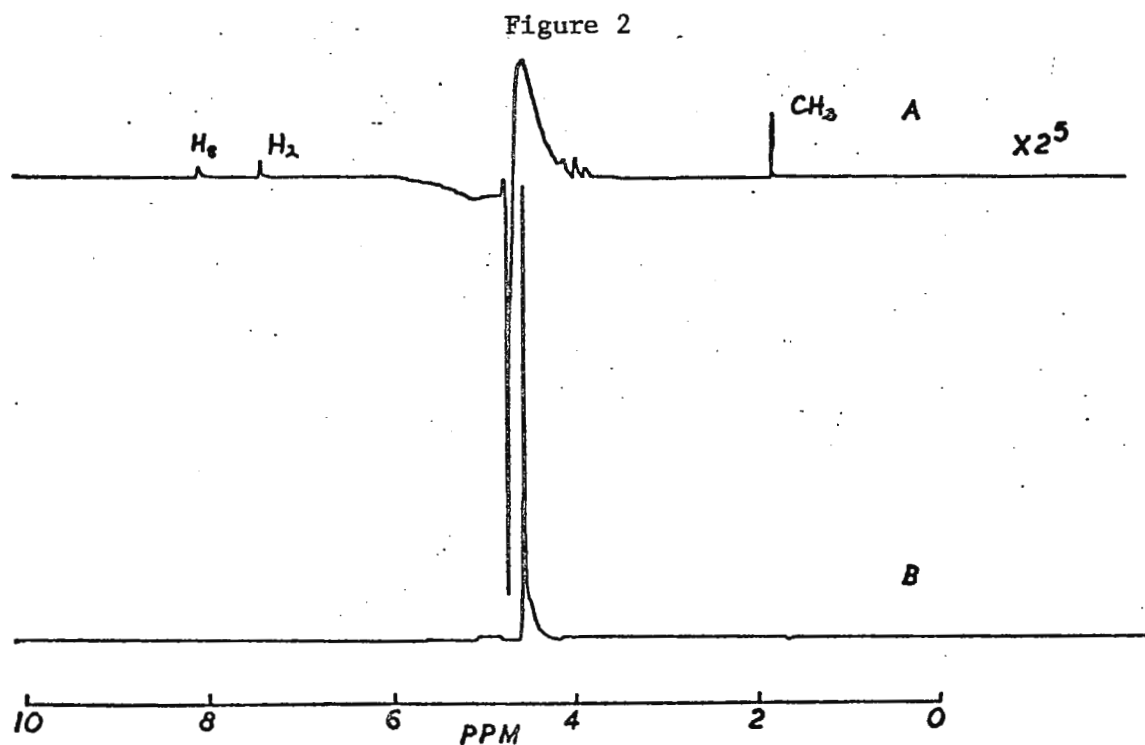
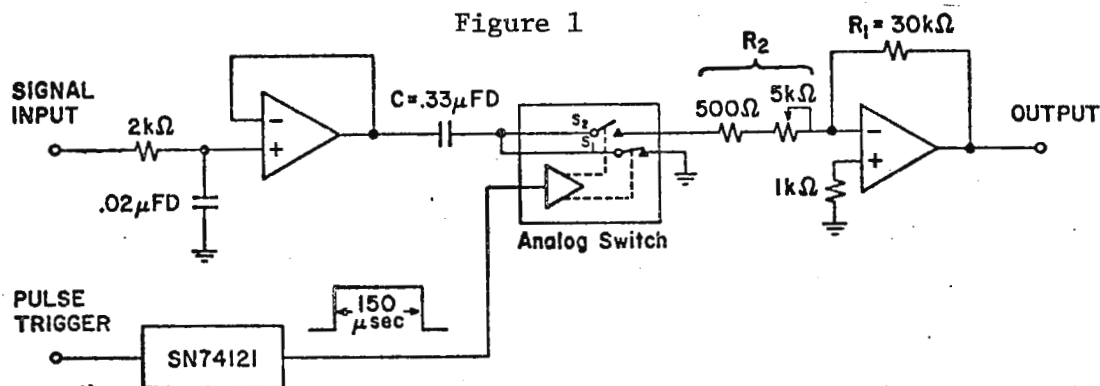
$$\frac{T_2^*}{RC} = 2\pi f_c T_2^*,$$

which can be expressed in terms of the cutoff frequency, f_c , and the transverse relaxation time T_2^* . The resulting spectrum, after complex transformation, will then consist of a broadline minus a narrow residual solvent resonance both

attenuated by $2\pi f_c T_2^*$.

The actual active RC circuit used is shown in Figure 1. The single channel quadrature method requires only one such filter whereas normal quadrature would require two.

The spectra in Figure 2 are of a $5 \times 10^{-3} M$ solution of 5'-O-phosphoryl-thymidyl-yl-(3'-5')-deoxyadenosine, d-(pTpA) prepared in 10% H_2O-D_2O . The ADC resolution was set to 10 bits and the signal amplitude was adjusted to make optimum use of the 10 bits in each case. Spectrum 2a, with solvent suppression is amplified by 2^5 and shows suppression of the H₂O peak by a factor of 40 over the normal spectrum in 2b. Suppressions of as much as a factor of 256 have been obtained under conditions where theory predicts 300.



Sincerely,

J.H. Prestegard
R.T. Pajer
I.M. Armitage

P.S. I expect to have a postdoctoral position available beginning as early as January 1 for work on NMR studies of Vesicular Membranes. JHP



THE UNIVERSITY OF NORTH CAROLINA
AT
CHAPEL HILL

Department of Chemistry

June 20, 1977

The University of North Carolina at Chapel Hill
Venable and Kenan Laboratories 045 A
Chapel Hill, N.C. 27514

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

Dear Professor Shapiro:

Variable Field ^1H T1 Measurement on an XL-100

We have installed a multinuclear modification on our XL-100 recently which is receiving much use. One application to which we have put our multinuclear NMR may be of interest to your readers.

One of our faculty had a need to measure ^1H T1's at low field with high resolution for which we had no specific instrument available. Since we needed an internal lock for stability, I calculated that lowering the field so that ^{31}P would resonate at 15.4 MHz (the deuterium lock frequency) would allow ^1H observation at 37.94 MHz. When the XL-100 magnetic field was lowered to 8.91 KG as measured with a Gauss meter and the probe was tuned for 37.94 MHz with our ^{31}P components, the proton signal from water was easily detected. After some initial tuning, the phosphorus lock signal in phosphoric acid was also easily detected. We had two problems with this set up. When the field-frequency flux stabilizer was locked, both error lights on the power supply stayed on, but this did not seem to impair the stability of the lock at all. The second problem was more serious. All of our spectra had 120 Hz sidebands. For the experiment we were performing, these sidebands did not interfere so we made no effort to remove them.

I was pleased with the success of the experiment and it seems to me that this might be a good technique for anyone who wants to study T1 changes with field.

Sincerely yours,

David L. Harris
Director, NMR Facility

DLH:jc
Enclosure

200

100

120 Hz Sidebands

Spinning Sidebands

5 sec.

2

1.5

1

.7

.5

.2

.10

.05

.01

T1 measurement on HD_2PO_4 at 25° at 37.94 MHz

$T1 = 1.06 \pm .02 \text{ sec.}$

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 Professor of Physical Chemistry and
 Head of Department.
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 Royal Society Research Professor.

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 UNITED KINGDOM
 TEL SWANSEA (0792) 25678

14th June 1977.

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

Dear Professor Shapiro,

Spin-coupling, Elections, Gambling and Incense Sticks

I thought that, as a complete change, your subscribers might be interested in a few points from my recent cross-disciplinary and historical research.

Every first-year chemistry undergraduate knows two electrons can couple to give a singlet or a triplet. As N.M.R. spectroscopists, we know the three ($s = \frac{1}{2}$) protons in a methyl group give a resultant $S = \frac{3}{2}$ and doubly degenerate $S = \frac{1}{2}$. Larger groups than this may not be common, but the six methyl protons in propane, although not fully equivalent - the distinction would be important in an anisotropic situation - are isochronous, and couple to give as resultant (degeneracies being given in brackets) : $S = 3(1)$, $S = 2(5)$, $S = 1(9)$ and $S = 0(5)$ (e.g. ref.1). The general formula for such a branching diagram is that the number of ways of obtaining a resultant spin S for N particles of spin $\frac{1}{2}$ is:

$$D_S(N) = \binom{N}{k} - \binom{N}{k-1} \equiv T_{N-k}^k \quad (1)$$

where $k = \frac{1}{2}N - S$, and $\binom{N}{k} = N!/[k!(N-k)!]$.

The proof from the Pascal triangle is straightforward.² When N is even, $N = 2n$, we have as a special case for coupling to a singlet,

$$D_0(2n) = \binom{2n}{n} - \binom{2n}{n-1} = \frac{1}{n+1} \binom{2n}{n} = T_n^n \equiv E_n. \quad (2)$$

These formulae give the degeneracy in the N.M.R. case, and the number of multiplets for open-shell atoms and for open-shell molecular electronic states. Indeed in the last case, not only does E_n enumerate the number of distinct singlets from a particular occupation of molecular orbitals, but also (for $2n$ electrons and $2n$ atomic orbitals) the number of linearly independent covalent singlet-coupled canonical valence bond structures (equal to the number of ways of joining $2n$ vertices pairwise by non-crossing lines - the famous Rumer diagrams^{3,4}).

Now the numbers of (1) are famous in several branches of pure mathematics, being known as Delannoy numbers or ballot numbers. A fine late-nineteenth-century text⁵ gives many examples of their occurrence in combinatorics, including chess-board problems. The special case of (2) is even more famous: they are (curiously) known as the Catalan numbers; they go back at least to Euler (1758 A.D.); the 1976 edition of a research bibliography lists no less than 431 references to them; and a recent article⁶ provides a non-technical introduction. I have noted with considerable surprise that the quantum-mechanical connection appears not to have been recognised hitherto, and so I propose briefly to illustrate a very small selection of examples enumerated by one or other of these two integer sequences (which can indeed be further generalised, but more on that elsewhere).

Since electrons - and protons - are sets of identical particles, this immediately suggests a connection with the Symmetric Group S_N of permutations on N objects.⁷ Indeed it is easy to show from standard formulae that, in S_N , the dimension of the irreducible representation corresponding to the partition of N into the two numbers k and $(N-k)$ is simply T_{N-k}^k ; as a special case, when N is even, $N = 2n$, and $k = n$, the dimension is E_n . My discovery of further such connections with the invariants of binary forms studied by nineteenth-century algebraists would doubtless not interest your readers. But any of you who are browsing in a library and care to glance at plate I opposite p.82 in ref.8 (dated 1878 A.D.) will be amused to see something closely resembling the Rumer diagrams (of half a century later) for cyclobutadiene and benzene portrayed, because the author felt that invariant theory ought to have some relevance to chemistry!

Why 'ballot numbers'? The term derives from the famous 'Problème de scrutin': the number of ways of counting votes in a two-candidate election with final vote L for candidate A and M for candidate B ($L \geq M$), such that throughout the count the vote of A is never less than that of B, is given by T_L^M . Not only is this identical to a nice little problem of Lucas' (ref.5) on two ranks of soldiers, and to the problem of enumerating proper Young tableaux in the theory of the Symmetric Group^{7,4}; it is also of considerable importance in the Theory of Probability.⁹ A related result, much cited in the same context,⁹ is one form of the 'Gambler's Ruin Problem' (or 'La Durée du Jeu'): Peter, who has n écus, gambles against Paul, who is infinitely rich; after each throw, one écu changes hands; the number of distinct sequences of throws, such that Peter is ruined after exactly m throws, is given by

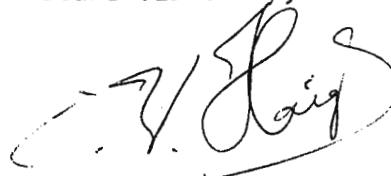
$$T_{\frac{1}{2}(m-n)}^{\frac{1}{2}(m+n)-1}$$

(provided m, n are both odd or both even; otherwise it is zero). This precise form of the result may indeed be of much later date, but I have discovered that it is implicit in a result published by Moivre in 1718 A.D.; indeed I have now expressed his complete solution of the more general problem as a double sum of ballot numbers.

For my last example, I delve back a thousand years into Japanese literature. 'The Tale of Genji', by Lady Murasaki, was published c.1004 A.D. This is the first Japanese novel; it is considered by those competent to judge such matters to be one of the world's great books; a new translation into English appeared earlier this year. Unfortunately the translations do not give the symbolic chapter-headings. This massive tome has 54 chapters, and all but the first and last have as headings patterns of five vertical incense-sticks, coloured in all the 52 distinct possible ways (52 is the fifth 'Bell number'). Let us draw a horizontal line to join incense sticks of the same colour: if we omit those with crossed lines, there remain 42, which is E_5 . As this enumerative result is valid for any number of sticks, we may call such patterns Murasaki diagrams. The figure shows the five ($=E_3$) patterns with three sticks (no crossed ones exist).¹⁰

I have now shown a simple and direct connection between Murasaki diagrams and a problem of spin-coupling. A pair of spin- $\frac{1}{2}$ particles can be coupled to a singlet (shown in my figure by an open circle) or a triplet (shown by an arrow). We then have the following result: the number of distinct ways in which N pairs of spin- $\frac{1}{2}$ particles (each pair being singlet- or triplet-coupled) can be coupled to give an overall singlet is h_N . There is a one-to-one correspondence with non-crossed Murasaki diagrams if a horizontal line between a number of incense-sticks represents triplet-pairs coupled to give an overall singlet, and incense-sticks without a tie-line represent singlet-pairs. For the case $N = 3$, this correspondence is illustrated in my figure.

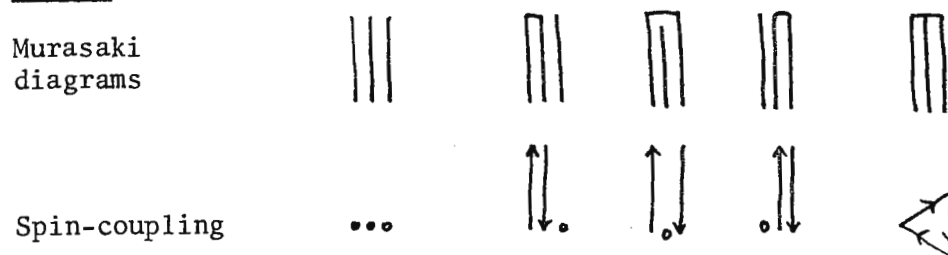
Yours sincerely,



C. W. Haigh.

1. R. C. Ferguson and D. W. Marquardt, J.Chem.Phys., 41, 2087 (1964).
2. P. L. Corio, "Structure of High-resolution N.M.R. Spectra", Academic Press, New York, 1966, p.121.
3. G. Rumer, Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Math.-Phys.Klasse, 338 (1932).
4. R. McWeeny and B. T. Sutcliffe, "Methods of Molecular Quantum Mechanics", Academic Press, London, 1969, p.67 et seq.
5. E. Lucas, "Théorie des Nombres", Tome I, Paris 1891; reprinted, Blanchard, Paris, 1961.
6. M. Gardner, Scientific American, June 1976, p.120.
7. For a discussion with special reference to its chemical relevance, see A. J. Coleman, Advances in Quantum Chemistry, 4, 83 (1968).
8. J. J. Sylvester, Amer.J.Maths. 1, 64 (1878).
9. W. Feller, "An Introduction to Probability Theory and its Applications", 2nd edn., Vol.I, Wiley, New York, 1957.
10. I am greatly indebted to Professor H. W. Gould, of West Virginia University, for introducing me to the Murasaki diagrams.

Figure





Eidg. Technische Hochschule
Zürich-Hönggerberg

Institut für Molekularbiologie und Biophysik

CH-8049 Zürich

Prof. Dr. K. Wüthrich

Tel. (01) 57 57 70

8049 Zürich, June 10, 1977

KW/as

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

Window Functions for Digital Resolution Enhancement

Dear Barry,

In a recent paper (A. De Marco and K. Wüthrich, J. Magn. Reson. 24, 201-204 (1976)), we suggested that the use of sinusoidal window functions is a particularly attractive technique for digital resolution enhancement. It was also suggested in this paper that a combination of the sine bell with additional treatments of the FID, e.g. multiplication with an increasing exponential, would yield results of practical interest. In the meantime, we have had additional experience with the use of such techniques for work with ^1H and ^{13}C NMR spectra of macromolecules, in particular proteins. For the present letter, we have selected two figures from a recent thesis (G. Wagner, Ph.D. Thesis, ETH Zürich 1977) to illustrate some results thus obtained.

Fig. 1 shows the aromatic region of the ^1H NMR spectrum of the Basic Pancreatic Trypsin Inhibitor (BPTI), a protein with molecular weight 6'500. The figure shows some spectra obtained with the combined use of multiplication of the FID with an increasing exponential and with the sine bell window. Fig. 2 shows a region of the ^1H NMR spectrum of the same protein which contains the aromatic and the amide proton resonances. It illustrates results obtained by multiplication with an increasing exponential combined with application of a phase-shifted sine bell window. Experimental details are given in the figure captions.

Sincerely yours,


G. Wagner


K. Wüthrich

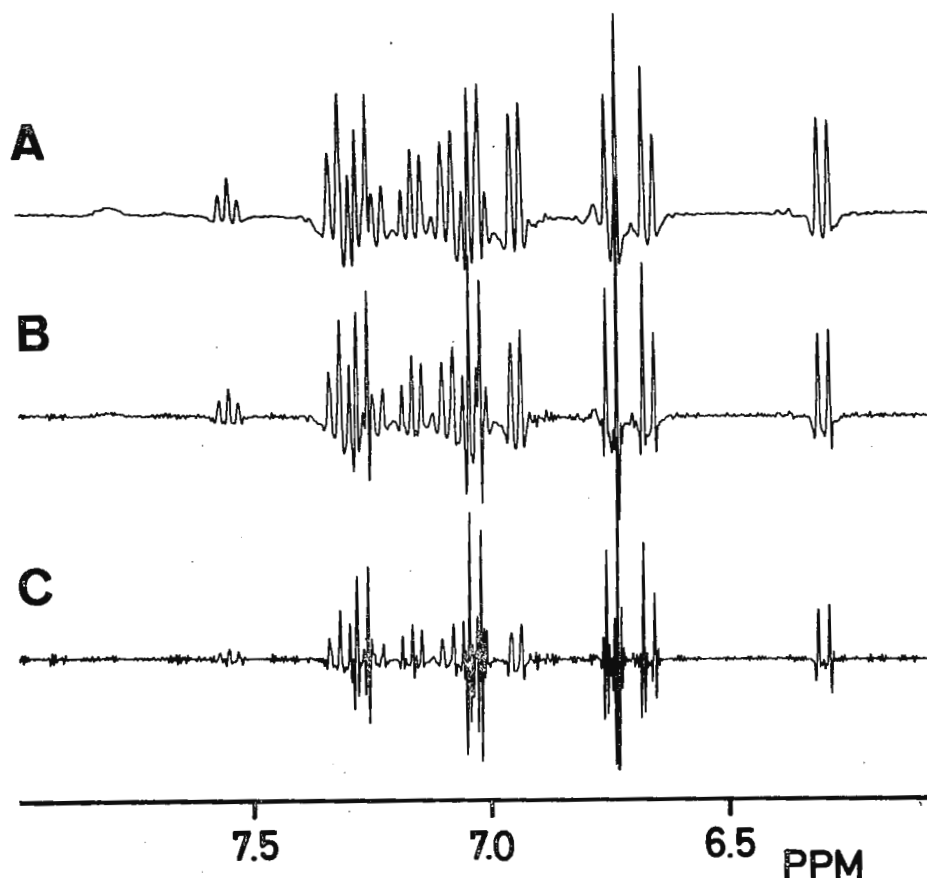


Fig. 1 360 MHz FT ^1H NMR spectra of the aromatic region of BPTI (5 mM solution in D_2O , $\text{pD} = 4.6$, $T = 56^\circ$, prior to this experiment the labile protons had been exchanged against deuterium) after accumulation of 5000 scans with an acquisition time of 0.5 sec.

- A. Digital filtering using the sine bell window function $\sin \frac{\pi t}{t_s}$, $t_s = 0.5$ sec.
- B. Same as A, but before application of the sine bell the FID had been multiplied with an increasing exponential $e^{\text{TC} \cdot t}$, with a time constant $\text{TC} = 3$ Hz (Note: Phe doublets are broader than Tyr-doublets).
- C. Same as B with $\text{TC} = 6$ Hz. The strong distortions of narrow lines are due to the apodization of the enhanced FID by the sine bell. For $T_E < t_s$, the line shape after the two digital manipulations is

$$L_1 \propto \frac{\left(\frac{\pi T_E}{t_s}\right)^2 \left(1 + \left(\frac{\pi T_E}{t_s}\right)^2 - (\Delta\omega T_E)^2\right)}{\left[1 + \left(\frac{\pi T_E}{t_s}\right)^2 - (\Delta\omega T_E)^2\right]^2 + 4(\Delta\omega T_E)^2}; \quad \frac{1}{T_E} = \frac{1}{T_2^*} - \text{TC}$$

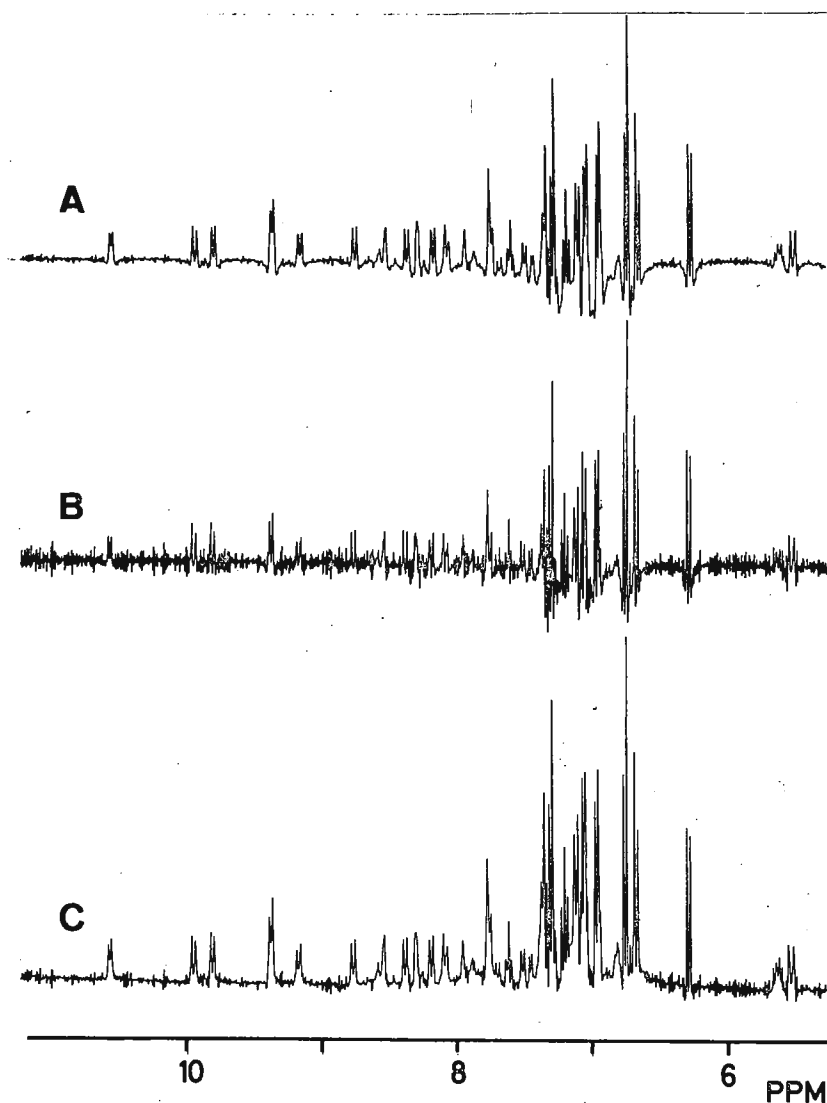


Fig. 2 360 MHz FT ^1H NMR spectra between 5.5 and 11 ppm of BPTI (5 mM solution in D_2O , $\text{pD} = 4.6$, $T = 36^\circ$), 5000 scans with an acquisition of 0.5 sec.

A. Same treatment as in Fig. 1 A.

B. Same as A, but before application of the sine bell, the FID had been multiplied by an increasing exponential with $\text{TC} = 4$ Hz.

C. Same as B, but using a phase-shifted sine bell function, $\sin(\pi \frac{t + t_0}{t_s})$, $\frac{t_0}{t_s} = \frac{1}{16}$. It is seen that without noticeable distortion of the line shape, the resolution enhancement in spectrum C is comparable to or even superior to that in spectrum A. For $T_E < (t_s - t_0)$, the resulting line shape is

$$L = L_1 \cos(\pi t_0/t_s) + L' \sin(\pi t_0/t_s)$$

$$L' = \frac{T_E \cdot (1 + (\frac{\pi T_E}{t_s})^2 + (\Delta\omega T_E)^2)}{[1 + (\frac{\pi T_E}{t_s})^2 - (\Delta\omega T_E)^2]^2 + 4(\Delta\omega T_E)^2}$$

with $L' \propto$



June 20, 1977

Professor Bernard L. Shapiro
Texas A and M University
College of Science
College Station, Texas 77843

Subject: Position Open

Dear Barry:

An opening exists in our laboratory for a person at the Bachelor's or Master's level which we hope to fill in the near future.

We are looking for someone to do semi-independent research on the physical properties of photographic dyes, polymers and other systems. Extensive use will be made of a Bruker WH-270 and a Varian CFT-20 spectrometer. There will be possibilities for development of specialized nmr techniques.

The candidate should have a good background in both organic and physical chemistry. While actual prior experience with nmr spectrometers would be helpful, it is not essential. Good ability in communication skills is important, since oral reports and written research papers will be required.

Interested qualified persons can write directly to me. Feel free to include this in the TAMU Newsletter.

Sincerely,

A handwritten signature in cursive script, appearing to read 'Mark', written in dark ink.

PMH:nc

P. M. Henrichs
Chemistry Division
Research Laboratories

Annnonce de réunion : RMN dynamique -
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Professor B.L. SHAPIRO
Department of Chemistry
TEXAS A.M. UNIVERSITY
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TEXAS 77843

Cher BARRY,

Après la première réunion organisée en 1977 par le G.E.R.M. sur le thème de la Dynamique Moléculaire dans les liquides, nous avons pensé qu'il serait intéressant de poursuivre cette expérience pour développer les contacts entre les utilisateurs des techniques de résonance. Il nous a semblé conforme à l'opinion générale de conserver à cette réunion un caractère pédagogique, tout en favorisant des discussions au niveau des applications directes des techniques de résonance à des problèmes de recherche :

Les thèmes de la réunion envisagée pour l'année prochaine :

- l'effet Overhauser Nucléaire
- phénomènes d'échanges inter- et intra-moléculaires

permettront de traiter les aspects suivants : présentation générale de l'effet Overhauser Nucléaire. Effet O.N. en présence d'échange. Mesure de l'effet O.N. par transformation de Fourier. Application de l'effet O.N. à l'étude des protéines. Théories de Kubo-Sack et de la matrice densité. Applications à la mesure de durée de vie de processus intra- et inter-moléculaires. Méthode de Forsen-Hoffmann.

Ces thèmes constituent une suite logique à ceux qui ont été développés en 1977 (Phénomènes de Relaxation). Six conférences de 1 H, six communications de synthèse de 1/2 H, une séance de communications spécifiques en nombre très limité et une table ronde sont prévues au programme de ces journées qui se dérouleront, comme en 1977,

A VICHY, les 16, 17 et 18 MARS 1978

Les conditions financières seront, en principe, les mêmes qu'en 1977 : 450 Francs. Les personnes intéressées par cette réunion sont invitées à s'adresser avant le 15 Novembre 1977 à :

G.J. MARTIN
L.C.O.P.
B.P. 1044
44037 NANTES Cédex

LE COMITE D'ORGANISATION,

C. BREYARD,	P. GRANGER,	G. MARTIN,	F. METRAS,	J. REISSE,	J.B. ROBERT,	B. ROQUET
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^oFor A60, typical usage is 4.5 kw and 60 gal/hr

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State University of New York
at Stony Brook
Stony Brook, New York 11794

Department of Chemistry
telephone: (516) 246-5050 / 5051

Stony Brook

June 30, 1977

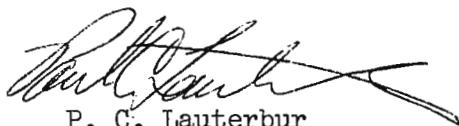
Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Dear Barry:

We should like to announce the establishment of an NIH-supported "Facility for Biomedical NMR on Radioactive Samples" at Stony Brook on September 1, 1977. The capabilities of the facility are centered around a multinuclear XL-100-12 FT spectrometer, equipped to observe ^3H , as well as most other nuclei, and an associated radiochemical laboratory. It is anticipated that the Facility will primarily be involved with the observation of tritium NMR spectra. Tritium offers some unusually interesting opportunities for investigations of complex systems because of its high resonance frequency (almost 7% higher than that of the proton), the corresponding high sensitivity, the narrow resonances possible from a spin $1/2$ nucleus that may be completely decoupled from all protons, and the absence of any measurable natural background signals. We invite inquiries from potential users, but, because of the special problems encountered in handling radioactive compounds, considerable advance planning may be required.

In connection with the establishment of the facility we are seeking a postdoctoral research associate. The person appointed will be involved in the modification of the XL-100-12 FT probe to increase the safety and convenience of experiments involving the observation of tritium NMR signals and studies of samples containing other radioactive nuclei, as well as in other hardware and software modifications and in the design and execution of various biochemical and biophysical studies. The starting salary is budgeted at \$12,000 per year, and the Facility has been funded for three years. We believe that there is an unusual opportunity here for interesting and productive work in a relatively new area of NMR, and we would like to hear from any students or post-docs who might be interested in the position.

Sincerely,


P. C. Lauterbur
Professor

L. J. Altman / ocl
L. J. Altman
Associate Professor

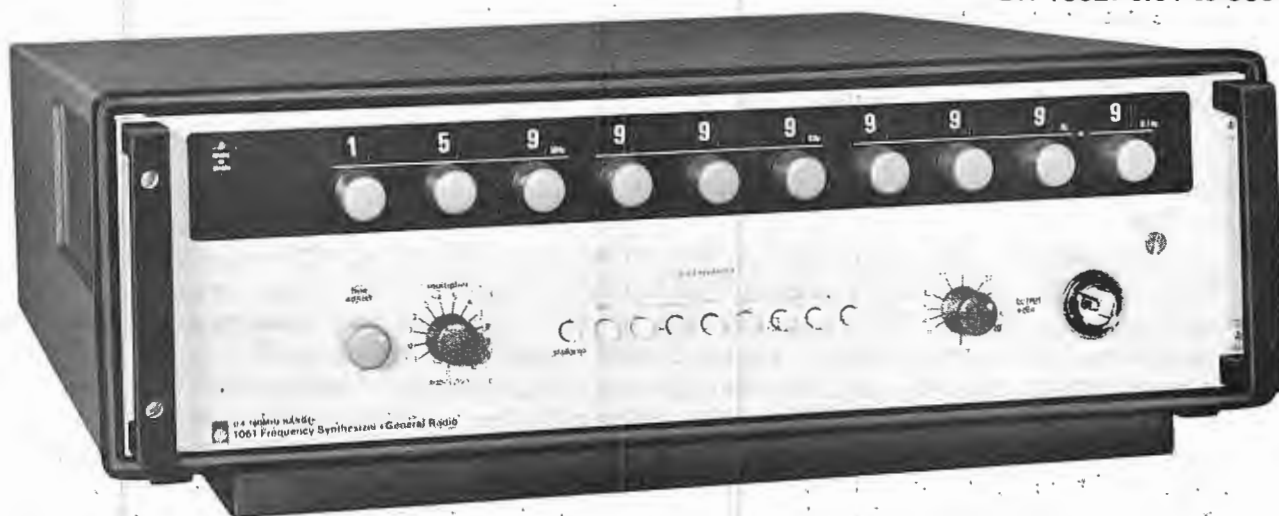
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DEPARTMENT OF CHEMISTRY

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June 21, 1977

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

"Short Sine Tables and Big Broad Lines"

Dear Barry:

We have been examining a couple of points regarding the Fourier transform in the average minicomputer which you may find interesting. When we first reported that a very strong peak which just fills memory may cause round-off error leading to noisy transforms, Bob Mooney of Sohio pointed out to me that the broader the large line the greater the possible dynamic range since its short T_2 will cause only a few channels of memory to be filled before the transform. After the transform it is the integral of the line rather than its intensity which has the value related to the amplitude of the original sine wave.

We therefore present below the results of a number of such 16K transforms for 16- and 20-bit computer words while varying the width of the large line, which is in these experiments at the Nyquist frequency.

<u>Line width</u>	<u>20-bit range</u>	<u>16-bit range</u>
0.2	59,600	3,124
1.0	145,512	12,496
2.0	227,368	15,624
3.0	355,272	15,624
5.0	693,888	30,512
10.0	867,360+	38,144
20.0	---	45,474

These data may be of use to those polymer spectroscopists contemplating examining some weak, sharp lines in the presence of some large, broad resonance.

UNIVERSITY OF MARYLAND

COLLEGE PARK, MARYLAND 20742

DEPARTMENT OF CHEMISTRY

June 30, 1977

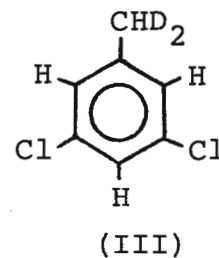
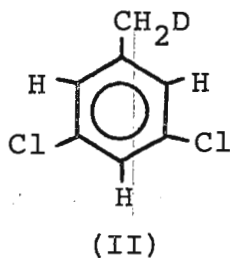
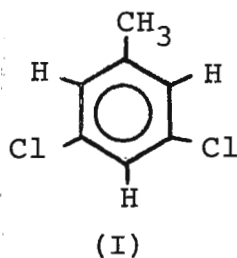
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

PROTON HOMONUCLEAR OVERHAUSER ENHANCEMENTS OF METHYL GROUPS

Dear Barry:

Although it is routine to observe homonuclear Overhauser enhancements of methine, olefinic, or aromatic protons when methyl resonances are saturated, the reverse type of enhancement has rarely, if ever, been observed above the significance level. This "asymmetry" of the NOE arises because the relaxation of the methyl protons occurs almost exclusively via pathways intrinsic to the methyl group: dipolar interactions among the methyl protons and, frequently, the spin-rotation mechanism. Substitution of two methyl protons by deuterons should reduce the dipolar relaxation rate of the lone remaining methyl proton, and make the intensity of this resonance a "nuclear Overhauser enhancement probe" of its environment.

To test this prediction, we have prepared the following compounds:



The proton T_1 's of the methyl groups are as follows: I, 6.9 s; II, 8.1 s; and III, 21.0 s (T_1 's \pm 5%). The NOE's of the methyl resonances when the resonances of the adjacent aromatic protons are saturated follow the expected trend: I, $1 \pm 2\%$; II, $3 \pm 2\%$; and III, $9 \pm 2\%$. The measurements were made at a temperature of $27 \pm 2^\circ$, on samples dissolved in $CDCl_3$. The corresponding NOE for III went up to 22% when the temperature was lowered to -40° , indicating that, as one could expect, intramolecular dipolar relaxation plays a more important role at the lower temperature.

Professor Bernard L. Shapiro
June 30, 1977

The NOE's were measured in FT mode. Our best results have been obtained using continuous, not gated decoupling. Because of the long T_1 's of the aromatic proton resonances (the proton between the two chlorines appears in each case to have a T_1 of about 150 s), extremely long delays (600 s and up) between the pulses have been used. These measurements have been facilitated by some hardware and software modifications of our XL-100 which enable the computer automatically to switch the decoupler frequency between two values, thus acquiring parallel control and enhanced spectra.

C.A. Kanagy, M. Regan, M. Mattingly, and Professor P.H. Mazzocchi have contributed to this work.

Sincerely yours,



Robert Rowan, III
Assistant Professor

RR/ssc

CONTINUED FROM P. 18

Dr. B. L. Shapiro

June 21, 1977

On another matter, we have had occasion to wonder whether the 512 or 1024 data points usually reserved in FT programs for the sine look-up table are sufficient. On running some 16 and 32K transforms for 16- and 20-bit computers we found that the transforms were identical for linear interpolation of 4096, 2048, 1024, 512, 256, and even 128-point look-up tables. Tables shorter than that, i.e. 64, 32 and 16-word tables, produced total garbage in which the spectrum could not even be observed. This fact may allow some workers trying to cram 11 pounds of you-know-what into an 8-pound bag some extra programming room. This fact may also cause those using more complex interpolation schemes or sine generation schemes to rethink their necessity since a short interpolation routine and a 128-point table seem to be all that are really necessary. These conclusions are included in a paper which has been submitted to J.Mag.Res. Preprints are available.

Regards,



James W. Cooper
Assistant Professor

ANORGANISCH-CHEMISCHES INSTITUT
DER
TECHNISCHEN UNIVERSITÄT MÜNCHEN
Univ.-Doz. Dr. F. H. Köhler

8 MÜNCHEN 2, den 28. 6. 1977
Arcisstraße 21, Postfach-Nr. 20 24 20
Ruf-Nr. (089) 2105/330/331/332 (Prof. Fischer)
333 (Prof. Fritz)
308 (Prof. Schmidbaur)

Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77 843
U.S.A.

Paramagnetic ^{13}C nmr on ferricenium ions: help from temperature dependent studies.

Dear Professor Shapiro,

the title compounds and your reminder have one thing in common, all are blue, the former being much deeper in colour. In addition ferricenium ions are paramagnetic. For some time now we have been studying organometallic radicals by means of ^{13}C nmr. An early example is the $(\text{RC}_5\text{H}_4)_2\text{Fe}^+$ system [1]. This system posed a problem in that we could not find the number of signals suggested by the ligand's symmetry, i.e. five for $(\text{C}_2\text{H}_5\text{C}_5\text{H}_4)_2\text{Fe}^+$. Instead only four resonances appeared at the spectrometer working frequency (see spectrum A).

Fig. A. ^{13}C nmr of
 $(\text{C}_2\text{H}_5\text{C}_5\text{H}_4)_2\text{Fe}^+\text{PF}_6^-$
S = acetone- d_6
temperature 316 K

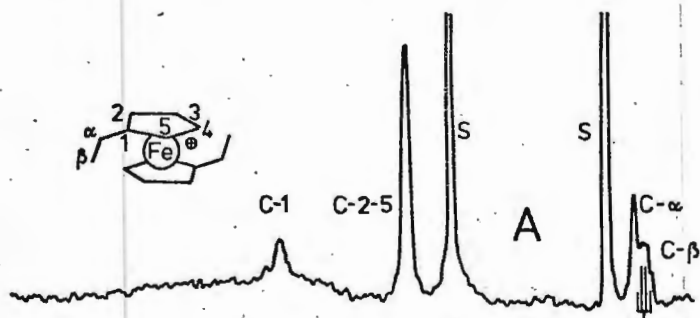
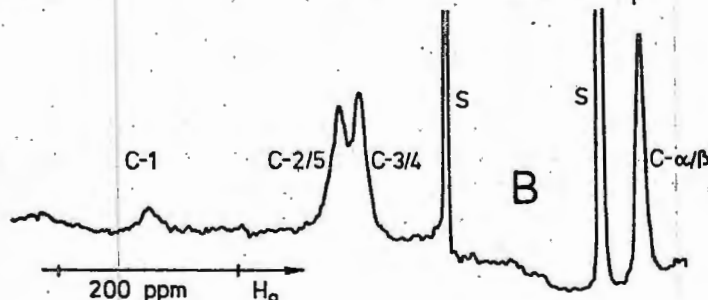


Fig. B. As fig. A
but with proton de-
coupling
temperature 215 K

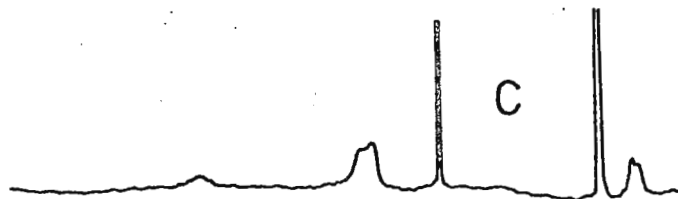


From the unsubstituted $(\text{C}_5\text{H}_5)_2\text{Fe}^+$ we know that the five-ring carbons resonate at low δ field. Together with the signal intensities in A it may be concluded that $\delta(\text{C}2/5) \approx \delta(\text{C}3/4)$.

[1] F.H. Köhler, J. Organometal. Chem. 64(1973)C27.

This is proved by a temperature dependent study: at 215 K all ring carbon signals are separated (see spectrum B). Surprisingly the α and β carbon signal now overlap. This seems to be a consequence of the fact that - contrary to what one expects - the β carbon is more shifted than the α carbon (c.f. the poorly resolved C-H quartett in A).

Fig. C. As fig. B
temperature 262 K



At intermediate temperatures all five signals may be observed (see spectrum C). Temperature variation also helps to understand the paramagnetic ^{13}C spectra of other mono and disubstituted ferricenium ions. The disubstituted species in turn allow the assignment of C2/5 and C3/4 in B and C. Details of this work will be published soon.

With this contribution I would like to support the subscription of Prof. H.P. Fritz.

Yours sincerely

Frank H. Köhn

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29.52.78 - 29.54.82 - 29.60.71

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

^1H -Spectra with ^{13}C insert.

Computer memory display on large screen.

Dear doctor Shapiro,

we would like to submit to you two practical details which could be useful to some of the readers.

1) We have found that in Bruker spectrometers of the HX series it is convenient to use the broad-band coil of the 10mm ^{13}C insert for measuring proton spectra. We use routinely this procedure for determining the proton shifts in the same n.m.r. tube in which then we perform the selective decoupling ^{13}C ^1H (without replacing the probe head).

The obtained S/N ratio is of the order of 200, which is not a problem considering the usual large concentration needed for this type of decoupling experiments. This procedure can be useful also for proton T_1 measurements due to the height of the broad band coil which results in a more homogeneous B_1 field.

2) The x and y input of the large screen scope in Bruker spectrometers of the HX series can be connected to the computer output of the NIC 1080 computer, in order to have a more detailed and persistent display of the memory content (FID and frequency spectrum after FT) which we have found useful in proton FT spectroscopy, particularly for shimming on FID. Adjustment of x and y position of the trace on the scope need a slight modification by replacing the 47 K Ω resistor connected to the slider of the adjustment pot. with a 12 K Ω resistor (see schematic of B-0A3h). The 100 K Ω resistor connected to the inverting input of the operational amplifier (X channel) is replaced with a resistor of 560 K Ω to reduce the ampl. gain. Finally in order to eliminating reciprocal interference between the x and y channels we have taken out the capacitor between ground and the base 2N3053 transistor in the x amplifier. Due to the rather narrow frequency response of the CRT the transformed spectrum must be displayed with reduced rate (i.e. in the CRT REAL TIME mode). Slight increase of the frequency response is obtainable by inserting a switch on the front panel to by-pass the y channel filter.

F. Cabassi
 (F. Cabassi)

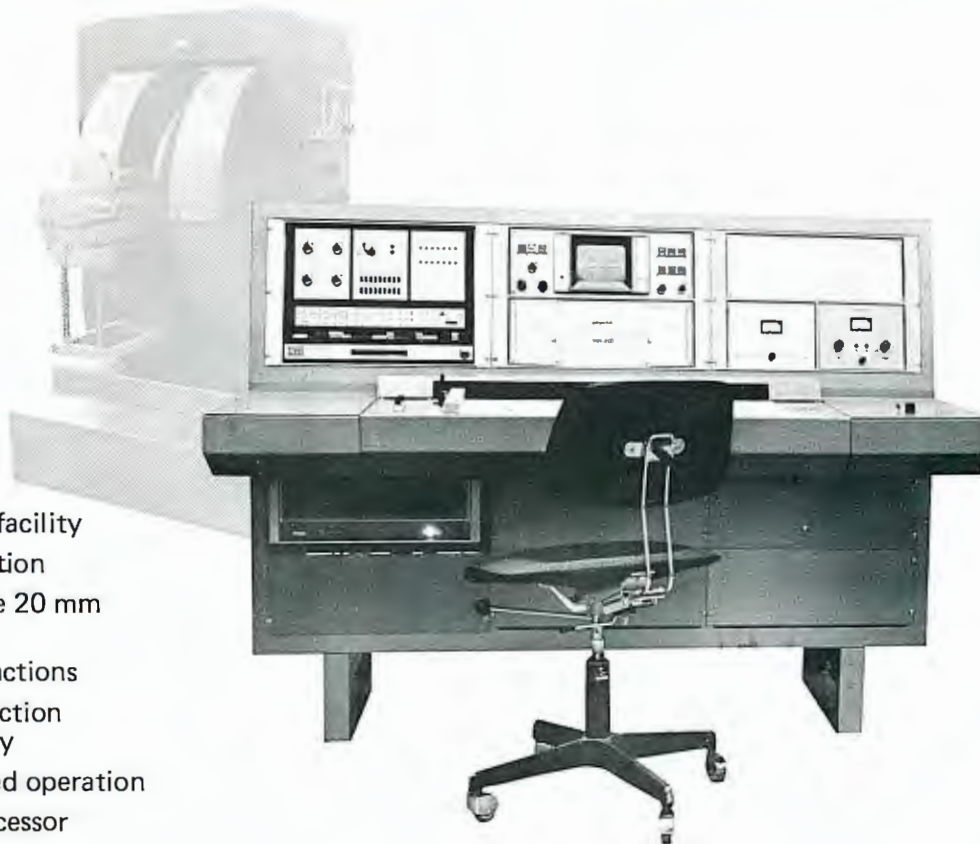
G. Gatti
 (G. Gatti)

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 Royal Society Research Professor.

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JMW/BH

21st June 1977

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

Dear Barry,

Disc System Malfunctions - a plea for help

I wish to take advantage of Claude Haigh's subscription to ask newsletter readers for advice. Over the past two years we have had regularly recurring malfunctions of our Diablo disc system (Varian L100 computer). These failures are extremely frustrating since we don't have the equipment for reloading the software package. The failures appear to be hardware failures, although an obscure software fault has not been excluded. The faults often begin with a failure to recall an FID via SYMON, a disc hardware failure or CDOS fail message being printed. Alternatively, SYMON may become corrupt. The disc heads were replaced last February and we hoped that with a reformatted and reloaded disc from Zug we might have trouble-free operation. Alas, this disc ran for only six days before malfunctioning. We have three discs and all have malfunctioned at different times. We get inconsistent results when we run the disc diagnostic test programme. Sometimes we get no errors; sometimes we get errors that don't make sense, for example:-

ERROR 076 ON UNIT 0
 CER 110001
 BAR SB 000102 IS 000102

We have made no changes to the disc software package as provided by Varian, and we carry out standard measurements of FT spectra, T_1 experiments, and make occasional use of the spin simulation programme (SIMEQ) and BASIC. If any of your readers have had similar disc problems and similar experiences with the disc diagnostic programme, I would be most grateful for any advice.

Yours sincerely,

J. M. Williams.

226-27

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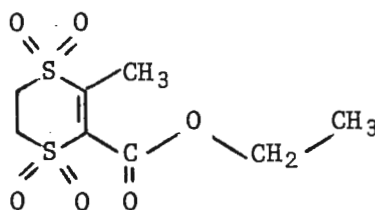
June 28, 1977

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

Dear Professor Shapiro:

Facile Synthesis of a New Compound in an NMR Tube

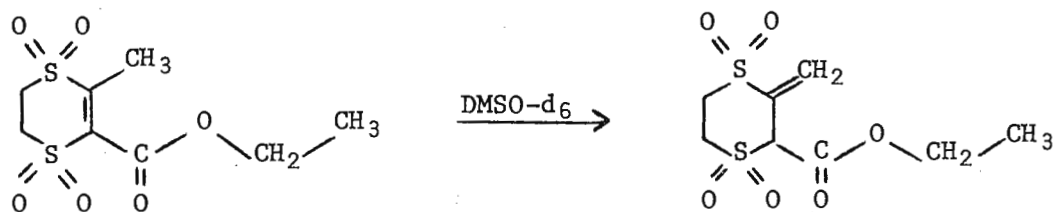
Please pardon my long relaxation time in responding to your notices - I won't waste space with my excuse, but it is a good one! Recently, I was studying the ^{13}C -NMR spectrum of the following dithiin compound:



The data were obtained from acetone- d_6 solution, in which the compound is sparingly soluble. In order to obtain off-resonance decoupled data more readily, I discovered that the compound is quite soluble in dimethylsulfoxide and so obtained my data from DMSO- d_6 solution. At this point, the following data were on hand:

<u>Chemical Shift (ppm from TMS)</u>		<u>Multiplicity (in DMSO)</u>
<u>Acetone Solution</u>	<u>DMSO Solution</u>	
159.4	162.8	singlet
147.7	139.8	singlet
136.8	131.8	triplet
64.0	69.6	doublet
50.0	63.5	triplet
49.4	50.1	triplet
14.2	49.0	triplet
12.3	14.5	quartet

Although there were other complications which are deleted for the sake of brevity, it was clear that my compound had changed as I attempted to examine it. When the chemical shifts and multiplicities were examined in more detail, it appeared that the following reaction had occurred:



The reaction is quite fast (time scale of minutes) and was almost complete before data were acquired. The reaction goes to completion, producing the single product in 100% yield. When the DMSO solution is cooled, the product precipitates out readily since it is much less soluble in DMSO than its precursor. The solvent does not appear to participate directly since no deuterium incorporation into the product is observed. So what started out as a complication in my NMR study turned out to be by far the easiest organic synthesis of my career!

Yours truly,

David G. Westmoreland
David G. Westmoreland

DGW:pt



Medical Research Council

National Institute for Medical Research
The Ridgeway, Mill Hill
London NW7 1AA

telegrams Natinmed London NW7
telex 922666 (MRCNAT G)
telephone 01-959 3666

reference

28th June, 1977.

Dr. Bernard L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, TX 077843,
U.S.A.

Dear Barry,

- 1) 3-Fluorotyrosine labelled Dihydrofolate Reductase (L. casei)
- 2) NMR Spectrometer (15" Varian Magnet) For Sale

Dihydrofolate Reductase

We have continued our NMR studies on substrate analogue binding to the enzyme dihydrofolate reductase. Even though the enzyme has a low molecular weight its ^1H spectrum is very complicated and only a few signals can be assigned to individual amino acid residues. We have overcome this problem by preparing selectively deuterated and fluorinated proteins to simplify their NMR spectra. For example, we have recently incorporated fluorine labelled amino acids into the enzyme by growing the organism on a medium containing all the normal amino acids except one which is replaced by a fluorine labelled amino acid. In this way we have prepared both 3-fluorotyrosine and 6-fluorotryptophan labelled dihydrofolate reductase. The ^{19}F spectra give well-resolved signals which can be monitored in the presence of substrate, substrate analogues and the coenzyme NADPH. The figure shows the ^{19}F proton noise decoupled (gated to avoid negative NOE) spectrum at 94.1 MHz of the 3-fluorotyrosine labelled enzyme. There are five tyrosine residues which give well-resolved resonances over a range of 2.66 ppm. Four of the five tyrosines are affected by the binding of substrate, inhibitors and/or coenzyme. We have also studied the binding of 2,4-diaminopyrimidine and p-aminobenzoyl-L-glutamate which can be considered as fragments of the inhibitor methotrexate (MTX) and these allow us to give a detailed description of the changes in chemical shift on ligand binding. Methotrexate causes a very large downfield shift of one of the resonances (N) (2.7 ppm) whereas the substrate folate has a much smaller effect suggesting a difference in binding between substrate and inhibitor. The binding of the coenzyme NADPH also causes a large downfield shift of this resonance and also a large upfield shift (1.3 ppm) of

another resonance (K). This upfield shift is most easily interpreted as resulting from a conformational change produced by coenzyme binding which moves a neighbouring residue away from this fluorine nucleus and thus removes an electric field (Van der Waal's) contribution from its overall shielding.

HA 100 For Sale

We wish to sell our HA 100. This is equipped with an excellent 15" Varian wide gap magnet and we have 5 mm + 12 mm probes for ^1H and ^{19}F operation. The instrument is in superb working order. We await reasonable (and unreasonable) offers from anyone interested.

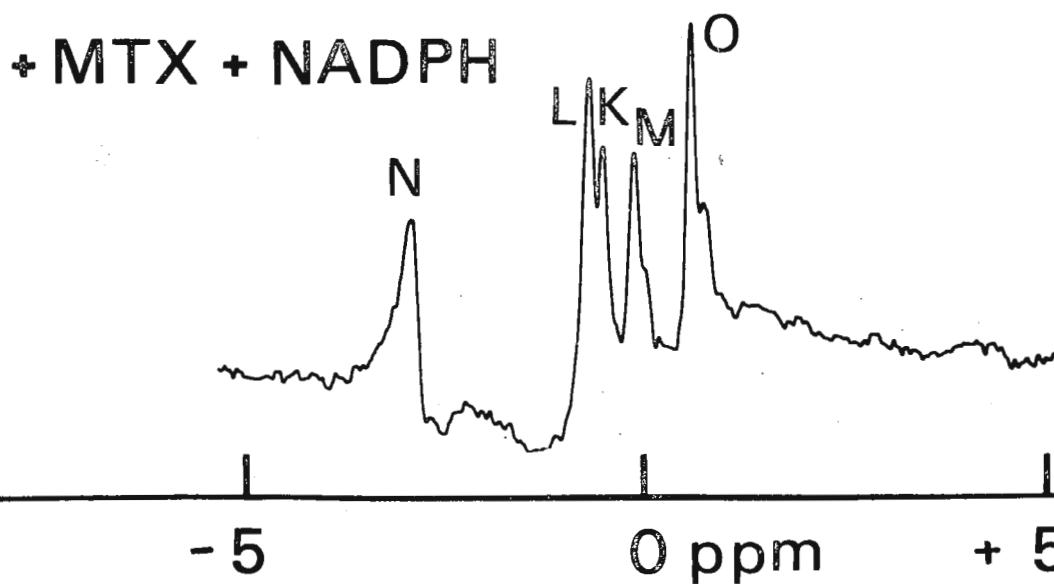
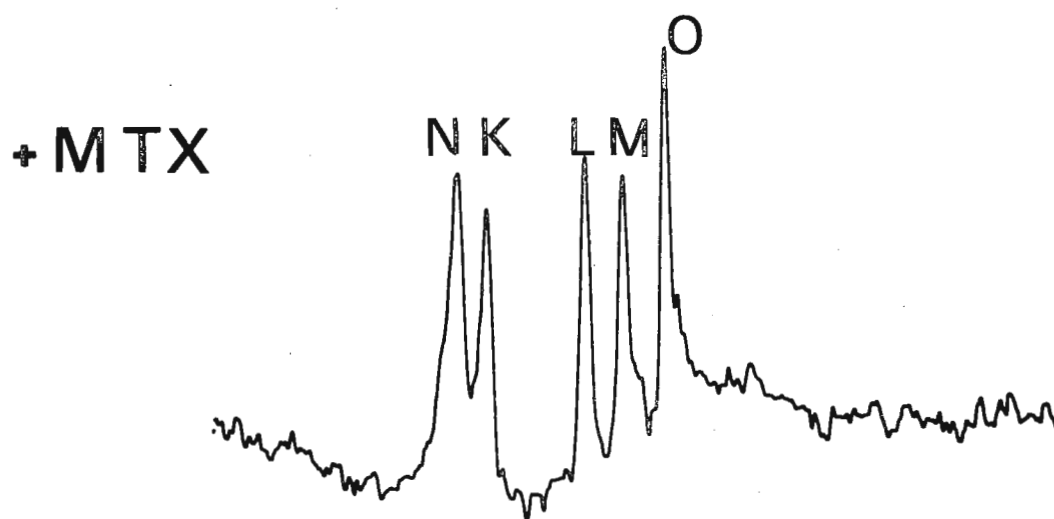
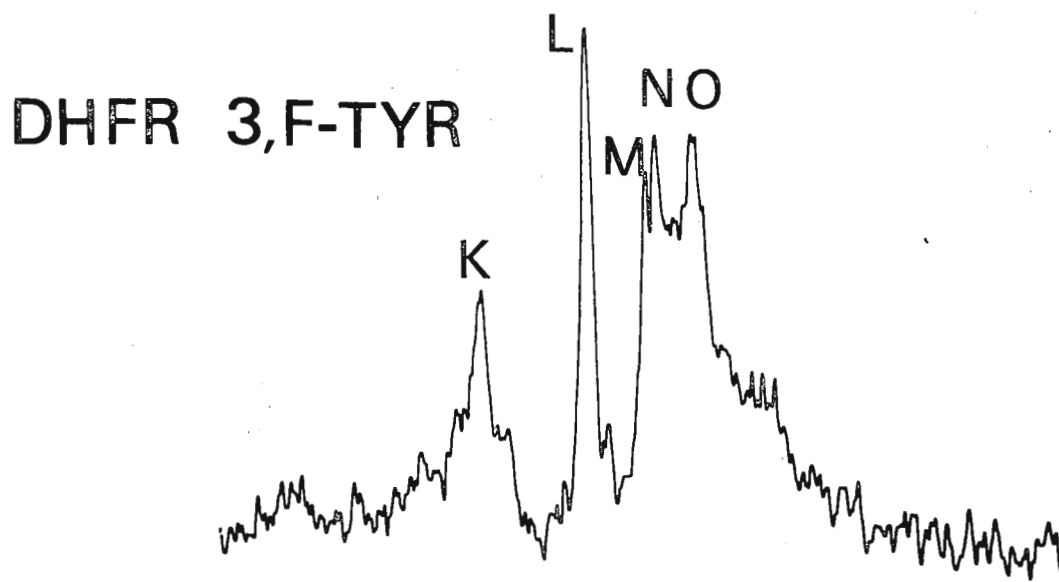
Yours sincerely,



J. Feeney.

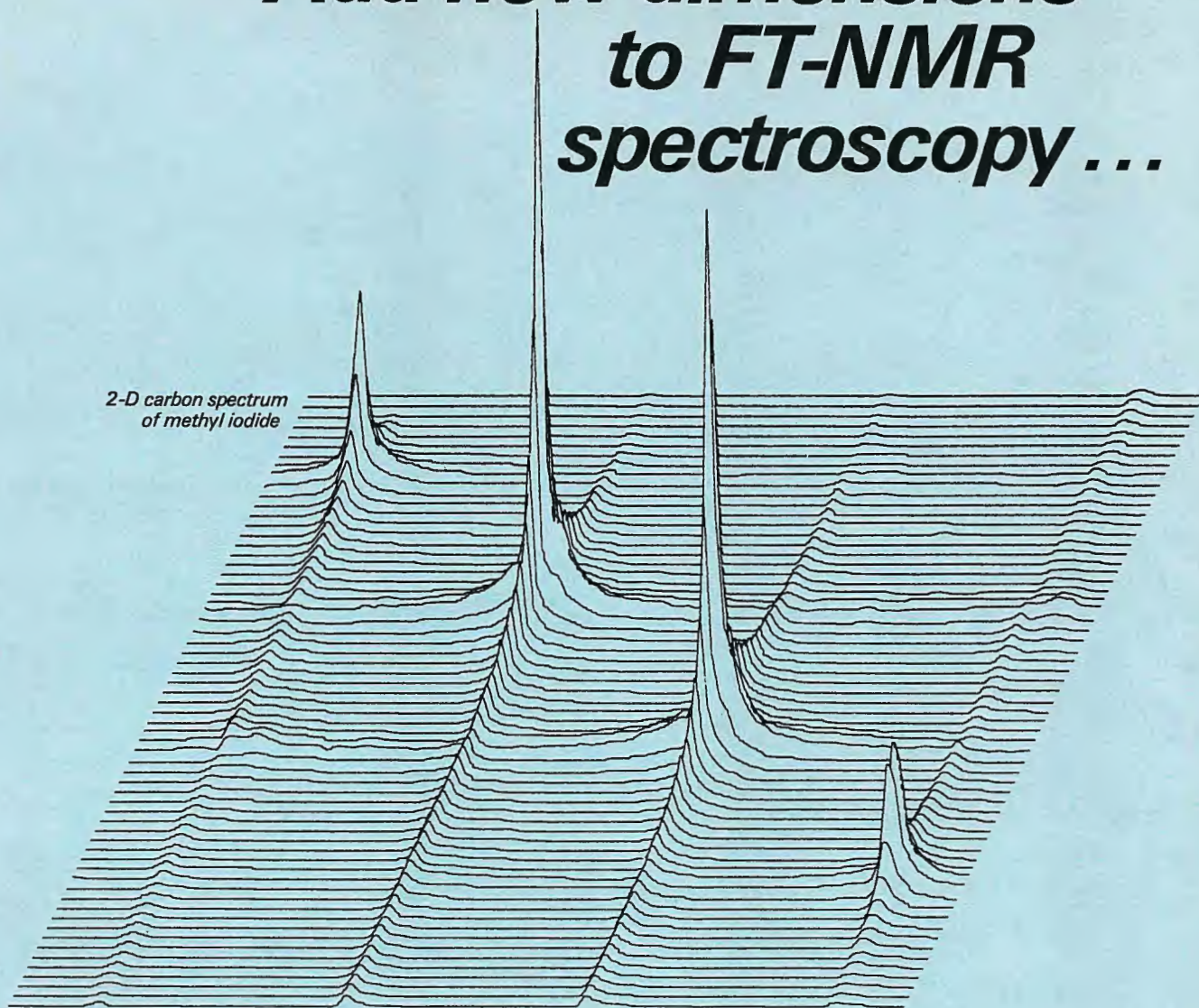


G.C.K. Roberts.



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*Broadband tunable probe —
for variable-temperature observation of nuclei
from ^{14}N to ^{31}P .*

*Broadband frequency source —
delivers 5 to 80 MHz at the turn of a dial.*

*$^1\text{H}/^{13}\text{C}$ switchable probe —
permits instant switchover.*

*Plug-in probe inserts for optimizing
receiver coil size to sample quantity.*

*24K-word computer — allows acquisition
of 16K-word data table.*

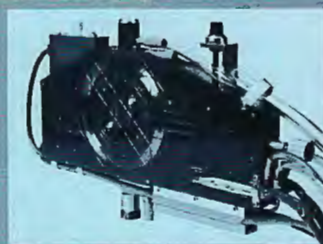
*13-Bit analog-to-digital converter —
offers extended dynamic range.*

*Software packages for 2-D spectra,
relaxation experiments.*

For further information contact your
local Varian representative or write to:
Varian Instruments, 611 Hansen Way,
Box D-070, Palo Alto, CA 94303.



Relative Intensities vs NMR Frequencies



- (DQD) DIGITAL Quadrature Detection System
- * ■ **Multi-Frequency TUNEABLE Probe observation**
- Dual Frequency probes
- 4-channel DIGITAL phase shifters (DPS)
- Comprehensive auto-stacking system
- Foreground/Background system
- Computer based pulse programmer with
Multiple Pulse Sequence Generator
- CPU Expandable to 65K words (MOS)
- 2-channel 12 bit AD/DA
- $T_{1\rho}$ /spin locking system
- Disc storage systems
- Multi-Mode HOMO/HETERO decoupling capabilities
- Multi-Mode TRIPLE Resonance
- Programmable Variable Temperature Unit
- Simplex Y/Curvature gradient controller