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No. 274

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

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DEADLINE DATES: No. 275 3 August 1981 No. 276 7 September 1981

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

May 14, 1981

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

Dear Barry:

We have been pursuing  ${}^{13}$ C studies at 50 MHz on relatively insoluble and scarce compounds using the 20 mm  ${}^{13}$ C probe on our Nicolet NT-200. In order to conserve the amount of compound used in each run and gain the maximum S/N we try to restrict the sample volume roughly to the height of the receiver coil, about 25 mm depth in the sample tube. In order to minimize inhomogeneity contributions it is desirable to have a liquid column twice the height of the receiver coil diameter. When doing pH titrations using the minimum volume extensive adjustments of the shims are required with each adjustment of the pH.

We have found that this can be avoided if one uses, as a vortex plug, an appropriate sized micro-cell filled with the same solvent used in the lower portion of the tube. For routine  ${}^{13}C$  work we use the Wilmad 20 mm OD; 18.04 mm ID tubes. Using a "micro cell" with a 18 mm OD and 15 mm height, attached to a 5 mm stem, nearly doubles the solvent column seen by the magnet. When doing titrations or other measurements involving frequent sample changes only  $z^1$  and  $z^2$  need to be touched up, making the overall operation much easier.

(INNE-

Anne H. Turner

Sincerely yours,

Carlyle B. Storm



NICOLET MAGNETICS CORPORATION A NICOLET INSTRUMENT SUBSIDIARY

July 2, 1981

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

Dear Barry:

It is my sad duty to inform your readers that, after an illness of several months, Ray Ettinger passed away on June 29th.

Although he joined Nicolet Magnetics as Marketing Manager only a year and a half ago, he had been in the "NMR game" about 20 years. He made a lot of friends during that time, and I am sure that he will be missed by all of them.

Ray will be particularly missed here at Nicolet Magnetics, where he was so very instrumental in developing our marketing efforts.

And, worst of all Barry, both you and I lost a close friend.

Sorrowfully yours,

LeRoy F. Johnson NICOLET MAGNETICS 274-2

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BMNC/81/12

Dr. Bernard L. Shapiro, Department of Chemistry, Texas A & M University, COLLEGE STATION, TX 77843, USA.

lst June 1981.

Dear Dr. Shapiro,

Another Use for Absolute Value NMR Spectra

Sometime ago we indicated the application of the Gaussian resolution enhancement function when producing absolute value spectra and suggested its use when projecting 2D-J resolved spectra to obtain a "proton-decoupled" proton spectrum (J. Magn. Reson. <u>36</u>, 277, (1979)). Our last TAMUNMR contribution (265-29) showed how to eliminate most of the information content in a <sup>13</sup>C spectrum using Gaussian deconvolution, so now here is a way to get back something that is usually considered lost forever.

Normally an FID that has overflowed is discarded completely but the figure shows what can be done in a favourable case with equal  $T_2^*$  values. The lowest trace is the normal <sup>1</sup>H FID and absorption spectrum from Me<sub>2</sub>CH.OCH<sub>2</sub>CH<sub>2</sub>.CO<sub>2</sub>H. If the ADC range is decreased by a factor of 4, then the result is the clipped FID in the centre trace and the absorption spectrum is full of nice sharp well-phased peaks that should not be there. Multiplying this FID by a Gaussian envelope to give the top FID results, if the absolute value mode is plotted, in the spectrum shown.

Yours sincerely,

DR. J.C. LINDON A. G. FERRIGE Department of Physical Chemistry

JCL/ag



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Prof. Dr. D. Ziessow

Berlin, den June 4, 1981 Tel.: (030) 314-4958 Az.:

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

#### SOLVENT DEPENDENCE OF R.F. PULSE LENGTHS

Dear Dr. Shapiro,

There are NMR experiments the success of which depends on the accurate adjustment of 90° and 180° R.F. pulses. It is quite common to determine the R.F. pulse length with a standard sample which delivers a single resonance line with a sufficiently short  $T_1$  relaxation time (f.i., in C-13 NMR, ethylene glycol has often been used for that purpose). It is then assumed that this 90° pulse length also applies to other samples, most notably in those cases where the concentration is too small in order to allow the pulse length determination. One has, however, to consider that the  $B_1$  magnetic field is dependent on the dielectricity constant of the sample. Thus, the R.F. pulse length may appreciably change with the solvent. The table below provides the interested reader with respective data.

Compound	ε(20-25 °C)	180° pulse length	
C6H12	2,0	64 µs	
<sup>с</sup> б <sup>н</sup> б	2,3	65	
СНСЈЗ	4,8	70	
CH2CL2	8,9	72	
(CH3)2CO	20,7	81	
снзон	32,7	86	
ČH <sub>3</sub> CN	37,5	90	
(CH <sup>2</sup> OH) <sup>5</sup>	37,7	94	
(сн <sub>з</sub> ) <sub>2</sub> so	46,7	96	
HMTA/H <sub>2</sub> 0 <sup>2)</sup>	80,4 (H <sub>2</sub> 0)	100	
HCONH <sub>2</sub>	111	130	

1) \* indicates observed nucleus 2) HMTA = Hexamethylentetramine

Yours faithfully,

Ride figt -6

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<sup>13</sup>C Sensitivity Test: Single transient following 90° pulse on 60%  $C_6D_6/40\%$  dioxane using the 10 mm 20-81 MHz broadband probe.



<sup>19</sup>C Sensitivity Test: Cholesteryl acetate, 100 mg/ml, 10 mm broadband probe. Transients accumulated using 90° pulses every 2.28 seconds with 0.5 Hz line-broadening.





13C Sensitivity Test: 0.02 molar cholesteryl acetate in a 16 mm tube, 200 transients.



<sup>15</sup>N Sensitivity Test: 90% Formamide in dmso-d<sub>6</sub>, 10 mm 20-81 MHz broadband probe. Upper trace: single-transient (with NOE) proton-decoupled. Lower trace: eight transients, coupled (with NOE) 8-second acquisition time, 20-second delay time.

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(TAA



Department of Chemistry

#### 6/4/81

Dear Barry:

Since I will be away from here for the next six months on leave, I thought that I had better let my next contribution come a little early as it is not clear how much NMR I will be doing in the near future.

Recently, Sievers and co-workers demonstrated the use of a binuclear complex formed from equivalent amounts of AgFOD and Yb(FOD), on the proton NMRs of a number of olefins. Of course, a natural extention of this would be to the <sup>13</sup>C NMRs. It is pretty well impossible to make much out of the complexation effects of silver ion alone on olefin chemical However, if one first notes the silver complex chemical shifts. shifts and then forms the binuclear complex in situ by the addition of the Yb(FOD), a rational picture emerges that resembles a normal LIS. Two examples of the relative Yb-LIS are given here for 0.1 equivalents of each reagent ( available incidently from Aldrich). As can be seen, the LIS falls off with distance and clearly reflects also a steric preference by the silver as to alternate sides of the double bond.



My address for the remainder of the year will be-The School of Molecular Sciences, University of Sussex, Falmer Brighton BN1 9QJ where I will be associated with Sir John Cornforth. See you next year.

Best regards,

William B. Smith



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Prof. B.L. SHAPIRO TEXAS A&M UNIVERSITY College of Science College Station, Texas 77843

Geneva, the 23th June 1981

Dear Prof. Shapiro,

In response to your note of June, 3, 1981, please find here after abstracts of recent publications of our group :

 "In situ" identification of human pathological fluids by nuclear magnetism in the earth's field"

B. Borcard, E. Hiltbrand, P. Magnin et G.J. Béné, Section de
Physique - Université de Genève - Suisse et H. Mehier et P.O. Peyrin
Biophysique - UER Médecine - Université LYON I - France
Société Française de Biophysique Paris 23.1.81

Abstract

The "in situ" determination of the free precession of protons has been observed for ascite water in the earth's magnetic field. This leads to determination of the volume of the fluid, in relative units, and to its protein concentration, in absolute units. The application of this method to medical diagnosis is promising. (to be published in the proceedings of this meeting)  Evolution of Spin-Network Relaxation Time T<sub>i</sub>, of Biological Water Protons in Haricot Seed Maturation André Grange, André Dupanloup, Pierre Descouts et Georges Béné présentée par

Pierre Grivet

C.R. Acad. Sc. Paris t.291 (15 décembre 1980)

Longitudinal relaxation time,  $T_1$  of biological water protons has been measured during Bean seed maturation. The important variation observed may be related to a physiological transition directing in the seed towards an active synthesis phase.

3) Variation of the proton relaxation in the low field range during the coagulation process

Emile Hiltbrand, Bernard Borcard, Patrick Magnin et Georges Béné(présentée par Pierre Grivet)

Abstract

The measurement of the relaxation time  $T_2$ , in the earth's field, of water protons of a recalcified plasma, leads to an identification and a description of the coagulation process. Contrary to other techniques, the relaxation measurements are sensitive to the first transformation : prothrombin into thrombin. (in press)



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ISOTOPE DEPARTMENT

#### June 4, 1981

מחלקת איזוטופים

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

#### A <sup>1</sup>H FT-PGSE Method to Study Small Molecule Diffusion in Liquid Crystalline Phases

Dear Professor Shapiro:

We have been involved in the development of a technique to study anisotropic selfdiffusion of small molecules in liquid crystalline phases utilizing proton Fourier transform pulsed-gradient spin-echo methods. We have tried to do this with a minimum of alterations to our WH-90/NIC 1180 system. The pulse sequence used is the tried-and-true Stejskal and Tanner pulsed-gradient experiment (1), holding T in the 90°-T-180°-T- echo acquisition sequence constant (to eliminate T<sub>2</sub> or homonuclear spin-spin coupling effects) while varying the pulsed-gradient duration.

The field gradients are generated by two quadropole coils, each consisting of 10 turns of 34 AWG coated copper wire, which are mounted together on a thin mylar sheet around the cylindrical glass insert of our 5 mm probe and fixed at 45° to one another in order to direct the field gradients along the z and x laboratory axes (2), as in Figure 1. The coils are driven by a simple software-controlled current pulser and produce z and x field gradients of 6 gauss/cm from 900 mA of pulsed current. This gradient strength is quite sufficient for studying small molecule diffusion, with typical pulsed gradient durations in the range of 1-100 ms. We have found that with careful winding of the coils there is sufficient room in the Bruker probes for coils of this small size, even with the addition of the D<sub>2</sub>O sample/RF coil assembly for our <sup>2</sup>H external lock.

We are quite pleased with the results. Individual self-diffusion constants on the order of  $10^{-9}m^2/s$  can be reliably determined within a few percent, while the lower limit of measureable diffusion rates (+ 20%) is roughly  $1x10^{-11}m^2/s$  for T<sub>2</sub> values of about 100 ms.

Some initial measurements of interest have concerned chloroform and dichloromethane (3 wt %) diffusion along the director,  $D_z$  and perpendicular to it,  $D_x$ , in nematic and smectic phases of 4'-n-octyl-4-cyanobiphenyl (8CB) and N-(p-butoxybenzylidene)-p-n-octylaniline (40,8). Solute self-diffusion anisotropy in the nematic phases is in the range  $D_x/D_z=0.9-0.7$ . Upon slow cooling however, the anisotropy in the smectic phases was found to be  $D_x/D_z=1-1.5$  in 8CB and from 6 to 13 in 40,8 at 26°C (typical experiments are shown in Figure 2). Whether the difference between the smectic phases of the



- Fig.1. Practical design of gradient coils. Z-gradient coil windings lie on diagonals, X-windings on axes, with alternating sign to show current direction. Z-coil on probe insert shown at right.
- Fig.2. <sup>1</sup>H FT-PGSE experiments on chloroform (3 wt.%) diffusion in 40,8 at 26<sup>o</sup>C. FT signal intensities are shown versus gradient durations ( $\delta = 1-50$  ms,  $\Delta = 85$  ms). Left, D = 0.17 ± 0.01 x 10<sup>-9</sup> m<sup>2</sup>/s perpendicular to director. Right, D<sub>z</sub> = 0.017 ± 0.003 x 10<sup>-9</sup> m<sup>2</sup>/s parallel to director.



two liquid crystals may be partially due to the effects of the interdigitated bilayer arrangement in 8CB on small molecule transport versus the more ordered monolayer arrangement in 40,8 is not yet clear. Further work may help clarify this as well as give some insight as to any effects of solute molecular shape and order and to problems of defect annealing, etc.

Please credit this contribution to the account of Dr. Rafi Poupko.

Sincerely,

Micha Moseler M. Moseley

1. E.O. Stejskal and J.E. Tanner, J. Chem. Phys. 42, 288 (1965).

2. G. Ödberg and L. Ödberg, J. Magn. Reson. 16, 342 (1974).



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

Position Available: NMR Spectroscopist/Biological Applications in Environmental Health Sciences

Dear Dr. Shapiro:

I have an opening for a research NMR spectroscopist in the Laboratory of Environmental Chemistry of this Institute.

We are seeking a Ph.D. scientist relatively young in career development but with a clear specialization in NMR spectroscopy who could assume a leadership role in planning and developing a solid program in NMR at the Institute. Our future plans include developing high field NMR capabilities for a wide range of biological applications. The incumbent would be expected to work closely with our existing program in bioorganic chemistry and mechanism elucidation.

Interested candidates should send to me an updated curriculum vitae/ bibliography and the names of two references within thirty days of the publication date of this letter.

Sincerely, M splimen

James D. McKinney, Ph.D. Chief, Laboratory of Environmental Chemistry

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62.8 MHz <sup>13</sup> C lineshape: 80% C <sub>k</sub> H <sub>s</sub> , 10 mm tube; linewidth at 0.55% peak height: 2.24 Hz	*[ <sup>13</sup> C <sub>2</sub> ]C <sub>6</sub> H <sub>6</sub> * <sup>*</sup> / <sub>1</sub> <sup>*</sup> / <sub>2</sub> ,24 Hz + 1 Hz +
(quod erat dem	onstrandum)
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JEAN L. DELAYRE, Ph.D. Research Associate in Biophysics



25 Shattuck Street Boston, Massachusetts 02115 617 · 732–1878

June 6, 1981

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

#### SODIUM NMR IMAGES OF A PACED RAT HEART

Dear Dr. Shapiro:

The first sodium images of a perfused rat heart [Science 212, 935 (1981)] showed two images at mid-ventricular level. With the acquisition of the NMR data being triggered by the heart beat, it was possible to show the difference between systole and diastole. In this case, though, one image was acquired 15 minutes after the other. Due to the short Tl value of sodium (50 msec), it is possible to collect several <u>different</u> FID's within the same cardiac cycle without loss in sensitivity. The experiment described here uses 4 FID's per cardiac cycle. A special 4-pulse sequence was designed, in which the first observed pulse is triggered externally by the heart beat and the three others occur at a regular interval after the first one. Each FID (projection) is thus a representation of the status of the heart at a particular position within the cardiac cycle.

To insure the stability of the beat, the heart was paced at a rate of 4Hz. The other experimental conditions are given below. Unfortunately, TAMU does not publish color pictures: it is thus impossible to show the images here.



Sincerely yours,

Jean L. Delayre

## GRUPPO LEPETIT SDB



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

nostro riferimento: PRD/Analytical Labs

data: Milan, June 15, 1981

AR/gt

Title - NMR spectra of erythromycins

Dear Professor Shapiro,

NMR spectroscopy has played an important role in structure determination of erythromycins, (1).

I think of interest to inform of the recent results obtained in our lab. as part of the program to completely interpret the NMR spectra of erythromycins.

In the figure the 270 MHz spectrum of erythromycin A and the enlarged zone between 0.8 and 1.5 ppm using the well known "sine bell" technique (2) are reported. All the  $CH_3$  groups are well separated and all attributions were possible by homodecoupling confirming previous assignements. Further investigations are planned in the zone 1.5-3 ppm for the near future.

Yours sincerely



Ambrogio Ripamonti

- J.R.Martin, R.S.Egan, A.W.Goldstein, P.Collum Tetra hedron vol.31 pp 1985-1989 (1975)
- 2) A.De Marco, K.Wüthrich J.M. Resonance 24, 201-204 (1976)





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JCM/YB/173-81/TAMU

Professor Bernard L.SHAPIRO Department of Chemistry Texas A and M University College Station, Texas 77843.

Dear Professor Shapiro,

#### $\gamma$ effect of trimethyltin group - Equipment for sale.

I - We have recently recorded the <sup>13</sup>C spectra of stereoisomeric organotin substituted cyclopentanes A<sub>1</sub>(trans) and A<sub>2</sub>(cis). Comparing the observed Nmr parameters (table 1) with those of parent compounds 1,1'-dicarbethoxy 3,4 dimethylcyclopentane (I) an estimate of  $\alpha,\beta$  and  $\gamma$  effects of trimethyltin group can be obtained (table 2). In return these increments can help in assigning a structure to other organotin derivatives. It could be objected that going from A<sub>1</sub> to A<sub>2</sub> not only the tin substituent but also the methylgroup suffer a configuration change. However it has been shown (1) that the  $\gamma$ -effect of the methyl group is almost independant of the position (axial or equatorial) of the group whichs allows to assign the shift entirely to the tin substituent.

II - The electronics (not transistorized) of our Jeol C6OH got dead as well as the magnet power supply. However the probe an the magnet itself are sound and for sale, as well as  $^{19}{\rm F}$  an  $^{31}{\rm P}$  decoupling attachments.

Т	а	b	1	е	1	

Carbon	Icis	I trans	Altrans	A <sub>2</sub> cis
C <sub>8</sub>	42,1	44	43,55	41,25
C <sub>9</sub>	37,5	42,6	45,83	41,25
C10	37,5	42,6	42,57	38,10
C12	14,8	18,6	14,66	11,65

Table 2

	γ (C <sub>8</sub> )	β (C <sub>9</sub> )	γ (C <sub>10</sub> )	α (C <sub>12</sub> )
A <sub>1</sub> trans	-0,45	+3,23	-0,03	-3,94
A <sub>2</sub> cis	-0,85	+3,75	+0,6	-3,15

Y.LIMOUZIN-MAIRE (

Sincerely yours.

J.NECCIARI

(1) M.CHRISTL, H.J.REICH, J.D.ROBERTS, JACS, 1971,

rue Henri Poincaré - 13397 MARSEILLE Cedex 4 tél.: 98-09-01 (570). Varian / 611 Hansen Way / Palo Alto / California 94303 / U.S.A. Tel. (415) 493-4000



June 12, 1981

Telex 34-8476

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

> Revision G XL-200 Software Release; 2D Heteronuclear Chemical Shift Correlation on Small Samples

Dear Barry:

We would like to alert XL-200 owner's that the G-release software is now available and can be ordered either from their local sales office or Sunnyvale (part #00-994501-04). A large number of new capabilities have been added, the principal one being 2D-related. To give an idea of the scale of improvements which have been made, thirty-three pages of manual have been written explaining the material. Importantly, the new software fits right into the existing "program" so that no change is necessary in the method of operation. The new material basically consists of about a dozen new pulse sequences and associated parameter sets, new user conveniences such as "manual-on-the-scope," games, optimum flip-angle and time of experiment programs, save display and return display capability (yes, the whole screen, including stacked plots), the capability of displaying stacked or contour plots, 90° pulse calibration MACRO's, HELP program, exponential fit displays, and full 2D package which lets the user do 2D for the first time with the convenience of 1D. The new pulse sequences include homo and heteronuclear 2D J spectroscopy, homo and heteronuclear chemical shift correlation, NOE correlated 2D, quadrupole echo, INADEQUATE, double-quantum <sup>13</sup>C excitation and APT.

The 2D software is particularly exciting since the disk-based nature of the XL-200 allows the very large data tables necessary for good 2D. Storage space is reserved for FID's, first, and second domain spectra. The nicest part is being able to display the 2D data directly on the screen, thus allowing choices to be made quickly. This is particularly important for contour plots, which are extremely useful in shift-correlated data.

The claim is often made that 2D is fine only when you have "buckets" of material. It does help if you have the sensitivity of the new generation XL-200 probes and I show here some data acquired on 40 mg of cholesteryl acetate using the new 10 mm broadband probe. This data resulted from a heteronuclear chemical shift correlated 2D pulse sequence with phase cycling to permit quadrature detection in both the carbon and proton dimensions<sup>1</sup>, thus minimizing data table requirements. 256 different values of the evolution period were used, collecting 480 transients for each, resulting in a total experiment time of 14 hours. The transform size was 2048 x 512. The shift ranges were 50 ppm for  $^{13}$ C and 2.5 ppm for  $^{1}$ H.

The presence of a resonance confirms a C-H bond and by extrapolation to the axes, the  $^{13}C$  and  $^{1}H$  shifts. As a bonus the splittings within a resonance are the H-H <u>homonuclear</u> splittings, even though the data were obtained at 50 MHz. In addition, I have plotted individual slices giving the proton spectrum for each proton involved in a C-H bond. Long relaxing protons can produce second-domain images and some of these are present. The phased slices permit facile identification of these, however.

Obviously, 2D experiments such as this can be very useful in structural determinations, even for  $^{13}$ C in reasonably small amounts. Proton homonuclear 2D usually only requires half-an-hour of acquisition for most experiments. The key to widespread use remains user convenience and innovation in data manipulation and output.

Sincerely yours,

Serge

George A. Gray NMR Applications Laboratory Varian Instrument Division

<sup>1</sup>A. Bax, R. Freeman and G. Morris, J. Magnetic Resonance, <u>42</u>, 169 (1981); A. Bax and G. Morris, J. Magnetic Resonance, <u>42</u>, 501 (1981).









P.O. Box 18, 6160 MD Geleen, Holland Geleen (04494) 6 91 11 ext.

Prof. B.L. Shapiro Dept. of Chemistry Texas A. and M. University College Station TEXAS 77843 USA

your letter of your reference our reference Geleen, 6874 CRO-AN 8 June 22nd, 1981 Dear Barry,

Т

In industrial ethylene-propylene (EP) co- and terpolymers an important factor that determines the crystallization capability is given by the methylene sequence length distribution.

The 75 MHZ  $^{13}$ C NMR spectrum of a particular EP copolymer, shown in fig. 1, was obtained at  $120^{\circ}$ C with a Varian SC 300 spectrometer<sup>‡</sup>. The sample concentration was 16% (w/v) in a solvent mixture of 80% 1, 2, 4-trichlorobenzene and 20% 1, 2 dideuterotetrachloroethane, which latter compound provided the internal lock signal.

Using Carman's assignments and Randall's approach (1,3), the weight and number average methylene sequence length distribution could be calculated on the basis of the measured intensities (2). The weight percentage methylene sequence length distribution has been fitted to a first order Markoff statistics, using Carman's approach (1) as can be seen in Fig. 2.

With best wishes,

Yours Asincerely

NBEMATUM

V. Mathot

lae

DSN

G. van der Velden

J. Beulen

Encl.

W79 601-7-2030

S.

1. C.J. Carman , R.A. Harington, C.E. Wilkes Macromolecules, 10, 536 (1977)

2. V. Mathot, M. Pijpers, J. Beulen, R. Graff, G. v.d. Velden, Proc. ESTA-2, September, 1981, Aberdeen

3. J.C. Randall, Macromolecules 11, 33 (1978)

\* The 75 MHZ <sup>13</sup>C NMR spectral measurements were carried out on the Varian SC-300 spectrometer of the Hoofdafdeling Maatschappelijke Technologie of TNO at Delft, The Netherlands.



Fig. 1. <sup>13</sup>C NMR spectrum of EP 45 (45 refers to the mole percentage ethylene). The notation of the CH<sub>3</sub> resonances has been changed, e.g.  $P\beta\beta$  is equal to  $P\gamma\gamma$  in ref. 1



Fig. 2. Weight-percentage methylene sequence length distributions by the NMR method and by calculation.  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_M$  are the calculated mole percentages for ethylene, the two types of propylene, and methylene. I is the inversion percentage,  $S_{n,M}$  is the number-average sequence length.



#### THE UNIVERSITY OF WYOMING LARAMIE, WYOMING 82071

June 10, 1981

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

Dear Dr. Shapiro:

#### Title: Varian HA-100 NMR spectrometer for sale.

The above instrument is for sale and includes the following items:

- 1. Console and magnet with V-3520 magnet coolant controller system
- 2. V-2100B magnet power supply
- 3. V-3506 Flux stabilizer
- 4. V-4333 100 MHz probe
- 5. V-4333 14.054 MHz probe for beryllium
- 6. 14.1 MHz RF unit for beryllium
- 7. V-4343 Variable temperature controller
- 8. Hewlett-Packard model 200 AB audio oscillator
- 9. Hewlett-Packard model 200 CD wide range oscillator

The spectrometer has been maintained and serviced regularly by a fulltime technician and is in excellent working order. We will consider any reasonable offer. Those interested may contact me or Dr. David A. Nelson at the above address or by telephone (307-766-4335 and 766-4357, respectively).

Sincerely yours,

Davil Q.

David A. Jaeger Associate Professor

#### **Oxford Research Systems Limited** Ferry Hinksey Road, Oxford OX2 0DT, England Telephone 0865 43294 Telex 83413



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

RESEARCH SYSTEMS				
Date	23 June 198	1		
Our Ref.	DS/SIE			

Your Ref.

Dear Barry,

Re: CORSET - Another Shaping Function!

When recording TMR spectra using the Topical Magnetic Resonance (TMR) technique, a line shape is obtained which is a mixture of two basic components. A set of narrow resonances originating from the region of the sample, which is in the "sensitive volume" superimposed upon a set of broadened lines from the part of the sample which is in the penumbral region outside the sensitive volume. Obviously it is advantageous to separate these and obtain the spectrum from the sensitive volume alone.

Manipulating an FID to change the final spectral characteristics is a well established NMR procedure, e.g. resolution or sensitivity enhancement and processing to remove broad lines. The latter operation is usually carried out by the convolution difference technique, but we have found that the resultant spectra can have base-line distortion and may be difficult to integrate. In TMR studies we continually have to remove broad lines (the unwanted hump!) so we have recently looked at alternative solutions to this problem.

The FID of a single line from a system in a profiled field is given by:

$$\left[\alpha \exp\left(-\frac{t}{T_{2}^{*}}\right) + \beta \exp\left(-\frac{t}{T_{2}^{*} + T_{PROF}}\right)\right] \cos\left[(\omega - \omega_{O})t\right]$$

the first term in square brackets gives the signal from the nuclei in the homogeneous region of the field yielding a narrow line in the spectrum, and the second term corresponds to the nuclei in the inhomogeneous region of the field yielding a broad line in the spectrum.

PROF .  $\alpha$  and  $\beta$  provide a measure of the number of nuclei in each region. Т the contribution to the effective transverse relaxation time caused by field inhomogeneity outside the sensitive volume.

To remove the broad component we want to multiply the total FID by a function  $\Psi$ such that:

$$\Psi\left[\alpha \exp\left(-\frac{t}{T_{2}^{*}}\right) + \beta \exp\left(-\frac{t}{T_{2}^{*} + T_{PROF}}\right)\right] = \alpha \exp\left(-\frac{t}{T_{2}^{*}}\right)$$
(1)

Directors: P. Hanley (Managing), G. B. Marson, D. Shaw Registered Office: Southampton House, 317 High Holborn, London WC1N 7NL Registered Number: 1494080

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/...

On solving equation (1) for  $\Psi$  we arrive at an analytical expression:

$$\Psi = \frac{1}{1 + \eta \exp \left(-\frac{t}{T_{\text{PROF}}}\right)} \quad \text{where } \eta = \frac{\beta}{a}$$

This function has two variables:

A value determined by the profile coils T<sub>PROF</sub>

n

- The ratio of the concentrations outside and inside the sensitive volume.

The first is known from the spectrometer's characteristics, the second is also calculable, but in practice if determined by iteration.

Being true blue spectroscopists we had to name the technique and settled on CORSET from:

Correction Of Redundant Spectral Error Terms

CORSET flattens the unwanted spectral humps Just like the corresponding waistline bumps!

We have found CORSET easier to use, particularly where integrals are required, since We have found CORSET easier to use, particular, more figure is flat and free of the line shape is more Lorentzian and the spectral baseline is flat and free of 31 distortions. A typical example is shown in the attached figure which is the spectrum and integral of an arm. The top spectra are processed spectra from the same raw data, the bottom spectra are the transforms of the raw data and the 'function' which was effectively subtracted.

A full comparison of the method is being prepared and will be submitted for publication. Preprints are available on request.

Yours sincerely,

I.D. CRESSHULL

Roy Gordon

D. SHAW

R.E. GORDON



### SYRACUSE UNIVERSITY

DEPARTMENT OF CHEMISTRY | 108 BOWNE HALL | SYRACUSE, NEW YORK 13210

TELEPHONE 315/423-2925 June 12, 1981

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

#### POSTDOCTORAL OPENING IN BIOPHYSICAL CHEMISTRY-NMR

Dear Barry:

I have a postdoctoral research position (salary \$12,500 to \$14,500 plus extensive benefits, depending on experience) available in my group at Syracuse University this coming year. The new Syracuse University NMR Laboratory will operate two fully multinuclear widebore supercon nmr spectrometer systems including a widebore Bruker WM360 as well as several low field spectrometers. The Laboratory will also operate with our WARPATH computer network, giving us unique and powerful software capabilities.

The position description follows:

PHYSICAL CHEMIST OR PHYSICAL BIOCHEMIST, "THEORETICAL AND EXPERIMENTAL STUDIES OF THE CONFORMATIONAL DYNAMICS OF DOUBLE AND SINGLE STRANDED DNA MOLECULES". We are currently obtaining an extensive <sup>13</sup>C nmr data set on carefully prepared native and denatured DNA samples. These data, obtained at dispersed magnetic fields include linewidths, T<sub>1</sub>s and NOEs, all functions of the overall and internal conformational dynamics of the DNA molecule. This project is a collaboration with Randolph L. Rill (biochemist, Florida State University) and Bob London (physical chemist, Los Alamos National Laboratory). The postdoctoral researcher will direct primary attention to the theoretical side of the project, but experimental work can be included. Programming experience in Fortran would be an asset.

I anticipate filling this position before November and urge candidates to write to me and have two letters of recommendation forwarded to me separately. I will be pleased to provide detailed information on these and other projects under way in my group. Incidently, I should point out that Syracuse is a city of <u>ca</u>. 300,000 in central New York state. Living costs in the community are quite moderate and while I cannot promise as much sun as in Florida, winter skiing is very convenient.

Yours sincerely, George C

Professor

GCL:sd

#### POSITION ANNOUNCEMENT - NMR SPECTROSCOPIST

Boehringer Ingelheim Ltd. is expanding its new Research and Development Center, located in historic Ridgefield, Connecticut, 60 miles from New York City. Additional construction now underway emphasizes Boehringer's commitment to creating a significant resource for the continuing challenge of pharmaceutical research. Combined with competitive salaries, an outstanding benefit package, and full relocation assistance, we offer an ideal environment for individual contribution and reward.

We require an MS graduate with several years of knowledge of and experience with state-of-the-art Fourier transform NMR instrumentation, and both routine and specialized analysis of molecular structure by NMR. Will consider BS graduate with proportionately wider experience.

Primary duties of the NMR Spectroscopist include:

- Operation of NMR Spectrometers (200 MHz IBM and 250 MHz Bruker) and interpretation of resulting spectra for submitting departments in Research, Development and Manufacturing
- Formulation of NMR approaches to scientists' research problems
- Active collaboration with colleagues in Analytical Chemistry and other departments
- Technical assistance with instrument maintenance
- Important qualifications include familiarity with work in a computer environment, good interactive communication skills, initiative and problem solving ability.

The position reports to the Senior Scientist, NMR.

Interested parties may contact:

Stuart E. Rapp Personnel Manager, R & D Boehringer Ingelheim Ltd. 90 East Ridge, Box 368 Ridgefield, CT 06877

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- Chemical dynamics studies.
- Temperatureprogrammed experiments.

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