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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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Postadresse: Institut für Molekularbiologie und Biophysik ETH - Hönggerberg CH - 8093 Zürich Prof. B.L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843 USA

Zurich, April 16, 1980

CIDNP for Studies of Proteins in Zurich

Dear Barry,

During the past few years Kaptein and his coworkers have introduced a CIDNP technique for studies of aromatic rings in the surface structure of biological macromolecular systems (R. Kaptein, K. Dijkstra, F. Müller, C.G. van Schagen and A.J.W.G. Visser, J. Magn. Reson. <u>31</u>, 171-176 (1978)). His success in the application of the new technique has prompted us to set up a CIDNP experiment on our 360 MHz ¹H NMR spectrometer. We have used a somewhat different probe design from that used in Groningen. This is described in this letter together with an illustration of the type of spectra recorded with our set-up.

The probe design is shown in Fig. 1. Starting from a commercial high resolution probe for 5 mm tubes a fiber-optic cable was used to bring the laser light close to the sample. There the beam is reflected by a 45° mirror through the loops of the radio frequency coil. To prevent reflection holes were drilled into the glass cylinder which supports the rf coil. The beam is thus applied perpendicular to the sample rotation axis. Fig. 2 shows a spectrum obtained with a small protein, the basic pancreatic trypsin inhibitor.

Sincerely yours,

2. Banne G.

R. Baumann

G. Wagner

K. Wüthrich





Fig. 1 Laser Photo CIDNP probe used in the Bruker HX 360 MHz instrument. A Spectra-Physics Argon Ion Laser working in the multi-line mode was used. The laser light leaving the fiber-optic light guide is reflected by a 45° mirror perpendicular to the rotation axis of the sample tube.



Fig. 2

360 MHz ¹H NMR spectra (200 Scans, acquisition time 1 sec, delay between pulses 6 sec) of a 1 mM solution of the basic pancreatic trypsin inhibitor at 22^o and pD 7.8 containing 0.4 mM Flavin S (3-N-propane-3sulfonic acid lumiflavin). A. Light spectrum (laser pulse 0.5 sec, 3 W) B. Dark spectrum C. = A. - B. The 3,5-protons of Tyr 10 at 7.07 and Tyr 21 at 6.78 ppm show a negative CIDNP effect, the 2,6-protons of Tyr 10 at 7.32 and the β -protons of Tyr 10 at 2.95 and Tyr 21 at 2.70 ppm show a positive effect.

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reference

21st April 1980.

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

Dear Professor Shapiro,

Fast Convolution Difference Technique

The convolution difference technique is in principle a three parameter technique

 $FID_{CD} = FID_{O}exp(-\pi LBI \cdot t) - K \cdot FID_{O}exp(-\pi LBI \cdot t) exp(-\pi LB2 \cdot t)$

The calculation of the CD-spectrum can be performed either in the time or frequency domain. Normally a compromise between line distortion, signal-tonoise ratio, and linewidth has to be found by trial and error. This timeconsuming process can be reduced by using the phase correction software routine as a very fast subtraction device for the determination of the optimal K-value.

This can be achieved by the following procedure:

- 1) Multiplication of the FID with LBI, FT transformation, phase correction, and storage of only the absorption part on disc.
- 2) as in 1 plus additional multiplication with LB2 before FT.
- Transfer of absorption part of spectrum 1 into the first and of spectrum 2 into the second half of the memory.
- 4) Entering the phase routine allows one to display the difference as a function of the zero th order phase parameter corresponding to K.

Yours sincerely,

K. Roth.

C. N. R.

Centro di Studio per le Sostanze Organiche Naturali

Istituto di Chimica del Politecnico

20133 MILANO - Piazza Leonardo da Vinci, 32 Tel 230845-6-7-8-9 May 7, 1980

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

Conformational Analysis in Solution of 2,7 - Dichlorothiantrene from Its

Spectrum in LICRI.

Dear Barry,

The most interesting geometrical perameter of tricyclic molecules such as thianthrene, phenothiazine, dibenzodioxine, etc., is the angle, ϕ , of folding about the axis which joins the two heteroatoms. In the case of biologically active compounds for instance, ϕ has been related to their biological activity. The molecular geometry of such substances has been studied mainly in the solid state. A few measurements of dipolar moments in solution have been performed and the angle of folding have been given, but the accuracy was rather poor. Thus the problem of the accurate determination of the angle of folding of the molecules in solution is still open.

We have investigated the possibility of an approach to this problem using the NMR Spectroscopy in liquid crystal solvents.

The results obtained for 2,7-dichlorothianthrene are satisfactory and promising enough. Since for this molecule there are nine different direct coupling constants and nine independent variables to be determined, a reasonable assumption has been made to decrease the number of independent variables, namely that the S-S axis is coincident with the z-direction and so the atoms 1 and 3 have the same x and y coordinates ($x_1 = x_3$, $y_1 = y_3$).

As shown in Table 1, the agreement between the experimental and calculated parameters for the bent structure is quite good. The calculations for the planar structure, also reported in Table 1, show that the errors between the experimental and calculated D_i are much greater. This suggests that the barrier for conformational interconversion is large enough

to let us assume that the molecule exists preferentially in two equivalent folded conformations.

Thus the molecular geometry given in Table 2 and in particular the value of angle of folding should be sufficiently correct.

Sincerely yours

iovanni Fronza fiouson Flourp

Rosanna Mondelli Nofolure Myinstell



Table 1. Experimental and computed parameters for 2,7-dichlorothiantrene dissolved in Phase IV.

Nuclei	D _{obs}	D _{obs} -	- D calc
		Planar geometry	Folded geometry
1 2	2502.155 <u>+</u> 0.099	-0.051	-0.001
1 3	49.918 <u>+</u> 0.897	-1.556	-0.164
14	14.974 <u>+</u> 0.544	-0.678	0.398
15	-21.239 <u>+</u> 0.080	-0.045	-0.021
16	-309.975 <u>+</u> 1.461	-7.290	0.414
2 3	180.937 <u>+</u> 0.805	1.183	0.034
25	-30.231 ± 0.544	1.667	0.588
26	-122.426 + 1.358	1.686	-1.009
36	-107.155 <u>+</u> 0.095	-0.618	0.001
WTRMS		0.297	0.080
Sxx		0.38090	0.34684
Szz		0.06984	-0.5703
S _{xz}		0.19570	0.1872

Table 2. Final parameters of 2,7-dichlorothianthrene.

		0
	Internuclear distances	(A)
$r_{12} = 2.555 \pm 0.022$		$r_{16} = 5.095 \pm 0.012$
$r_{13} = 5.153 \pm 0.037$		$r_{23} = 4.377 \pm 0.010$
$r_{14} = 7.293 \pm 0.037$		$r_{25} = 9.549 \pm 0.000$ (a)
$r_{15} = 8.160 \pm 0.019$		$r_{26} = 7.299 \pm 0.009$
		$r_{36} = 7.198 \pm 0.012$
Angle of folding	ϕ = 143.14 <u>+</u> 1.72 °	

(a)_{Assumed}

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EIDG. TECHNISCHE HOCHSCHULE ZÜRICH

Laboratorium für Physikalische Chemie

> Prof. Dr. R. R. Ernst mü

CH - 8006 Zürich, May 8/1980 Universitätstrasse 22 Tel. (01) 32 62 11

Prof. B.L. S H A P I R O Department of Chemistry Texas A & M University College Station, Texas 77843 U S A

Double Quantum Cross-Polarization

Dear Barry,

The observation of forbidden multiple quantum transitions has become quite fashionable during the past few years, breaking all the traditional rules of good behavior in NMR spectroscopy. For their excitation, and particularly for their detection, it is necessary to transfer coherence between allowed single quantum transitions and the forbidden multiple quantum transitions. Most double quantum experiments so far have utilized coherence transfer between transitions of the same nuclear species, e.g. deuterium double quantum transitions were observed by Pines and his research group through polarization transfer to and from the deuterium single quantum transitions.

For reasons of sensitivity, it is often more advantageous to transfer coherence to and from a different nuclear species with a higher gyromagnetic ratio. We have successfully performed experiments which demonstrate this principle through the indirect excitation and detection of nitrogen-14 double quantum transitions via proton resonance. For this purpose, we made a detailed study of Hartmann-Hahn cross-polarization between single quantum transitions of an I spin and double quantum transitions of an S spin.

The results are as follows:

- (1) Double quantum cross-polarization is indeed possible.
- (2) A modified Hartmann-Hahn condition taking into account the effective radio frequency field acting on the double quantum transition must be fulfilled for maximum transfer rate.
- (3) Surprisingly, the transfer rate for double quantum crosspolarization is four times as fast as single quantum cross-polarization under comparable conditions.

This faster transfer of coherence can be explained by the doubling of the effective dipolar interaction between I and S spins when double quantum transitions are involved, and the fact that the cross-polarization rate is proportional to the square of the second moment of the S spins due to IS coupling. A full account of these experiments and calculations will be published soon in the Journal of Chemical Physics.

Sincerely yours,

une M. Keinhold Michaul

P. Brunner

M. Reinhold

R.R. Ernst

DEPARTMENT OF BIOCHEMISTRY



THE UNIVERSITY OF ALBERTA EDMONTON, CANADA T6G 2H7

PHONE: (403) 432-5460

May 12, 1980.

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

Dear Barry:

Susceptibility Linebroadening of Lanthanide Shifted Resonances in Proteins

Lana and I have been studying the interaction of lanthanides such as Yb^{+3} with the calcium binding protein parvalbumin. The Yb^{+3} bound to parvalbumin causes very large shifts (in the slow exchange limit) in the ¹H NMR spectrum of the protein. The low field region of the 270 MHz spectrum is shown in Figure 1B. We have been interested in the relaxation behavior of these lanthanide shifted resonances and have shown that the linewidths are caused in part by the susceptibility relaxation mechanism discussed by Vega & Fiat (1) and Gueron (2). This contribution is given by

1	= 1	$\omega_{I}^{2}g_{L}^{4}\beta^{4}J^{2}(J+1)^{2}$	$\int 4\tau_{\rm R} + \frac{3\tau_{\rm R}}{2}$)
^T 2χ	5	$r^{6}(3kT)^{2}$	$\frac{1+(\omega_{\rm I}^2\tau_{\rm R}^2)}{1+(\omega_{\rm I}^2\tau_{\rm R}^2)}$	\$

and is distinguished by its dependence on field strength shown in Figure 1A for 200, 270 & 400 MHz. We have used this contribution to calculate distances of the shifted nuclei from the metal ion.

Best regards,

Lana Lee and 1

Brian D. Sykes Professor of Biochemistry

BDS/d1w

ENCL:

(1) Vega, A.J. & Fiat, D. (1976) Mol. Phys. <u>31</u>:347-355.

(2) Gueron, M. (1975) J. Magn. Reson. <u>19</u>:58-66.





B



U.S. Department of Energy Laramie Energy Technology Center P.O. Box 3395, University Station Laramie, Wyoming 82071

May 22, 1980

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

Spin-Lattice Relaxation Times Measurements For Naphtha and Light Distillate Saturate Fractions From Shale Oil

Dear Barry:

Because of the energy crisis, there is an increasing need to characterize shale oil and to explore new methods which would enable one to confirm or complement information obtained from existing methods, provide additional information and/or provide a more rapid means for accessing the properties of shale oil.

A number of applications of spin-lattice relaxation times have appeared in the literature. Most relaxation studies have been conducted on single molecular species but only a few investigations of relaxation times have been conducted on systems composed of many different molecules.

Table 1 lists the chemical shifts, carbon types and relaxation times for the major resonance signals identified in the spectra of the saturate cuts from the naphtha and light distillate fractions. A survey of the data in Table 1 shows that (1) the relaxation times for the two shale oil fractions are shorter than those measured for neat linear or branched alkanes, and (2) the 13 C relaxation times measured for the naphtha fraction are longer than the corresponding 13 C relaxation times measured for the light distillate fraction.

The relaxation times for the five carbons, C_1 to C_5 , representing the n-alkanes in the naphtha saturate fraction are 4.03, 4.22, 3.79, 3.50 and 3.27 sec., respectively. Except for the methyl carbon, a monotonic decrease is observed for the relaxation time as a function of the distance a given CH_2 group is from the end of the carbon chain. This decrease has been noted for neat n-alkanes and is due to segmental motion of the methylene carbons within molecule. The same effect is also observed for the n-alkane carbons in the light distillate saturate fraction (3.81, 3.65, 3.22, 2.52, and 2.11 sec.).

The motional properties of molecules are related to viscosity, density and molecular size and shape which in turn effect the measure relaxation time. Within a homologous series, the dipolar spin-lattice relaxation time for a given carbon atom is indirectly related to the molecular weight of the molecule. As a first approximation many of the computational problems of the molecular dynamics associated with molecules within these mixtures can be simplified if the ratio of the relaxation times for a given carbon atom within these two similar fractions is compared to the ratio of the average molecular weights of the fractions. If one further assumes that the kinematic viscosities of the naphtha and light distillate saturates are nearly identical, then the ratio of the average relaxation times, $T_1(ave)$, should be equal to the ratio of the average molecular weights, MW(ave), as shown in eq. 1.

 $\frac{T_1^{LD}(ave)}{T_1^{N}(ave)} = \frac{MW^{N}(ave)}{MW^{LD}(ave)}$

where the superscripts N and LD refer to naphtha and light distillate fractions, respectively.

It was shown by both NMR and MS that the normal alkanes (accounting for 76% of the molecular types) in the light distillate fraction have an average carbon chain-length of $\sim C_{15}$ and, thus, a higher average molecular weight than the normal alkanes in the naphtha fraction (average carbon chain-length of $\sim C_{11}$). Table 1 also lists the relaxation time ratios for each carbon common to both the naphtha and light distillate fraction as well as the overall relaxation time ratio (0.748) based upon the average of the relaxation times is in effect determining the relaxation time for the envelope of alkane carbons.

The calculated ratio of the average molecular weights based upon the average chain-length of C_{11} for the naphtha fraction and C_{15} for the light distillate fraction is 0.736. Thus, agreement between the relaxation time ratio and the molecular weight ratio is good. In fact, the results are quite surprising considering the number of assumptions made.

Sincerely,

D.a. Ner

D. A. Netzel Section Supervisor Spectroscopic Methods Section

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Chemical Shift	Accignment	<u>Spin-lattice re</u> Naphtha Fraction	laxation time (sec) Light distillate Fraction	$\frac{T_{1}^{LD}}{T_{1}^{N}(ave)}$	$\frac{MW_{C_{11}}^{N}}{MW_{C_{15}}^{LD}}$
<u>(</u> hhii)		'1(ave)	'1(ave)		
14.2	CH ₃ n-alkane (C ₁) ^a	4.03 <u>+</u> 0.09	3.81 <u>+</u> 0.10		
19.8	CH_3 Isoprenoid $(C_{13})^b$	2.77 <u>+</u> 0.21	2.22 <u>+</u> 0.09		
20.4	CH_2 Branched alkane $(C_2)^C$	3.88 <u>+</u> 0.13			
22.9	CH₂ n-alkane (C₂)	4.22 <u>+</u> 0.10	3.65 <u>+</u> 0.10		
24.7	CH ₂ Isoprenoid (C ₈)		1.85 <u>+</u> 0.07		
25.1	CH ₂ Isoprenoid (C ₄)	3.07 <u>+</u> 0.21	2.24 <u>+</u> 0.12		
28.2	CH Isoprenoid (C ₂)	4.69 <u>+</u> 0.38	3.58 <u>+</u> 0.11		
29.7	CH ₂ n-alkane (C ₄)	3.50 <u>+</u> 0.07	2.52 <u>+</u> 0.05		
30.0	CH ₂ n-alkane (C ₅)	3.27 ± 0.08	2.11 <u>+</u> 0.04		
32.2	CH ₂ n-alkane (C ₃)	3.79 <u>+</u> 0.11	3.22 <u>+</u> 0.10		
32.8	CH Branched alkane (C_4)	3.74 <u>+</u> 0.18	*		
33.1	CH Isoprenoid (C ₆)		2.69 <u>+</u> 0.10		
37.6	CH_2 Isoprenoid (C_5, C_7)	2.82 <u>+</u> 0.31	1.77 <u>+</u> 0.06		
39.7	CH ₂ Isoprenoid (C ₃)	3.00 <u>+</u> 0.21	2.34 ± 0.13		
Overall A	lverage	3.57	2.67	0.748	0.736

(,

¹³C Spin-Lattice Relaxation Times for Shale Oil Saturate Cuts

a b c

n-Alkane carbon designation based on n-decane Isoprenoid carbon designation based on farnesane Branched alkane carbon designation based on 4-methyldecane

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STATUS	DECR	RCVROFF	MOD
ASSIGN	INCR	RND	MOD4
Ability to one	the and you	v phone and r	andiror

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- Use of indirect variables for phase control
- Up to three nested loops for repetitive action Ability to execute simultaneous observe
- and decoupler pulses
- External device control under sequence control
- Use of floating-point parameter format
- User-creation of new delay, pulse, frequency, integer and flag parameters
- Flexible branching within sequences
- Ability to phase-shift within a pulse with no dead times
- Use of math statements for sequence timing calculations

- Complete separation of sequence code from parameter sets
- Dynamic variable calculations
- Use of indirect parameter labels in sequence code
- User control of parameter display characteristics
- Example sequences

Standard two-pulse Carr-Purcell-Meiboom-Gill T2 Quadrupole echo Cross-polarization Miltiple-contact cross-polarization Selective excitation Quadrature selective excitation INEPT INEPT with refocussing and decoupling PREP J-Cross polarization Refocussed J-cross polarization Noise off-resonance spin echo Inversion-recovery spin echo Multiple quantum 2D Proton-carbon correlated 2D

Heteronuclear enhanced 2D Double quantum ¹³C-¹³C spectroscopy

Acquisition Processor

- Independent 32-bit anthmetic bit-slice 32K CPU
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Almost everyone knows about the XL-200's reliability and ease of operation. But are you aware of its power, flexibility and sophisticated research capabilities?

Beneath its basic exterior, the XL-200 offers you true research power to perform complex experiments.

-

2

For example, you can frequently obtain enhanced sensitivity from low-y nuclei through INEPT sequences on the XL-200. See: Freeman and Morris, J. Amer. Chem. Soc., 102, 72 (1979); and, Morris, J. Amer. Chem. Soc., **102**, 428 (1980).

Illustrated here is a simple implementation of these ideas.

- FIFO architecture for event streaming at 50-ns resolution
- State-of-the-art LSI construction
- 50-kHz spectral widths standard
- Pulse timing to 0.1 microsecond
 Automatic filter selection
- Four observe phases under CPU control
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- Quadrature detection
- Single or double precision acquisition with 32-bit data path
- Direct periodic data save to non-volatile memory
- Transmitter and decoupler frequencies under CPU control
- Decoupler gating under CPU control
- Decoupler modulation under CPU control-CW, noise, square wave and external
- Decoupler modulation frequency under CPU control
- Decoupler high/low power switch under CPU control
- Precision decoupling power in 60 one-dB steps below one watt under CPU control
- Computer controlled VT
- Low/High and High/Low VT mode switch under . CPU control
- Up to three simultaneously arrayable acquisition parameters
- Dynamic phase selection in multi-transient data collection
- 48-bit microprogram specialized instruction set
- Noise amplitude and scaling limit checking
- Lock/VT/high noise interlocks



U.S. Department of Energy Laramie Energy Technology Center P.O. Box 3395, University Station Laramie, Wyoming 82071

May 30, 1980

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

> 22nd Rocky Mountain Conference: NMR Symposium on Macromolecules 3rd International Symposium on EPR

Dear Barry:

Enclosed is the preliminary program for the NMR and EPR Symposia to be held at the 22nd Rocky Mountain Conference in Denver, Colorado, August 11-14, 1980. Again, as was for the last two years, an excellent program has been arranged. The NMR sessions cover such topics as solid state NMR, fuels, biopolymers and polymers and the EPR symposium covers a wide range of topics including spin labels, defect centers in solids, biological systems polymers, metal complexes, ENDOR, pulsed EPR and saturate-transfer EPR. Paper will be presented in lectures and poster sessions. An invitation is extended to all readers of the Newsletter to attend the conference.

For additional information contact:

NMR: Dr. Francis P. Miknis Laramie Energy Tech. Center Laramie, WY 82071 307-721-2307 EPR: Dr. Garett R. Eaton Department of Chemistry University of Denver Denver, CO 80208 303-753-2507

Sincerely,

F. P. Miknis NMR Symposium Chairman

* Program is <u>not</u> enclosed. For specific information, write either of the two persons listed above.

Telephone OXFORD (0865--) 53322



SOUTH PARKS BOAD OXFORD OX1 30Z

From: Ad Bax Ray Freeman Gareth Morris

Dear Barry,

"INADEOUATE"

An experiment that offers an alternative to synthetic chemistry can't be all bad. We have been working on a technique for studying carbon-carbon spin couplings in natural abundance material, obviating the need for specific isotopic enrichment procedures. The idea is due to Ad Bax, who is working here in Oxford on leave from the University of Delft. It involves the momentary creation of double-quantum coherence, and in that sense is related to two-dimensional NMR.

If we wish to study the weak carbon-13 satellites which appear in conventional carbon-13 spectra, the basic problem is not so much one of sensitivity, but rather the difficulty of identifying these weak lines amid a jumble of spinning sidebands, impurity lines and spurious modulation effects in the flanks of the strong central resonance, often a result of incomplete proton decoupling. For natural abundance samples, we need consider only two coupled carbon-13 spins in the molecule, so the spectra are AX or AB, and the spin system possesses the key property of a double-quantum energy gap. We may therefore generate a double-quantum coherence, whereas the molecules with only a single carbon-13 spin can never exhibit this effect. The pulse sequence used to excite this double - quantum coherence is

$$90^{\circ}(X) - \tau - 180^{\circ}(+Y) - \tau - 90^{\circ}(X)$$

and the transfer is optimized for the cyclic condition $(2n+1)\tau = 1/(4J)$. This is similar to the condition for "INEPT" magnetization transfer. The protons are noise decoupled throughout the experiment.

Now double-quantum coherence is not directly observable, but once the information has been stored in this form, it can be retrieved by reconversion into transverse nuclear magnetization by a fourth pulse, $90^{\circ}(\Phi)$. We do this as soon as possible (after 10 microseconds) so there is no evolution of the doublequantum coherence. Discrimination against the strong central signal (M_) hinges on the fact that double-quantum coherence is uniquely sensitive to the phase Φ of this last pulse. If Φ is changed by 90° of this last pulse. If Φ is changed by 90°, the signal derived from the double-quantum coherence (M₂) shifts phase by 270°. Thus if Φ is cycled counterclockwise in 90° steps, M₂ apears to cycle clockwise in 90° steps. The receiver phase is made to follow this clockwise rotation, and all other signals cancel, having a different dependence on Φ . Phase alternation of the 180^o pulse helps suppress signals arising from pulse imperfections. The usual "CYCLOPS" is also used, giving a 32 step sequence altogether.

On our XL-200 it proved possible to achieve suppression ratios exceeding 1000 : 1, allowing a clear view of the inner satellites due to long-range C-C coupling. Longer T values are used for small couplings, and the direct couplings can be included in the same spectrum by judicious choice of T and n. The C-C couplings in pyridine are shown in the diagram. This was an early attempt; better suppression was obtained by careful attention to pulse length calibration and the establishment of a steady-state regime before starting the main sequence.

In fact the real reason for this note is to suggest a name for this technique \backslash before it becomes submerged in a mire of half-remembered pulse sequences. We wanted to get Ad's name into it, and at the same time continue the tradition of "INEPT" so we favour, INADEQUATE, the Incredible Natural Abundance DoublE Al Ray Goned QUAntum Transfer Experiment.

Kindest regards,



Bax, Freeman and Morris: Carbon-carbon splittings in pyridine observed by INADEQUATE pulse sequence. The two components of each doublet are always antiphase, up-down if n is odd, down-up if n is even.

261-20

PHILIPPS-UNIVERSITÄT MARBURG

FACHBEREICH CHEMIE

Dr.Stefan Berger



FB CHEMIE HANS-MEERWEIN-STR. D-3550 MARBURG Professor B.L.Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843

MARBURG. DEN 20.5.1980 TELEFON (06421) 28-1 DURCHWAHL: (06421) 28 5520 TELEX 482372

Dear Professor Shapiro,

DATA TRANSFER FROM A XL-100 TO A COMPUTER CENTER

-1

Advanced line shape fitting programs like DNMR5 and DAVINS (D.S.Stephenson and G.Binsch, QCPE No 365 and 378) require digitized nmr spectra as input.XL-100 owners who do not have a magnetic tape unit like the program authors could possibly punch their spectra on paper tape with the teletype using the VARIAN AID program.However,the tapes punched in this manner have a very special format and contain besides the spectral intensities the core addresses,checksums and other data which are difficult to disassemble in a FORTRAN routine.

I have therefore written a little punch program which punches the 16 bit word of the VARIAN 620 computer in two subsequent bytes on the standard 8 channel teletype paper tape.Furthermore the program punches after a leader of O300 blanks 2 bytes of a visual starting mark.The next two bytes contain the number of words to follow.Tapes in this format should be readable at any computer center.

Our procedure to transfer data from the XL-100 to the computer center now stands as follows:

a) Record spectrum and store it on disc with the SV/S command.

- b) Exit to CDOS and load the spectrum into core using the LP command.
- c) Load the punch program and enter into its two first addresses the starting and the end address of the part of the nmr spectrum of interest.
- d) Start the punch program at location 01010.
- A copy of the punch program is enclosed.

7

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001000 (000000)	• Start address	001042	(071002)	, STX	
001001 (000000)	• End address	001043	(006017)	, LDAE	
	•	001044	(101002)	,	
001003 (000777)	• Mask	001045	(002000)	, JMPM	
001000 (177777)	• Mark	001046	(001070)	,	
001005(000300)	• Leader	001047	(005041)	, TXA	
001006 (000000)	2	001050	(006147)	, SUBE	
001007 (000000)	,	001051	(001001)	,	
001010 (005002)	• TZB	001052	(005144)	, IXR	
001011 (005001)	• TZA	001053	(001002)	, JAP	
001012 (002000)	JMPM	001054	(001010)	9	
001013 (001060)	و	001055	(001000)	, JMP	
001014 (005122)	● IBR	001056	(001042)	و	
001015 (005021)	• TBA	001057	(000000)	و	
001016 (141005)	, SUB	001060	(000000)	Subroutine	Output
001017 (001002)	JAP	001061	(101101)	SEN, TTY	
001020 (001023)	و	001062	(001065)	,	
001021 (001000)	, JMP	001063	(001000)	ቃ JMP	
001022 (001011)	و	001064	(001061)	,	
001023 (001040)	, JXZ	001065	(103101)	• OAR	
001024 (001026)	و	001066	(001000)	∍ JMP	
001025 (000777)	• HLT	001067	(101060)	9	
001026 (005002)	, TZB	001070	(000000)	Subroutine	Shift
001027 (011004)	, EDA	001071	(005012)	, TAB	
001030 (002000)	, JMPM	001072	(004350)	LSRA,8	
001031 (001060)	و	001073	(002000)	JMPM	
001032 (002000)	JMPM	001074	(001060))	
001033 (001060)	9	001075	(005021)		
001034 (011001)	, LDA	001076	(151003)	, ANA, MASK	
001035 (141000)	, SUB	001077	(002000)	JMPM	
001036 (005111)	, IAR	001100	(001060)	•	
001037 (002000)	, JMPM	001101	(001000)	JMP	
001040 (001070)	9	001102	(101070)	•	
_001041 (031000)	, LDX				

Sincerely yours



International Business Machines Corporation

C. S. Yannoni K34/281 5600 Cottle Road San Jose, California 95193

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

Dear Barry:

As you know, we have been interested in applications of variable temperature magic-angle spinning (VT-MAS) for the past two years. Currently, we are engaged in the investigation of polymer dynamics in the solid state using C-13 NMR. In principle, resolution of individual carbon resonances in bulk polymers allows relaxation experiments to be performed which can be interpreted in terms of main chain and side chain motions in the solid. This is a distinct advantage over the more common proton NMR relaxation experiments where efficient spin-diffusion usually results in the averaging of the relaxation behavior over the ensemble of protons. Fundamental to the characterization of molecular motion in polymers is the measurement of relaxation data over a range of temperature. In this regard, we are using our VT-MAS capability to obtain results on the T₁ and T_{1p} behavior for the carbons in a 90% isotactic, 70% crystalline sample of poly(propylene), PP.

The initial T₁ relaxation results on PP over a temperature range from 24°C to -195°C are summarized in the Figure. The T_1 data were collected using a pulse sequence developed by Torchia¹ which allows cross-polarization enhancement of the signals. As indicated in the Figure, each of the carbons displays individual relaxation rates. The CH and CH₂ carbons have a T₁ minimum at <u>ca</u>. -110°C, nearly the same temperature as that reported by McBrierty et al.2 for the proton T₁ minimum in isotactic PP. This result suggests, if it is assumed that a C-H heteronuclear dipolar relaxation mechanism is operative, that methyl protons dominate the relaxation behavior of these carbons over much of the temperature range studied despite the $1/r^6$ dependence of the mechanism. The shorter T_1 for the CH as compared to the CH, then arises from the shorter distance between the methine carbon and methyl protons. Apparently, the contributions to spectral density in the MHz region of the frequency spectrum due to backbone motions is minor relative to the sidegroup motion.

Relaxation data for the methyl carbon could be measured only down to <u>ca</u>. -125° C; below this temperature, line broadening is so severe that the resonance is lost in the baseline. The broadening may arise, in part, from incomplete decoupling as the re-orientation rate of the methyl group about the C₃ - axis becomes comparable to the strength of the decoupling field. Substantial fluctuations of the heteronuclear dipolar coupling at the decoupling frequency reduce the decoupling efficiency. This phenomenon has been observed by Garroway for methyl groups in epoxy resins.³

A full report of the relaxation work on PP will be published within the next few months.

Bill

W. W. Fleming

Best wishes,

J. R. Lyerla

Jem

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C. S. Yannoni

- 1. D. A. Torchia, J. Magn. Resonance, 30, 613 (1978).
- V. J. McBrierty, D. C. Douglass, and D. R. Falcone, JCS Faraday Trans. II, <u>68</u>, 1051 (1972).
- 3. A. N. Garroway, Naval Research Laboratories, Washington, D.C. Private Communication.



Carbon -13 spin-lattice relaxation times for the methyl (triangles), methylene (filled circles), and methine (open circles) carbons of PP as a function of temperature at 1.4T.

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<u>(</u>;



THE UNIVERSITY OF ARIZONA

TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS DEPARTMENT OF CHEMISTRY

May 24, 1980

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

Dear Barry:

"Conformational Dependence and Signs of ${}^{5}J(H-C_{\alpha}-C(0)-N-C_{\alpha}-H)$ Coupling Constants in Peptides"

Interproton coupling constants over five bonds in the peptide moiety have been presumed (1) to depend on the associated ϕ and ψ angles in a manner analogous the the angular dependence of homoallylic H-H coupling constants (2). Our INDO-FPT MO calculations for a large number of model peptides indicates a much more complicated dependence than the simple $\sin^2\theta \sin^2\theta'$ formula(1). In fact, both signs are predicted depending on conformation whereas homoallylic coupling constants are invariably much larger in magnitude and of positive sign (2,3). Because of the small size of the five bond coupling constants, relative sign determinations are not easy. Spin tickling results for cyclo-[Gly-Tyr], which were obtained on our recently installed WM-250 spectrometer, at least convince us that the signs of the syn and anti coupling constants over five bonds in this compound are both negative. However, the analysis was not as clean as we would like, so that we will wait to report the data for a more suitable model compound now being prepared by Victor Hruby's group. Unfortunately, the MO results for the cyclo-[Gly-Tyr] indicated that the coupling constants should be opposite in sign; this appears to be one more example in which the INDO-FPT method does not give reliable results for those cases in which an amide bond is involved (4).

Sincerely yours,

Wine

Mike Barfield Steve Walter

- (1) D. B. Davies and Md. A. Khaled, J. Chem. Soc. Perkin II, 1327 (1976), and references cited therein.
- (2) M. Barfield and S. Sternhell, J. Am. Chem. Soc., 94, 1905 (1972).
- (3) Recent results for coupling over dual vicinal and homoallylic paths in a series of benzocyclobutenes and related compounds [M. Barfield and A. A. Abia, Org. Magn. Reson., 000 (1980)] seem only to be compatible with "homoallylic" coupling constants of negative sign.
- (4) K. D. Kopple, A. Ahsan, and M. Barfield, <u>Tetrahedron Lett.</u>, 3519 (1978).



The University of Sydney Department of Organic Chemistry

N.S.W. 2006

IN REPLY PLEASE QUOTE:

TELEPHONE: 692 1122.

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

May 21, 1980

Dear Barry,

ORTHOBENZYLIC COUPLING CONSTANTS. STERIC DEPENDENCE OF BOND-ORDER DEPENDENCE.

We have a very long-standing interest in benzylic coupling constants and have previously reported both on the steric dependence [TAMUNMRN <u>192</u>, 16 (September 1974)] and bond-order dependence [TAMUNMRN <u>212</u>, 7 (May 1976)] of <u>orthobenzylic</u> coupling constants. We now have some evidence that the bond-order dependence exhibits a steric dependence (i.e., there are wheels within wheels).

The three sets of data shown below were all obtained in these laboratories by Mr M.J. Collins, Dr C.J. Fallick and Miss Kazumi Hata, except, of course for the base results for toluene [Williamson, Castellano and Kostelnik, <u>J. Chem. Phys.</u>, 49, 2218 (1968)].

Set 1: The average conformation of the isopropyl group should place the benzylic proton more often in the plane of the benzene ring than is the case for the protons of the methyl group. This is confirmed by relative magnitudes of the <u>orthobenzylic coupling constants in toluene and isopropyl benzene</u>. The bondfixing pair (4-OH/3-NO₂) is seen to have more effect on <u>orthobenzylic coupling in</u> the toluene system than in the <u>isopropyl benzene system</u>, as seen from the consideration of the average values of <u>orthobenzylic coupling constants</u> (Av) and their ratios (R). Similar (although less unequivocal) conclusions can be drawn from <u>sets 2 and 3</u>. Overall, it appears that the variation with bond-order has a greater effect on benzylic protons which are more out of the plane of the aromatic ring. This is not unexpected in view of the importance of π -electrons in this type of coupling.

With best regards.

Yours sincerely (1d)

Sev Sternhell



University of Illinois at Urbana-Champaign

School of Chemical Sciences Urbana, Illinois 61801

May 28, 1980

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

Dear Barry:

New High-Resolution Solid-State Technique: NMR of Protein Crystals by Magnetic Ordering

We have recently been carrying out a series of solid-state NMR experiments aimed at obtaining structural information on condensed phases, such as proteins and membranes. We have been using field ordering techniques to produce "pseudo-single-crystal" type spectra in which we can deduce orientations of particular groups using say a ²H NMR quadrupole splitting, or ¹³C chemical shift.

For molecules in solution, magnetic energies are <<kT so only the smallest effects on NMR spectra are expected. For condensed phases however, the interactions scale up with particle size, so for even the smallest visible microcrystalline particles, large ordering effects are predicted. The following spectra illustrate what happens:



The top spectrum is a ²H powder pattern obtained from two chemically (rather than biosynthetically) ²H-labelled methyl groups in the 18,000 Dalton protein myoglobin (from <u>Physeter catodon</u>). The sample here consists of protein microcrystals, obtained by filtering off aqueous ammonium sulphate supernatant.

The bottom spectrum is obtained when the crystals are resuspended in ammonium sulphate mother liquor. The torque of the magnetic field is sufficient to perfectly align all the suspended particles and we get a single-crystal type spectrum. The crystals have the following appearance in an ordered sample of the high-spin ferric form:



Magnetic Field

X100

X200

From this and other experiments, it's possible to deduce the orientations of the labelled groups and, of course, to do relaxation studies on numerous resolved sites. Calculations show that even low levels of high spin iron (say one Fe³⁺ in 20,000,000 Daltons) will still give excellent ordering, at high magnetic field strengths.

Eric Oldfield Assistant Professor of Chemistry

Sincerely yours,

Cide

T. Mike Rothgeb

EO/TMR:msh



Department of Chemistry University of Canterbury Christchurch 1 New Zealand

22 May 1980

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

Dear Dr Shapiro,

Determination of Disubstituted Alkene Stereochemistry by means of ¹³C SFORD Spectra.

Over the past few years we have encountered a number of examples where the stereochemistry of a 1,2-disubstituted alkene could not be determined from the ¹H nmr spectrum because the alkene proton resonances were either hidden or had identical chemical shifts. An example of the latter case was afforded by

 $C_{6}H_{5} C(CH_{3})_{2} CH = CH C_{6}H_{5}$.

The ¹³C SFORD spectrum of this compound had a complex pattern for the marked carbon, as shown below, due to secondorder effects arising from the strong coupling of the two protons. Simulations of this resonance pattern using expected values for $J_{\rm HH}$ (15Hz for the (E) - isomer, and 7Hz for the (Z) - isomer), allowed a clear determination of the stereochemistry of this isomer.

Yours sincerely,

John W. Blunt WMM/ MMM/ MMM/ MMM JHH ISHE JHH 7HE



PUBLIC HEALTH SERVICE NATIONAL INSTITUTES OF HEALTH BETHESDA, MARYLAND 20205

May 22, 1980

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

> NIH/EPA Chemical Information System: New NMR Literature Search System (NMRLIT) Available

Dear Dr. Shapiro,

We are pleased to announce that the latest Component to be added to the NIH/EPA Chemical Information System (CIS) is a search system for NMR literature citations, called NMRLIT. The NMRLIT interactive retrieval programs search a data base of over 34,000 citations drawn from subject, author, and journal indices to "Nuclear Magnetic Resonance Abstracts and Index" published since 1964 by Preston Publications, Inc., Niles, IL. Currently abstracts published through December 1979 are covered.

Searching in NMRLIT is accomplished in a straightforward fashion, with AUTHOR, NUCLEUS, SUBJECT and JOURNAL searches. Up to three authors' names are retained from the original article along with the journal name, volume and page reference. The subject coding, done by the NMR Abstracts Board of Editors at the time of abstract preparation, covers some 150 categories ranging from nmr parameters (e.g. chemical shifts, coupling, relaxation times), experimental techniques (e.g. multiple resonance, variable temperature, pulse studies) to characterizations of the substances studied. Each NMRLIT citation gives the Preston Abstracts number for easy reference to the published abstract, and lists a phrase descriptive of the NMR content of the article. Perhaps the most useful aspect of the NMRLIT retrieval system is the NUCLEUS search illustrated in the example below. Citations tungsten are retrieved with only 3 commands and for a total for cost of under \$2.

> NMRLIT Example: (User input is underlined)

NIH-EPA CIS (Version 3.7) 10:56 8-May-80

Component Mnemonic? (H for HELP): <u>NMRLIT</u>

NMRLIT - NMR Bibliographic Search System-Version 2.00/2.0 Latest news for NMRLI . . . 5 May 80; Getting Started With NMRLIT NMRLIT Search System

Option? <u>NUC</u>

Nucleus Search Enter element symbol preceded by isotope mass if known Nucleus: W

(D)irect/(I)ndirect/(B)oth - (D)? B

File 1 has 42 entries Nucleus = W measured directly and/or indirectly Nucleus:___

Option? <u>TYPE 1</u>

All Preston Abstract years (Y/N) (Y)? N

Enter desired years - Last 2 digits only Years: <u>78 79</u>

ABS # = 790786 ACERETE HAMMER BAKER TUNGSTEN; 183-W NMR; TUNGSTATES J. AM. CHEM. SOC. VOL = 101 PAGE = 0267

ABS # = 790355 BROWNSTEIN FLUORINE BRIDGING CAN. J. CHEM. VOL = 056 PAGE = 0343

ABS # = 780400 MALISCH ALSMANN 1-H, 31-P; (C5H5) (CO)3M-PXCL2, M=CR,MO,W; X= NIL,S,SE ANGEW. CHEM. GERMAN ED. VOL = 088 PAGE = 0809

ABS # = 780397 ALT PHOTOCHEM. ADDN. OF ACETYLENE TO (CO) 3-CP.-CH3-M (M=MO, W); 1-H; 13-C ANGEW. CHEM. GERMAN ED. VOL = 088 PAGE = 0800

ABS # = 780394 ANDERSEN GALYER WILKINSON DITUNGSTEN COMPLEX WITH BRIDGING CARBYNE UNIT; 13-C ANGEW. CHEM. GERMAN ED. VOL = 088 PAGE = 0692

ABS # = 780392 FISCHER KALDER FRANK PENTACARBONYL (3-DIMETHYLAMINO-3PHENYLALLENYLIDENE) TUNGSTEN; 13-C; J(W,C) ANGEW. CHEM. GERMAN ED. VOL = 088 PAGE = 0683

Option? <u>TYPE 1/2/790355</u>

ABS # = 790355 BROWNSTEIN FLUORINE BRIDGING CAN. J. CHEM. VOL = 056 PAGE = 0343F NUCLEI (DIR. OBS.); APPLICATIONS ; HIGH RESOLUTION; SPIN-SPIN COUPLING; 1-BOND COUPLING; CHEMICAL SHIFTS; 2-BOND COUPLING; EXCHANGE PHENOMENA; MISCELLANEOUS EXCHANGE STUDIES; SIGNAL-TO-NOISE IMPROVEMENT ; FT ; VARIABLE TEMPERATURE; STEREOCHEMISTRY; CONFIGURATIONAL ASSIGNMENTS ; ORGANOMETALLICS; 11B NUCLEI OBS.) ; 95MO NUCLEI (INDIR. OBS.); 97MO NUCLEI (INDIR. (INDIR. OBS.); W NUCLEI (INDIR. OBS.)

Option? LOGOFF

Your approximate total CIS session cost is \$ 1.53 User [73,17] job 19 ISC#3 off TTY17 at 10:59 PM Thu 8-May-80 Connect time 0:03 CRU'S 1111

As a component of the CIS, NMRLIT benefits from the availability of many CIS "utility" programs and also from the presence within the CIS of a variety of other searchable data bases including a Carbon-13 NMR Search System, CNMR, and Structure and Nomenclature Search System, SANSS. Transfers from one CIS component to another are routine, since subscribers to CIS have automatic access to all components.

The CIS is run on a commercial computer accessible world-wide via the GTE/TELENET telecommunications network. An annual subscription fee of \$300 per organization is charged (<u>waived for</u> <u>educational institutions</u>), and use of NMRLIT is priced at \$36 per connect hour. Further information on access to the CIS may be obtained from the CIS staff at Information Sciences Corporation, 918 16th Street, N.W., Suite 500, Washington, D.C., 20006 (800-424-9600 or 202-223-6503).

Sincerely yours,

E.D. Becker Lab. of Chemical Physics NIAMDD

W.A. Milne

Chine Fisk

lne C. L. Fisk Lab. of Chemistry NHLBI

Conseil national de recherches Canada

Division of Biological Sciences

Division des sciences biologiques

File Référence 30 May 1980

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

Dear Barry,

VISUALIZATION OF THE MOBILITY OF METHYL GROUPS IN THE SOLID STATE BY ²H NMR

Most researchers in high resolution NMR know that the methyl groups of compounds in solution rotate rapidly. Recently we have been studying by ²H NMR the binding of specifically-deuterated sugars to wheat germ agglutinin, and have found that when bound to the protein, the pyranose ring of N-acetylglucosamine is strongly immobilized, whereas the methyl group rotates orders of magnitude more rapidly. Ancillary to this, we ran ²H NMR spectra of a series of solid sugars deuterated in the methyl group. The ²H powder spectra are excellent indicators of the intrinsic mobility of the methyl groups in the solid.

The Figure shows the 46 MHz ²H NMR powder patterns obtained on solid samples of N-acetyl-²H₃-glucosamine and α -methyl-²H₃-glucoside. Note that in each case the quadrupole splitting is about 40 kHz, much less than the theoretical maximum of 130 kHz. This is the value expected for rotation about the axis of attachment of the methyl group; rotation about other axes would reduce the quadrupole splitting even further. Note that in the reducing sugar, separate quadrupole splittings are observed for the α - and β -anomers. This suggests that the amplitudes of motional averaging are not identical in the two anomers, a consequence of different steric interactions, either intraor intermolecular.

With very best personal regards,

Yours sincerely,

Ian C.P. Smith

Klaus J. Neurohr

lenry H. Mantsch



 2 H NMR (46.1 MHz) spectra, of the solid compounds indicated, acquired on a Bruker CXP-300 using the quadrupole echo sequence 90°x- τ -90°y- τ -Echo-AT: (A) SW = 1 MHz, AT = 4.1 ms, τ = 60 μ s, (B) SW = 125 KHz, AT = 16.4 ms, τ = 20 μ s. The recycle time in both cases was 1.0 s.

THE UNIVERSITY OF ROCHESTER COLLEGE OF ARTS AND SCIENCE RIVER STATION

ROCHESTER, NEW YORK 14627

DEPARTMENT OF CHEMISTRY

May 20, 1980

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

Dear Barry:

RE: Higher Isolation Gate and Position Available

Since our last contribution in the News Letter, organic users were introduced on our PFT-100 which necessitated the following modi-fication which I believe is of an interest to your readers.

The modification described below was implemented to make the lock receiver free from XMTR leakage and indeed, an improvement of 20 dB or better was attained.



S1: Solid state switch
 by Watkins-Johnson,
 70 dB of on-off ratio
 (.5 - 20 MHz) replaced
 the ZAD-1H by Min.
 Circuit Lab.

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Our Department has an immediate opening for an instrument specialist with an emphasis in running and maintaining our Mass-Spec Lab (his/her knowledge in NMR will help). Candidates with electronics background having done mass spectrometry are preferred, but can be visa-versa. Interested candidates should send their resumes to: Mrs. Virginia Leport - Personnel Department - University of Rochester, Rochester, N.Y. 14642 - Phone 716-275-4643. Candidates may also contact me (716-275-4705) for further details.

Needless to say, the University of Rochester is an equal opportunity employer (M/F).

Sincerely,

Yukio Kuroda

P.S. Professor Tom Krugh may have a progress report forthcoming on Bruker WH-400.

Hunter College

OF THE CITY UNIVERSITY OF NEW YORK | 695 PARK AVENUE, NEW YORK, N.Y. 10021 | DEPARTMENT OF CHEMISTRY

May 5, 1980

(212) 570-5666

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

Dear Barry:

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Title: Senior Postdoctoral Position Available

I have an additional opening in my laboratory for a Senior Postdoctoral Fellow beginning July 1980. For a salary of \sim \$18,000 plus fringe benefits, the successful candidate will participate in research in ¹⁵N NMR spectroscopy, as well as supervise much of the operation of the laboratory. I am particularly seeking an individual who can work independently in carrying out research and can assist in developing new areas. Some teaching will also be required. The position will run through August 1981; extension beyond that time depends on the availability of funds.

Candidates should submit a curriculum vitae and arrange to have 2-3 letters of recommendation sent to me at the above address. Hunter College is an affirmative action/equal opportunity employer.

Regards from the Big Apple!

Sincerely yours,

Robert L. Lichter Professor and Chairman

RLL:bd

Department of Chemistry

The Florida State University Tallahassee, Florida 32306



May 12, 1980

Title: Postdoctoral Opening

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

Dear Barry:

We anticipate a postdoctoral opening in our project using natural abundance C-13 NMR to study the conformational dynamics of native DNA (see our first communication, Journal of the American Chemical Society, 102, 418 (1980)). This position can begin as early as summer and preferably before October 1, 1980. The salary level is \$11,500-14,000, depending on experience.

For this project we prepare short, homogeneous length double-stranded DNA. Carbon-13 NMR spectra, including spinrelaxation data, are obtained to elucidate the flexibility of conformation at each carbon site. This project combines biochemistry with physical chemistry. The primary need is for a theoretically-oriented physical chemist to use our new data sets to establish realistic models for the complex, rapid internal motions apparent in these DNA molecules. At the option of the postdoctoral associate, experimental work may also be included. We are utilizing state of the art spectroscopy, including specially-designed probes on two supercon spectrometers (150 and 270 MHz for protons).

If you know anyone who would be interested in this position, please have them write either of us. Please also have them arrange to have two letters of recommendation forwarded.

Yours sincerely George Levy

Professor

Randolph Rill Associate Professor

GCL/RR/1h



Rensselaer Polytechnic Institute Troy, New York 12181

UNIVERSITY POSITIONS AVAILABLE

Instrumentation Specialist. The Department of Chemistry at Rensselaer Polytechnic Institute is seeking a full-time specialist for its nmr and mass spectroscopy facilities. Applicants should have had graduate training in nmr (or mass spectrometry) techniques and be knowledgeable in the operation and maintenance of computer-interfaced instrumentation. Responsibilities will include the maintenance, operation, and supervision of instruction of postdoctorals and graduate students in the use of these instruments where appropriate. Collaboration with faculty research programs and the preparation of major equipment proposals are strongly encouraged. A Ph.D. graduate with experience in either of the above areas is preferred but others with commensurate experience will be considered. This is a staff position with a 12 month salary commensurate with experience, and a superior benefit package is also available. Applications should include a curriculum vitae and a description of past experience. These and three letters of recommendation should be submitted directly to Professor K. T. Potts, Chairman, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. An Affirmative Action/ Equal Opportunity Employer.

Instrumentation Technician. The Department of Chemistry at Rensselaer Polytechnic Institute is seeking a full-time instrumentation technician for its instrumentation facility. The successful applicant should have a B.S. or M.S. in electronics, analytical chemistry or some related area, and preferably be experienced in maintaining instruments used in chemical research. Others with commensurate experience will also be considered. Knowledge of computerinterfaced instrumentation would be desirable but is not essential. The appointee will be primarily responsible for maintaining major instruments in the Department's Instrumentation Facility such as FT and CW NMR instrumentation and GC-MS equipment. This is a staff position with a 12 month salary commensurate with experience, and an excellent benefit package is also available. Applications should include a curriculum vitae and a description of past experience. These and three letters of recommendation should be submitted directly to Professor K. T. Potts, Chairman, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. An Affirmative Action/ Equal Opportunity Employer.

Mobil Chemical Company

RESEARCH AND DEVELOPMENT LABORATOMES

P.O. BOX 240 EDISON. NEW JERSEY 08817

May 27, 1980

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

Dear Dr. Shapiro:

The Analytical Department in the Mobil Chemical R&D Laboratory in Edison, New Jersey may have an opening for a spectroscopist whose major initial responsibility would be FT/NMR. The person would solve problems involving ¹³C and ³¹P NMR, operate and maintain the instrument, and assure that routine ¹HNMR spectra obtained on a smaller instrument by a technician are run properly. Mobil Chemical's products include petrochemicals, polymers, plastics products, coatings, agricultural chemicals, and inorganic and organic phosphorus compounds. The Edison Lab is involved in all these areas. Current instrumentation includes a JEOL FX-60Q ($^{1}H/^{13}C/^{31}P/F/B$) and a Varian EM-360. Acquisition of multi-nuclear capability for the JEOL is planned for 1980. In addition, FTIR will be added to the department in 1980, and it is expected that if a person is hired he/she will assume some responsibility in that area as well.

If you have or know of any students who might be interested in this position, please have them send me a resume.

Thank you.

Yours truly Arleigh V: Hartkopf

AVH:mft

NT-Series Fourier Transform Superconductive Magnet NMR Spectrometers

The NT-Series has been conceived and designed to provide optimum performance while being fully adaptable to new techniques with minimal cost and difficulty. More than just a collection of instruments, the NT-Series represents a completely modular approach to FT-NMR instrumentation that allows the user to expand his system as his research needs grow and to easily accommodate new experimental techniques as they develop.

Outstanding NT-Series features include these:

- A full range of superconductive magnets from 3.5T to 11.7T in both wide-bore and narrow-bore configurations.
- Multinuclear observation with a wide variety of fixed-tune and broadband probes.
- Simultaneous acquisition, processing, and plotting for greater sample throughput.

- Simplified control of spectrometer operations and parameters by using easy keyboard commands.
- Advanced Nicolet-1180 Data System with the most comprehensive FT-NMR software package available.
- Extended dynamic range performance with 40-bit acquisition and floatingpoint processing.
- An expandable pulsesequence library, including T₁, T₂, Redfield, 2D-FT, etc.
- Convenient computercontrol of field shimming, observe and decoupling frequencies, sample temperature.
- Precise digital plotting with full annotation of spectral parameters and flexibility of hardcopy format.

The multiple-technique NT-Series spectrometers provide the user with the ability to easily adapt to the newest techniques and experimental configurations.

Some of these are:

- High-resolution studies of solids with Waugh-Pines crosspolarization and magic-angle spinning
- High-sensitivity wide-bore ¹³C studies of high molecular weight polymers.
- Automated T₁ and T₂ measurements.
- Chemical dynamics studies.
- Temperature-programmed experiments.
- ³¹P experiments on living organs.



145 East Dana Street Mountain View, California 94041 Telephone: 415/969-2076

FX SERIES FT NMR SYSTEMS

FX-90Q OMNI Probe™ System 10mm, 5mm, micro inserts

FX-60Q

Solids Probe (¹³C) with Magic Angle Spinning High Resolution Probe (¹³C/¹H) Dual Probe (¹³C/¹H) Broad Band (¹⁵N to ³¹P) 50 KHz Spectral Width

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System Features

- Light Pen Control System
- Foreground/Background
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- Multi Frequency Observation
- Programmable Multi Pulser
- Module Performance Indicator Lights
- Comprehensive Auto Stacking
- T₁-rho
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- Floppy; MH Disc Storage
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