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Newsletter

No. **265**

October, 1980

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	No. 267	1 December 1980

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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DMR/VJN

29th August, 1980

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

EUROPIUM SHIFT REAGENT BINDING CONSTANTS

Dear Professor Shapiro,

I am going to risk excommunication of the entire Lilly Organisation from the TAMU newsround by admitting that we receive a spare newsletter in the UK by kind courtesy of our parent company in Indianapolis. In return for this welcome privilege, Doug Dorman has suggested (!) that we make a short contribution regarding our unpublished work on the equilibrium binding constants (K) of lanthanide shift reagents with organic substrates. Would you please, therefore, credit it to the Lilly Indianapolis account?

The incremental dilution procedure of Bouquant and Chuche[1] serves as a simple procedure for measuring K. With equimolar concentrations of shift reagent and substrate the maths is considerably simplified and reduces to a plot of lanthanide induced shift versus molar concentration. We are aware of the need for 1:1 complexes in solution and restrict ourselves to the non-fluorinated reagents, particularly $Eu(thd)_3$. The Table shows the binding constants obtained for some nitrogen heterocycles and for two $N \rightarrow O$ and $S \rightarrow O$ substrates. Fuller details of these should appear in Spectroscopy Letters in the autumn[2].

.../

These, and earlier, results show that K is quite sensitive to changes in basicity (e.g. compounds 1, 6 and 7, K increasing with pKa) but extremely susceptible to steric hindrance near the donor binding site. Thus although the basicities of 1 to 3 rise there is a forty fold fall in K with methyl substitution around the pyridine nitrogen atom. Acridine (8) also shows this steric hindrance to binding. The need for a pyridine-like nitrogen in the heterocycle is evident from the zero binding seen for 4 and 5.

We were interested to find that formation of the N-oxide 9 both increases the "hardness" of the donor (which therefore binds more strongly to the hard shift reagent) and also increases the value of K. The same effect is more dramatically seen in the sulphide/sulphoxide pair 10 and 11.

With good wishes,

David M. Rackham

References
1. J. Bouquant and J. Chuche, Bull. Soc. chim. Fr. 959 (1979).
2. D.M. Rackham, Lanthanide Shift Reagents, Papers 17 and 18, to appear in Spectroscopy Letters.

TABLE Binding Constants for $Eu(thd)_3$ with organic substrates (Varian EM 360, $CDCl_3$, $27°$).

COMPOUND		K	pKa
1.	$R=R^1=H$	333	5.21
2.	$R=Me, R^1=H$	83.1	5.94
3.	$R=R^1=Me$	8.7	6.60
4.		0.0	–
5.		0.0	–
6.		51.3	2.04
7.		1620	7.2
8.		9.4	5.5
9.		1680	–
10.	Ph_2S	0.0	–
11.	$Ph_2S \rightarrow O$	277	–

Prof. B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College Station,
TEXAS 77843,   U. S. A.

Diagnostic Proton Chemical Deshielding caused by Peri Nitrogen Lone Pair Action.

Dear Barry,

We want to report here about the structural assignment of a monosubstituted pyridine imidine derivative 2 on the basis of its ^1H NMR chemical shift parameters.

Imidines like 1 react readily with amines to form mono- or disubstituted compounds.

When 5,7-diimino(5H,7H)-pyrrolo(3,4-b)pyridine (1) reacts with morpholine in ethanol only one monosubstituted isomer was obtained, which was determined to have the morpholino group next to the pyridine N atom (2, X = CH, Y = N). The other isomer (2, X = N, Y = CH) could not be isolated. In Table 1 some proton chemical shift data of 2 and related compounds are collected.

From this table it follows that an isoindole system such as in 4, causes a downfield shift of about 1.3 ppm for the methylene hydrogens adjacent to the morpholine nitrogen atom, whereas the oxygen methylene hydrogens (H_3, and H_5,) are deshielded for about 0.1 ppm. These effects might be due to the partial positive charge induced on the morpholine nitrogen by conjugation with the imidine system. [which also precludes the morpholine ring to rotate freely around the C-N bond with the imidine (hence the anisochronism of H_2,(3') and H_6,(5'))]. Furthermore, when a nitrogen atom is present in the aromatic ring at the same side of the morpholino substituent, as in 3 and 2 , one group of methylene hydrogens (H_2,) shows an additional downfield shift of 0.7 ppm (cf. 2 vs. 5) presumably due to the anisotropy of the lone pair electrons of the pyridine (of pyrazine) nitrogen atom.

TABLE 1. Chemical Shift Values (ppm)(CDCl$_3$/TMS)

	2	3	4	5	6
H$_{2'}$	4.97	4.84	4.20	4.23	2.87 (H$_3$)
H$_{3'}$	3.93	3.94	3.82	3.95	3.67 (H$_2$)
H$_{5'}$	3.92	3.94	3.80	3.92	
H$_{6'}$	4.19	4.21	4.04	4.15	

This deshielding effect is even more pronounced, when cis-2,6-dimethylmorfoline is used in the reaction, in which ring-inversion of the morfolino fragment is prohibited. The ^{1}H NMR-spectrum of 7-[3',5'-dimethylmorfolino]-5-oxo-(5H)-pyrrolo(3,4-b)pyridine shows that it is the equatorial H$_{2'}$-proton that is very intensively affected by the local paramagnetic field of the nitrogen lone pair (downfield shift of 1.3 ppm !) whereas the axial H$_{2'}$-proton exhibits a deshielding effect of only 0.2 ppm. The mean value of 0.7 ppm for the methylene hydrogen atoms, observed in morfolino compounds 2 and 3, is in good agreement with these observations.

It is clear that these spectacular deshielding effects provide an excellent way of discriminating between positional isomers of 2.

Sincerely yours,

M.J.O. ANTEUNIS   L. SPIESSENS

September 29, 1980
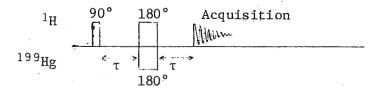
Dr. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:
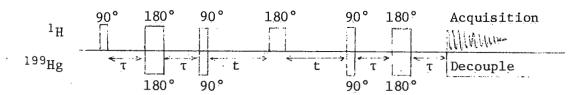
Title: S E D and S E I D ^{199}Hg-NMR

We have begun investigating the interaction of the organomercurial
ethyl mercury phosphate (EMP) with various amino acids and nucleotides by
natural abundance ^{199}Hg-NMR. Millimolar concentrations and small volumes,
which are often the case with biological samples, generally prohibit direct
observation in a reasonable length of time.

We have resorted to spin echo[1] detection (S E D) to estimate the
mercury frequency to within ± 500 Hz (^{1}H = 270 MHz, ^{199}Hg = 48.3 MHz).
The chemical shift and the line width of the ^{199}Hg decoupled spectrum
can be determined exactly using a "Sensitivity Enhanced Indirect Detection"
two dimensional technique (SEID). Both methods, illustrated by the pulse
schematics below, have been described in more detail elsewhere.[2,3]

Spin Echo Detection

Both theoretically and experimentally for EMP and nitrogen and oxygen
adducts, $\tau = (2J)^{-1}$ is the optimal time interval in the spin echo program
leading to inversion of the satellite upon irradiation of the appropriate
^{199}Hg resonance. However, the value of τ is not as critical as one might
expect. Provided that $\tau < (2J)^{-1}$, the ^{199}Hg resonance frequency can be
determined easily, although the inversion rapidly becomes a dispersion
signal with $\tau \leq (5J)^{-1}$ (Fig. 1).

This makes SED quite attractive, particularly in cases where other
^{1}H nuclei obscure accurate determination of $J_{1_{Hg}199_{Hg}}$. In a similar

fashion, while SEID is optimized with $\tau = (4J)^{-1}$, τ-values of $(2J)^{-1}$ and $(3J)^{-1}$ also produce acceptable ^{199}Hg spectra (Fig. 2). This sloppiness may be the result of the long ^{199}Hg pulse widths (100 μsec) used, and in any event is useful to us.

However, an equimolar solution of EMP and cysteine (or β-mercaptoethanol) behaves in a contrary fashion. With $\tau = (2J)^{-1}$, the satellites null rather than invert at the ^{199}Hg frequency. Furthermore, with SEID use of $\tau = (4J)^{-1}$ produces noise, while use of $\tau = (2J)^{-1}$ leads to a respectable ^{199}Hg peak.

This behavior is exhibited, as far as we can determine, only among EMP-sulfur compound complexes (it is also pH-independent). Ethyl mercury-nitrogen or oxygen adducts appear to be well behaved.
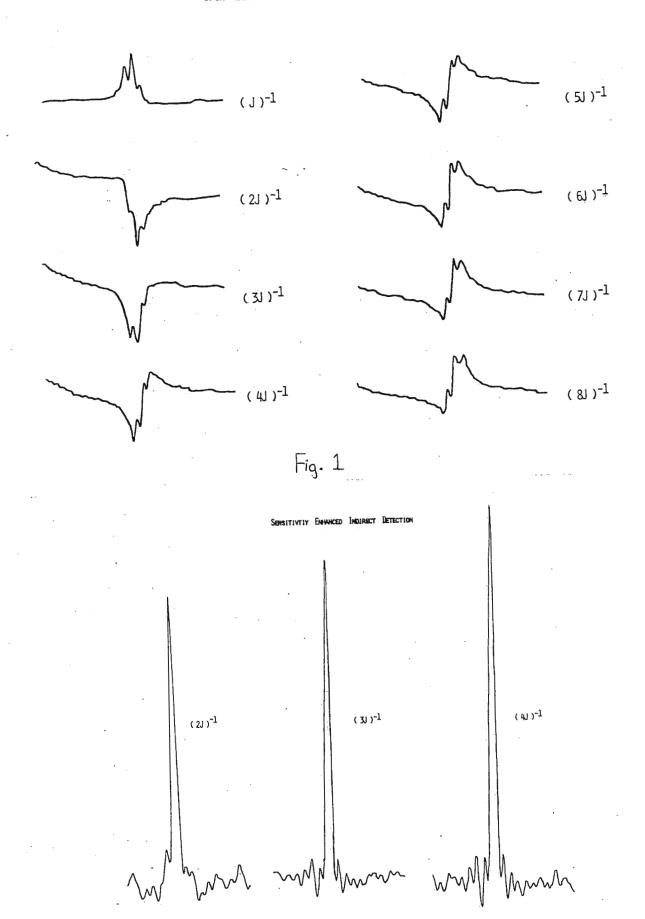
We suspect that unexpected exchange or unusual relaxation behavior is behind these observations.

Any theories/suggestions/explanations from the NMR community would be welcome and appreciated.

Sincerely,

David A. Vidusek
David A. Vidusek

Mary F. Roberts
Assistant Professor of
Chemistry
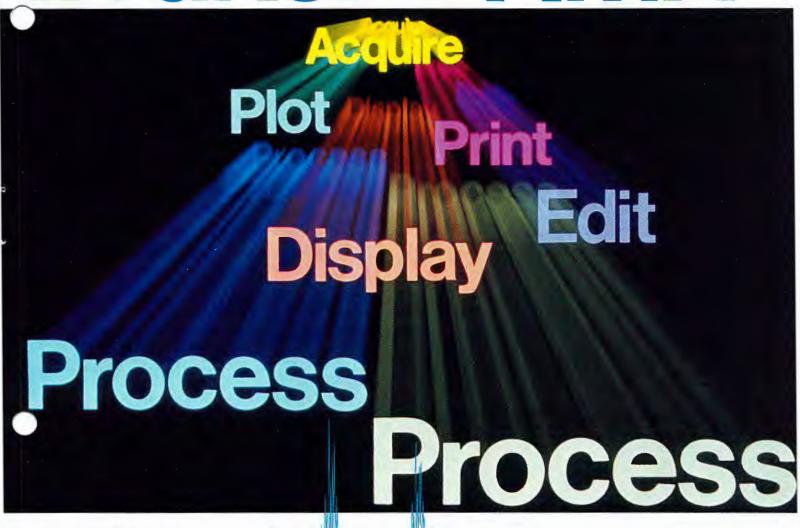
1. Emshwiller, M. etal. (1960) Phys Rev. 118, 414.
2. Bodenhausen, G., and Ruben, D.J. (1980) Chem. Phys. Lett. 64, 185.
3. Roberts, M.F. etal. (1980) FEBS Lett. 117, 311.

SPIN ECHO SEQUENCE - VARIATION OF τ

(J)$^{-1}$

(2J)$^{-1}$

(3J)$^{-1}$

(4J)$^{-1}$

(5J)$^{-1}$

(6J)$^{-1}$

(7J)$^{-1}$

(8J)$^{-1}$

Fig. 1

SENSITIVTIY ENHANCED INDIRECT DETECTION

(2J)$^{-1}$

(3J)$^{-1}$

(4J)$^{-1}$

Fig. 2

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September 30, 1980

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

"Position Available - Pascal in NMR"

Dear Barry:

To inaugurate my new subscription I would like to note that
the Pascal compiler for the Aspect 2000 has been receiving heavy
use here. We have developed matrix manipulation and simplex
routines, real and integer Fourier transforms and a text justif-
ication program. Copies of these programs will be reproduced in
my new textbook to be published by Wiley next spring.

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Sincerely,

James W. Cooper
Vice President for Software Development

/g

UNIVERSITY OF UMEÅ   Sept 1, 1980

Department of Organic Chemistry

Professor B. L. Shapiro

Department of Chemistry

Texas A & M University

College Station, Texas 77843, USA

Dear Barry,

Interpretation of NMR SCS - WM 250 - Postdoc Wanted

Papers dealing with the interpretation of NMR SCS, especially ^{13}C NMR
SCS, seem to occupy an ever increasing part of the literature in
physical organic chemistry. However, the aim or the results of these
studies are seldom clearly stated, whether it is to get a deeper under-
standing of the substituent transmission mechanisms or if the used
correlation model will be useful for predictive purposes, confirming
signal assignments etc.

Irrespectively of the ambition, one surely has spoiled the chances to
get relevant information if one uses any of the common, fixed dual sub-
stituent parameter models (DSP) without showing that the correlation
for the present data set is statistically better than using a one-para-
meter model (F-test). It is rather discouraging to find papers in
well-respected journals where authors mention a successful correlation
to a single parameter (ie σ_p or σ_R^0) but still without improving the
correlation report data obtained from a DSP analysis. The regression
parameters are then said to be a relevant measure of the relative con-
tribution of different "effects". I am rather pessimistic about future
changes in this handling of NMR SCS data but one can always have a
dream that authors could treat their data in this way:

1. Choose substituents which describe the whole substituent domain as
   good as possible. A minimum basis set of 6-7 substituents has been
   suggested[1].

2. Fit NMR SCS to a single σ-scale by least squares and calculate the
   residual standard deviation and confidence interval for the slope.

3. Plot the residuals against the observed SCS. Especially, if the
   plot indicates systematic patterns of residuals test for DSP and
   check significance by F-tests.

4. Test for significance using any of the well-accepted criteria for
   goodness of fit. If a dual substituent parameter equation is needed

report the multiple parameter correlation coefficient and the calculated confidence intervals of the regression coefficients.

Much more enjoyable (hopefully) is the fact that we are currently installing a Bruker WM-250 (fully broadbanded with high-density disk) at our institute. Being a small department / having very few biochemists mean that we could promise a well-qualified application-oriented post-doc a nice share of experimental time, starting from the 1st of July 1981 or later. Interested candidates with some postdoctoral experience in NMR applied to molecular dynamics, organometallics (reactive intermediates) or metal-biomolecule interactions could send me a letter.

PS. 18 hrs after charging the magnet we obtained a ^{13}C sensitivity of 80:1 on 10% ETB using the 10 mm broadbanded probe. Not bad at all. DS

1. S. Ehrenson, R.T.C. Brownlee, R.W. Taft, <u>Prog. Phys. Org. Chem.</u>, 1973,<u>10</u>,1

Best regards

Ulf Edlund

MICHIGAN STATE UNIVERSITY

COLLEGE OF NATURAL SCIENCE · DEPARTMENT OF CHEMISTRY   EAST LANSING · MICHIGAN · 48824
CHEMISTRY BUILDING

October 3, 1980

NMR TECHNICAL SERVICES COORDINATOR TO MANAGE DEPARTMENTAL MAGNETIC RESONANCE FACILITY CONSISTING OF A BRUKER WM-250, WH-180, HFX-90; MODIFIED VARIAN DA-60, 56/60, CFT-20; A VARIAN E-4 AND BRUKER ER-200D; AND OTHER SMALLER UNITS. EMPLOYEE WILL PLAN, RESEARCH, DESIGN AND CONSTRUCT STATE-OF-THE ART MAGNETIC RESONANCE EQUIPMENT, DIAGNOSE AND REPAIR INSTRUMENT PROBLEMS, COORDINATE AND OVERSEE OPERATION, MAINTENANCE AND USE OF SPECTROMETERS. EXPERIENCE IS REQUIRED IN THE DESIGN, FABRICATION, OPERATION AND REPAIR OF MAGNETIC RESONANCE INSTRUMENTATION; ELECTRONIC THEORY AND TECHNIQUES; COMPUTER OPERATIONS. SEND RESUME AND THREE LETTERS OF REFERENCE TO MICHIGAN STATE UNIVERSITY, G.J.KARABATSOS, DEPARTMENT OF CHEMISTRY, EAST LANSING, MI. 48824, OR CALL 517-355-9717.

Professor Bernard L. SHAPIRO
Department of Chemistry
Texas A & M University

COLLEGE STATION, Texas 77843

U.S.A.

GRENOBLE, LE 2 Septembre 1980

Dear Dr Shapiro,

In comparison with the very many data which exist on the influence of the molecular geometry on the phosphorus chemical shift, there exist relatively few studies concerned with the geometrical dependence of the individual components of the chemical shift tensor components σ_{rs}. As a first step for further investigations in this direction we took a set of cyclic organophosphorus molecules 1, 2, 3, 4 which have the same chemical environment around the phosphorus atom.

The molecular structure as obtained by X-ray diffraction shows that the parameter which shows the largest variation is the intracyclic O-P-O bond angle α (Table 1). For these four molecules 1,2,3,4 solid state high resolution n m r spectra were run on our new CXP 200 BRUKER spectrometer. The spectra were recorded using the Proton Enhanced Nuclear Introduction Technique. In each of the samples under study the phosphorus nuclei are crystallographically equivalent and thus contribute to one and the same powder pattern.

The results are quoted in the Table. One may notice the large anisotropy of the ^{31}P chemical shift (> 200 ppm). A good linear correlation of the assymetry parameter η ($\eta = \dfrac{\sigma_{22} - \sigma_{11}}{\sigma_{33}}$) with the O-P-O bond angle is observed.

Sincerely yours.

J.B. ROBERT

L. WIESENFELD

		σ_{11}	σ_{22}	$\sigma_{33}=\sigma$	$\eta(\%)$	$\Delta\sigma$	$\alpha(°)$	space group
(structure)	1	-126	-4	130	94	256	98	$P2_1/c$
(structure)	2	-110	-32	142	55	252	103	$P2_12_12_1$
(structure)	3	-94	-39	133	41	227	105	$P2_1/c$
(structure)	4	-81	-44	125	30	206	108.2	$P2_1/m$

Table : Principal values (σ_{11}, σ_{22}, σ_{33}) in ppm of the ^{31}P shielding tensor. For each compound, the chemical shift origin is defined by Tr $\sigma = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$. $\sigma = \sigma_{33}$ (ppm)and

$\eta = \dfrac{\sigma_{22} - \sigma_{11}}{\sigma_{33}}$ (%) are the asymmetry parameters of the σ tensor [g], $\Delta\sigma = \sigma_{33} - \sigma_{11}$(ppm) characterizes the anisotropy. α(degrees) is the intracyclic O-P-O bond angle.

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

September 2, 1980

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

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

^{15}N NMR of 1, 1-Diazenes

Dear Barry,

Recently we have been examining the ^{15}N NMR spectrum of N(2, 2, 6, 6-tetra-methylpiperidyl(nitrene), 1. The study has allowed us to gain some interesting insights into the 1, 1-diazene functional group, and has also given us a good excuse for using the new Bruker WM-500 which is now up and running at the Southern California Regional Facility here at Caltech.

As seen from spectrum A (taken on our JEOL FX-90Q spectrometer), the doubly ^{15}N-labeled 1, 1-diazene shows doublets at 917. 0 and 321. 4 ppm (J = 15. 5 Hz). The 1, 1-diazene dimerization product, tetrazene, has resonances at 418. 5 and 164. 6 ppm (J = 6. 4 Hz). Spectrum B (taken on the WM-500 with a gain in sensitivity of approximately 6) is of a mixture of mono-labeled 1 and 2 and allows assignment of the 917-ppm resonance to the "nitrene" nitrogen of the 1, 1-diazene chromophore.

The ^{15}N spectrum of this 1, 1-diazene shows a very large difference in electronic environments of the two adjacent nitrogens. The large downfield shift of the nitrene nitrogen is consistent with a large paramagnetic shift term which can be ascribed to mixing into the ground state of an excited state corresponding to a low-lying n-π* transition (λ_{max} = 543 nm). The amino nitrogen is shifted almost 600 ppm upfield of the nitrene nitrogen resonance and thus appears to have a much smaller paramagnetic shift term. Its lone pair is therefore much less involved (if at all) in an excited state contribution corresponding to an n-π* transition and, presumably, is substantially delocalized into the empty p orbital of the nitrene nitrogen. This is consistent with both experimental and theoretical evidence which characterize 1, 1-diazenes as having N=N π bonds.

With all good wishes,

Sincerely,

Michael E. Squillacote   Peter B. Dervan   Paul M. Lahti,   Alan P. Sylvester

John D. Roberts
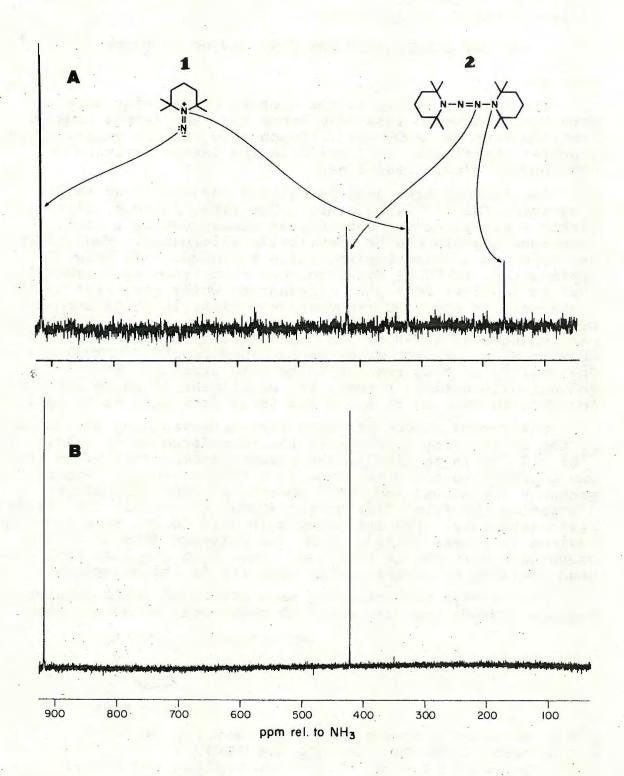
Figure 1.

varian / instrument group
25 hanover road / florham park / new jersey 07932
telephone (201) 822-3700

September 10, 1980

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

SOLVENT ELIMINATION AND TIME SAVING BY INEPT

Dear Barry,

The history of nmr is the history of learning more and more about less and less (one hopes the same is not true of contributions to TAMU-NMR!). Recent progress in polarization transfer experiments in liquids is the latest exciting development along these lines.

Two factors have gone relatively unappreciated in the burgeoning INEPT[1-5] literature. The first is that, given either a pre-pulse[4] or appropriate phase-cycling[5], natural-abundance signals can be identically eliminated. Thus INEPT can serve as a solvent elimination technique. In this application, INEPT is distinguished from other techniques in that it achieves 100% peak elimination while requiring no adjustment of times or frequencies. Alas, it would seem to be applicable only to ^{13}C. For ^1H observation in H_2O, one can conceive of a C→H or N→H INEPT experiment to reveal only CH's or NH's, or even an H→C→H or H→N→H double INEPT experiment. The utility of this remains to be demonstrated. For ^{13}C solvent elimination, though, the experiment is quite straight-forward, as seen in Figure 1 [D2 is τ_1 from Ref. 4; D3 is τ_2].

The second aspect of INEPT that deserves more attention is the sensitivity gain due to the dependence on ^1H T_1's. ^{29}Si and ^{15}N in particular can possess intolerable T_1's; the use of INEPT to overcome these is a real blessing. Figure 2 presents the normal and INEPT spectra of HMDS, run after discarding the first four pulses (SS=4) to exhibit the steady-state intensity. The intensity gain here is 35, or a time savings in excess of 10^3. Even for polymers (Figure 3) a comparable gain can be realized. Note that the lack of a one-bond coupling to protons is no obstacle to the experiment.

I've always thought there were plenty of INEPT spectros-copists around; now with any luck there will be even more!

Sincerely,

Steve

Steve Patt

1. G.A. Morris and R. Freeman, J. Am. Chem. Soc. 101, 760 (1979).
2. G.A. Morris, J. Am. Chem. Soc. 102, 428 (1980).
3. P.H. Bolton and T.L. James, J. Am. Chem. Soc. 102, 1449 (1980).
4. D.P. Burum and R.R. Ernst, J. Magn. Reson. 39, 163 (1980).
5. G.A. Gray, Varian Instruments at Work NMR-14, September, 1980.

1

EXP3 PULSE SEQUENCE: INEPTR

ACQUISITION		DEC. & VT	
TN	13.250	DN	1.250
SW	10000.0	DO	0
AT	0.800	DM	YY
NP	16000	DMM	EE
PW	6.3	DMF	200
D1	5.000	DHP	Y
TO	-500	DLP	20
NT	128		
CT	128	PROCESSING	
MULT	1	SE	0.318
J	0	LB	1.000
PP	45.0	FN	16384
D2	3.57E-3	MATH	I
D3	2.90E-3		
FB	5500	DISPLAY	
BS	16	SP	0
SS	4	WP	10000.0
IL	N	VS	800
IN	N	SC	130
DP	Y	WC	120

EXP4 PULSE SEQUENCE: INEPTR

ACQUISITION		DEC. & VT	
TN	13.250	DN	1.250
SW	10000.0	DO	0
AT	0.800	DM	NY
NP	16000	DMM	CE
PW	12.0	DMF	200
D1	5.000	DHP	Y
TO	-500	DLP	20
NT	1.00E 9		
CT	128	PROCESSING	
MULT	1	SE	0.318
J	140.0	LB	1.000
PP	45.0	FN	16384
D2	3.57E-3	MATH	I
D3	2.90E-3		
FB	5500	DI PLAY	
BS	16	SP	0
SS	4	WP	10000.0
IL	N	VS	800
IN	N	SC	0
DP	Y	WC	120

INSENSITIVE NUCLEI ENHANCED
 BY POLARIZATION TRANSFER
 WITH REFOCUSSING
85% HMDS

EXP4   PULSE SEQUENCE: INEPTR

ACQUISITION		DEC. & VT	
TN	29.000	DN	1.750
SW	500.0	DO	0
AT	8.000	DM	NY
NP	8000	DMM	CE
PW	13.0	DMF	200
D1	10.000	DHP	Y
TO	200	DLP	20
NT	4		
CT	4	PROCESSING	
MULT	1	FN	8192
J	6.7	MATH	I
PP	45.0		
D2	7.46E-2	DISPLAY	
D3	2.13E-2	SP	250.2
FB	300	WP	25.0
BS	128	VS	31
SS	4	SC	0
IL	N	WC	120
IN	N	IS	100
DP	N	RFL	0
		RFP	0
		TH	40
		INS	1.000
		AI	

POLYDIMETHYLSILOXANE
 TETRAMETHOXY-TERMINATED
INEPT EXPERIMENT
8/22/80
SLP
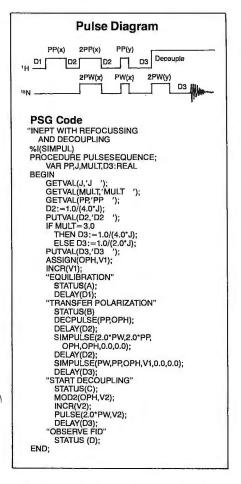
EXP1   PULSE SEQUENCE: INEPTR
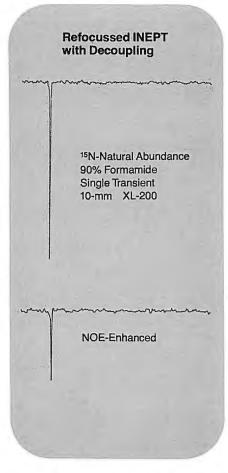
ACQUISITION		DEC. & VT	
TN	29.000	DN	1.750
SW	500.0	DO	0
AT	8.000	DM	NY
NP	8000	DMM	CE
PW	13.0	DMF	200
D1	2.000	DHP	Y
TO	-1000	DLP	20
NT	4		
CT	4	PROCESSING	
MULT	3	FN	8192
J	7.3	MATH	I
PP	45.0		
D2	6.84E-2	DISPLAY	
D3	3.00E-2	SP	250.0
FB	300	WP	100.0
BS	128	VS	1500
SS	4	SC	0
IL	N	WC	120
IN	N	IS	100
DP	Y	RFL	0
		RFP	0
		TH	60
		INS	1.000
		AI	

2

3

How much do you know about the Varian XL-200?

Pulse Diagram

PP(x)   2PP(x)   PP(y)

1H   D1   D2   D2   D3   Decouple

15N   2PW(x)   PW(x)   2PW(y)   D3

PSG Code

```
"INEPT WITH REFOCUSSING
   AND DECOUPLING
%I(SIMPUL)
PROCEDURE PULSESEQUENCE;
   VAR PP,J,MULT,D3:REAL
BEGIN
   GETVAL(J,'J   ');
   GETVAL(MULT,'MULT   ');
   GETVAL(PP,'PP   ');
   D2:=1.0/(4.0*J);
   PUTVAL(D2,'D2   ');
   IF MULT=3.0
     THEN D3:=1.0/(4.0*J);
     ELSE D3:=1.0/(2.0*J);
   PUTVAL(D3,'D3   ');
   ASSIGN(OPH,V1);
   INCR(V1);
   "EQUILIBRATION"
      STATUS(A);
      DELAY(D1);
   "TRANSFER POLARIZATION"
      STATUS(B);
      DECPULSE(PP,OPH);
      DELAY(D2);
      SIMPULSE(2.0*PW,2.0*PP,
        OPH,OPH,0.0,0.0);
      DELAY(D2);
      SIMPULSE(PW,PP,OPH,V1,0.0,0.0);
      DELAY(D3);
   "START DECOUPLING"
      STATUS(C);
      MOD2(OPH,V2);
      INCR(V2);
      PULSE(2.0*PW,V2);
      DELAY(D3);
   "OBSERVE FID"
      STATUS (D);
END;
```

Refocussed INEPT with Decoupling

15N-Natural Abundance
90% Formamide
Single Transient
10-mm   XL-200

NOE-Enhanced

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.

For example, you can frequently obtain enhanced sensitivity from low-γ 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.

The XL-200's Pulse Sequence Generation capabilities were used to perform the enhanced sensitivity experiment above. Acquisition Processor features are another important benefit for XL-200 owners.

Pulse Sequence Generation

- PASCAL language-based code with resident compiler
- English-like sequence code
- Error checking compiler
- Large text library for source code storage
- Sophisticated editor for convenient programming in PASCAL
- Use of PASCAL statements within sequence code
- Simple PSG components such as:

PULSE	OFFSET	SPAREON	HLV
OBSPULSE	DELAY	SPAREOFF	DBL
DECPULSE	IFZERO	DECPHASE	ADD
SIMPULSE	LOOP	RCVRON	SUB
STATUS	DECR	RCVROFF	MOD2
ASSIGN	INCR	RND	MOD4

- Ability to specify and vary phase and receiver off-times dynamically
- 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 ^{13}C-^{13}C spectroscopy

Acquisition Processor
- Independent 32-bit arithmetic bit-slice 32K CPU
- 50-nanosecond hardware timing
- Software-programmed for highest flexibility

- 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
- Four decoupler phases under CPU control
- Explicit and relative mode phase selection
- 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

In NMR research the XL-200 is first among first-class spectrometers. Following are lists of other features that make the XL-200 your logical choice for complex and sophisticated research NMR.

Standard Features
- Computer controlled VT
- $^{19}F/^1H$ 5-mm VT probe
- ^{15}N-^{31}P 10-mm VT broadband probe
- ^1H universal transmitter cards for observe, decouple and lock
- Built-in printer, plotter, keyboard, TV display and 5M-word dual disk
- 32K acquisition processor memory
- 32K main CPU memory
- Large, calibrated chart paper
- Interactive display knobs
- Autolock for automatic locking, even after sample change
- Pulsed/timeshared lock modes
- Universal fixed and broadband rf transmitters with interchangeable functions
- 3-month helium hold-time with only 25 liters needed for refill, *including* transfer loss
- 14-day nitrogen hold-time—45 days with optional refrigerator
- Welded dewar
- 25-watt rf transmitter output—200-watt pulse amplifier
- 10-μsec ^1H 90° pulse/15-μsec ^{13}C 90° pulse
- Internal ^2H lock
- Pushbutton PROM-based program loading
- Disk-based data system
- Flicker-free TV display with graphics capability
- Simplified 1-meter probe tuning
- 0.4 to 1.6 MHz offset synthesizer
- 13-bit ADC

Accessories
- ^{19}F transmitter
- Large sample and 5-mm broadband probes
- Nitrogen refrigerator
- Magnet power supply
- Maintenance kit
- Magic-angle/cross-polarization solids probes

Data System
- PASCAL language
- State-of-the-art operating system
- Disk-based using modular design software concept
- Concurrent and sequential PASCAL
- Floating-point data and math format
- Multitasking-simultaneous acquire, plot, print, display, parameter entry
- Queuing of acquisitions, plots, prints and calculations
- Spooling of plots and prints
- Disk-resident data tables
- Separate FID and spectral storage
- System resident PASCAL compiler for user programming
- User access to data files

- Expandable user-defined command and parameter architecture
- Floating-point or integer transform
- Convolution difference/gaussian apodization functions
- Parameter set libraries
- 2D transform
- Plot graphics
- T1, T2, 3-parameter least-squares-fit analysis programs
- Spin simulation
- LAOCOON with magnetic equivalence
- User-definable disk libraries
- PASCAL system source code availability
- NOE calculation
- Add-subtract-convolution spectral manipulation

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September 3, 1980

Prof. Bernard L. Shapiro
Dept. of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

A MgATP THERMOMETER FOR ^{31}P NMR STUDIES OF BIOLOGICAL SYSTEMS

A common problem in ^{31}P NMR studies of biological systems is accurate measurement of sample temperature. Because of the widespread use of ^{31}P NMR in biological research, it is desirable to have an NMR thermometer based on the ^{31}P nucleus for convenient measurement of sample temperature. We propose a MgATP thermometer for this purpose. The chemical shift difference between the αP and βP resonances in neutral pH solutions of MgATP (e.g., 20 mM metal free ATP + 40 mM Mg^{2+}) shows a sizeable temperature-dependence (0.012 ppm/°C at pH 7.2 and $\mu = 0.15M$, i.e., 0.5 Hz/°C at 40.5 MHz and 2.4 Hz/°C at 202.5 MHz ^{31}P NMR frequency). Since ^{31}P resonances of MgATP are sharp and narrow (≤ 1 Hz), and ATP is very soluble in aqueous medium to permit the attainment of good signal to noise ratio in a few minutes of time-averaging, it is possible to measure the chemical shift difference with an accuracy of a few tenths of a Hertz. It is therefore possible to measure sample temperature in high field spectrometers using the MgATP thermometer quite accurately. Since, in the MgATP thermometer, only the difference in chemical shift of two resonances in a single spectrum is measured, the actual measurement is easier than those based on absolute chemical shifts.

Sincerely yours,

Raj K. Gupta

Pratima Gupta

P.S. Please credit this contribution to the account of Al Mildvan.

jdi

DEPARTMENT OF CHEMISTRY

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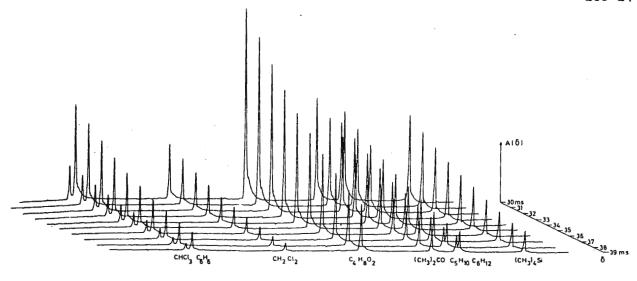
BERGEN, NORWAY Sept., 3, 1980.

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

Dear Professor Shapiro,

My previous contribution "Quantitative Off-resonance Studies made Easier" (Nov. 1979) and its "official" counterpart (Anal. Chem. 52 (1980)569) seem to have triggered some cases of severe deja vu. Of course, most nmr spectroscopists have used peak heights instead of splittings in various kinds of experiments in a qualitative or semiquantitative sense in the search for optimum irradiation frequencies (e.g. shift determination through audio side-band methods on the old CW-spectrometers). I have never claimed to have invented this approach; what I wanted to point out was that the ultimate evaluation method in the case of linear splitting-frequency relations should be non-linear least-squares fitting to Lorentzian functions, and that the conventional evaluation method for off-resonance experiments is often useless for practical purposes. Credit must be given to J.B. Grutzner, however, who already in 1972 used the "peak-height approach" in ^{13}C off-resonance studies (LLOYDIA, 35 (1972)375), using a triangular function. This reference was unknown to me at the time of writing.

An now for something completely different. Self-diffusion measurements can be done on FT-spectrometers through the experiment suggested by James and McDonald (J. Magn. Reson., 11 (1973) 58). We (M.E. Moseley, B. Lindman, J. Roots, B. Nystrøm and myself) have applied the method to several types of problems (Chemica Scripta, Polymer and J. Magn. Reson., in press). It works remarkably well even with the weak gradients obtained through the standard Homospoil on the JEOL FX-100 ($\sim$ 1 G cm^{-1}) and diffusion coefficients two magnitudes lower than for e.g. pure water can be determined with good precision.

The figure illustrates diffusional effects on proton echo amplitudes in the first ever (maybe last) 8-component system to be studied by this method (mixture designed by M.E. Moseley). The precision of the experiment is very good; D for each component can be determined to better than ±1%. A homospoil unit with slow rise and decay times cannot be used in this type of application.

I hope that this contribution keeps my subscription running.

Yours sincerely

Peter Stilbs

Peter Stilbs

UNIVERSITY OF MISSOURI-COLUMBIA

College of Arts and Science

Department of Chemistry

123 Chemistry Building
Columbia, Missouri 65211
Telephone (314) 882-2439

THE UNIVERSITY OF MISSOURI-COLUMBIA

DEPARTMENT OF CHEMISTRY

is consolidating its NMR instrumentation into a facility which will include 60, 90, and 300 MHz capabilities. The department is now recruiting a

SENIOR LEVEL

FACULTY MEMBER

in conjunction with this facility. In addition to maintaining an active research program using NMR, the candidate is expected (in lieu of substantial teaching duties) to supervise the maintenance and periodic upgrading of the facility and to offer technical advice to other faculty members who contemplate the use of NMR to solve problems in chemistry, biochemistry, and biology. Candidates should supply a graduate transcript, curriculum vitae, resume of future re- search plans, and have three letters of recommendation sent to : Dr. Pierre Crabbé, Chairman, Department of Chemistry, University of Missouri, Columbia, MO 65211. AN AFFIRMATIVE ACTION/EQUAL EMPLOYER.

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September 11, 1980.

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

Observation of 1,5 acyl transfer by ^{13}C NMR

The 1,5 acyl transfer undergone by enol esters of
1,3-diketones is easily observable by ^{13}C NMR. The accompanying
spectra were recorded at +30° and -50° on our Bruker WP-60
(15.08 MHz, spectral width 3750 Hz, acquisition time 1.089 s,
pulse angle 30°, Fourier number 8K, 1000 transients). We are
currently using this technique to obtain the thermodynamic
parameters for the degenerate rearrangement of the enol
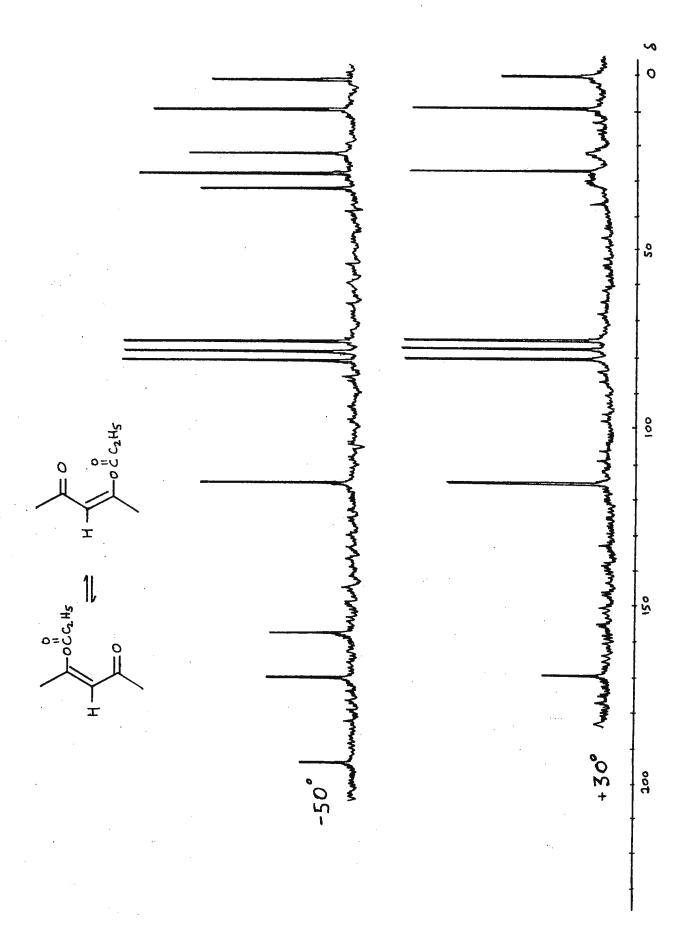propionate ester of pentan-2,4-dione.

Yours sincerely,

H. L. Holland   T. R. B. Jones   T. A. Bardsley.

P. S. Please credit this communication to the subscription of
Professor Jack M. Miller of our Department.

FACULTEIT DER WISKUNDE EN NATUURWETENSCHAPPEN

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

Uw kenmerk   Uw brief van   Ons kenmerk

Datum September 12, 1980

Onderwerp

Selective NOE experiments yield detailed information about gene-5-protein
DNA interactions.

Dear Dr. Shapiro,

Gene-5-protein (GVP, molecular weight 10.000) is a DNA double helix
destabilizing protein, which is encoded by the filamentous bacteriophage
M13. In the lifecycle of the phage GVP plays an important role during
the DNA replication process. Therefore studies of the binding of the
protein to DNA are of considerable importance. At present we are
investigating which of the amino acid residues in the protein are
involved in interaction with DNA. Particularly interesting results were
obtained at 500 MHz for the GVP-d(A)$_8$ complex. The aromatic spectrum of
the protein recorded between 6.0 and 7.5 ppm downfield from DSS in the
absence and the presence of the DNA fragment is shown in Fig. 1a and
Fig. 1b respectively.

Earlier we were able to assign several of the resonances to phenyl-
alanyl or tyrosyl residues via CIDNP and selective deuteration
experiments (1,2). In the present experiments we have elucidated the
complete aromatic spectrum of GVP (Fig. 1a) and of the GVP-d(A)$_8$ complex
(Fig. 1b) by performing selective NOE experiments. Comparison of these
spectra shows that significant shifts occur for the resonances of the
residues designated Phe I, Tyr I and Tyr IV upon complex formation
indicating that these residues are involved in the interaction with DNA.
Selective irradiation of the adenine ring protons of the oligonucleotide
in the complex gives rise to Overhauser effects for the ring protons of
these residues.

This demonstrates the proximity of the aromatic rings to the adenine
rings. In combination with the shifts discussed above, these results
show that the aromatic residues are involved in the interaction with
DNA most likely by stacking interactions. Future experiments will be
directed towards the determination of the DNA structure in the complex
so that a basis for the protein unwinding mechanism can be provided.

Sincerely Yours,

N. Alma   W.E. Hull   B. Harmsen   J. van Boom   C.W. Hilbers
              (Bruker-Physik AG   (University of
               Rheinstetten-   Leiden)
               Forchheim, FRG)

1) G.J. Garssen, R. Kaptein, J.G.G. Schoenmakers and C.W. Hilbers
   (1978) Proc. Natl. Acad. Sci. USA 75, 5281.

2) G.J. Garssen, G.I. Tesser, J.G.G. Schoenmakers and
   C.W. Hilbers (1980) Biochemica et Biophysica Acta 607, 361.
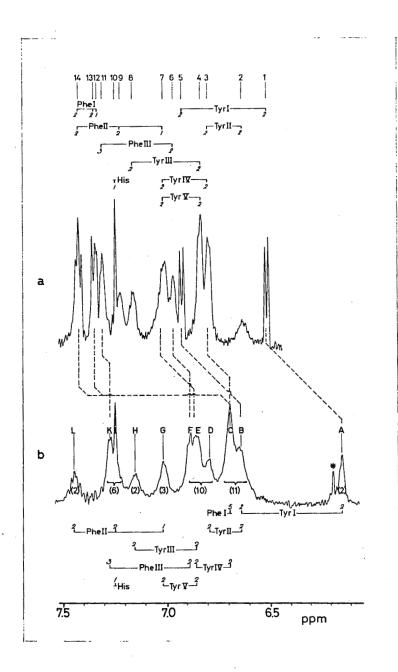
Figure 1.
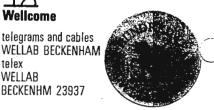
Comparison of the aromatic part of the 500 MHz ^{1}H NMR spectra of the free protein (a) and the protein-$d(A)_8$ complex (b). Prominent shifts are indicated with dashed lines. The interpretation of the spectra is given above (a) and underneath (b). Residue numbers are arbitrary but a particular residue has the same number in a and b. The number of protons of a certain residue resonating at the indicated position is given in italics. The peaks labelled A to L in the spectrum of the protein-$d(A)_8$ complex are protein resonances. The triplet marked with an asterisk belongs to a H_1' sugar proton of the $d(A)_8$. The number of protons resonating at a certain spectral position is denoted in parentheses.

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

12th September 1980

Dear Dr. Shapiro,

Selective Detection of Quaternary Carbons

Everybody has his or her own favourite method of achieving
a required result, most of which mean a lot of hard work in
order to throw away most of the information content in a
spectrum. We are no exception in looking for easy interpretations
and recently we have been looking at the discrimination of
quaternary carbons in a complex ^{13}C spectrum.

A number of methods have appeared in the literature and
these include the use of off-resonance noise-modulated
decoupling with the proton-bearing carbons giving broad
resonances, suppression of which is possible using convolution
difference or spin-echo techniques. We have found that good
sensitivity and resolution is obtained if the FID resulting
from the off-resonance noise-decoupled nuclei is subjected
to a Lorentzian-Gaussian transformation, severely over-
enhanced to produce a net zero integral in the absorption
spectrum and then displayed in absolute value mode.

The example shown is the 22.63MHz ^{13}C spectrum of the cardiac
glycoside digoxin (R=H) in dmso-d_6. The lower trace is the
result of 800 scans with normal noise decoupling and the upper
trace arises from 15000 scans with low power off-resonance
noise decoupling and Gaussian magnitude spectrum presentation.

Yours sincerely,

J.C. Lindon
Department of Physical Chemistry

A.G. Ferrige.

265-31

Section de Physique

CH - 1211 GENÈVE 4

UNIVERSITÉ DE GENÈVE

Professeur B.L. SHAPIRO
Department of Chemistry
Texas A & M.University
College of Science
College Station Texas
77843 U.S.A.

V/REF.   N/REF. GJB/md   GENÈVE, LE   23 septembre 1980

Cher Professeur Shapiro,

Merci de votre lettre de rappel du 3 septembre 1980.

Publications récentes du groupe
----

1) "Medical diagnosis by nuclear magnetism in the earth field range"

   (to be published in NMR Basic principles and progress vol. 19 - march 1981)

   Abstract : In this paper we study the application of nuclear magnetism in the weak field and in particular in the earth's field to medical diagnosis.

   After a review of the technique used, the free precession of the nuclear magnetization, we show how essential parameters, the equilibrium magnetization and the relaxation times can be obtained.

   We then give some examples to show the dependence of these parameters on the properties of the biological tissues, in particular healthy or pathological physiological fluids.

   Finally, we describe the results of some preliminary in situ measurements of physiological fluids, and discuss the possibilities offered by these techniques.

./..

Professeur B.L. Shapiro

2) "Diagnosis of meconium in amniotic fluid by nuclear magnetic resonance spectroscopy"

(Bernard C. BENE, Clinique Obstétricale, Université Lyon I, Hôpital de la Croix Rousse, 69317, Lyon Cedex 1, France) (to be published in Physiological Chemistry and Physics vol. 12 - 1980)

Abstract : Some 40 samples of amniotic fluid were studied by nuclear magnetic resonance (NMR) spectroscopy as the first step in developing techniques for analysis of amniotic fluid in vivo without amniocentesis. Il was found possible to distinguish amniotic fluid containing meconium (foetal feces) from all other kinds of amniotic fluid (hydramnios or normal fluid) by proton NMR, but precise chemical or cytological analysis seemed unavailable. Also reported are results of in vitro analysis of amniotic fluid, and of measurements performed in vivo on other biologic fluids to investigate possible in situ detection of pathological amniotic fluid.

3) "In situ identification of human physiological fluids by nuclear magnetism in the Earth's field"

(G.-J. BENE, B. BORCARD, E. HILTBRAND and P. MAGNIN) Phil. Trans. R. Soc. Lond. B289 501-502 (1980)

4) "Proton spin T_1 relaxation dispersion in liquid H_2O by slow proton-exchange"

(V. GRAF and F. NOACK, Physikalisches Institut der Universität Stuttgart)

(F.-J. BENE, Section de Physique de l'Université de Genève) J. Che. Phys. 72 861-863 (1980)

Abstract : We have measured the longitudinal proton spin relaxation time T_1 in pure water as a fonction of temperature (10, 37, 80°C) and Larmor frequency (50 Hz $\leq \nu_o \leq$ 50 kHz) by means of field-cycling techniques. T_1 becomes frequency dependent below $\nu_o \approx$ 5 kHz due to the slow proton-exchange between

Professeur B.L. Shapiro

---

different oxygen environments (^{16}O, ^{17}O, ^{18}O), which modulates the magnetic ^1H - ^{17}O interaction. The proton-exchange time τ_e was found to be Arrhenius-like with activation energy 13.4 kJ/mol and pre-exponential 1.5×10^{-6}s ($37^{\circ}C$: τ_e = 2.6×10^{-4}s). This is in fairly good agreement with results obtained previously in the literature by more indirect NMR methods. The new access to proton-exchange reduces the expérimental error limits and allows measurements at extrememly small frequencies, where the familiar $T_{1\rho}$ technique no longer works.

Next ampere meetings

1) 6th Ampere Summer School
     Schloss Seggau bei Leibnitz
     Steiermark, Austria
     September 6-16, 1981

   <u>Topics</u> : Basic principles of NMR; New Techniques – 2DfT, Relaxation Analysis, CIDNP Studies of Molecular Conformation by NMR; Protein and Nucleic Acid Structure and Dynamics; Enzymic Mechanisms, Membrane Dynamics; NMR <u>in vivo</u>: Study of Phosphorus Metabolism by ^{31}P NMR; Regulation of Metabolic Pathways by ^{13}C NMR; NMR monitoring of Hypoxia; NMR Imaging

2) 5th Specialized Colloque Ampere NMR in Solids
     Uppsala (Sweden)
     August 17-21, 1981

   <u>Topic</u> : The 5th Specialized Colloque Ampere will be devoted to recent developments in NMR spectröscopy applied to solids, in particular to techniques giving selective information about the interactions of nuclei with the environment, such as resolved chemical shielding or quadrupole interactions. This includes for examples multiple quantum spectroscopy, multiple pulse techniques, double resonance and magic angle spinning.
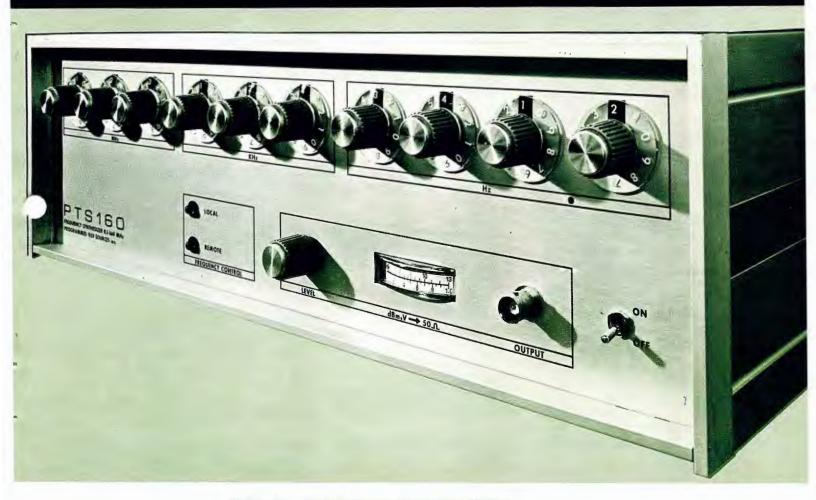
Avec mes sentiments très cordiaux.

Professeur G.J. BENE

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The PTS 160 is a generator of precision frequencies. It transfers the accuracy and stability of a frequency standard (built-in or external) to any output frequency between .1 MHz and 160 MHz. Steps as fine as 0.1 Hz are available and all functions are remotely programmable.

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This new system of synthesis has drastically cut complexity and parts count. The attendant reduction of primary power input and dissipation (less than 50% of that of competitive designs) is a major factor in the reliability which is further enhanced by the use of ceramic ICs, all metal-can transistors and a packaging system maximizing mechanical integrity and stability while keeping weight low. For ease of service most modules are identical and of plug-in design.

SPECIFICATIONS

FREQUENCY	Range:	0.1MHz to 160 MHz
	Resolution:	0.1Hz to 100KHz steps (optional in decades)
	Control:	Local by 10-position switches. Remote by TTL-BCD, 1248, buffered par. entry or by IEEE 488 BUS. (option)
	Switching Time:	20 micro-sec. (within 0.1rad at new frequency)
OUTPUT	Level:	+3 to +13dBm, (1V) into 50 ohms, metered in dBm and volt
	Flatness:	±0.5dB
	Impedance:	50 ohms
	Control:	Manual by F/P-control, remote by voltage, (+0.63 to +2.00V)
	Settling Time:	20 micro-sec.
SPURIOUS OUTPUT	Discrete:	—75dB
	Harmonics:	—35dB at full output, (—40dB at lower level)
	Phase Noise:	—63dBc, (0.5Hz to 15KHz), incl. effects of int. standard
	L (1Hz):	100Hz/105dBc; 1KHz/115dBc; 10KHz/123dBc; 100KHz/130dBc.
	Noise Floor:	—135dBc/Hz
FREQUENCY STANDARD	Internal:	3×10^{-9}/day or 1×10^{-8}/day (optional)
	External Drive:	5.000 orr 10.000MHz, 0.5V into 300 ohms
	Aux. Output	10.000MHz, 0.4V into 50 ohms
GENERAL	Oper. Ambient:	0 to 55°C, 95% R.H.
	Power:	105-125V, 50-400Hz, 45 Watts
	Dimensions/Weight:	19 x 5¼ x 18" Relay rack or bench cabinet, 35 lbs.

PRICES (domestic)	Resolution:	100KHz	10KHz	1KHz	100Hz	10Hz	1Hz	0.1Hz
	$	3,250.—	3,450.—	3,650.—	3,850.—	4,050.—	4,250.—	4,450.—

	Freq. Standards: (Option)	3×10^{-9}/day, $450.— (oven) 1×10^{-8}/day, $200.— (TCXO)
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Department of Chemistry

The Florida State University
Tallahassee, Florida 32306

September 4, 1980

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

Re: "POSTDOCTORAL OPENING: NMR OF SYNTHETIC POLYMERS"

Dear Barry:

Once again we have an opening for a postdoctoral researcher doing joint work with the two of us. (We keep having this opening because these people are in demand by employers.) This next position begins after this coming January, although an earlier start might be possible. A 12-month appointment with a stipend of $12,000-13,500 is offered with a possible renewal.

One difference this year is that our polymer collaboration will be geographically split in the fall of 1981 when G.C.L. is going to take up a new faculty position in the Chemistry Department at Syracuse University. The new postdoctoral fellow will remain at Florida State University, but will continue interactions with Dr. Levy (some visits to S.U. may be anticipated).

Interested candidates should write directly to one of us.

Warmest regards,

George C. Levy
Professor

Leo Mandelkern
Professor

GCL/LM/lh

CASE WESTERN RESERVE UNIVERSITY · CLEVELAND, OHIO 44106

September 15, 1980

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

Dear Barry:

^{29}Si NMR of Methyl Phenyl, Dimethyl Siloxane Copolymers

For the past year we have been interested in ^{29}Si NMR of siloxane polymers and aqueous silicate solutions in preparation for a solid phase study of these compounds. The encolsed spectra are of dimethyl siloxane, methyl phenyl soloxane copolymers which have not been previously observed to our knowledge. The nomenclature follows that of the literature:
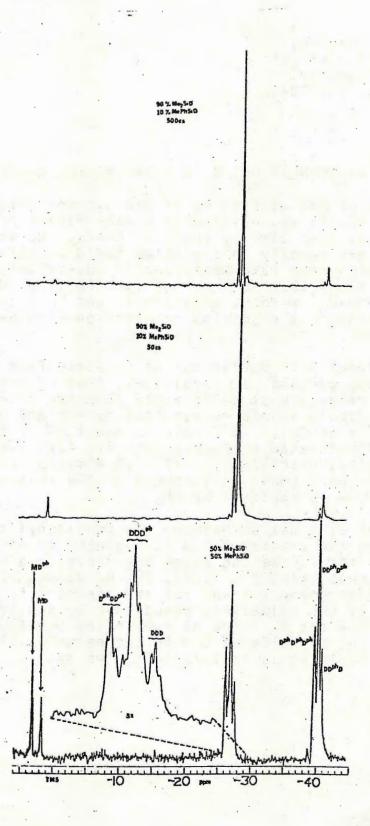

The triad and diad fine structure for the middle and end groups respectively are assigned in the spectra. Unassigned pentad and triad fine structure for the middle and end groups are also evident.

The samples were generously donated by Dr. Lee Smith at Dow Corning. They were doped with 2.87×10^{-3} M Gd(fod)$_3$ as a relaxation agent and run on an XL-100-15 NMR.

Sincerely,

Dr. W.M. Ritchey

P.S. We are currently constructing a low field 1.4 T solid state NMR from a
      Bruker console with NIC -14 and a Varian HA-60 wide gap magnet. We need
      a computer (preferably NIC 1080 or 1180 series) to complete the system.
      Information on available systems would be greatly appreciated.

Department of Chemistry

90 % Me₂SiO
10 % MePhSiO
500cs

90% Me₂SiO
10% MePhSiO
50cs

DDDᵖʰ

MDᵖʰ

MD

Dᵖʰ DDᵖʰ

DDD

50% Me₂SiO
50% MePhSiO

DDᵖʰDᵖʰ

Dᵖʰ Dᵖʰ Dᵖʰ

DDᵖʰD

Sₓ

TMS   -10   -20 ppm   -30   -40

CONCORDIA UNIVERSITY

DEPARTMENT OF CHEMISTRY

September 17, 1980

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

Dear Barry,

STRUCTURAL ASSIGNMENT USING ^{1}H SPIN-LATTICE RELAXATION RATES

Assignment of the structures of the two mono-N-methyl
derivatives of uracil was originally a non-trivial problem whose
solution required some time by chemical means. We were interested
in finding out how readily this problem could be solved using [1]H
spin-lattice relaxation rate measurements (R_1-values), carried
out under conditions used for routine spectra (i.e. 0.1 M
solutions in DMSO-d_6, without degassing), and in a self-contained
set of experiments, not requiring correlation with data from
model compounds.

The structural information can be obtained from the relaxation
rates of the ring protons, in particular, that of H-6. This
proton must be relaxed most efficiently (because of the $1/r^6$ distance
dependence for dipole-dipole relaxation) by H-5 and protons
located at N-1 (H or CH_3). H-6 relaxes about 50% faster than
H-5 in the non-deuterated compounds (uracil, 48%; 1-methyl uracil
(1a), 53%; 3-methyl uracil (2a), 47%; 1,3-dimethyl uracil, 50%).
There appears to be a small enhancement of the relaxation rate
of H-6 when N(1)-H is replaced by CH_3.

A clear cut distinction between the monomethyl compounds
can be made when the remaining N-H is replaced by deuterium
(1b, 2b). When the relaxation rates are normalized with respect
to the methyl group rates (= 1.00), the R_1 values of H-5 and H-6
in the 1-methyl compound (1a and 1b) are essentially unaffected
by replacement of the relatively remote 3-H by deuterium (1a vs 1b).
In contrast, while the R_1-value of 5-H in the 3-methyl compound
is unaffected, the R_1-value of 6-H is decreased by 17% when the
neighbouring 1-position is deuterated (2a vs 2b).

1a   1b

2a   2b

It is important that relaxation rates be normalized with respect to the rate of protons remote from the site of change (in this case, the N-CH$_3$ protons) when R_1-values of different molecules are to be compared. In this way, the effects of differences in experimental conditions, e.g. temperature, are minimized.

These experiments were carried out using the XL-200 spectrometer at McGill University. We thank the McGill Chemistry Department for making the spectrometer available, and Dr. Jeremy Everett for running the spectra.

Best regards.

Yours sincerely,

L. D. Colebrook   S. Lokuge   O. S. Tee

FACILITIES:
Bioinstrumentation
Biostatistics
Electron Microscope
Environmental Stress
Instrument Shop
Nuclear Magnetic Resonance
Scientific Computer

Mailing Address:
P. O. 6998 (933 Bldg.)
Chicago, IL 60680

Location:
1940 West Taylor Street
Chicago, IL 60612

September 17, 1980

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

"Water-Wik" stops unsightly ice build-up.

Dear Barry:

Since assuming the maintenance responsibilities for the CXP-180 at the Medical Center, I have been trying to eliminate the ice that formed in the vent arm of the LN_2 dewar. This hidden ice was forming because the external ice on the vent tubing was continuously melting, the resultant water was pooling on the nut holding the vent tubing, and the water was working its way past the protective O-ring under the nut and into the LN_2 vent arm. Replacing the O-ring did not significantly reduce the problem; then I discovered "Water-Wik", and my unsightly ice build-up was virtually eliminated.
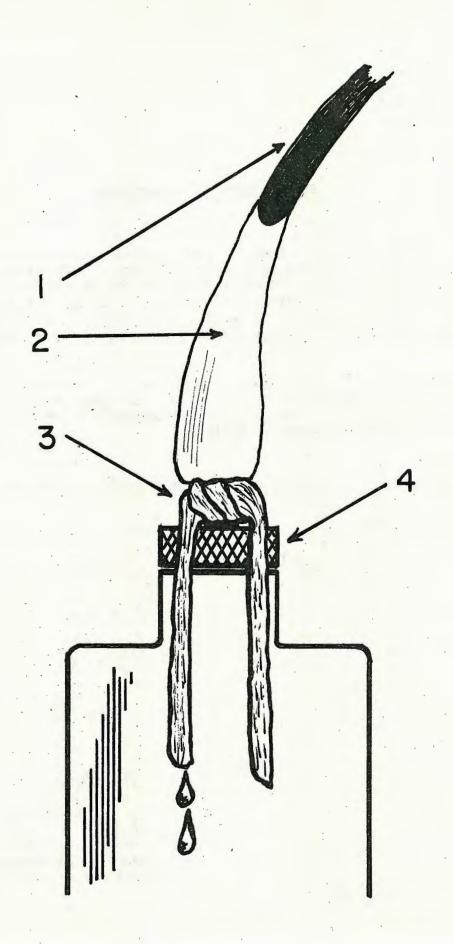
"Water-Wik" is a new improved strip of ordinary cotton gauze (3) that snugly, just above the nut (4), upon which the melting ice (2), surrounding the LN_2 vent tubing (I), is tied.

"The "Wik" is worth several times its cost in those emergency situations when unexpected humidity arrives, and you cannot find a proper O-ring anywhere in the lab.

I recommend "Water-Wik" for your readers who are troubled by unsightly ice build-up.

Sincerely,

Robert A. Kleps

RAK:lo

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
HEALTH EFFECTS RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

Professor B. L. Shapiro   September 17, 1980
Tamunmr Newsletter
Department of Chemistry
Texas A & M University
College of Science
College Station, Texas   77843

Conformations of a Pterophane

Dear Barry:

Mike Caspar of East Carolina University and I have been interested for some time in the possibilities of face-to-face interactions of the aromatic rings in pterophanes. The potential conformers and an ambient temperature 60 MHz ^{1}H spectrum of one pterophane are shown in Figure 1. The ultraviolet spectrum rules out the presence of significant amounts of the conformer III at ambient temperature. The ^{13}C NMR spectrum at ambient temperature exhibits seven peaks, corresponding to rapid interconversion of IIA and IIB.

At low temperatures, only the asymmetric conformer II is present, as evidenced by twelve peaks in the ^{13}C NMR spectrum at -107.7°C. Lineshape analysis of the ^{13}C spectra as a function of temperature gives the thermodynamic parameters in Table 1. The ^{13}C NMR chemical shifts are given in Table 2.

TABLE 1

THERMODYNAMIC PARAMETERS FOR IIA $\rightleftharpoons$ IIB

$\Delta G^{\ddagger}$ = 9.33 ± 0.03 kcal mol^{-1}

$\Delta H^{\ddagger}$ = 5.88 ± 0.16 kcal mol^{-1}

$\Delta S^{\ddagger}$ = -18.5 ± 1.4 cal deg^{-1} mol^{-1}
at -81.2°C.

TABLE 2
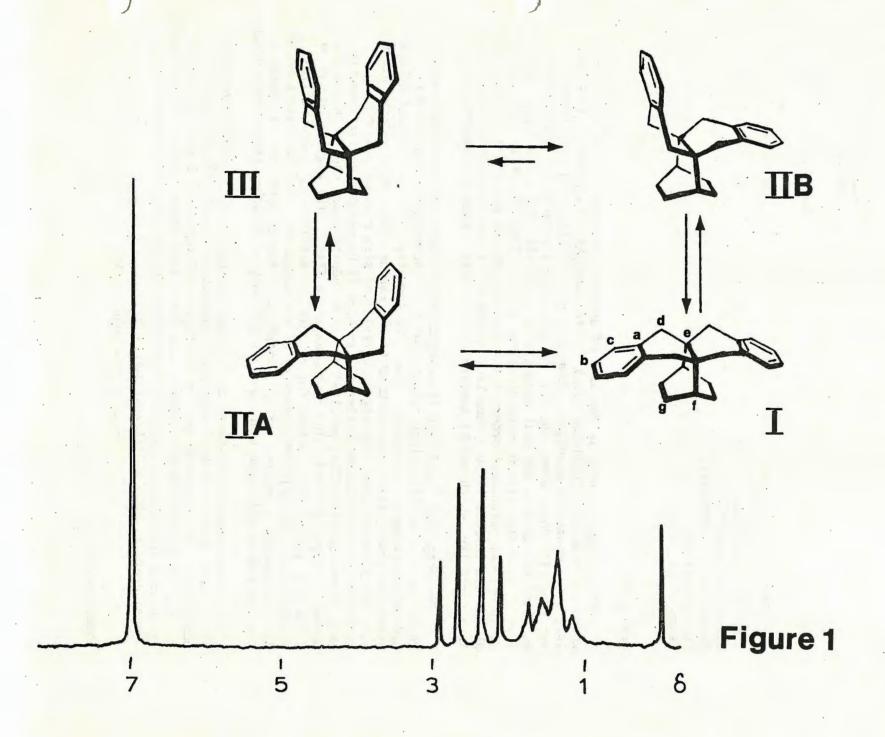
^{13}C NMR CHEMICAL SHIFTS OF A PTEROPHANE

Carbons	δ, 10.8°C	δ, -106.6°C	
a	138.99	139.43	138.63
b	127.20	128.08	126.12
c	125.86	126.04	125.62
d	42.18	42.97	40.29
e	40.81	40.47	
f	38.03	37.74	
g	24.12	23.68	23.74

With best wishes.

Sincerely yours,

Nancy K. Wilson, Ph.D., Chief
Chemical Characterization Section
Analytical Chemistry Branch (MD-69)

Figure 1

University of Waterloo

September 18, 1980

Dr. Bernard L. Shapiro,
Editor and Publisher,
TAMU NMR Newsletter,
Texas A&M University,
Department of Chemistry,
College Station,
Texas 77843, U.S.A.

Dear Barry,

We continue to work in the area of aqueous lyotropic liquid crystals, where the component building blocks of the mesophases are finite (but rather large) non-spherical micelles. Some time ago we discovered that there were two types (J. Phys. Chem. 80, 174, 1976). Type I with finite cylindrical micelles and $\Delta X > 0$ - the bulk diamagnetic susceptibility anisotropy, and Type II with disc-like bilayer micelles $\Delta X < 0$. There is still some question as to whether positional order of the micelles in the mesophase is completely absent and therefore the system truly nematic. I want to address this letter to a curiosity, which may be answered in the near future by experiments.

For both Type I and Type II mesophases the pseudo-extended hydrocarbon chains of the micelles align perpendicular to the magnetic field and to a hydrophobic/aqueous interface. Since the symmetry axis of the micelles for type I CM phases lies perpendicular to the chains, then these systems align with the director along the magnetic field and simultaneously along the interface of the micelle as always. In type II DM mesophases the symmetry axis of the micelles lies parallel to the pseudo-extended chains and so the director aligns perpendicular to the magnetic field. The symbols CM and DM after the type of phase, stand for cylindrical micelles and disc micelles, which properly describe the symmetry of the situation. The dominant part of the diamagnetic anisotropy of the mesophase is the co-operative alignment of the individual and known diamagnetic anisotropy of extended hydrocarbon chains.

In some chemical systems, it is possible to provoke a phase transition type I CM → type II DM by adding small amounts of electrolyte or neutral amphiphile. Of course we may, in principle fool ourselves because a change in sign of ΔX does not necessarily mean there is a phase change. If we could change the diamagnetic susceptibility anisotropy of individual micelles of either symmetry then a ΔX transition, e.g.,

type I CM → type II CM

should occur.

Such a $\Delta\chi$ transition in the same phase would have some interesting NMR characteristics. The quadrupole splittings of deuterium in say D_2O in the mesophase would change exactly by a factor -2 at the change in sign of $\Delta\chi$. This has never been observed previously. We think we know how to do it!

Kind regards,

Len Reeves

Len Reeves

UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

DEPARTMENT OF CHEMISTRY
(803) 777-5263

September 16, 1980

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

Dear Dr. Shapiro:

We would like to offer for sale a used Perkin Elmer 90 MHz CW permanent magnet NMR Spectrometer. This instrument is equipped for observation of ^1H and ^{19}F, variable temperature, internal lock, spin decoupling and Indor. We have 2 probes for this spectrometer, one of which has been modified to the Mark II spinner configuration. At the time we declared this instrument surplus (Aug. 1980) we were operating well above new instrument specifications for sensitivity and resolution. We will consider any reasonable offer.

We would also be interested in hearing from anyone who has a used FT data system, preferably Nicolet, which they would be interested in selling. We would like to acquire the mini computer, software, a working disk drive, and a pulse programmer, but are willing to discuss purchase of any portion of the above package.

Please send inquiries to myself or Dr. J. D. Odom, at

Department of Chemistry
University of South Carolina
Columbia, SC 29208

Please indicate if you are interested in buying, selling, or trading.

Sincerely,

Ron G.

Albert R. Garber, Ph.D.
Manager, NMR Services

GBF

Gesellschaft für
Biotechnologische
Forschung mbH

GBF   Mascheroder Weg 1   D-3300 Braunschweig-Stöckheim

Professor B.L. Shapiro
Texas A & M University
Department of Chemistry

College Station, TX 77843

USA

Abteilung

Physikal. Meßtechnik

Ihre Nachricht vom	Telefon 05 31/70 08-1	Telefondurchwahl	Datum
		05 31/70 08 306	September 18, 1980

Dear Dr. Shapiro:

ELIMINATION OF PARAMAGNETIC IMPURITIES FROM NMR SAMPLES

Cozzone and Jardetzky[1] have strongly recommended the removal of paramagnetic impurities from ^{31}P NMR samples by chromatography on 'Chelex-100' ion-exchange resin or by treatment with complexing agents such as dithizone or 8-hydroxy-quinoline.
For our continuing studies on long-range P,P coupling constants[2], we normally achieve the elimination of paramagnetics by shaking $CDCl_3$ solutions of our compounds with aqueous EDTA in a separating funnel. This method works well, but is only applicable if the compound to be investigated is better soluble in the organic phase than in water. Otherwise the 'Chelex' treatment becomes necessary. This is most easily carried out by transfering a small amount of resin into a Pasteur pipette and having the solution to be measured run through it[3]. The Figure shows the efficiency of this treatment. The bottom trace is a proton decoupled ^{31}P NMR spectrum of triethyl phosp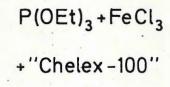hite in $CDCl_3$ (line width ca. 1 Hz). The middle trace shows the spectrum of the solution which had been maltreated with a very small crumb of ferric chloride. This caused the line width to increase to 150 Hz and the peak position to shift by ca. 2 ppm. After the solution had been run through 'Chelex', the line width returned to its old value and the chemical shift regained the original value to within 0.2 ppm (top trace). I hope that this example will convince your readers of the usefulness of this technique.
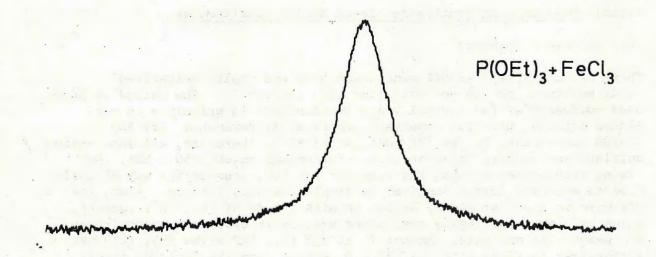
Yours sincerely,

Ludger Ernst

Ludger E r n s t

1) P.J. Cozzone & O. Jardetzky, Biochemistry 15, 4853 (1976).

2) L. Ernst, Org. Magn. Reson. 9, 35 (1977); JCS Chem. Commun. 375 (1977).

3) If solutions in organic solvents are subjected to this treatment, they may have to be dried afterwards, because 'Chelex' contains ca. 70% of water.

Encl. (Figure)

P(OEt)$_3$ + FeCl$_3$

+ "Chelex-100"

P(OEt)$_3$ + FeCl$_3$

P(OEt)$_3$

10 ppm
(405 Hz)

SFU

September 19, 1980

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

Title: Multinuclear Synthesizer-Based XL-100 Spectrometer

Dear Professor Shapiro:

There may still be XL-100FT owners who have not 'multinuclearized'
their machines, or are not satisfied with the result. The method we have
used successfully for several years is identical in principle to pub-
lished methods, with two important practical differences: (1) The
XL-100 is operated in the ^{19}F mode (94.13 MHz), therefore, all interesting
multinuclear observe frequencies are far enough below (<40.5 MHz) the
mixing frequencies so that the transmit and L.O. frequencies may be puri-
fied to whatever degree required by simple low-pass filters. Also, the
mix up/down synthesizer may be set on either side of the ^{19}F frequency,
which is a great advantage over other systems if broadcast transmitters
are nearby (in our case, Channel 8, at 500 ft., ERP = 164 kW); (2) The
synthesizer is mixed with the ^{19}F L.O. rather than the incoming signal,
which greatly reduces the danger of introducing spurious responses and
noise figure effects. The console modification required is trivial and
reversible (see Figure).

 The transmitter mixer module is constructed of standard components in a
large cast aluminum box. The receiver mixer module is constructed in a
much smaller cast box, and installed in the "RF Module". The L.O. line
is removed from its original destination and brought to the box, and a
jumper made and installed to continue to the L.O. destination. One coaxial
cable is brought into the console to carry the synthesizer signal. The
module is activated by pressing "Multinuclear" (formerly "B") which also
selects the ^{19}F modules. Since we use the synthesizer and power amplifier
for other purposes, transmitter connections are made manually, but relay
selection would be easily arranged. The synthesizer is usually set on the
"low side" so the console "observe offset" operates normally. The probe

Professor B.L. Shapiro
September 19, 1980

tuning, balancing, adjust mode lock, and CW sweep all operate exactly
as for the original modules, except "RF Field" is set ~20 dB higher.
The 10 MHz synthesizer reference and a 1 MHz counter reference are ob-
tained from a VCXO locked to the ^{2}H master in such a way as to give exact
and rational counter readings and synthesizer settings. Depending on the
synthesizer used, a filter may be required at its output to minimize har-
monic responses.

We have found that the XL-100 requires a relatively high gain preamp to
control the noise figure. There is no observed interaction with the
^{19}F external lock. We would estimate that ^{1}H modules could be used
in this system even in the presence of high power, ^{1}H noise decoupling,
but very careful engineering would be required.

Please credit this contribution to R.J. Cushley.

Yours sincerely,
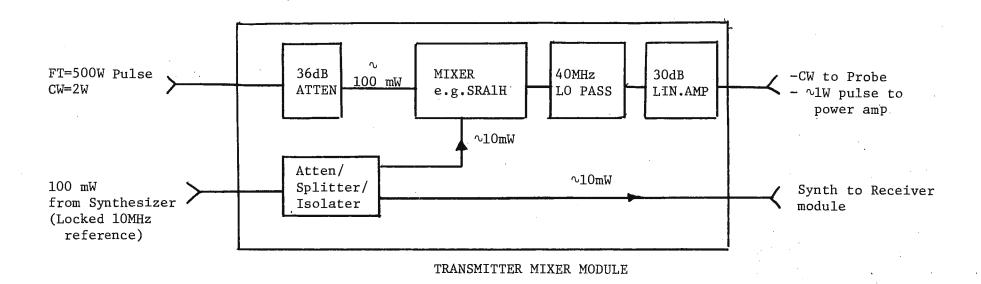
A. Brooke.
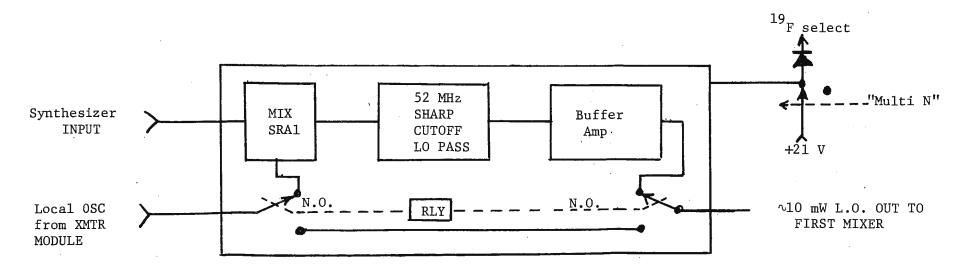
A. Brooke
N.M.R. Spectrometrist
Department of Chemistry

AB:LV

BLOCK DIAGRAM   XL100FT   MULTINUCLEAR

FT=500W Pulse
CW=2W

| 36dB ATTEN | $\sim$ 100 mW | MIXER e.g.SRA1H | 40MHz LO PASS | 30dB LIN.AMP |

-CW to Probe
- $\sim$1W pulse to power amp.

$\sim$10mW

Atten/ Splitter/ Isolater

100 mW
from Synthesizer
(Locked 10MHz
reference)

$\sim$10mW

Synth to Receiver module

TRANSMITTER MIXER MODULE

^{19}F select

Synthesizer
INPUT

| MIX SRA1 | 52 MHz SHARP CUTOFF LO PASS | Buffer Amp |

"Multi N"

+21 V

Local OSC
from XMTR
MODULE

N.O.   RLY   N.O.

$\sim$10 mW L.O. OUT TO FIRST MIXER

RECEIVER MIXER MODULE

The
Guelph-Waterloo Centre
for Graduate Work in Chemistry

Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1   519/824-4120

20 August 1980

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

Deuterium Isotope Effect on $^1J(^{15}N, ^{13}C)$ in Hydrogen Cyanide

Dear Barry:

Ken Friesen and I have recently prepared a mixture of neat ^{15}N-enriched HCN and ^2HCN and studied the ^{13}C nmr spectrum with and without proton decoupling. The following scalar coupling constants were obtained: $^1J(^{15}N, ^{13}C) = 18.5 \pm 0.10$ Hz and $^1J(^{13}C, H) = 267.3 \pm 0.10$ Hz in $H-C\equiv^{15}N$; $^1J(^{15}N, ^{13}C) = 18.8 \pm 0.10$ Hz and $^1J(^{13}C, ^2H) = 40.95 \pm 0.10$ Hz in $^2H-C\equiv^{15}N$. We are confident that the secondary isotope effect on $^1J(^{15}N, ^{13}C)$ is real; we have found it reproducible using acquisition times of 12.8 s in all experiments and as long as 32.77 s in some. To our knowledge only primary isotope effects on coupling constants have been previously reported (1-3). The measured value of $^1J(^{15}N, ^{13}C)$ in hydrogen cyanide is in excellent agreement with the value of -18.8 Hz calculated by Schulman and Venanzi (4). The above-mentioned isotope effect and others will be described in J. Magn. Reson..

I am presently on sabbatical in Colin Fyfe's laboratory at the University of Guelph. Best wishes.

Yours sincerely,

Rod

Rod Wasylishen

(1)   J.M.A. Al-Rawi, J.A. Elvidge, J.R. Jones, and E.A. Evans, J. Chem. Soc. Perkin Trans. II, 449 (1975).
(2)   R.R. Fraser, M.A. Petit, and M. Mislow, J. Am. Chem. Soc. 94, 3253 (1972).
(3)   J.P. Bloxsidge, J.A. Elvidge, J.R. Jones, R.B. Mane, and M. Salioughian, Org. Magn. Reson. 12, 574 (1979).
(4)   J.M. Schulman and T. Venanzi, J. Am. Chem. Soc. 98, 4701 (1976); J.M. Schulman, J. Magn. Reson. 28, 137 (1977).

UNIVERSITÄT
GESAMTHOCHSCHULE
SIEGEN

FACHBEREICH 8
Naturwissenschaften II (Chemie/Biologie)
Organische Chemie II
Prof. Dr. H. Günther

Universität-Gesamthochschule-Siegen - Postfach 210209 - 5900 Siegen 21

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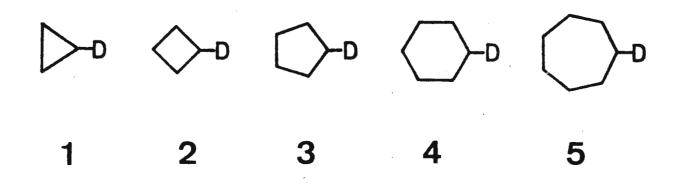College Station
Texas 77843

U. S. A.

5900 Siegen 21, 23 Sept., 1980
Adolf-Reichwein-Straße
Postfach 210209
Telefon (0271) 7401
Durchwahl 740– 4390/4400

Negative ^{2}H/^{1}H Isotope Effects.

Dear Barry,

thanks for your green one!

In connection with our work on ^{13}C,^{2}H coupling constants[1] we have found –to our surprise – negative (downfield) ^{2}H/^{1}H isotope effects on ^{13}C chemical shifts in two hydrocarbons: $^3\Delta$ in cyclopentane and $^4\Delta$ in cycloheptane (see spectra and table). Presently we are studying other simple hydrocarbons and substituted systems to see whether any rationalization of this puzzling behavior is possible.

1　　**2**　　**3**　　**4**　　**5**

Sincerely yours,

H. Günther　　　R. Aydin

1) R. Aydin and H. Günther, Z. Naturf. <u>34b</u>, 528 (1979).

Table 1. Deuterium Isotope Effects on Carbon Chemical

Shifts $^n\Delta$ (ppm); positive values are shifts to higher field;

	$^1\Delta$	$^2\Delta$	$^3\Delta$	$^4\Delta$
$\underline{1}^c$	0.3087	0.0641	---	---
$\underline{2}^c$	0.3630	0.1466	0.0272	---
$\underline{3}^d$	0.3737	0.1031	-0.0121	---
$\underline{4}^d$	0.4180	0.1037	0.0249	---
$\underline{5}^d$	0.4125	0.1098	0.0267	-0.0140
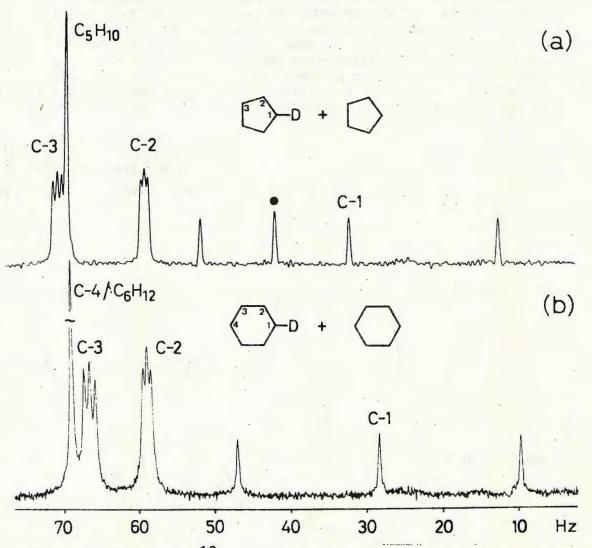
Fig. 1. 100.6 MHz ^{13}C NMR spectra of cyclopentane/cyclopentane-d_1 (a) and cyclohexane/cyclohexane-d_1 (b) with ^{1}H broadband decoupling; signal marked with (•) is due to unknown impurity.

STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

STANFORD MAGNETIC RESONANCE LABORATORY

(415) 497-4062
(415) 497-6153

October 3, 1980

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

2-Dcoupling

Dear Dr. Shapiro:

We were recently posed with a problem which seemed to require deuterium decoupling, in order to distinguish and measure a proton proton coupling for assignment of the stereochemistry in several stages of a reaction. Since we did not have a proton probe with a deuterium decoupling coil, and attempts to use the deuterium lock channel for decoupling failed miserably (as might be expected), we turned to the modern battery of experiments which seem able to do anything -- 2 dimensional NMR. With a moment's thought it is obvious that the normal 2D J spectroscopy will remove all of the hetero couplings in one dimension, and all of the homonuclear couplings in the other, with the usual constraint of a first order spectrum. Although this is a trivial experiment, we know of no previous application of it, and somehow it seems convenient to spread out everything in two dimensions. We hope that the accompanying pictures are sufficient to keep the Newsletter coming.

Sincerely,
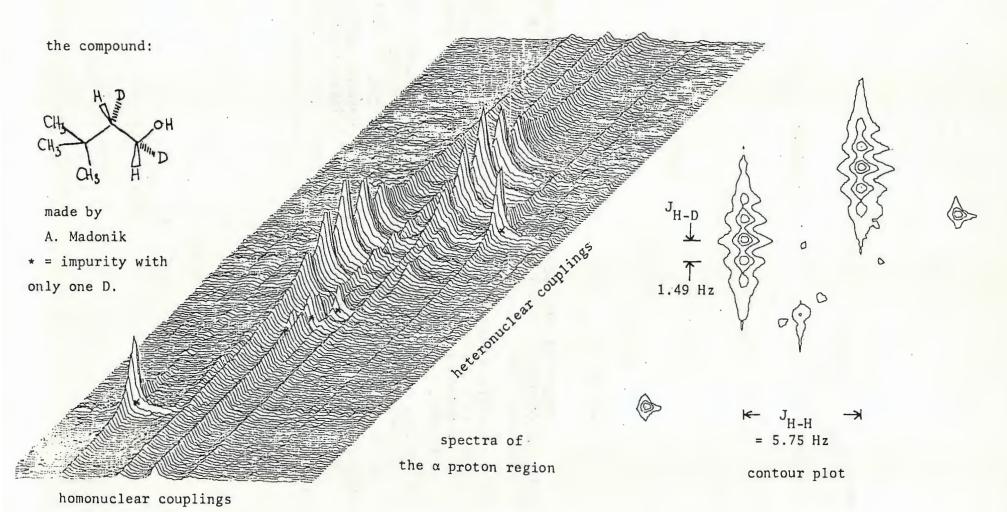
David Wemmer   Oleg Jardetzky

2D J projection

normal spectrum

the compound:

made by
A. Madonik
* = impurity with
only one D.

homonuclear couplings

heteronuclear couplings

spectra of
the α proton region

J_{H-D}

1.49 Hz

$\overset{\longleftarrow \quad J_{H-H} \quad \longrightarrow}{= 5.75 \text{ Hz}}$

contour plot

Professeur PIERRE LASZLO

Institut de Chimie
Université de Liège
Sart-Tilman par 4000   *Liège* 1, *Belgique*

Professor B.L. SHAPIRO
Texas A&M University
College of Science
College Station, TX 77843   September 5, 1980

<u>Preprints available.</u>

Dear Barry,

Rather than excerpting from these some results of interest
to the nmr community, I shall simply list the titles of recent products
from this laboratory :

with A. Delville, C. Detellier, A. Gerstmans : "Chelation of the sodium
   cation by polyamines : a novel approach to preferential solvation, and
   to the understanding of ^{23}Na chemical shifts and quadrupolar coupling
   constants", <u>J. Am. Chem. Soc.</u>, in press.

with the same co-authors, "On the theoretical interpretation of sodium-23
   nmr chemical shifts and quadrupolar coupling constants, as supported
   by new experimental evidence", <u>J. Magn. Resonance,</u> in press.

with A. Delville, J. Grandjean, Ch. Gerday, Z. Grabarek, and W. Drabikowski,
   "Sodium-23 nmr as an indicator of sodium binding to calmodulin and tryptic
   fragments, in relation with calcium content", <u>Eur. J. Biochem.</u> in press.

"^{23}Na NMR studies of cation binding by natural and synthetic ionophores",
   <u>Bull. Magn. Res.</u>, in press.

With best regards,

Cordially yours,

Pierre Laszlo

PL:nd

FX SERIES
OF
FT NMR SYSTEMS

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

FX-60Q
Solids Probe (^{13}C) with
 Magic Angle Spinning
High Resolution Probe ($^{13}C/^{1}H$)

FX-200
Dual Probe ($^{13}C/^{1}H$)
Broad Band (^{15}N to ^{31}P)
50 KHz Spectral Width

System Features

- Light Pen Control System
- Foreground/Background
- Digital Quadrature Detection
- Multi Frequency Observation
- Programmable Multi Pulser
- Module Performance Indicator Lights

- Comprehensive Auto Stacking
- T_1-rho
- Double Precision (32 bit word length)
- Floppy; MH Disc Storage
- 50KHz Spectral Width
- CPU Expansion to 65K

JEOL