Texas A&M University

N-M-R Newsletter

October, 1980

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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 that we make a short contribution regarding our unpublished work on the equilibrium binding constants (K) of lanthanide shift reagents with organic substrates.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. 

.../
These, and earlier, results show that $K$ is quite sensitive to changes in basicity (e.g. compounds 1, 6 and 7, $K$ increasing with $pK_a$) 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

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$K$</th>
<th>p$K_a$</th>
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<tr>
<td>1. $R=R_1=H$</td>
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<td>2. $R=Me, R_1=H$</td>
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<td>4.</td>
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<tr>
<td>5.</td>
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<td>-</td>
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<tr>
<td>6.</td>
<td>51.3</td>
<td>2.04</td>
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<td>7.</td>
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<td>8.</td>
<td>9.4</td>
<td>5.5</td>
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<td>9. $N\rightarrow O$</td>
<td>1680</td>
<td>-</td>
</tr>
<tr>
<td>10. $Ph_2S$</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>11. $Ph_2S \rightarrow O$</td>
<td>277</td>
<td>-</td>
</tr>
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</table>
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 imidene derivative \( \mathcal{E} \) on the basis of its \( ^1 \)H NMR chemical shift parameters.

Imidines like \( \mathcal{E} \) react readily with amines to form mono- or disubstituted compounds.

![Chemical Reaction Image]

When 5,7-diimino(5H,7H)-pyrrolo(3,4-b)pyridine (\( \mathcal{E} \)) reacts with morfoline in ethanol only one monosubstituted isomer was obtained, which was determined to have the morfoline group next to the pyridine N atom (\( \mathcal{E}_1, \ Y = \text{CH}, \ Y = \text{N} \)). The other isomer (\( \mathcal{E}_2, \ X = \text{N}, \ Y = \text{CH} \)) could not be isolated. In Table 1 some proton chemical shift data of \( \mathcal{E}_1 \) and related compounds are collected.

From this table it follows that an isoindole system such as in \( \mathcal{E}_1 \), causes a downfield shift of about 1.3 ppm for the methylene hydrogens adjacent to the morfoline nitrogen atom, whereas the oxygen methylene hydrogens (\( H_2 \), and \( H_5 \)) are deshielded for about 0.1 ppm. These effects might be due to the partial positive charge induced on the morfoline nitrogen by conjugation with the imidene system. Which also precludes the morfoline ring to rotate freely around the C-N bond with the imidene (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 morfoline substituent, as in \( \mathcal{E}_2 \), one group of methylene hydrogens (\( H_2 \)) shows an additional downfield shift of 0.7 ppm (cf. \( \mathcal{E}_1 \) vs. \( \mathcal{E}_2 \)) presumably due to the anisotropy of the lone pair electrons of the pyridine (of pyrazine) nitrogen atom.
This deshielding effect is even more pronounced, when cis-2,6-dimethylmorpholine 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 $\xi$ and $\zeta$, 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 $\xi$.

Sincerely yours,

M.J.O. ANTEUNIS  
L. SPIESSENS
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 detection (SED) 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

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 $\tau$ 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 $\tau \geq (5J)^{-1}$ (Fig. 1).

This makes SED quite attractive, particularly in cases where other $^{1}$H nuclei obscure accurate determination of $J_{\text{Hg199Hg}}$. In a similar
fashion, while SEID is optimized with \( \tau = (4J)^{-1} \), \( \tau \)-values of (2J)\(^{-1} \) and (3J)\(^{-1} \) also produce acceptable \( ^{199}\text{Hg} \) spectra (Fig. 2). This sloppiness may be the result of the long \( ^{199}\text{Hg} \) pulse widths (100 \( \mu \text{sec} \)) used, and in any event is useful to us.

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

Mary F. Roberts
Assistant Professor of Chemistry

Spin Echo Sequence - Variation of $\tau$

(Fig. 1)

(Fig. 2)
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Institute/Company: ______________________________________________________

Address: ______________________________________________________________
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 justification program. Copies of these programs will be reproduced in my new textbook to be published by Wiley next spring.

I have an immediate opening for an assembly language programmer to work in the field of NMR and IR software, programming our Aspect 2000 and some microcomputers. Suitable candidates should have at least a B.S. in physical science and some familiarity with NMR. We will consider candidates at all levels and could offer the chance of some publishable research to a post-doctoral student. Bruker, of course, are equal opportunity employers.

Sincerely,

Jim

James W. Cooper
Vice President for Software Development

/g
Dear Barry,

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 understanding of the substituent transmission mechanisms or if the used correlation model will be useful for predictive purposes, confirming signal assignments etc.

Irrespective of the ambition, one surely has spoiled the chances to get relevant information if one uses any of the common, fixed dual substituent parameter models (DSP) without showing that the correlation for the present data set is statistically better than using a one-parameter model (F-test). It is rather discouraging to find papers in well-respected journals where authors mention a successful correlation to a single parameter (i.e. $\sigma_p$ or $\sigma_R^0$) 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 contribution 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.

2. Fit NMR SCS to a single $\sigma$-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


Best regards

Ulf Edlund

MICHIGAN STATE UNIVERSITY

COLLEGE OF NATURAL SCIENCE • DEPARTMENT OF CHEMISTRY
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.
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 $\sigma_{ij}$. 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 $\mathrm{O-P-O}$ bond angle $\alpha$ (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 $^{31}\mathrm{P}$ chemical shift (> 200 ppm). A good linear correlation of the asymmetry parameter $\eta$ ($\eta = \frac{\sigma_{32} - \sigma_{11}}{\sigma_{33}}$) with the $\mathrm{O-P-O}$ bond angle is observed.

Sincerely yours.

J.B. ROBERT

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

$n(\%) = \frac{\sigma_{22} - \sigma_{11}}{\sigma_{33}}$ (\%) are the asymmetry parameters of the $\sigma$ tensor. $\Delta \sigma = \sigma_{33} - \sigma_{11}$ (ppm) characterizes the anisotropy. $\alpha(\text{degrees})$ is the intracyclic O-P-O bond angle.

<table>
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<tr>
<th></th>
<th>$\sigma_{11}$</th>
<th>$\sigma_{22}$</th>
<th>$\sigma_{33}$</th>
<th>$n(%)$</th>
<th>$\Delta \sigma$</th>
<th>$\alpha(\text{°})$</th>
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<td>130</td>
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Dear Barry,

Recently we have been examining the $^{15}$N NMR spectrum of $N(2, 2, 6, 6$-tetramethylpiperidyl)nitrene, $\cdot$. The study has allowed us to gain some interesting insights into the 1,1-diazen 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-diazen shows doublets at 917.0 and 321.4 ppm ($J = 15.5$ Hz). The 1,1-diazen 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-diazen chromophore.

The $^{15}$N spectrum of this 1,1-diazen 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 $n-\pi^*$ transition ($\lambda_{\text{max}} = 543$ 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 $n-\pi^*$ 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 $N=N$ $\pi$ bonds.

With all good wishes,

Sincerely,

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

John D. Roberts
Figure 1.
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 INEPT1-5 literature. The first is that, given either a pre-pulse4 or appropriate phase-cycling5, 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 $^1$H. For $^1$H observation in H$_2$O, one can conceive of a C+H or N+H INEPT experiment to reveal only CH's or NH's, or even an H+H+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 straightforward, as seen in Figure 1 [D$_2$ is $^2$T$_1$ from Ref. 4; D$_3$ is $^3$T$_2$].

The second aspect of INEPT that deserves more attention is the sensitivity gain due to the dependence on $^1$H 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 spectroscopists around; now with any luck there will be even more!

Sincerely,

Steve Patt

"NORMAL EXPERIMENT" USING ERMST ANGLE OPTIMIZED FOR T1=15 SEC.
8/22/80
SLP

EXP3 PULSE SEQUENCE: INEPT

ACQUISITION DEC. & UT
TH 15.250 ON 1.250
SV 10000.0 DD 0
RT 0.000 DM VV
NP 16000 DMM EE
PW 6.3 DNF 200
DI 5.000 DHP V
TD -500 DLP 20
NT 120
CT 120 PROCESSING
MULT 1 SE 0.310
J 0 LB 1.000
PP 45.0 FN 16364
D2 3.57E-3 MATH 1
D3 2.19E-3
FB 5500 DISPLAY
BS 16 SP 0
SS 4 UP 10000.0
IL N US 0
IN N SC 120
DP Y UC 120

SOLVENT ELIMINATION USING INEPT EXPERIMENT
10% EMTYLENZENE IN ACETONE-D6
8/22/80
SLP

EXP4 PULSE SEQUENCE: INEPT

ACQUISITION DEC. & UT
TH 15.250 ON 1.250
SV 10000.0 DD 0
RT 0.000 DM NV
NP 16000 DMM CE
PW 12.0 DNF 200
DI 5.000 DHP V
TD -500 DLP 20
NT 1.00E 9
CT 120 PROCESSING
MULT 1 SE 0.310
J 140.0 LB 1.000
PP 45.0 FN 16364
D2 3.57E-3 MATH 1
D3 2.19E-3
FB 5500 DI PLAY
BS 16 SP 0
SS 4 UP 10000.0
IL N US 0
IN N SC 0
DP Y UC 120
INSENSITIVE NUCLEI ENHANCED BY POLARIZATION TRANSFER WITH REFOCUSING 85% HMDS

EXP 4 PULSE SEQUENCE: INEPT

ACQUISITION DEC. & UT
TN 29.000 DN 1.750
SW 500.0 DD 0
RT 0.000 DM NY
PW 8000 DMM CE
D1 10.000 DHP Y
T0 200 DLP 20
CT 4
MULT 1 FN 8192
J 6.7 MATH 1
PP 45.0
D2 7.46E-2 DISPLAY
D3 2.13E-2 SP 250.2
FB 300 WP 25.0
BS 128 US 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

EXP 1 PULSE SEQUENCE: INEPT

ACQUISITION DEC. & UT
TN 29.000 DN 1.750
SW 500.0 DD 0
AT 8.000 DM NY
PW 8000 DMM CE
D1 15.0 DMP Y
TN 1.000 DLP 20
CT 4
MULT 3 FN 8192
J 7.3 MATH 1
PP 45.0
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FB 300 WP 100.0
BS 128 US 1500
SS 4 SC 0
IL N WC 120
IN N IS 100
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RFP 0
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AI
How much do you know about the Varian XL-200?

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-


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
- Use of PASCAL statements within sequence
- PASCAL language-based code with resident 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 SPARE0 HLV
  - ORSPULSE DELAY SPARE0 DBL
  - DECPULSE IZERO DECPHASE ADD
  - SIMPULSE LOOP RCVRON SUB
  - STATUS DECIN RCVRON MOD2
  - ASSIGN INCR (ND) MOD4
- Ability to specify and vary phase and receiver offsets 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 time
- Use of math statements for sequence timing calculations

**Example sequences**
- Standard two-pulse
  - Carr-Purcell-Meiboom-Gill T2
  - Quadrupole echo
  - Cross-polarization
  - Multiple-contact cross-polarization
  - Selective excitation
  - Quadrature selective excitation
  - INEPT with referencing and decoupling
  - PREP J-Cross polarization
  - Refocused 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 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 special widths standard
- Pulse timing to 0.1 microsecond
- Automatic filter selection
- Four observe phases under CPU control
- Exploit 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
- 48-bit microprogram specialized instruction set
- Transmission and decoupler frequencies
- Decoupler high/low power switch under CPU control
- Precise 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
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- Noise amplitude and scaling limit checking
- Look-Up Table
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- Look-Up Table
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/$^1$H 5-mm VT probe
- $^{31}$P 9-mm VT broadband probe
- $^1$H 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 refrigeratorter
- Welded dewar
- 25-watt rf transmitter output—200-watt pulse amplifier
- 10-µsec $^1$H 90° pulse/15-µsec $^{13}$C 90° pulse
- Internal $^1$H 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
- Multifasting-simultaneous acquire, plot, print, display, parameter entry
- Queuing of acquisitions, plots, prints and calculations
- Spooling of prints 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/interpolation/gaussian apodization functions
- Parameter set libraries
- 2D transform
- Plot graphics
- T1, T2, 3-parameter least-squares-fit analysis programs
- Spin simulation
- LAOCOON with magnetic equivalences
- User-definable disk libraries
- PASCAL system source code availability
- NOE calculation
- Add-subtract-convolution spectral manipulation
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 $\alpha$P and $\beta$P 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 $\mu$ = 0.12N, i.e., 0.5 Hz/°C at 40.6 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.
Professor B.L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Tx 77843  
U. S. A.

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 déjà 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. Nyström and myself) have applied the method to several types of problems (Chem. 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 (≈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

UNIVERSITY OF MISSOURI-COLUMBIA

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 research plans, and have three letters of recommendation sent to:

Dr. Pierre Crabbe, Chairman, Department of Chemistry, University of Missouri, Columbia, MO 65211. AN AFFIRMATIVE ACTION/EQUAL EMPLOYER.
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 −30° 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.
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 phenylalanyl 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. Harmen J. van Boom C.W. Hilbers

(Bruker-Physik AG Rheinstetten- Porchheim, FRG)


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.
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 22.63 MHz $^{13}$C spectrum of the cardiac glycoside digoxin (R=H) in dmsol-d. 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

A.G. Ferrige.

Department of Physical Chemistry

12th September 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.
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. It 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)

4) "Proton spin T₁ relaxation dispersion in liquid H₂O by slow proton-exchange"

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

Abstract: We have measured the longitudinal proton spin relaxation time T₁ in pure water as a function of temperature (10, 37, 80°C) and Larmor frequency (50 Hz ≤ ω₀ ≤ 50 kHz) by means of field-cycling techniques. T₁ becomes frequency dependent below ω₀ ≈ 5 kHz due to the slow proton-exchange between...
different oxygen environments \( (^{16}\text{O}, ^{17}\text{O}, ^{18}\text{O}) \), which modulates the magnetic \( ^1\text{H} - ^{17}\text{O} \) interaction. The proton-exchange time \( T_e \) was found to be Arrhenius-like with activation energy 13.4 kJ/mol and pre-exponential \( 1.5 \times 10^{-8} \) s \( (37^\circ\text{C} : T_e = 2.6 \times 10^{-8} \) 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 experimental error limits and allows measurements at extremely small frequencies, where the familiar \( T_1 \) technique no longer works.

Next Ampere meetings

1) 6th Ampere Summer School
   Schloss Seggau bei Leibnitz
   Steiermark, Austria
   September 6-16, 1981
   **Topics**: 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 in vivo: Study of Phosphorus Metabolism by \(^{31}\text{P} \) NMR; Regulation of Metabolic Pathways by \(^{13}\text{C} \) NMR; NMR monitoring of Hypoxia; NMR Imaging

2) 5th Specialized Colloque Ampere NMR in Solids
   Uppsala (Sweden)
   August 17-21, 1981
   **Topic**: The 5th Specialized Colloque Ampere will be devoted to recent developments in NMR spectroscopy 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.

[Signature]

Professeur G.J. BENE
160 MHz

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PTS 160 FREQUENCY SYNTHESIZER

- 0.1 MHz to 160 MHz
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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.

The PTS 160 is a direct frequency synthesizer of novel design providing high performance for many demanding applications. With its low spurious outputs, fast switching, low phase noise and wide choice of resolution (finest step), it is suited for a range of uses from NMR to communications or ATE.

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**
- 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 x 10⁻⁹/day or 1 x 10⁻⁸/day (optional)
- External Drive: 5.000 or 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**

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**IEEE 488 Interface:** $650.— (This option replaces standard parallel entry BCD interface)

**IEEE 488 Interface:** Delete Front Panel Controls: —$200.—

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**PROGRAMMED TEST SOURCES, inc.**

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160A/80-000
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/1h
September 15, 1980

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

Dear Barry:

29Si NMR of Methyl Phenyl, Dimethyl Siloxane Copolymers

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

\[
\begin{align*}
D^\bullet &= \text{Me} \quad - \quad \text{Si} \quad - \quad \text{O}_y^- \\
M^\bullet &= \text{Me} \quad - \quad \text{Si} \quad - \quad \text{O}_x^- \\
E^\bullet &= \text{Me} \quad - \quad \text{Si} \quad - \quad \text{O}_z^- \\
D^{\text{rh}} &= \text{O}_y^- \quad - \quad \text{Si} \quad - \quad \text{O}_x^- \\
M^{\text{rh}} &= \text{O}_y^- \quad - \quad \text{Si} \quad - \quad \text{O}_z^- \\
E^{\text{rh}} &= \text{Me} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
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).
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-CH₃ protons) when R₁-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
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 LN2 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 LN2 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 LN2 vent tubing (1), 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. Kieps

RAK:lo
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 1H 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 13C 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 13C NMR spectrum at -107.7°C. Lineshape analysis of the 13C spectra as a function of temperature gives the thermodynamic parameters in Table 1. The 13C NMR chemical shifts are given in Table 2.

TABLE 1
THERMODYNAMIC PARAMETERS FOR IIA \( \rightleftharpoons \) IIB

<table>
<thead>
<tr>
<th></th>
<th>( \Delta G^\circ )</th>
<th>( \Delta H^\circ )</th>
<th>( \Delta S^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal mol(^{-1})</td>
<td>kcal mol(^{-1})</td>
<td>cal deg(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td>IIA ( \rightleftharpoons ) IIB</td>
<td>( 9.33 \pm 0.03 )</td>
<td>( 5.88 \pm 0.16 )</td>
<td>( -18.5 \pm 1.4 )</td>
</tr>
<tr>
<td></td>
<td>( -81.2 )°C</td>
<td>( -107.7 )°C</td>
<td>( -18.5 \pm 1.4 )</td>
</tr>
</tbody>
</table>

TABLE 2
13C NMR CHEMICAL SHIFTS OF A PTEROPHANE

<table>
<thead>
<tr>
<th></th>
<th>10.3°C</th>
<th>-106.6°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>138.99</td>
<td>139.43</td>
</tr>
<tr>
<td>b</td>
<td>127.20</td>
<td>128.08</td>
</tr>
<tr>
<td>c</td>
<td>125.86</td>
<td>126.04</td>
</tr>
<tr>
<td>d</td>
<td>42.18</td>
<td>42.97</td>
</tr>
<tr>
<td>e</td>
<td>40.81</td>
<td>40.47</td>
</tr>
<tr>
<td>f</td>
<td>38.03</td>
<td>37.74</td>
</tr>
<tr>
<td>g</td>
<td>24.12</td>
<td>23.68</td>
</tr>
</tbody>
</table>

With best wishes.

Sincerely yours,

Nancy K. Wilson, Ph.D., Chief
Chemical Characterization Section
Analytical Chemistry Branch (MD-69)
Figure 1
September 18, 1980

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 \( \Delta X \) 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 \( \Delta X \) transition, e.g.,

\[
\text{type I CM} + \text{type II CM}
\]

should occur.
Such a $\Delta X$ transition in the same phase would have some interesting NMR characteristics. The quadrupole splittings of deuterium in say D$_2$O in the mesophase would change exactly by a factor -2 at the change in sign of $\Delta X$. This has never been observed previously. We think we know how to do it!

Kind regards,

Len Reeves
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-hydroxyquinoline.

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 transferring 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 phosphite 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

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)
$$\text{P(OEt)}_3 + \text{FeCl}_3 + "\text{Chelex-100}"$$

$$\text{P(OEt)}_3 + \text{FeCl}_3$$

$$\text{P(OEt)}_3$$

10 ppm (405 Hz)
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 published 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 purified 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
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 obtained from a VCO locked to the \(^2\text{H}\) 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 harmonic 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 \(^{19}\text{F}\) external lock. We would estimate that \(^1\text{H}\) modules could be used in this system even in the presence of high power, \(^1\text{H}\) noise decoupling, but very careful engineering would be required.

Please credit this contribution to R.J. Cushley.

Yours sincerely,

A. Brooke
N.M.R. Spectrometrist
Department of Chemistry

AB:LV
FT=500W Pulse
CW=2W

100 mW
from Synthesizer
(Locked 10MHz
reference)

36dB ATTEN
\( \sim 100 \text{ mW} \)

MIXER
e.g. SRA1H

40MHz LO PASS
30dB LIN.AMP

\( \sim 10\text{mW} \)

Atten/
Splitter/
Isolater

\( \sim 10\text{mW} \)

Synth to Receiver
module

- CW to Probe
- 1W pulse to
power amp

\( 36\text{dB} \)
\( 100 \text{ mW} \)
ATTEN

\( \sim 10\text{mW} \)

TRANSMITTER MIXER MODULE

MIX SRA1

52 MHz
SHARP
CUTOFF
LO PASS

Buffer
Amp.

\( \sim 10\text{mW} \)
L.O. OUT TO
FIRST MIXER

SYNTHESIZER
INPUT

Local OSC
from XMTR
MODULE

"Multi N"

\( 19 \text{F select} \)

421 V

\( \sim 10 \text{ mW} \)
LO OUT TO
FIRST MIXER

RECEIVER MIXER MODULE
20 August 1980

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

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

Dear Barry:

Ken Friesen and I have recently prepared a mixture of neat $^{15}$N-enriched HCN and $^{2}$HCN and studied the $^{13}$C nmr spectrum with and without proton decoupling. The following scalar coupling constants were obtained: $^{1}J(^{15}N, ^{13}C) = 18.5 \pm 0.10 \text{ Hz}$ and $^{1}J(^{13}C, H) = 267.3 \pm 0.10 \text{ Hz}$ in $^{13}$C:$^{15}$N; $^{1}J(^{15}N, ^{13}C) = 18.8 \pm 0.10 \text{ Hz}$ and $^{1}J(^{13}C, ^{2}H) = 40.95 \pm 0.10 \text{ Hz}$ in $^{2}$H:$^{15}$N. We are confident that the secondary isotope effect on $^{1}J(^{15}N, ^{13}C)$ 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 $^{1}J(^{15}N, ^{13}C)$ in hydrogen cyanide is in excellent agreement with the value of $-18.8 \text{ Hz}$ 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 Wasylishen

Dear Barry,

thanks for your green one!

In connection with our work on $^{13}\text{C}, ^{2}\text{H}$ coupling constants\(^1\) we have found to our surprise negative (downfield) $^{2}\text{H}/^{1}\text{H}$ isotope effects on $^{13}\text{C}$ chemical shifts in two hydrocarbons: $\Delta^3$ in cyclopentane and $\Delta^4$ 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.

Sincerely yours,

H. Günther

Table 1. Deuterium Isotope Effects on Carbon Chemical Shifts $^{n}\Delta$ (ppm); positive values are shifts to higher field;

<table>
<thead>
<tr>
<th></th>
<th>$^{1}\Delta$</th>
<th>$^{2}\Delta$</th>
<th>$^{3}\Delta$</th>
<th>$^{4}\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{1}{c}$</td>
<td>0.3087</td>
<td>0.0641</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$^{2}{c}$</td>
<td>0.3630</td>
<td>0.1466</td>
<td>0.0272</td>
<td>---</td>
</tr>
<tr>
<td>$^{3}{d}$</td>
<td>0.3737</td>
<td>0.1031</td>
<td>-0.0121</td>
<td>---</td>
</tr>
<tr>
<td>$^{4}{d}$</td>
<td>0.4180</td>
<td>0.1037</td>
<td>0.0249</td>
<td>---</td>
</tr>
<tr>
<td>$^{5}{d}$</td>
<td>0.4125</td>
<td>0.1098</td>
<td>0.0267</td>
<td>-0.0140</td>
</tr>
</tbody>
</table>

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.
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,

[Signature]

2D J projection

normal spectrum
the compound:

\[
\text{H} \quad \text{D} \\
\text{H} \quad \text{D} \\
\text{H} \quad \text{D} \\
\text{H} \quad \text{D} \\
\text{H} \quad \text{D}
\]

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

spectra of the a proton region

homonuclear couplings

heteronuclear couplings

\( J_{\text{H-D}} = 1.49 \text{ Hz} \)

\( J_{\text{H-H}} = 5.75 \text{ Hz} \)
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 the same co-authors, "On the theoretical interpretation of sodium-$^{23}$nmr chemical shifts and quadrupolar coupling constants, as supported by new experimental evidence", J. Magn. Resonance, in press.


With best regards,

Cordially yours,

Pierre Laszlo
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- Digital Quadrature Detection
- Multi Frequency Observation
- Programmable Multi Pulser
- Module Performance Indicator Lights
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- \( T_\text{rho} \)
- Double Precision (32 bit word length)
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