J. Oakes and E. G. Smith
Investigation of Solutions of MnEDTA2− .......................... 1

Y. Marat
Tickling Anywhere, Particularly 19F. ................................ 3

A. Steigel
Diastereotopicity as Probe to Lactam-Lactim Tautomerism .......... 9

A. L. Batch, G. B. Matson and C. H. Lindsay
Isotopomer Identification Through SPT Experiments ................ 9

G. Freudenthal
13C Shifts in Benzenium Ions ....................................... 11

J. Brondeau, B. Diter and D. Canet
Writing with an Analog Plotter and a Nicolet 1180 Computer .... 13

R. H. Cox
Glutathione Conjugates of Epoxides .................................. 15

J. A. Ferrerri
Studies on Molecular Motions of Biological Peptides ................. 18

A. Boyd
XL-100 Program Patch .................................................. 19

H. S. Gutowsky
NMR and ESR Studies of Thylakoid Membranes; Postdoctoral Opening ....................................................... 21

A. R. Turner, C. B. Storm and M. D. Swann
Scatchard Plots in the Analysis of DNMR Spectra ..................... 23

P. Pyykko and L. Wiesenfeld
Relativity, Lone Pairs and Spin-Spin Coupling ........................ 25

P. H. Bolton
DANTE vs. "Lousy Samples" ........................................... 27

W. T. Ford
13C Relaxation in Crosslinked Polystyrene Gels ....................... 29

V. Wray
One-Bond J(CC) .............................................................. 31

O. Lutz
Hetero-Nuclei in Solid State .......................................... 33

G. Mavel, C. Santini, F. Mathay and R. Mankowski-Favelier
Further Phosphole Structures by 1H, 13C, 31P NMR ................ 35

G. L. Elchhorn
Position Available ....................................................... 36

A. G. Marshall
New Campus Instrument Center at Ohio State University .......... 36

P. Diehl
Direct Couplings Providing Poor Structural Information .......... 37

J. Oldfield
500, 360 MHz Postdoctoral Positions ................................ 39

G. E. Maciel
Permanent NMR Staff Position ....................................... 40

J. B. Lambert
Position Available for NMR Manager ................................. 41

X. L. Nunnally
Who Shot J.R., and Does Anyone Have a Used Pulse Spectrometer for Sale? .................................................... 42

J. B. N. Engberts
Position Available ....................................................... 43

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

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Dear Professor Shapiro

Investigation of Solutions of MnEDTA$^{2-}$

Although ethylenediamine tetra acetate (EDTA) has found widespread use as a sequestrant, the structures of many of its complexes with metal ions in aqueous solution await confirmation. The MnEDTA$^{2-}$ complex is known to be seven co-ordinate in the solid state. We have carried out investigations using water proton relaxation times to ascertain the number of water molecules, $n$, co-ordinated to the metal ion in aqueous solution. Whilst this has been the major objective of this work, it has also been demonstrated that secondary sphere solvation i.e. water molecules hydrogen bound to complexed EDTA, plays an important part in determining the overall water relaxation times.

Contributions to overall relaxation rates from second solvation sphere water can be estimated experimentally by using larger, more flexible liquids than EDTA capable of octahedrally co-ordinating to Mn$^{2+}$ or theoretically, using constants obtained from the crystal structure. Typical contributions to $T_1^{-1}$ due to secondary sphere water are $2s^{-1}$ at 60 MHz and 293K for an overall relaxation rate of $3.8s^{-1}$.

Measurements of $T_1$ for the complexes have been obtained from frequency dependence of $T_1^{-1}$ (FIG 1) a method which does not assume prior knowledge of $D = \frac{6 S(s+1)}{r^6} \gamma_2^2 g^2 B^2$. $^1$

Values of $T_1$ for Mn$^{2+}$, MnEDTA$^{2-}$, and MnEGTA$^{2-}$ obtained are $4.2 \times 10^{-11}s$, $6.3 \times 10^{-11}s$, and $8.9 \times 10^{-11}s$, respectively. $T_1$ decreases from $1.5 \times 10^{-8}s$ to $1.67 \times 10^{-9}s$ at 60 MHz upon complexation.

Values for $n$, calculated at various frequencies, range from 1.0 to 1.1, suggesting that the number of water molecules bound to Mn$^{2+}$ in its complex with EDTA is one. It thus seems likely that the crystal structure of MnEDTA$^{2-}$ retains its integrity in aqueous solution.

We apologize for the delay in sending this contribution.

Yours sincerely

J. Oakes

19 MAY 80

[Signature]

EG Smith
Figure 1.

Graph showing reciprocal relaxation times ($T_1^{-1}$) as a function of experimental frequency (MHz) for different species:

- $\text{Mn}^{2+}$
- $\text{MnEOTA}^{2-}$
- $\text{MnEGTA}^{8-}$

The graph illustrates the decrease in $T_1^{-1}$ with increasing frequency.
June 27, 1980

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

Dear Dr. Shapiro:

Re: Tickling anywhere, particularly $^{19}\text{F}$.

We have recently made two modifications to our Bruker B-SV3 B decoupler that may be of interest to other owners of this unit.

The first modification removes the fixed frequency ($^{31}\text{P}$ at 36.44 MHz in our case) 80 W power amplified and connects a jumper across the coax connectors in the "main frame". Because the 10 W driver amplifier is of broad-band design, the decoupler will now provide 10 to 12 W over the entire multinuclear range of our WH-90. The decoupling frequency is provided by the Shomandl synthesizer in the spectrometer. We have used this decoupler for a number of experiments requiring $^{19}\text{F}$ decoupling and have found that 10 W is more than sufficient to decouple the one-bond carbon-fluorine coupling in a CF$_3$ group; provided that the decoupling frequency lies within about 100 Hz of the fluorine resonance. An external power amplifier may be added, if desired, but the effective range appears to be limited more by modulator bandwidth than by power available. The 90 MHz decoupler circuit in the Bruker probes may be tuned to 84.7 MHz with a slight adjustment of the "resonance" capacitor. To decouple $^{19}\text{F}$ and $^1\text{H}$ simultaneously, or to extend the range below 84.7 MHz, it would be necessary to build a matching network to double-tune the decoupler coil.

The other modification adds an external modulation jack and switch to the B-BM1 modulator (figs. 1 and 2). This allows modulation of the decoupling frequency with an external signal or gating of the decoupler with a TTL logic pulse from the pulse programmer (NIC 293A).

con't 

.......

We have also used this input to mix the $90 + \Delta F_2$ MHz signal from the WH-90 proton decoupler with a 5.32 MHz signal from the Shomandl synthesizer to obtain $84.70 + \Delta F_2$ MHz, allowing computer-controlled offset when decoupling or "tickling" fluorine. The advantage of this approach is that the offset-synthesizer has a much smaller step size than the Shomandl: 0.007 Hz compared to 1 Hz.

Figure 3 shows the results of a $^1H - ^{19}F$ double resonance experiment using this system.

Please credit this letter to Ted Schaefer's account.

Sincerely,

Kirk Marat

Figure 1
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Diastereotopicity as Probe to Lactam-Lactim Tautomerism

Dear Professor Shapiro,

Our previous $^{13}$C NMR study (Newsletter 251-7) on the prototropic lactam-lactim tautomerism of 1 and 2 did not provide conclusive evidence for the preferred tautomeric structure. We now wish to show that information on the prototropic and silatropic tautomerism of 2-5 can be obtained by $^1$H NMR using the methylene signals as structural probe.

The method is based on the finding that, in contrast to the fixed dilactam compound 6, the methylene protons are diastereotopic in the fixed lactam-lactim compounds 2. The shift difference of 0.08 - 0.09 ppm in the latter compounds can be explained by the different anisotropy of the carbonyl and OR groups.

In view of this effect, the observation of isochronous methylene protons in the potentially tautomeric compound 2 indicates the predominance of structure 2a. However, in the case of 1 the isochrony of the methylene protons does not allow a discrimination between the presence of structure 1a and a fast tautomerization in structure 1b. On the other hand, the methylene protons of the trimethylsilyl derivatives 3-5 are diastereotopic (shift difference 0.08 - 0.10 ppm) showing the presence of the lactam-lactim structures 3b-5b.

Yours sincerely,

Alois Steigel
Isotopomer Identification Through SPT Experiments

Dear Dr. Shapiro:

Selective population transfer (SPT) experiments in FT NMR are normally accomplished by selective inversion of a single transition followed by a non-selective observation pulse. Under appropriate conditions which include a small flip angle observation pulse, only transitions directly connected to the inverted transition are altered in intensity. Subtraction of this spectrum from an unperturbed spectrum results in a difference mode display bearing a close resemblance to an INDOE response in CW NMR. Utilization of a larger flip angle can result in intensity alterations of all transitions connected to the inverted transition. The use of SPT experiments for elucidation of carbon-proton as well as proton-proton spin-spin couplings has been aptly demonstrated. Here we report the use of SPT experiments in 31P NMR to make isotopomer identifications and enable determinations of 31P-31P and 31P-195Pt couplings. The isotopomers of Pt2(µ-S)(CO)(PPh3)3, arising because of the 34% natural abundance of 195Pt (the only Pt isotope possessing a magnetic moment), are shown at the top of Figure 1 (Pt* indicates 195Pt). The resulting 31P [H] NMR spectrum (spectrum A) shown in Figure 1 is complicated because of contributions from each of the isotopomers. However, selective inversion of one of the stronger lines gives rise to the difference mode spectrum (spectrum B) which displays just the (nearly) ABX splitting of the unlabeled isotopomer. Further SPT experiments were used to identify the spectra of all but the doubly labeled isotopomer. A more complete description of the experimental parameters along with the 31P-31P and 31P-195Pt couplings obtained by spectral simulation will be presented in a forthcoming publication. We note that the ability of the Nicolet NT-200 spectrometer (on which the spectra were obtained) to switch from high to low power under computer control made implementation of the experiment a trivial matter. Please credit this contribution to the account of Prof. G.N. La Mar.

Sincerely,

A.L. Balch
Professor
Department of Chemistry

G.B. Matson
Operations Manager
UCD NMR Facility

References

GBM:kg
Figure 1. The isotopomers of Pt₂(µ-S)(CO)(PPh₃)₃, arising because of the 34% natural abundance of ^{195}Pt, are shown at the top of the figure. Spectrum A shows the normal $^3P^1{[^1H]}$ spectrum, while spectrum B displays the difference mode spectrum resulting from inversion of the strong line just under 20 ppm. Spectrum B clearly identifies the (nearly) ABX pattern resulting from $^31P-^31P$ coupling in the unlabeled isotopomer.
In response to the dreaded pink note, some thoughts on the alleged charge shift relationship for π carbons in carbenium ions. We recently had occasion to examine $^{13}$C shifts in benzenium ions. The shifts vary widely with substituents, solvent, and temperature, yet a satisfying regularity ensues from the following treatment.

Let's assume these shifts have contributions from a) the carbon skeleton, b) a medium effect which acts uniformly at all carbons and what's left is c) due to charge. For a) we choose $^{13}$C shifts in neutral model compounds in skeletal environments which most closely resemble those for carbons in the carbenium ions. Once the neutral model shifts, $\delta_m$, have been subtracted from the carbenium shifts, $\delta^+$, the shifts which remain are internally almost the same for each $R^+$ but are displaced from one $R^+$ species to another. This displacement turns out to be equal to $\delta^+_i - \delta_m$ (neutral C$_3$). If we take the sum for all the ring carbons, it comes close to 166 ppm each time, almost the charge shift index. In other words, the introduction of a charge of +1 into the neutral model system results in a total 166 ppm downfield shift provided we subtract $\delta^+ - \delta_m$ from all the shifts. The latter must represent an environmental effect from solvent (for instance electric field) that acts at all carbons equally.

One could argue that second order differences cancel out all the interesting effects. However, the treatment does lead to a common number ~ 166 ppm/e-. Also, it seems we have to include the shift of the saturated ring carbon.

Examples with model structures and results follow below.

Best wishes,

Gideon Fraenkel
Professor of Chemistry
\[ R^+ \]

MODELS

\[ \sum (\delta_1^+ - \delta_{M1}) - (\delta_2^+ - \delta_{M2}) \]

I\(^+\) CF\(_3\)CO\(_2\)^- in CF\(_3\)CO\(_2\)H 165.5 ppm

I\(^+\) AlCl\(_3\) in CH\(_2\)Cl\(_2\) 167.4

II\(^+\) FSO\(_3\)^- in SbF\(_5\) 167.0

III\(^+\) Al\(_3\)Cl\(_7\) in CH\(_2\)Cl\(_2\) 165.2
Title: writing with an analog plotter and a Nicolet 1180 computer

Dear Professor Shapiro,

Your yellow remainder arrived during the examination period and since all undergraduate students are now on vacation, we have the feeling it is time to answer. Anyway, we are afraid we have lost at least one issue of your newsletters.

For many reasons (practical as well as esthetic), we were eager to make our Nicolet 1180 computer draw axis or write comments on a spectrum sheet. This appeared, at first, impossible since we could not afford a digital plotter and since, regarding analog devices, the Nicolet Basic software just allows to plot a curve. We therefore decided to adapt the digital plotter software to our situation.

Basically, it consists in replacing each instruction specific to the digital plotter by a set of instructions which allows to drive the analog plotter (SEFRAM TGM 101 in our case) in a proper way. This is essentially achieved by controlling the speed of the pen according to direction changes. As an example, an horizontal straight line will be drawn quickly whereas the pen will move slowly when a curve is to be plotted. This is done in order to get rid of the inherent inaccuracy of an analogic plotter. All the required modifications are included in a dedicated routine (STDPL) which is simply called just before PLOTS (Nicolet initialization plotting routine). This routine has to be loaded by the linking loader at the basic program generation stage.

In order to obtain a good quality of presentation, some minor adjustments on the plotter may be necessary (increase of the sensitivity and decrease of the time constant). The joined figure has been obtained in less than 5 minutes. The program is available on request.

Sincerely yours,

J. BRONDEAU  B. DITER  D. CAZET

Equipe de recherche associée au CNRS n° 22  Case postale 140  54037 NANCY Cedex — Tél. (88) 28 93 93
DEUTERIUM SPECTRUM OF D2O IN A LYOTROPIC PHASE
Glutathione Conjugates of Epoxides

One of the major biotransformation pathways for epoxides is conjugation with glutathione (GSH). Further metabolism of the GSH conjugates gives rise to the mercapturic acids (N-acetylcysteine conjugates). We have been interested in the stereochemical aspects of this important detoxication reaction because of the influence of stereochemistry on the metabolism and/or excretion of GSH conjugates.

Studies of the $^{13}$C NMR spectra of the glutathione and mercapturic acid conjugates of styrene oxide, phenanthrene 9,10-oxide and pyrene 4,5-oxide show that the peak separation (0.1-0.4 ppm) between diastereoisomers for the carbons which were formerly the epoxide ring (CHOHCHSR-) is sufficient to allow quantitation of the mixture of isomers. We have recently assigned the relative stereochemistry of the GSH and mercapturic acid conjugates of styrene oxide (four isomers each, two positional isomers as a mixture of diastereoisomers) by preparing the conjugates from (+)- and (-)-styrene oxide.

In related work, $^{13}$C NMR analysis of the GSH conjugates formed from (+) benzo(a)pyrene 4,5-oxide-4,5-$^{13}$C by a purified glutathione transferase from little skate (Raja erinacea) liver demonstrated that equivalent amounts of the positional isomers (4-hydroxy-5-glutathionyl and 5-hydroxy 4-glutathionyl) were formed as single diastereoisomers. This was confirmed by comparison with the spectrum of the synthetically produced isomers (mixture of four stereoisomers) and HPLC. Whether this stereochemical behavior is restricted to the purified fish liver enzyme, the substrate, or this particular combination is actively being pursued by the use of other arene oxide substrates and with purified glutathione transferases from other sources.

Manuscripts of this work are in preparation and I will be happy to send preprints to anyone interested.

Sincerely,

Richard H. Cox, Ph.D.
How much do you know about the Varian XL-200?

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
- Use of indirect variables for phase control
- Ability to specify and vary phase and receiver off-times dynamically
- Use of indirect variables for phase control
- Use of direct periodic data save to non-volatile memory
- Use of math statements for sequence timing calculations
- Complete separation of sequence code from parameter sets
- Dynamic variable calculations
- Use of PASCAL statements within sequence
- User control of parameter display characteristics
- Example sequences
  - Standard two-pulse
  - Carr-Purcell-Meiboom-Gill T2
  - Quadrupole echo
  - Cross-polarization
  - Multiple-contact cross-polarization
  - Selective excitation
  - Quadrature selective excitation
  - INEPT
  - INEPT with refocussing and decoupling
  - Decoupling and decoupler frequencies under CPU control
  - Decoupler gating under CPU control
  - Decoupler modulation under CPU control
  - CW, pulse, square wave and external
  - Flexible phase selection in multi-transient
  - CW, noise, square wave and external
  - Dynamic phase selection in multi-transient
  - 48-bit microprogram

Acquisition Processor
- Dynamic phase selection in multi-transient
- 48-bit microprogram
- Software-programmed for highest flexibility
- FIFO architecture for event streaming at 50-ns resolution
- State-of-the-art LSI construction
- J-Cross polarization
- Proton-carbon enhanced 2D
- Dynamic phase selection in multi-transient
data collection
- Noise amplitude and scaling limit checking
- lock/VT, high noise interlocks

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?

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- Computer controlled VT
- 19F/1H 5-mm VT broadband probe
- 13N/31P 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 simple 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 13C 90° pulse
- Internal 1H 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
- 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-refinable disk libraries
- PASCAL system source code availability
- NOE calculation
- Add-subtract-convolution spectral manipulation

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

MAG-3842 (Printed in U.S.A.)
Professor Barry Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

We have recently been studying molecular motions in a series of hormone peptides and trying to understand the relationship between conformational constraints and biological activity. In the course of this work we have carried out a temperature and magnetic field strength dependence of the $^{13}$C $T_1$ values of a Bradykinin. The data are summarized below for each of the backbone $\alpha$-carbon atoms.

<table>
<thead>
<tr>
<th></th>
<th>$T = 14^\circ$</th>
<th>$T = 38^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15.1MHz</td>
<td>67.9MHz</td>
</tr>
<tr>
<td>Arg</td>
<td>.102</td>
<td>.212</td>
</tr>
<tr>
<td>Pro</td>
<td>.095</td>
<td>.183</td>
</tr>
<tr>
<td>Pro</td>
<td>.082</td>
<td>.195</td>
</tr>
<tr>
<td>Gly</td>
<td>.106</td>
<td>.214</td>
</tr>
<tr>
<td>Phe</td>
<td>.080</td>
<td>.167</td>
</tr>
<tr>
<td>Ser</td>
<td>.084</td>
<td>.176</td>
</tr>
<tr>
<td>Pro</td>
<td>.082</td>
<td>.173</td>
</tr>
<tr>
<td>pNO$_2$Phe</td>
<td>.078</td>
<td>.169</td>
</tr>
<tr>
<td>Arg$^c$</td>
<td>.083</td>
<td>.207</td>
</tr>
</tbody>
</table>

It is necessary to determine the field strength dependence of the $T_1$ values in order to correctly characterize the motional behavior in terms of the relevant rotational correlation times. We have analyzed these data using a model which assumes isotropic overall rotation with independent internal correlation times. The overall correlation time ranges from $4 \times 10^{-8}$ sec at $14^\circ$C to $7 \times 10^{-10}$ sec at $38^\circ$ whereas the internal correlation times are around $1 \times 10^{-10}$ and change by no more than a factor of two over the same temperature range. This analysis yields computed $T_1$ values within experimental error of the measured values and also correctly predicts the observed NOE factors.

Please credit this contribution to the subscription of Dr. R. J. Highet.

Sincerely yours,

James A. Ferretti
Dear Professor Shapiro,

Here is yet another modification to the old XL-100 programme, 99k100-E and -D. It enables a plotter speed change while plotting, by typing S for slower and F for faster. The PT command is eliminated. The DC command is also rationalised. Typing DC now clears the drift correction and jumps to the scope routine without needing any more input.

With apologies for the brevity of this note.

Yours sincerely,

 Alan Boyd
Dear Barry:

This is a note to update the research my group (S. Rajan and I) have been doing with some of the local biophysicists (Govindjee and Rita Khanna) on photosystem II, the oxygen-evolving part of photosynthesis in green plants.

It has been proposed that manganese is an integral part of photosystem II. In an effort to better understand the nature and role of the manganese we have made parallel NMR and ESR measurements of thylakoid membranes in aqueous suspension under a variety of conditions. Also, total Mn content was determined by neutron activation and oxygen evolution monitored. In other earlier work two pools of bound Mn have been identified, a loosely-bound pool related to O₂ evolution and a tightly-bound pool. Our experiments indicate that the loosely-bound pool has at least two components of which the most loosely-bound is not related to O₂ evolution. Also, it appears that the tightly-bound pool is associated with the light harvesting complex.

The aqueous proton relaxation rate (R₂ = 1/T₂) is known to be sensitive to the amount and oxidation state of Mn present and to the extent and nature of its binding in a complex. Also, changes in binding can affect the correlation times that govern R₂ or change the accessibility of Mn to the aqueous protons. In ESR, free aqueous Mn(II) gives a distinctive six-line spectrum while other oxidation states and bound Mn(II) give at most very broad, weak absorption. The two types of measurement give confirmatory and supplementary evidence of changes in oxidation state and binding of Mn.

Among our findings for pea thylakoids are the following:

(a) Aging of thylakoids at 35 °C causes a parallel decrease in O₂ evolution activity, in R₂ and in Mn content, confirming that R₂ monitors bound Mn related to O₂ evolution.

(b) Addition of 1 to 20 mM MgCl₂ causes a decrease in R₂ and an increase in the six-line ESR spectrum for free Mn(II), without any effect on O₂ evolution activity, indicating the presence of a pool of non-functional, loosely-bound Mn.

(c) The decrease of R₂ by MgCl₂ is probably due mainly to the smaller molar relaxivity of free compared with bound Mn(II). Mg ion is known to cause structural changes in membranes, (e.g., grana stacking) but not in trypsinated membranes. However, MgCl₂ has the same effects upon the R₂ and ESR of trypsinated membranes.

(d) The isolated light harvesting Chl a/Chl b preparation (LHC) contains ~1/3 of the bound Mn in the thylakoids; this may be the tightly-bound
Professor B. L. Shapiro

Mn pool.

(e) Treatment of thylakoids with NH₂OH increases R₂ by up to nearly two-fold, presumably by the reduction of higher oxidation states of Mn to Mn(II). Also, the progressive release of bound Mn with [NH₂OH] is shown by the growth of the six-line Mn(II) ESR spectrum, by the progressive loss of O₂ evolution and by the decrease in R₂ at [NH₂OH] ≥ 1 mM. However, the release of Mn is not complete even at 100 mM NH₂OH, confirming the presence of a tightly-bound pool. H₂O₂ also increases R₂.

(f) Reduction of thylakoids with tetraphenyl boron (TPB) causes R₂ to nearly double. The titration curve exhibits three sharp endpoints, the first at [TPB] ~ 2.5 mM corresponding to complete inhibition of O₂ evolution. The endpoints may correspond to the reduction of Mn to Mn(II) in each of three pools.

Further work is continuing along these lines. In particular, we hope to characterize in more detail the species involved in the titration curves, for example, by removing some of the Mn and seeing the effect upon the titration.

I have a postdoctoral opening for someone interested in such studies. At least general familiarity with pulsed-NMR instrumentation would be helpful. If you're interested or know of someone who might be, please give me a call (217/333 0710) or send me a note, preferably with a curriculum vitae.

Sincerely yours,

H. S. Gutowsky
Professor of Chemistry

akh
Scatchard plots are often used in the analysis of NMR data (1, 2). We have been examining the exchange dynamics of tetraphenylporphyrinato Zn(II) with pyridine and N-methylimidazole at 200 MHz and have found a version of a Scatchard plot most useful in assessing the values of several parameters needed in the analysis of the DNMR. The reaction considered is ZnTPP + L ⇌ ZnTPPL, which is in rapid exchange at room temperature with \( \nu_0 = X_0 \nu_f + X_b \nu_b \). If one makes up a sample of ZnTPP and ligand in CDCl₃ and records the spectrum at several different dilutions the ligand frequencies will shift down field due to progressive dissociation of the complex. A plot of \( \Delta_1/(\text{ZnTPP})_0 (\Delta_1 = \delta_f - \delta_b) \) vs. \( \Delta_1 \) gives a straight line with the extrapolation to the \( \Delta_1 \) axis giving \( \nu_0 \) for the fully formed complex in rapid exchange at that particular \( (\text{ZnTPP})/L \) ratio (Fig. 1). From this one can easily determine the mole fraction free and bound and the equilibrium constant under a variety of conditions. A plot of these intercepts \( (\Delta_f) \) vs. \( (\text{ZnTPP})/L \) ratio gives a straight line with a sharp break at \( (\text{ZnTPP})/L = 1 \) (Fig. 2). For pyridine the \( (\text{ZnTPP})/L > 1 \) still has a slope, for N-methylimidazole it appears to have a slope of zero. We believe that the low slope for pyridine in the \( (\text{ZnTPP})/L > 1 \) region is due to π-complexing and we use that slope to correct our other observed values for the π-complexing. The point of the break at \( (\text{ZnTPP})/L = 1 \) permits an accurate assessment of \( \delta_f - \delta_b \).


Sincerely yours,

A. H. Turner

C. B. Storm

M. B. Swann
Figure 1

Pyridine $\alpha$-protons at various ratios of [ZnTPP]/[L].

Figure 2

$\Delta_{0}$ in ppm vs. $[\text{ZnTPP}]/[\text{L}]$ for L = N-Methylimidazole and L = Pyridine.
Relativity, lone pairs and spin-spin coupling

Dear Professor Shapiro,

We have recently written a program which calculates nuclear spin-spin coupling tensors using the "Relativistically Parameterized Extended Hückel Method (REX)" /1/ and the relativistic equivalent of Ramsey's non-relativistic theory /2/. All the parameters are taken from ab initio atomic calculations, relativistic or non-relativistic, thus permitting an analysis of relativistic effects. Any element can be treated. The largest molecule we have looked at so far is \( \text{Pb}_2(\text{CH}_3)_6 \).

The trends when descending down a column of the periodic system are shown on the following page. These trends are quite typical for the cases with and without lone pairs, respectively, as discussed qualitatively earlier by several workers (Kennedy & McFarlane, Birchall & Pereira, etc.). A new piece of insight is that relativistic effects seem to play a role in making \( \Delta K \) negative, already for elements as light as Se or Te. The relativistic increase of \( \Delta K(XH) \) in case (b) is again beautifully confirmed.

We still keep finding that relativistic effects increase the anisotropy \( \Delta K = K_\parallel - K_\perp \), as predicted in /2/, and have tracked down this to an \( s(A) - p_{1/2}(B) \) contribution, for which \( K_\parallel = -K_\perp \).

Sincerely yours,

[Signature]

Pekka PYYKKÖ

[Signature]

Laurent WIESENFELD


(a) Lone pairs
(SnH₃, SnMe₂, SbH₃, H₂Te, HI, etc.)

(b) No lone pairs
(PbH₄, PbMe₄, TlMe₃, SnH₃⁺, etc.)
July 18, 1980

Dear Dr. Shapiro,

One of the many goals of the spectroscopist is to obtain good spectra from lousy samples. For those of us in NMR the main sources of poor spectra (besides malfunctioning spectrometers and operators) are either field and/or sample inhomogeneity. Recently people have started putting a whole new class of inhomogeneous samples into NMR tubes: intact cells and tissues. As a distinguished colleague has said: "These samples are inherently not isotropic and it will be years until those genetic engineers get any isotropic organisms for us to study." In the meantime it is of interest to find ways in getting the information which is obscured by the poor quality of living samples. One approach is to use DANTE to selectively excite a magnetically homogeneous portion of the sample while proton decoupling is applied. If the FID is then acquired without proton decoupling the proton coupled spectrum from a magnetically homogeneous sample can be obtained. The ability to resolve proton couplings might offer information that could aid in assigning the $^{31}$P peaks as well as obtaining some conformational information about cellular phosphates in vivo. An example is shown in the figure. The bottom spectrum is of $^{2}$'CMP in an inhomogeneous field. If a DANTE pulse train is applied to excite the center of the $^{31}$P peak and then a non-selective pulse applied to the $^{31}$P nuclei the middle spectrum results. This illustrates the width of the selective excitation relative to the inhomogeneous linewidth. If the sample is excited only by the selective pulse train in the presence of proton decoupling and then the FID acquired without proton decoupling then the top spectrum is obtained. The proton-phosphorus coupling is about 7 Hz. The method has fairly good signal to noise and the spectra shown were all obtained by accumulating 4 transients. The method has not been tested on any real live samples yet.


Sincerely,

Philip H. Bolton
Assistant Professor
2',CMP

\[ \text{\( ^{31} \text{P NMR SPECTRA} \)} \]

PROTON COUPLED HOLE

PROTON DECOUPLED WITH HOLE

PROTON DECOUPLED
Dear Professor Shapiro:

Interest in determining the role of crosslinked polystyrene structure in polystyrene-supported catalysts led us to investigate chain mobility in these crosslinked, solvent-swollen gels. The polymers contain varied amounts of divinylbenzene as crosslinker and 25 wt % chloromethylstyrenes to be used for binding catalysts. Spectra were obtained at 25.2 MHz on our Varian XL-100(15)-Nicolet TT-100 system at 30°C with the polymers swollen or dissolved in CDC13.

Representative data are in the table. The T1s decrease with crosslinking up to 4% divinylbenzene and may increase slightly with 6% divinylbenzene, suggesting that the T1 minimum occurs at ~4% crosslinking. The linewidths increase with crosslinking from values nearly the same as those of soluble polymers at ~1% crosslinking to broad bands at 10% crosslinking. The linewidths depend on crosslinking, not on polymer concentration, because the uncrosslinked polymer has identical linewidths in 10, 19, and 25% solutions in spite of a tremendous increase in viscosity. NOE ratios, determined by gated decoupling and fully decoupling successive spectra, decrease as crosslinking increases. The most interesting data arose from the discovery in NOE measurements that the aliphatic carbon signal areas in polystyrenes were always smaller than theoretical values when compared with the aromatic signal areas. On a per carbon nucleus basis the aliphatic signal decreases from ~87% of its theoretical area in uncrosslinked samples to ~20% in the 10% crosslinked sample when compared with a polyethylene glycol internal standard. The relative signal areas were obtained from both gated decoupled and fully coupled spectra, and by both electronic and cut-and-weigh integrations. Results using all of these methods agree to within 10% in all but one sample. We attribute the signal area decrease to increasing numbers of dipolar coupled carbon nuclei in the polymer backbone as the crosslinking increases. Our results are the first systematic study of crosslinking level on 13C relaxation in polymer gels of which we are aware.

Please credit this contribution to the Oklahoma State University account.

Sincerely,

Warren T. Ford
Associate Professor

WTF:wp
<table>
<thead>
<tr>
<th>Sample^{a}</th>
<th>Wt % Polymer in CHCl₃</th>
<th>T₁, msec</th>
<th>α,β Methine</th>
<th>-CH₂Cl</th>
<th>Linewidth, Hz</th>
<th>α,β Methine</th>
<th>P Methine</th>
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<td>95</td>
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<td>20</td>
<td>14</td>
<td>15</td>
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<td>0.82</td>
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<td>Uncrosslinked copolymer</td>
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<td>--</td>
<td>--</td>
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<td>0.84</td>
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<tr>
<td></td>
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<td>123</td>
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<td>--</td>
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<td>--</td>
<td>0.48</td>
<td>0.20</td>
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</tr>
</tbody>
</table>
Dear Professor Shapiro,

The wealth of data that now exists in the literature for $J(\text{CC})$ has been tabulated in two recent reviews $^1,^2$, where all the data up to the beginning of 1980 have been collated. By far the most numerous are those for coupling over one bond. These have been summarised in the enclosed scheme which we hope will be of practical use for those chemists and biochemists working in this area of NMR.

The scheme shows the range and distribution of $^1J(\text{CC})$ values, abscissa, according to the formal hybridisation of the coupled carbons which is indicated along the left-hand ordinate as follows:

- A—both coupled carbons formally with sp$^3$ hybridisation,
- B—one coupled carbon formally with sp$^3$ hybridisation and the other with sp$^2$ hybridisation,
- C—one coupled carbon formally with sp$^3$ hybridisation and the other is a carbon of a carbonyl function,
- D—one coupled carbon formally with sp$^3$ hybridisation and the other with sp hybridisation,
- E—one coupled carbon formally with sp$^3$ hybridisation and the other with sp$^2$ hybridisation (other than aromatic and carbonyl carbons),
- F—both coupled carbons formally with sp$^2$ hybridisation (both aromatic or aromatic and olefinic carbons),
- G—both coupled carbons formally with sp$^2$ hybridisation, one of which is a carbonyl function,
- H—one coupled carbon formally with sp$^2$ hybridisation and the other with sp hybridisation, and
- I—one coupled carbon formally with sp hybridisation.

This work was done in collaboration with Dr. P.E. Hansen of Roskilde University, Denmark.

Yours sincerely,

Victor Wray

- Vitamin B₁₂ (to C₅, C₁₀ & C₁₅)
- -C=C=O, X=O or N
- -C=C=O
- Porphyrins (to meso carbons)

- -C₂H₅ - C₂H₅
- -C₂H₅
- (CH₃)₂C⁺
- C₁-C₂ carbohydrates
- Cyclopropane ring
Hetero-Nuclei in Solid State

Dear Professor Shapiro,

Extending our NMR studies of heteronuclei in liquids to the solid state we succeeded in the following topics:

1) For the spin 1/2-nuclei $^{77}$Se and $^{125}$Te large chemical shifts and partly small line widths have been observed in IIb- and Pb-selenides and tellurides (1).

2) The anisotropy of the shielding of $^{207}$Pb found in lead nitrate powder (A. Nolle, Z. Naturforsch. 32a, 964(1977)) has been investigated now in a lead nitrate single crystal (a gift by Prof. Haussühl, Köln). The shielding tensors and the characteristic vectors could be given (2,3).

3) For $^{125}$Te in CdTe, HgTe and PbTe powders a line splitting was observed which has been analyzed in terms of direct dipole-dipole-coupling and isotropic and anisotropic indirect spin-spin-coupling (4). The procedure could be confirmed by a comparison with a single crystal measurement in CdTe (A. Nolle, Z. Physik B34, 175(1979)).

4) For the quadrupolar nuclei $^{33}$S and $^{67}$Zn, which have rather low receptivities, narrow signals have been detected in powdered chalcogenides. Absolute shielding constants could be given for $^{67}$Zn (5).

A typical signal of $^{67}$Zn in zinc selenide powder is given in Fig. 1.
Fig. 1: $^{67}\text{Zn}$ NMR signal in ZnSe powder, Larmor frequency at 2.11 T: 5.633 MHz, line width: 49 Hz, number of FID: 10800, measuring time: 15 h.

Sincerely yours

(0. Lutz)

(1) $^{77}\text{Se}$ and $^{125}\text{Te}$ Nuclear Magnetic Resonance Investigations in II - VI and IV - VI Compounds

(2) Angular Dependence of the $^{207}\text{Pb}$ NMR linewidth in Pb(NO$_3$)$_2$ due to $^{14}\text{N}$-$^{207}\text{Pb}$ Direct Dipole-Dipole-Interaction

(3) Nuclear Magnetic Shielding Tensors of $^{207}\text{Pb}^{2+}$ in Pb(NO$_3$)$_2$

(4) $^{125}\text{Te}$ - NMR Studies of Indirect and Direct Dipole-Dipole-Coupling in Polycrystalline CdTe, HgTe, and PbTe

(5) $^{67}\text{Zn}$ and $^{33}\text{S}$ Nuclear Magnetic Shielding in Zinc Chalcogenides
M. Haller, W.E. Hertler, O. Lutz, and A. Nolle
Dear Barry,

In a preceding letter we have described the "4 + 2" dimerization of 1-phenyl-3,4-dimethylphosphole by reaction with Mo(CO)$_6$ under U.V. However, when reacting 1-phenylphosphole with molybdenum hexa-carbonyl under U.V., a "2 + 2" dimer is obtained instead of the expected "4 + 2" dimer:

$$\begin{align*}
\text{Mo(CO)}_6 & \rightarrow \text{THF, 20h} \\
\text{Mo(CO)}_4 & \rightarrow \text{THF, 20h}
\end{align*}$$

The original "head to head" structure of complex (2) was established by NMR and mass spectroscopy: $^1$H NMR (CDCl$_3$, internal TMS, 100 MHz, $^3$P decoupling): 3.12 (d x m, J(H-P) 17.7 Hz, 2H, saturated cyclic CH); 6.15 (ABX system, J(H-H) 7.64 Hz, 2H, olefinic cyclic C=H); 6.37 (ABX system, J(H-P) 25 Hz, 2H, olefinic cyclic C=H); 7.16 (m, 6H, Ph meta-para); 7.61 (m, 4H, Ph ortho) ppm. $^{13}$C NMR (CDCl$_3$, internal Me$_4$Si, $^1$H decoupling): 46.2 (d, J(C-P) 19 Hz, saturated cyclic C$-$); 53.7 (s, saturated cyclic C$-$); 128.2 - 132.2 (m, Ph and olefinic cyclic C$-$); 140.2 (s, olefinic cyclic C$-$) ppm.

Since only minor changes in the $^{13}$C chemical shifts are observed when complexing a chelating diphosphine with a Mo(CO)$_4$ moiety (1), the attributions have been made for (2) by comparison with the $^{13}$C spectrum of 1-phenylphosphol-2-ene. The perfectly symmetrical structure of complex (2) is well in evidence on the $^1$H and $^{31}$P NMR spectra.

We have no explanation for this result at the present time.

Best regards,

G. MAVEL, C. SANTINI, F. NATHHEY, R. MANKOWSKI-
PAVELIER

Siège Social, Direction Générale, 18 bis, bd de la Bastille, 75012 Paris. Tél. (1) 340.38.98

Centre de Recherche BP n°1 - 91710 Vert-le-Petit c.c.p. 9005.68 L au nom de l'agent comptable de l'Iroha - Tél.: 620.520 F Tél. (1) 493.24.75
Professor Barry Shapiro  
Texas A & M University  
College Station, Texas 77843

July 9, 1980

Dear Professor Shapiro:

I am looking for a recent Ph.D. who is highly skilled in NMR techniques to work with me on a number of projects that involve mechanisms of biological processes. Applicants who are not citizens of the U.S. will be considered under the Fogarty fellowship program. If you know of a qualified individual, please let me know, or have the person contact me directly.

Thank you very much for your attention.

Sincerely,

Gunther L. Eichhorn  
Chief, Laboratory of Cellular & Molecular Biology

THE UNIVERSITY OF BRITISH COLUMBIA  
395 WOODWORTH MALL  
VANCOUVER, B.C., CANADA  
V6T 1W5

8 July, 1980

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

Dear Barry,

I have the pleasure to announce that I will be joining the faculty of Ohio State University in September, 1980, as professor of chemistry and biochemistry, and director of the campus instrument center.

The center equipment will initially include: Bruker WH-300 FT-NMR spectrometer, Kratos MS-25 GC-mass spectrometer, and computerized Kratos MS-9 mass spectrometer. Further expansion in NMR and mass spectroscopy is contemplated over the next few years. Users will initially include members of the chemistry, biochemistry, and pharmacy departments.

Our own research on NMR (¹H, ¹⁹F, ³¹P) of 5S RNA, and dispersion-absorption plots for analyzing NMR line shapes will continue at O.S.U., and I will be sending a contribution shortly to TAMU in these areas.

Sincerely,

Alan G. Marshall  
Associate Professor
Direct couplings providing poor structural information

Dear Barry,

In the field of NMR of oriented molecules we quite often come across cases of direct couplings which turn out to carry very poor structural information, i.e. the coupling can be interpreted by a large range of internuclear distances with almost negligible change in bond angle. As the analysis is always performed by computers nobody has tried to explain this peculiarity and to give a general condition for its occurrence. In the present newsletter I would like to make up for this neglect.

The relation for a direct coupling:
\[ D = \frac{-k}{r^3} [(S_x - S_y) \cos^2 \alpha + S_y] \]

may be interpreted as a graph in two dimensions:
\[ \frac{1}{r^3} [(S_x - S_y) \cos^2 \alpha + S_y] + \frac{D}{k} = 0 \]

\[ \frac{1}{ax} + \frac{b}{bx} + \frac{D}{k} = 0 \]

This relation corresponds to a hyperbola with the following two asymptotes:
\[ x = \frac{1}{r^3} = 0 \]
\[ y = -\frac{b}{a} = \frac{S_y}{(S_y - S_x)} \]

Since \( y = \cos^2 \alpha \), only the part of the hyperbola which lies between \( y = 0 \) and \( y = 1 \) is a solution of the problem.
It now becomes immediately obvious that if the asymptote \( y = \frac{Sy}{(Sy-Sx)} \) lies in the allowed range between \( y = 0 \) and \( y = 1 \), the corresponding direct coupling defines the internuclear distance very poorly (see the figure!).

The condition \( 0 < \frac{Sy}{(Sy-Sx)} < 1 \) is fulfilled if \( Sx \) and \( Sy \) have opposite signs. Here we have the simple reason for the well known fact that if the molecular plane contains directions of \( S = 0 \), the structure of the molecule is usually poorly defined.

Yours sincerely

[Signature]

Peter Diehl
July 22, 1980

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

Dear Barry:

500, 360 MHz Postdoctoral Positions

I shall have several postdoctoral positions opening up in my group for the coming year, for work on the NMR of systems of chemical and biological interest using our new 500 and 360 MHz widebore spectrometers.

Areas of primary interest are as follows:

1) $^{13}$C and $^2$H NMR of solids at 11.7 Tesla (500 MHz $^1$H frequency), with special reference to studies of membrane and protein-crystal dynamics.

2) $^{13}$C 2D-FT at 360 MHz (Oxford WB-360 and Nicolet 1180 data system), studying in particular magnetically ordered protein crystals and oriented membranes.

3) Metal-ion NMR (Fe, Mo, Zn) in systems of biological interest.

4) High-field magic-angle spinning

Candidates should submit a letter of application, a curriculum vitae with a list of publications, and arrange to have three letters of recommendation sent to me at the following address:

Professor Eric Oldfield
School of Chemical Sciences
University of Illinois at Urbana-Champaign
Urbana, Illinois  61801

The starting salaries are negotiable and the appointments are renewable for up to three years. I will be happy to answer any preliminary inquiries by phone, at (217) 333-3374 or (217) 333-8328.

Best regards,

Yours sincerely,

Eric Oldfield
July 24, 1980

Title: Permanent NMR Staff Position

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

Dear Barry:

I hope that some of your readers will be interested in the following announcement.

Colorado State University seeks an NMR Spectroscopist for a permanent staff position in the Department of Chemistry. The starting annual salary will be in the range $16,000 to $20,000, depending on background and experience. The candidate must have an advanced degree in chemistry and a strong background in nmr. The responsibilities will be weighted heavily toward providing nmr service on the Department’s spectrometers, and will also involve supervision, spectrometer instruction, maintenance, and repair. Collaboration with faculty on NMR problems is encouraged. Applications should include curriculum vitae, bibliography and three letters of recommendation, and should be sent to D.F.S. Natusch, Chairman, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Colorado State University is an EEO/Title IX Employer. Equal Opportunity Office: 314 Student Services Building.

Sincerely,

Gary S. Maciel
Professor of Chemistry
Dear Barry:

We are looking for a manager of our NMR equipment. The following ad describes the position.

**NMR Specialist**

Challenging position in the Chemistry Department Analytical Laboratory for a professional with experience in the operation and maintenance of NMR spectrometers and/or expertise in high-frequency analog and digital electronics. Knowledge of organic chemistry desirable. Current NMR instrumentation includes: JEOL FX-90Q, Varian CFT-20, T-60, and EM-360, and Perkin-Elmer R-20B. In addition, it is expected that a 250 MHz superconducting FT-NMR system will be acquired. Opportunity to work with other instruments, such as the Nicolet FT-IR spectrometer. Must have an advanced degree or comparable experience.

Send resume to: Manager of Employment, Northwestern University, 720 University Place, Evanston, IL 60201

An equal opportunity affirmative action employer m-f.

Sincerely,

Joseph B. Lambert

Title: Position Available for NMR Manager
July 28, 1980

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

Title: "Who shot J.R., and does anyone have a used pulse spectrometer for sale?"

Dear Dr. Shapiro:

In initiating my subscription to the Newsletter, I should like to let your readers know that after a very fruitful and instructive tenure with Dr. Donald Hollis, I am starting my own NMR laboratory at the University of Texas Health Science Center at Dallas. It is my intention to pursue NMR studies of cellular metabolism and also to investigate the potential of high field imaging based on metabolic states. It is envisioned that this second area will be directed toward basic research in physiologic (and pathophysiologic) studies of perfused organs and in vivo in small animals. It is likely that I will be able to support a postdoctoral fellow to work in these areas by late spring or early summer of 1981. Well qualified senior graduate students planning on completing their degrees within this time frame are encouraged to contact me.

Dr. Donald Twieg (also at this institution) is interested in obtaining a used pulse spectrometer (without computer) in good condition. Please contact him at 214/688-2259 or write to him at this address:

Department of Radiology
University of Texas Health Science Center
5323 Harry Hines Blvd.
Dallas, Texas 75235

if you have a used spectrometer for sale.

Sincerely,

Ray L. Nunnally, Ph.D.
Assistant Professor

5323 HARRY HINES BLVD. DALLAS, TEXAS 75235 (214) 688-2295
Dear Janos,

We would like to bring to your attention our interest in offering a highly qualified Ph.D. a one, two or three year appointment (tenure not absolutely excluded) in our Division starting in September 1980 or January 1981. The candidate must be well-versed and experienced in modern NMR techniques and willing to devote up to 50% of his time to the service aspects of our XL-100 (with 13C probe) and the 200 MHz Nicolet apparatus, which will arrive in December of this year. We would strongly encourage research although our first need is high quality service. The technical assistance will consist of (at least) one part or full-time technician and at least one or possibly two, (part-time) graduate students as assistants. Our Organic Division consists of six full Professors of which five have an active research program. The Division has at present sixty graduate students and ten technicians. The salary ranges from US$ 20-25,000,- depending on age and experience and has all the advantages of a civil-service appointment.

I enclose:

a) Recent biographical data on members of the Division.

b) Summary of the structure of the Chemistry Department.

c) Additional data on Groningen and the University.

If you can recommend someone strongly for this position please let him write to the Chairman of the Division (Prof. Dr. H. Wynberg). The candidate should enclose biographical data and names of two persons familiar with his work, who can provide letters of reference.

We would expect the candidate to be between 24 and 35 years of age, to have completed the requirements of the Ph.D. degree or its equivalent and be motivated to enter academic life by way of NMR research, theory, perhaps a teaching task and service duties. Willingness to devote time and energy to work with graduate students and staff members on NMR problems connected with their research is essential.

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

Outstanding NT-Series features include these:

- A full range of superconductive magnets from 3.5T to 11.7T in both wide-bore and narrow-bore configurations.
- Multinuclear observation with a wide variety of fixed-tune and broadband probes.
- Simultaneous acquisition, processing, and plotting for greater sample throughput.
- Simplified control of spectrometer operations and parameters by using easy keyboard commands.
- Advanced Nicolet-1180 Data System with the most comprehensive FT-NMR software package available.
- Extended dynamic range performance with 40-bit acquisition and floating-point processing.
- An expandable pulse-sequence library, including T1, T2, Redfield, 2D-FT, etc.
- Convenient computer-control of field shimming, observe and decoupling frequencies, sample temperature.
- Precise digital plotting with full annotation of spectral parameters and flexibility of hard-copy format.

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

Some of these are:

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

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