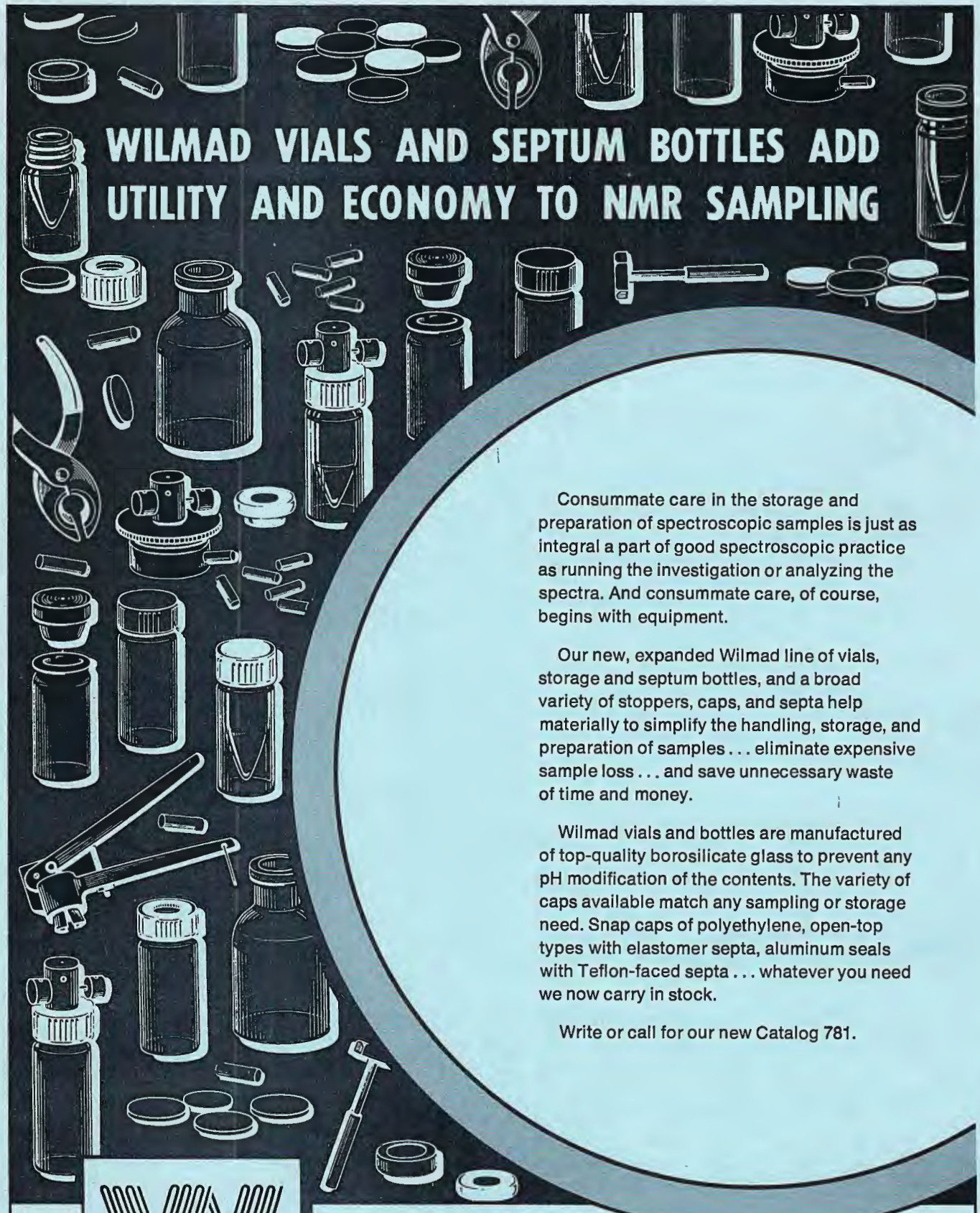
Texas A&M University
N-M-R Newsletter

No. 246

March, 1979



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DEADLINE DATES: No. 247: 2 April 1979
No. 248: 7 May 1979

All Newsletter Correspondence, Etc. Should Be Addressed To:

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 246

246-1

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reference

31st January 1979.

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

Dear Professor Shapiro,

^{31}P nmr studies of coenzyme-enzyme interactions

As part of our continuing study of the binding of small molecules to dihydrofolate reductase, we have been using ^{31}P nmr to examine the binding of the coenzyme $NADP^+$, and a series of structural analogues.

The ^{31}P signal from the 2'-phosphate group shifts downfield approximately 2.7 ppm when the coenzyme binds to the enzyme at pH 6.5. With $NADP^+$ itself, this signal shows straightforward slow-exchange behaviour, separate signals for free and bound coenzyme being clearly resolved. This is not the case, however, for the thionicotinamide analogue, $ThioNADP^+$. As shown in Fig.1, for this compound a single 2'-phosphate signal is observed, which shifts progressively as the $ThioNADP^+$ concentration is increased. This is the kind of behaviour one would expect for fast exchange, and indeed the concentration-dependence of the chemical shift can be fitted quite satisfactorily by an equation based on the assumption of fast exchange. However, the binding constant obtained from this fit is a factor of 20 higher than that obtained by independent measurements.

The assumption of fast-exchange is in fact wrong, and the full lineshape equation for exchange between two sites must be used to fit the data. For a given set of parameters, the theoretical lineshape is simulated at each concentration of $ThioNADP^+$ and the chemical shift and linewidth are 'read off'. These are compared with the measured values, and the parameters adjusted automatically to obtain the best (least-squares)fit to the data. The 'optimal' fits to the shift and linewidth data are shown in Fig. 2a and b; note the marked maximum in the linewidth at about 2 equivalents of ligand. This analysis provides reliable estimates of the bound shift, the binding constant and the dissociation rate constant (here $250 \pm 50\ s^{-1}$).

Concerned that the incorrect assumption of fast-exchange might lead to many errors in the measurement of equilibrium constants by nmr, we have explored this further by simulation methods, and a paper describing this will appear shortly in J.Mag.Res. (Feeney, Batchelor, Albrand and Roberts). The crucial test turns out to be the observation of the maximum in the linewidth, which requires measurements at as low ligand/protein ratios as possible.

Yours sincerely,

Gordon Roberts Lisa Hyde Jim Feeney

G.C.K. Roberts E.I. Hyde J. Feeney

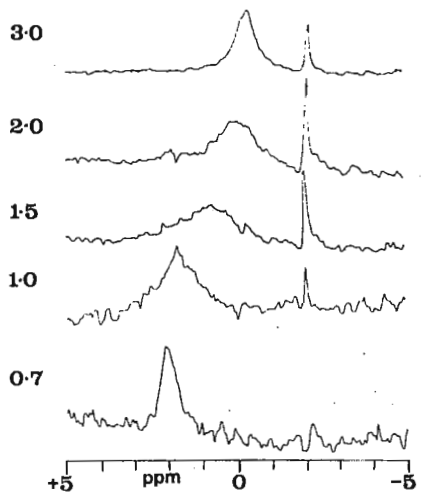


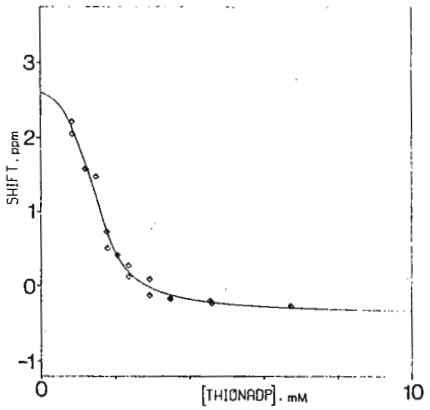
Fig. 1 (left)

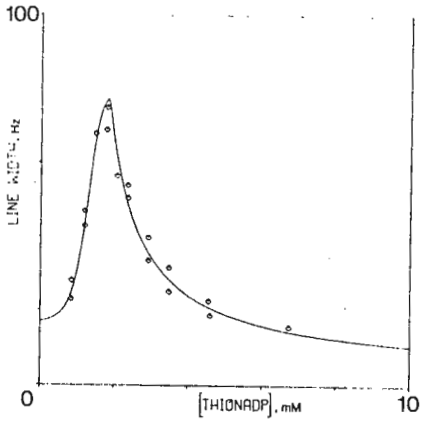
^{31}P resonance of the 2'-phosphate of $TNADP^+$ in the presence of dihydrofolate reductase as a function of the TNADP/enzyme ratios.

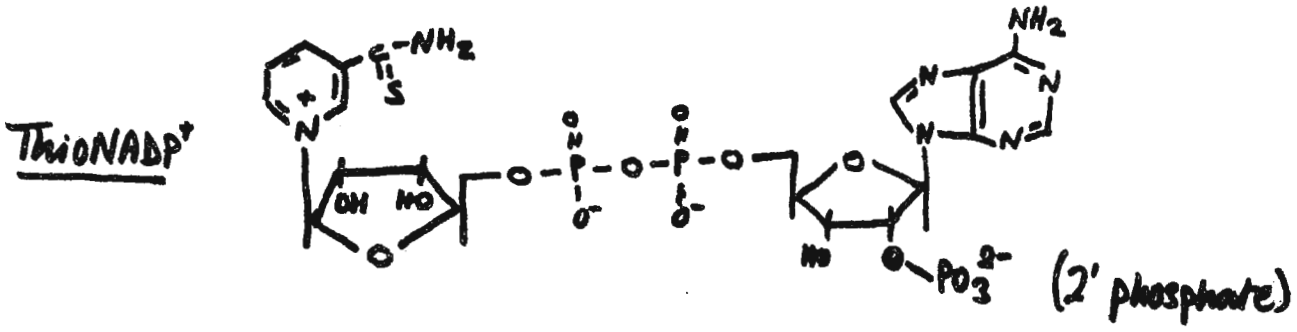
(XL-100 ; 11°C)

Fig.2(a) and (b) below

Concentration dependence of shift and linewidth, from data such as Fig.1, as a function of $[TNADP^+]$, and the best fit curves, based on the full lineshape equation.







OSU

The Ohio State University

Department of Chemistry
140 West 18th Avenue
Columbus, Ohio 43210
Phone 614 422-2251

February 7, 1979

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

Chow's Tables or
Elements of the Quadrupole Relaxation Matrix

In deriving density matrix equations to calculate NMR line-shapes, it is often necessary to include effects due to different relaxation mechanisms. This is done by adding the appropriate relaxation term to the density matrix equations, $R(\rho - \rho_0)$. The relaxation operator in the extreme narrowing limit has the form

$$R(\rho - \rho_0) = -\sum_{\alpha, \underline{i}} j^{+}(\alpha\omega)[\mathcal{I}_{\underline{i}}^{\alpha}, [\mathcal{I}_{\underline{i}}^{-\alpha}, \rho - \rho_0]]$$

where α is the order of the tensor, j^{+}'s are spectral densities, $\mathcal{I}$'s spin operators and $\underline{i}$ sums over spins. Consider the quadrupole relaxation operator for conditions of extreme narrowing and low RF power. One can drop ρ_0. Then expanded out $R_q \rho$ have to be evaluated by computer; however, in the product representation one can do it by hand, with some patience, since each element of one of the 33 operators only gives one value or zero. Better yet, the entire element $(R_q \rho)_{i,j}$ can be generalized with closed formulas, see (1). We have calculated out all the typical element of $R_q \rho$ for $I = 1$ to $I = 3$, $m_i - m_j = +1$ and $m_i = m_j$. The results, known as Chow's Tables, will soon be available on application to the authors. These tables allow fast, painless evaluation of elements of the quadrupole relaxation matrix, even for multinuclear species. From now on, there will be no excuse to avoid using the operator in its proper form. Soon we shall do the same thing for dipole dipole relaxation.

Best wishes.

Albert Chow

Gideon Fraenkel
Professor

P.S. $j_0^{+} = \frac{1}{5}A^2\tau$

$$j_1^{+} = j_2^{+} = \frac{1}{10}A^2\tau$$

$$A = \frac{e^2qQ}{\hbar} \cdot \frac{1}{4I(2I-1)}$$

GF:ras

$$
\begin{aligned}
&- \langle m_i | R_q \rho | m_j \rangle \\
&= \Big\{ 9 j_0^+ (m_i + m_j)^2 (m_i - m_j)^2 \\
&\quad + j_1^+ \Big[(2m_i - 1)^2 [I(I+1) - m_i(m_i - 1)] + (2m_j + 1)^2 [I(I+1) - m_j(m_j + 1)] \\
&\qquad + (2m_i + 1)^2 [I(I+1) - m_i(m_i + 1)] + (2m_j - 1)^2 [I(I+1) - m_j(m_j - 1)] \Big] \\
&\quad + j_2^+ \Big[[I(I+1) - m_i(m_i - 1)][I(I+1) - (m_i - 1)(m_i - 2)] \\
&\qquad + [I(I+1) - m_j(m_j + 1)][I(I+1) - (m_j + 1)(m_j + 2)] \\
&\qquad + [I(I+1) - m_i(m_i + 1)][I(I+1) - (m_i + 1)(m_i + 2)] \\
&\qquad + [I(I+1) - m_j(m_j - 1)][I(I+1) - (m_j - 1)(m_j - 2)] \Big] \Big\} \rho_{m_i, m_j} \\
&\quad - 2 j_1^+ (2m_i - 1)(2m_j - 1)[I(I+1) - m_i(m_i - 1)]^{1/2} [I(I+1) - m_j(m_j - 1)]^{1/2} \rho_{m_i - 1,\ m_j - 1} \\
&\quad - 2 j_1^+ (2m_i + 1)(2m_j + 1)[I(I+1) - m_i(m_i + 1)]^{1/2} [I(I+1) - m_j(m_j + 1)]^{1/2} \rho_{m_i + 1,\ m_j + 1} \\
&\quad - 2 j_2^+ [I(I+1) - m_i(m_i - 1)]^{1/2} [I(I+1) - (m_i - 1)(m_i - 2)]^{1/2} \\
&\qquad \times [I(I+1) - m_j(m_j - 1)]^{1/2} [I(I+1) - (m_j - 1)(m_j - 2)]^{1/2} \rho_{m_i - 2,\ m_j - 2} \\
&\quad - 2 j_2^+ [I(I+1) - m_i(m_i + 1)]^{1/2} [I(I+1) - (m_i + 1)(m_i + 2)]^{1/2} \\
&\qquad \times [I(I+1) - m_j(m_j + 1)]^{1/2} [I(I+1) - (m_j + 1)(m_j + 2)]^{1/2} \rho_{m_i + 2,\ m_j + 2}
\end{aligned}
$$

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UNIVERSITY OF LONDON

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MILE END ROAD
LONDON E1 4NS
Tel. 01-980 4811

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

2nd January, 1979.

Dear Professor Shapiro,

Natural Abundance ^{15}N Spectra of Gramicidin A

In continuing our studies of peptides by natural abundance ^{15}N n.m.r., we have now looked at the linear peptide gramicidin A (M.W. 1880):- HCO-L-Val^{1}-Gly^{2}-L-Ala^{3}-D-Leu^{4}-L-Ala^{5}-D-Val^{6}-L-Val^{7}-D-Val^{8}-L-Tryp^{9}-D-Leu^{10}-L-Tryp^{11}-D-Leu^{12}-L-Tryp^{13}-D-Leu^{14}-L-Tryp^{15}-$NHCH_2CH_2OH$.
The spectra obtained are shown in the Figure. A is a predicted spectrum arrived at in the manner previously described[1] for gramicidin S with allowance for the peptide sequence effects determined by the Roberts group.[2] Spectrum B is the broad-band ^{1}H decoupled spectrum at 34° which, in addition to the high frequency resonances from the indole side chain of the Tryp residues, shows six (possibly 7) peptide nitrogen resonances. Under these conditions the other peptide nitrogen resonances are nulled by the restricted motional effect upon the ^{15}N-(^{1}H) n.O.e. This is shown in spectrum C (at 34°) in which the ^{1}H decoupler was gated to supress the ^{15}N-(^{1}H) n.O.e. but retain decoupling, and in spectrum D which was recorded with full ^{1}H broad-band decoupling but at 80°. At the elevated temperatures the decreased effective correlation times for the N-H groups no longer produce the "nulling" condition for the n.O.e.

Our interpretation is that in spectrum B we only see resonances from amino acid residues near to the ends of the chain due to segmental motion along the chain. Two additional features of interest are (i) in spite of there being only 6 chemically different residues in the chain we observe 15 resolved backbone nitrogen resonances out of 16 possible in spectrum C; (ii) in spite of the relatively low molar concentration (80 mM) we were still able to obtain good spectra in a reasonable time. These spectra were obtained in collaboration with Bill Hull of Bruker and we wish to thank Bruker for the use of the instrument (WH-360). Please credit this contribution to Ed Randall's account.

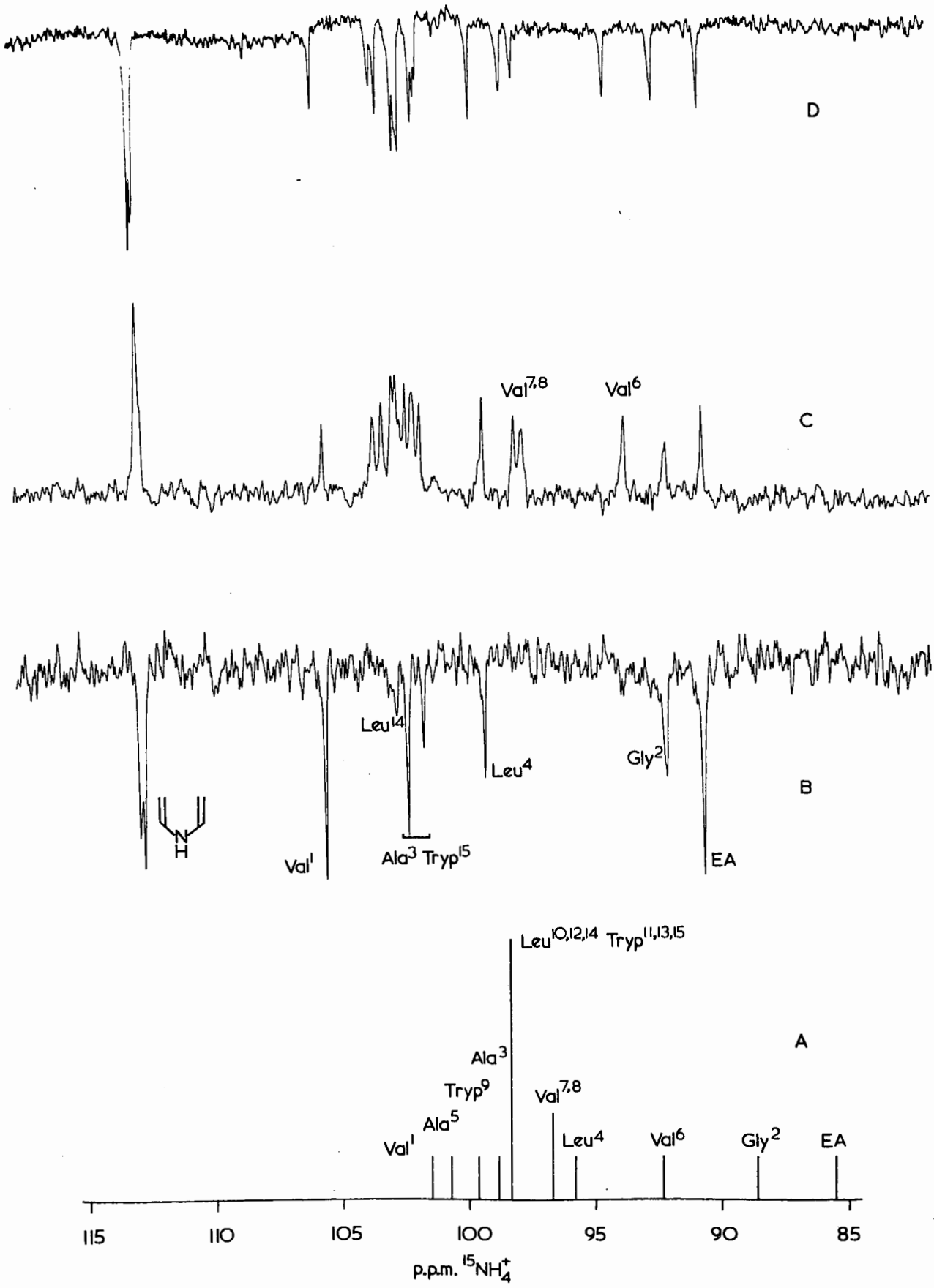
1. G.E. Hawkes, E.W. Randall and C.H. Bradley, Nature, 1975, 257, 767.
2. T.B. Posner, V. Markowski, P. Loftus and J.D. Roberts, Chem. Comm., 1975, 769.

Figure Caption - Natural abundance 36.48 MHz ^{15}N spectrum (WH-360) of gramicidin A, 15 mm o.d. sample, 80 mM in DMSO-d_6; A predicted spectrum; B broad-band ^{1}H decoupled spectrum at 34°, 26,590 scans in 10.2 h.; C inverse-gated ^{1}H decoupled spectrum at 34°, 13,823 scans in 12.9 h.; D broad-band ^{1}H decoupled spectrum at 80°, 50,000 scans in 18.9 h.

Yours sincerely,

Geoff Hawkes

Dr. G.E. Hawkes


D
Val7,8
Val6
C
Leu14
Leu4
Gly2
B
Val1
Ala3 Tryp15
EA
Leu10,12,14 Tryp11,13,15
A
Ala3
Tryp9
Val7,8
Ala5
Val1
Leu4
Val6
Gly2
EA
115
110
105
100
95
90
85
p.p.m. 15NH4+

246-9

Prof. Dr. Horst Kessler
Institut für Organische Chemie
der Johann Wolfgang Goethe-Universität
Frankfurt am Main

February, 8, 1979

Chemiegebäude
Niederurseler Hang
D-6000 Frankfurt am Main 50
Telefon (06 11) 58 00-91 30/31

Professor
Bernard L. Shapiro
Texas A & M University
College of Science
Department of Chemistry

College Station, Texas 77843
U S A

The Boat Conformation of cyclo[L-Pro-L-Pro-D-Pro]

Dear Barry,

Getting your insistent letter for a technical contribution I will tell you something about our cyclotripeptide work.

The backbone conformation of cyclotripeptides is either a crown or a boat[1,2]. Whereas cyclotripeptides containing at least one achiral amino acid (sarcosin or benzylglycine) exhibit conformational equilibria, for steric constraint cyclo[L-Pro_3] can only form a crown. For cyclo[L-Pro_2D-Pro][3] a boat was predicted[1]. The 270 MHz ^1H NMR spectrum of the latter was analyzed by spin decoupling in $CDCl_3$ solutions containing various amounts of benzene[4] and the ^{13}C signals were correlated to the proton signals by selective ^1H decoupling experiments.The boat form was proven with the following arguments:

The α proton signals appear as two tripletts (4.30 and 4.41 ppm) and one doublet (4.57 ppm). The tripletts correspond to the αH-signals in the boat (M) of cyclo[Pro_2Bzl.Gly][1].

The ^{13}C signals of the proline rings are in close analogy to those of M[1] (figure). Characteristic downfield shifts are observed for C^α and C^β of Pro 2 caused by the $+30^o$ ψ angle (N-C^α-C-N') in the boat conformation.

---

1) H. Kessler, P. Kondor, G. Krack, and P. Krämer, J.Am.Chem.Soc. 100, 2548 (1978); 2) H. Kessler, G. Krack, and P. Krämer, Peptides 1978 Proceedings of the 15th European Peptide Symposium at Gdansk; 3) Sample by Prof. Rothe, University of Ulm; 4) The complete analysis of the three 7-spin system is in work.

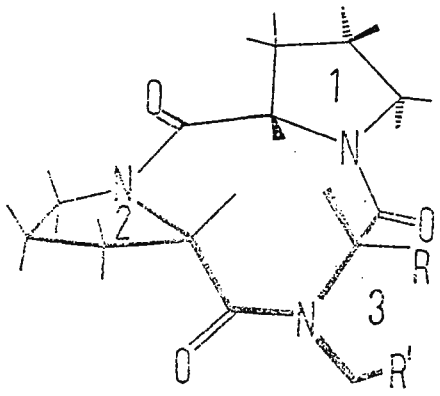
Yours sincerely,

Axel Friedrich

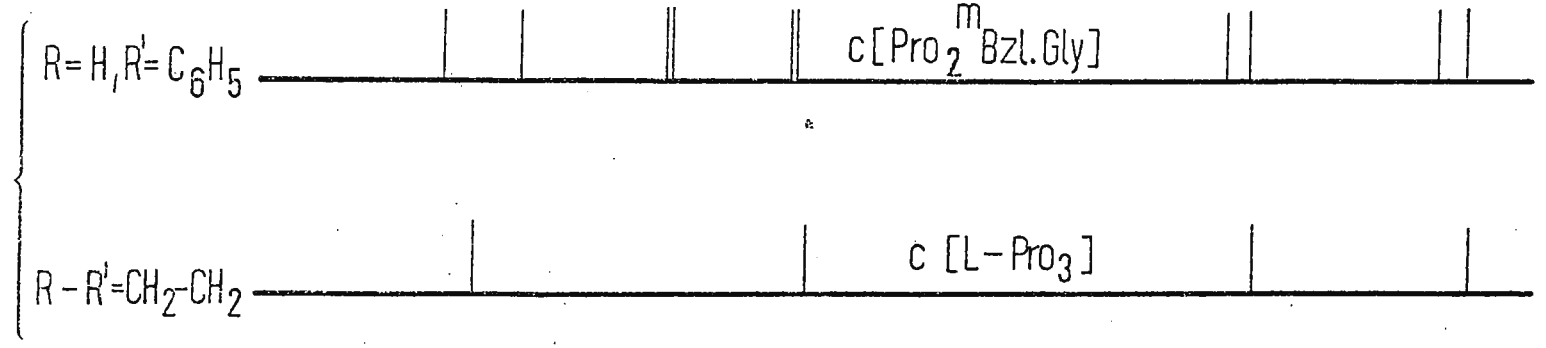
Axel Friedrich

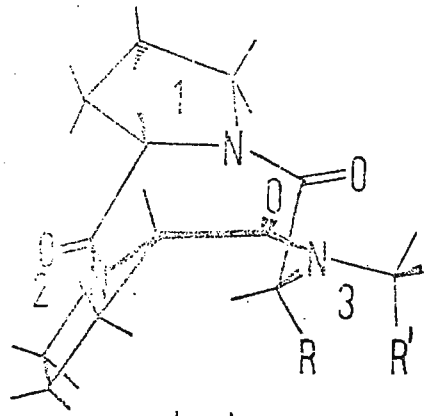
Horst

Horst Kessler

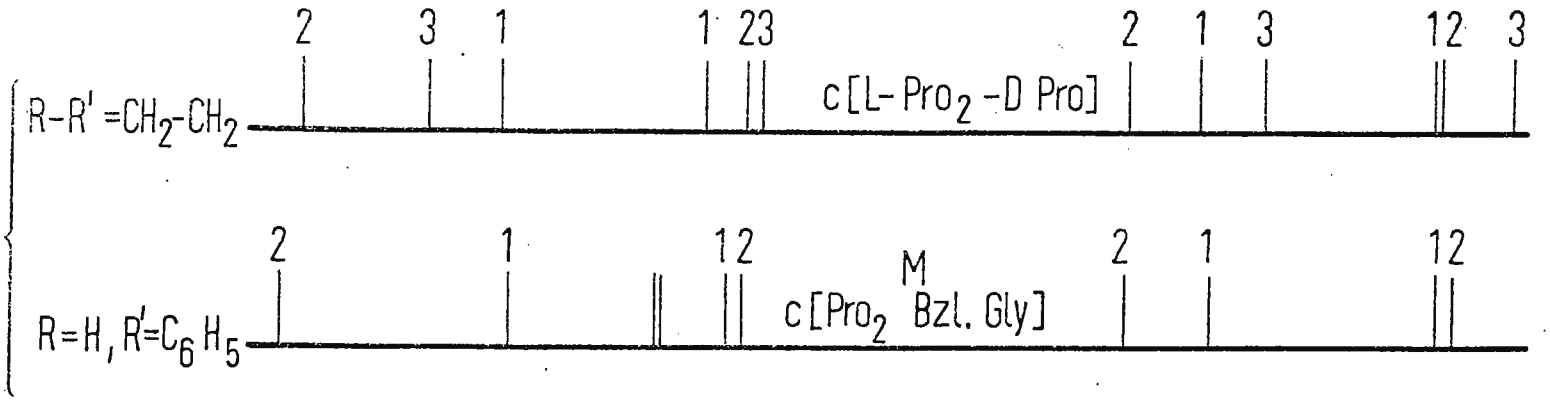

1
2
3
O
N
R
R'

crown


R=H, R'=C6H5
c[Pro2 m Bzl. Gly]
R-R'=CH2-CH2
c [L-Pro3]
ppm
60
50
40
30
20


1
2
3
O
N
R
R'

boat


R-R'=CH2-CH2
2 3 1 1 23 2 1 3 12 3
c[L-Pro2-D Pro]
R=H, R'=C6H5
2 1 12 2 1 12
M
c[Pro2 Bzl. Gly]

Hunter College

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

(212) 570-5666

12 February 1979

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

Dear Barry:

Title(s): 1) ^{15}N Chemical Shifts of Secondary Piperidines Are Not Influenced by Lone-pair Orbital Orientation
2) Postdoctoral Positions Available

Recently, Duthaler *et al.* suggested that ^{15}N chemical shifts of secondary (N-H) piperidines are not influenced by N-H (lone-pair) orientation.[1] To address this question, we have independently determined ^{15}N chemical shifts of axial and equatorial 8-methyl- and 8-*t*-butyl-*trans*- decahydroquinolines (1-4, see Table). These compounds were chosen because infrared spectroscopic measurements have shown independently that a methyl group at C-8 is relatively ineffective in influencing the N-H equilibria of 1 and 2, but that 8-*t*-butyl groups bias the N-H conformation to be predominantly equatorial in 3 and predominantly axial in 4.[2] As seen in the Table, the ^{15}N chemical shift difference between 1 and 2 is 1.8 ppm, and that between 3 and 4, for which the conformational difference is even more profound, is even smaller, only 1.4 ppm. This result shows unambiguously that N-H (hence lone-pair) conformation does not influence ^{15}N resonance positions in piperidines, and conversely that ^{15}N chemical shift determinations are of little value in probing lone-pair orientations in these compounds.

Postdoctoral positions, as previously announced in the TAMU Newsletter, are still available in our laboratories.

Sincerely yours,

George T. Furst

FWV RL

Friedrich W. Vierhapper[3]

Rob

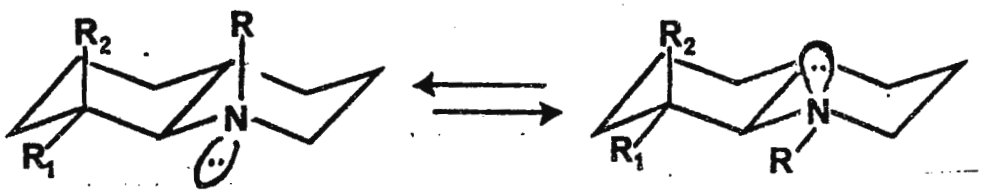
Robert L. Lichter

(1) R.O. Duthaler, K.L. Williamson, D.D. Giannini, W.H. Bearden, and J.D. Roberts, J. Am. Chem. Soc., 99, 8406 (1977).

(2) F.W. Vierhapper and E.L. Eliel, J. Org. Chem., in press.

(3) Institüt für Organische Chemie der Universität Wien, A-1090 Wien, Austria.

Table I. ^{15}N Chemical Shifts of 8-Substituted-trans-decahydroquinolines[a]



R_1	R_2	R = H		R = CH_3	
		Predominant Conformation[3]	δ_N, ppm	Predominant Conformation[2a]	δ_N, ppm
H	CH_3	B	51.4(1)	B	45.8(1m)
CH_3	H	B	49.6(2)	A	26.0(2m)
H	$(CH_3)_3C$	B	55.7(3)	B	46.9(3m)
$(CH_3)_3C$	H	A	54.3(4)	A	282.(4m)
H	H	B	54.3(5)	B	48.5(5m)

[a] In $CHCl_3$, concentration ~1M. Chemical shifts measured with respect to external $CH_3{}^{15}NO_2/CD_3NO_2$, converted to anhydrous liquid ammonia scale via relationship $\delta^{NH_3} = \delta^{CH_3NO_2} + 380.2$ ppm. Positive values denote deshielded resonances relative to reference.

Diamond Shamrock

T. R. Evans Research Center

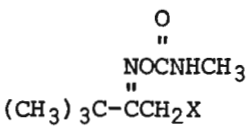
January 26, 1979

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

Subject: ^{13}C NMR of Ketoxime Carbamate Insecticides

Dear Barry,

As part of a program to correlate biological activity of carbamate insecticides and molecular geometry, we have recorded the ^{13}C NMR spectra of the E and Z isomers of some compounds with the general structure below.[1]



The ^{13}C shifts of three such isomeric pairs, plus one pair of oximes, are given in the Table. A number of features of this data are worthy of note. As previously reported,[2] a carbon α to the imine carbon in ketoximes is most sensitive to E-Z isomerism. This behavior is seen here for the N-methyl oxime carbamates. With X=SCH_3, the difference for the α-methylene carbon between E and Z isomers is about 10 ppm, which decreases upon going to the corresponding sulfoxide and sulfone. The exception is the tertiary butyl group, which does not exhibit large chemical shift differences between E and Z isomers. In addition, carbons on the oxime side chain are insensitive to geometry.

Further work will center on correlation of ^{1}H and ^{13}C NMR shifts and on "absolute" determinations of stereochemistry in solution, when only one isomer is available.

Sincerely,

Richard A. Komoroski

Richard A. Komoroski

dp

[1] T. A. Magee and L. E. Limpel, J. Agric. Food Chem., 25, 1376(1977).

[2] G. E. Hawkes, K. Herwig, and J. D. Roberts, J. Org. Chem., 39, 1017(1974).

dp

Attach.

TABLE

	$X=SCH_3$		$X=\overset{O}{\overset{\|\|}{S}}CH_3$		$X=SO_2CH_3$		$X=SCH_3$, oxime	
Carbon	E	Z	E	Z	E	Z	E	Z
C=N	165.8	168.7	163.6	164.6	162.6	161.6	160.4	163.6
C=O	155.7	155.9	155.1	154.9	154.8	154.7	—	—
C_{quat}	37.5	37.9	37.8	37.8	38.0	37.9	36.6*	37.2
tBu	28.1	28.3	27.8	27.5	28.0	27.5	27.7	28.3
CH_2	36.1	26.8	58.2	53.6	57.6	53.6	36.3*	25.8
NCH_3	27.6	27.6	27.5	27.7	27.8	27.7	—	—
SCH_3	14.7	17.2	39.0	41.0	40.9	45.0	14.6	17.3

*Indicates ambiguity of assignments. Shifts are in ppm from internal TMS in $CDCl_3$.

CONT'D. FROM P. 246-15

Professor Bernard L. Shapiro
Texas A and M University
February 14, 1979

As expected, T_1 is long; the full signal is obtained only after sample polarization for 8-12 hours. We are evaluating various aspects of relaxation in diamond and other dilute-spin solids.

Sincerely yours,

Mark Henrichs Ralph Young J. M. Hewitt

[1]H. L. Retcofsky and R. A. Friedel, J. Phys. Chem. 77, 68 (1973).

February 14, 1979

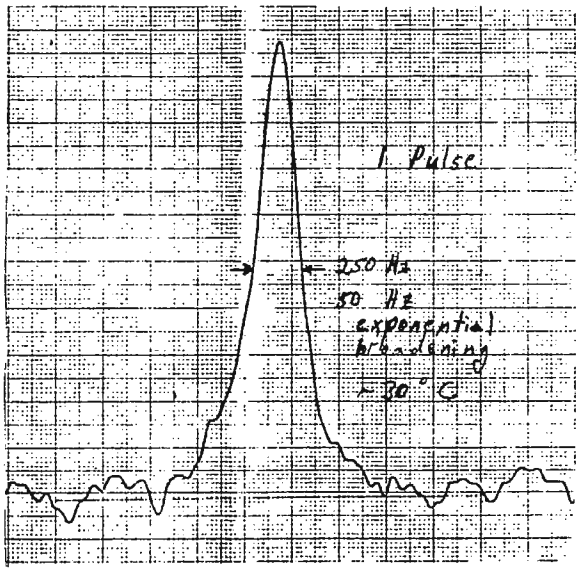
Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

"Poor Man's" High-Resolution NMR of Solids

Dear Barry:

To get narrow lines in solids, one must normally overcome broadening effects such as dipolar interactions and chemical-shift anisotropy with one of the special techniques developed in recent years. Nothing special is needed, however, for solids in which the magnetically active nuclei are so dilute as to minimize dipolar interactions, and the nuclei of interest are in a symmetric environment so that chemical shifts are isotropic.

Diamond is such a solid. We get a ^{13}C-NMR line 250 Hz wide (with 50 Hz exponential broadening) at 67.89 MHz from a 700 mg (3.5 carat) sample consisting of 13 randomly oriented single crystals. It is not yet certain that we are seeing the natural linewidth rather than the effect of magnetic field distortions by the sample. Nevertheless, a preliminary spectrum at 20 MHz has approximately the same linewidth, and we cannot produce a spin echo even after times as short as 8 msec. An even broader line has previously been found for diamond on a lower resolution spectrometer.[1]



Cont'd. bottom of p. 246-14

ABBOTT

Pharmaceutical Products Division

Abbott Laboratories
North Chicago, Illinois 60064

January 31, 1979

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

Dear Professor Shapiro:

Abbott Laboratories is seeking a nuclear magnetic resonance spectroscopist at the experienced Ph.D. level. The primary responsibilities of this position will be the supervision of the NMR laboratory in the Analytical Research Department. Responsibilities will also include the consultative interpretation of PMR and CMR spectra with the laboratory staff and submitters.

A thorough understanding of the underlying principles of and operation of CW and FT NMR instruments as well as experience in the use of NMR data in the solution of structural problems is required.

The successful candidate must coordinate and expedite challenging problems of a wide variety and be competent to communicate the results achieved both orally and in written reports. A firm knowledge of organic chemistry is mandatory and experience in natural product chemistry would be helpful. The position requires participation in an integrated approach to structural solutions with other instrumental techniques. Industrial laboratory experience as well as an understanding of routine instrument maintenance is desirable.

Qualified applicants should send their resumes including salary requirements in strict confidence to:

Victor Papendick
Analytical Research Dept.
1400 N. Sheridan Road
North Chicago, IL 60064

Sincerely,

Victor E Papendick

Victor E. Papendick

VEP:dmp

246-17

Dr. Joan Mason
Chemistry Department
The Open University,
Walton Hall,
Milton Keynes,
MK7 6AA.

Telephone Milton Keynes 74066
(6 3606 Direct Line)

THE OPEN UNIVERSITY

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

6th February, 1979

Dear Dr. Shapiro,

Here, with apologies for lateness, is our contribution to TAMU NMR Newsletter:

^{15}N NMR Spectroscopic Studies of Dinitrogen Complexes of Molybdenum and Tungsten

We have been measuring the ^{15}N nmr spectra of model compounds in which 'nitrogen fixation' can be observed, using ^{15}N-enriched metal complexes made at the Agricultural Research Council's Unit of Nitrogen Fixation, University of Sussex (J. Chatt, M.E. Fakley, and R.L. Richards) and measured at 18.24 MHz at the Physicochemical Methods Unit, Harwell, Oxon. (I.A. Stenhouse).[1] Dinitrogen complexes of molybdenum and tungsten are prepared from $^{15}N_2$ gas, and treatment with acid in methanol gives ammonia (and sometimes some hydrazine).[2]

The Table compares our measurements of molybdenum and tungsten dinitrogen complexes with Bercaw's results on titanium[3] and zirconium[4] complexes (which contain bridging as well as terminal dinitrogen). The spread of the M-NN resonances is remarkable, covering 280 p.p.m. from tungsten to titanium (or 360 p.p.m. if bridging dinitrogen is included). This may be related to the different structures (octahedral and tetrahedral), d-electron configurations (d^6 and d^4), and so on.

The assignment of the resonances to α-(metal-bound) and β- (terminal) nitrogen is tricky, and Bercaw has (wisely) not attempted this. We have the advantage of observing the coupling of nitrogen to the phosphorus ligands: but still we have to assume, for our tentative assignments, that $^2J(NP) > {}^3J(NP)$, despite some well-known counter-examples such as that of pyridine for which the C-N coupling constants increase $^1J < {}^2J < {}^3J$. However, there are special explanations for the relatively large values of $^3J(CN)$ in pyridine and other aromatic compounds.[5] Further, Schulman

has demonstrated (by (INDO) coupled Hartree Fock calculations) a "one-bond lone-pair effect" which explains the small coupling constants to nitrogen by the approximate cancellation, in the Fermi contact term, of the (normal) negative contribution from the bonding orbitals by a large positive contribution from an s-hybridized lone pair on nitrogen.[6] This theory is in accord with the small values (Table) observed for $^{1}J_{(NN)}$, and suggests to us that there is no reason why the N-P coupling constants should not be attenuated with distance in the usual way, as was found for ethyl diazoacetate.[7] We hope that Dr. Schulman agrees with our application of his theory!

[1] J. Chem. Research, in the press

[2] J. Chatt, A.J. Pearman, and R.L. Richards, J.C.S. Dalton, 1977, 1852.

[3] J.E. Bercaw, E. Rosenberg, and J.D. Roberts, J. Amer. Chem. Soc., 1974, 96, 612; J.E. Bercaw, J. Amer. Chem. Soc., 1974, 96, 5087; J.M. Manriquez, R.D. Sanner, R.E. Marsh, and J.E. Bercaw, J. Amer. Chem. Soc., 1976, 98, 8358.

[4] J.M. Manriquez, D.R. McAlister, E. Rosenberg, A.M. Shiller, K.L. Williamson, S.I. Chan, and J.E. Bercaw, J. Amer. Chem. Soc., 1978, 100, 3078.

[5] F.J. Weigert and J.D. Roberts, J. Amer. Chem. Soc., 1972, 94, 6021.

[6] J.M. Schulman and T. Venanzi, J. Amer. Chem. Soc., 1976, 98, 4701, 6739; J.M. Schulman, J. Ruggio, and T.J. Venanzi, J. Amer. Chem. Soc., 1977, 99, 2045.

[7] R.L. Lichter, P.R. Srinivasan, A.B. Smith, R.K. Dieter, C.T. Denny, and J.M. Schulman, J.C.S. Chem. Comm., 1977, 366.

Table ^{15}N chemical shifts and coupling constants in dinitrogen complexes

Compound[a]	$\delta(^{15}N)$[b]			J/Hz[c]		
	α	β	μ-N_2	^1J(NN)	^2J(NP)	^3J(NP)
trans-$[Mo(N_2)_2(dppe)_2]$ (thf)[d]	-46.5	-46.2	-	~4.4(5)	-	-
trans-$[W(N_2)_2(dppe)_2]$ (thf)	-63.5	-52.0	-	5.4(1)	1.9(1)	0.9(1)
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$ (thf)	-42.6	-34.9	-	6.3(5)	trans 5.2(5)	-
cis-$[W(N_2)_2(PMe_2Ph)_4]$ (thf)	-61.2	-35.9	-	6.2(3)	trans 16.7(3)	0.9(3)
					cis 1.2(3)	
$[\{Ti(C_5Me_5)_2(N_2)\}_2N_2]$ (tol, -61 °C)[e]	165,215		299	7(2)		
$[\{Zr(C_5Me_5)_2(N_2)\}_2N_2]$ (tol, -28 °C)[f]	4.5,73.5		172.5	6.2		

[a] Measured at 18.24 MHz, and at 30 °C unless otherwise described. dppe is $Ph_2PCH_2CH_2PPh_2$. No tungsten satellites were observed. [b] Chemical shifts relative to external $MeNO_2$ (liquid CD_3NO_2 containing $[Cr(acac)_3]$), downfield positive. The provisional assignment to α- and β-nitrogens is explained in the text. [c] No signs have been measured. In parentheses, spectral resolution in Hz. [d] Signals very nearly coincident, making measurement of coupling constant difficult. [e] Ref. 3. Chemical shifts originally referred approximately to 11M Et_4NCl(aq), for which we assume δ-316. Spin-spin coupling evidence for the assignment of the α- and β-nitrogen resonances is lacking for the titanium and zirconium complexes. [f] Ref. 4. Chemical shifts originally referred to HNO_3 of unspecified concentration: referenced here with the authors' shift of -65.5 p.p.m. for N_2(tol) taken as -78 relative to $MeNO_2$(l).

Yours sincerely,

Joan Mason

Dr. Joan Mason

UNIVERSITY OF MINNESOTA
TWIN CITIES

Department of Chemistry
Kolthoff and Smith Halls
207 Pleasant Street S.E.
Minneapolis, Minnesota 55455

February 13, 1979

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

Amplifier Research Model 60LA with Noise Blanking
Interfaced to Varian XL-100 Spectrometer

Dear Barry:

As part of our multinuclear capability, we have replaced the Varian tuned, 100W pulse cards with an Amplifier Research broadband power amplifier. This unit also has provision for noise blanking which improves its on/off characteristics dramatically, as well as providing an edge of safety. The amplifier is essentially in a standby state as long as the blanking circuits are activated, thus prohibiting a blast of CW power from being sent to the probe. To deactivate the noise blanking, we use the leading edge of the pulse at pin BB(TP-19) at the Gate and Relay Driver board (Schematic 87-109-810) and the trailing edge to activate. XL-100 timing is set up such that the actual transmitter pulse follows the pulse at pin BB by 10 usec. To allow sufficient time for deactivation we increased this delay by 20 usec. giving a total of 30 usec. between the leading edge at pin BB and the actual transmitter pulse.

This change in hardware delay requires that one add 20 usec. to all pulse widths or adjust the pulse width timings accordingly. We have done the latter. On the Logic card (Schematic 87-109-753) in the FT Control module we recalibrated the pulse width with R-17 so the front panel control reads correctly. To correct the software required that the PW timing in each program be altered. This required that the PW software overhead be changed as follows: (for 30 usec. delay):

	FT-16E (994100-E) and SSFT			
Currently	3441	140054	SUB	ONE
Change to		120074	ADD	DEC 20
	T-1 RESEARCH SPECIAL (20309-M)			
Currently	2613	120127	ADD	ONE
Change to		120125	ADD	DEC 22

and in some free location, such as 125, put:

125	000026	DEC 22	

We suggest that these adjustments be checked with a scope.

Yours truly,

Robert M. Riddle Lenas J. Hedlund Frank D. Blum

RMR/LJH/FDB/cmb

Oklahoma State University

Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74074

February 12, 1979

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

TITLE: Miniaturization of Spectra on the XL-100 NMR Spectrometer

Dear Barry:

One of the problems involved in the reproduction of spectra for publication (or for theses) is the high cost of photoreductions. It occurred to us that a simple modification of our XL-100(15) unit would permit us to obtain reduced spectra directly on the unit at a reasonable cost and with a minimum of time and effort. The modification involves wiring three precision potentiometers into the y-axis servo assembly circuit board of the XL-100 through a three-pole,double throw switch (see Fig. 1). When the switch is in the "reduce" position, the new potentiometers alter the y-axis gain and the characteristics of two transitors which govern the high and low level electronic stops of the y-axis. In the normal position, the original circuitry is restored. The switch and potentiometers can be mounted on the recorder panel conveniently and connected to the y-axis servo assembly card through spare clip pins on the bottom of the card. Furthermore, the new circuitry was specifically designed to be removed easily from the card to facilitate repair or replacement. Since the modification is to the recorder, reduced spectra can be obtained from data collected from the CW or FT mode. The actual printing of the spectrum involves setting the switch to the "reduce" position and then increasing the desired plot width (either through the computer-ours is a Nicolet TT-100-, or directly through the XL-100 in the CW mode) by a factor of 5/2 (for a plot scaled down from 50 cm to 20 cm, for example). In order to obtain reductions of full spectra suitable for theses or publications, we have designed a chart paper which meets thesis margin requirements (for us at least) and includes spaces for all ancillary parameters which can be typed in later (see Fig. 2). These charts may thus be used directly in the thesis at a cost of less than $0.03/sheet and are also very space saving with respect to storage of spectra. The modification permits our technician to produce these reductions in less time than it takes to obtain a normal spectrum. The total cost of the parts was less than $10 and the modification required an afternoon to install. We plan to publish the entire operation, including a photo of the switch installed on the XL-100(15) unit,shortly.

Best regards.

Sincerely yours,

D. J. O'Donnell
Research Associate

Stan Sigle
NMR Operator

K. D. Berlin
Regents Professor

Y-Axis Servo Assembly
Pub. No. 87-125-742
Varian XL-100

1 - Switch 3PDT, subminiature
3 - Precision Cermet Trimmer Potentiometers # 960-20
Total Cost - Less than $ 10.00

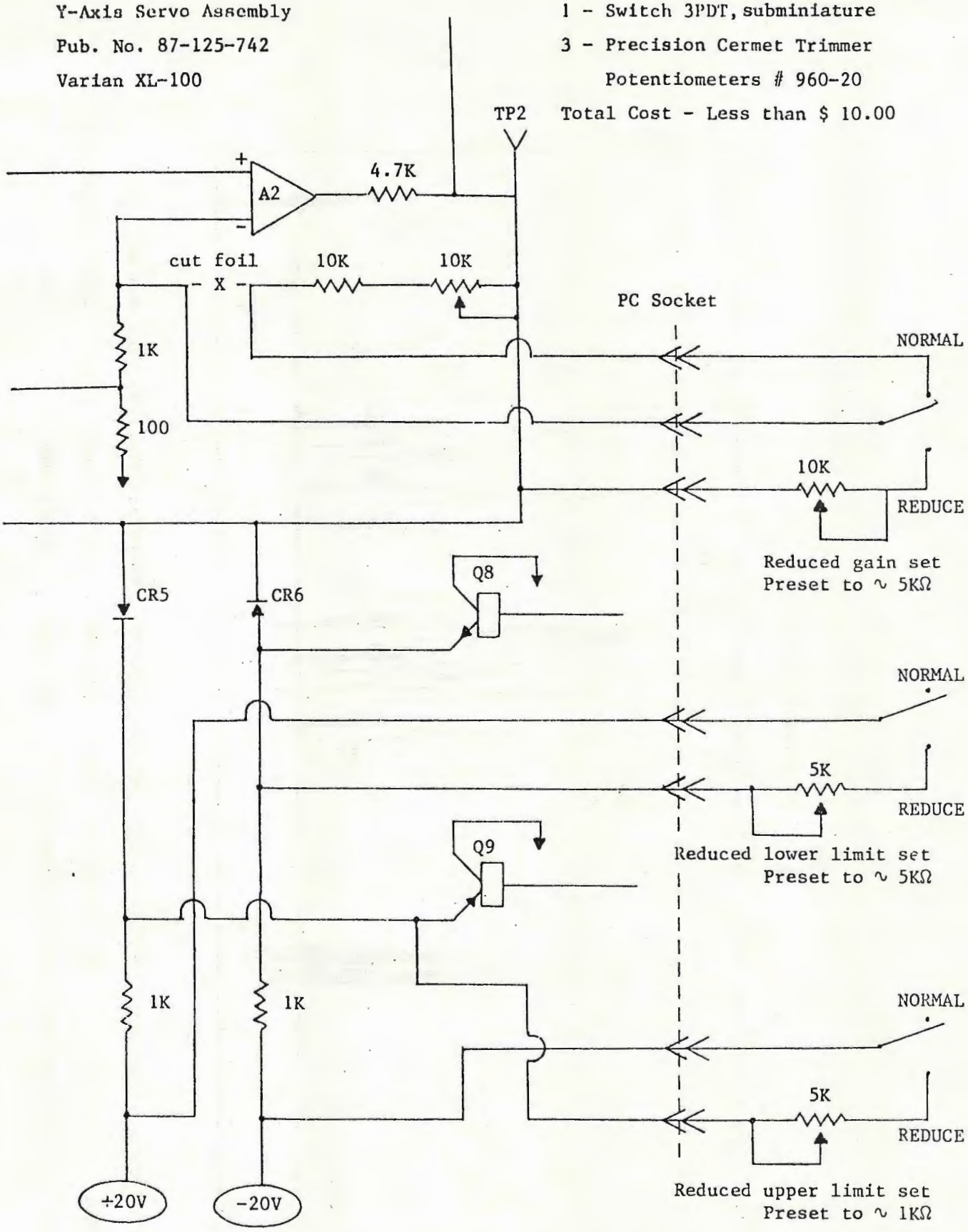
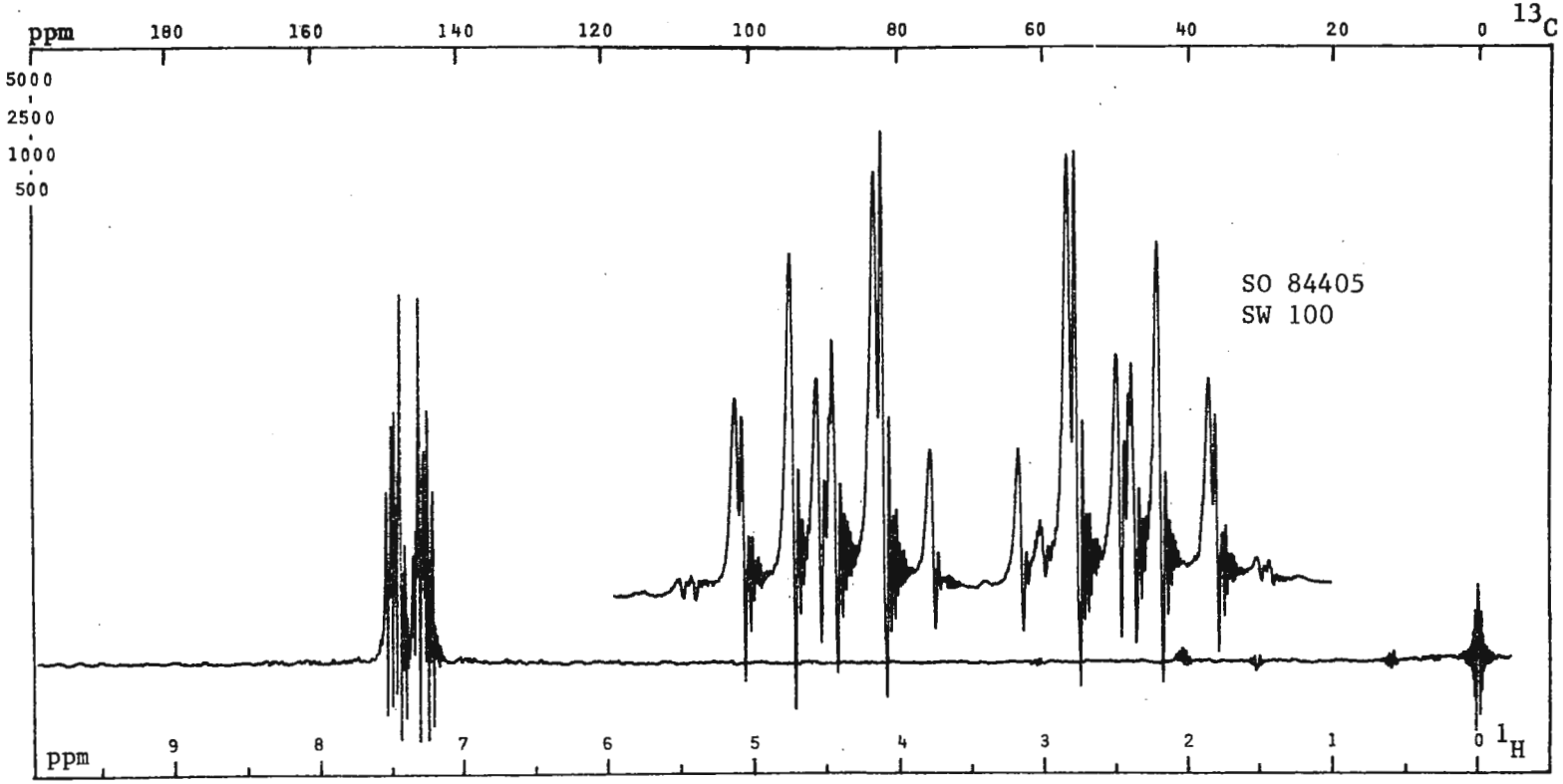


FIGURE 1

o-DICHLOROBENZENE



PFT _ CW X ; Solvent. . $(D_3C)_2C=O$; SO. . 83705 Hz; PW. . 1010 Hz; T. . 37 °C; Acq/SA. . 0.50

Size. . K; P2/RF. . 50 µs/dB; SF. . 100.1 Hz; FB. . 2 Hz; Lock. . ^1H ; D5/ST. . 1000 s

DC. . ; Gated Off. . ; Offset. . Hz; RF. . W/dB; NBW. . Hz

FIGURE 2

A hot performer at a cool 4.2°K

Varian introduces: The XL-200 superconducting FT NMR spectrometer

In a cost- and resource-conscious world, the new XL-200 with 47-kG superconducting magnet makes a lot of sense. To begin with, its high-field performance and advanced design come in a truly affordable package. And economy characterizes the XL-200 spectrometer in other ways, too—such as the low-loss dewar unit, which lets the system operate over three months on only 25 liters of liquid helium!

The basic instrument is designed for ^{1}H (200 MHz) and ^{13}C (50.3 MHz) observation, but it will accommodate a host of other nuclei with the optional 20-80 MHz broadband accessory.

The XL-200's data management system tops all conventional concepts of versatility and convenience. There are two processing units working in tandem—one 32 bits wide and very fast for data acquisition, the other programmed in a high-level language and extremely flexible for data manipulation. Both operate continuously and, together with the XL-200's full complement of built-in I/O devices, offer you unique multi-tasking capability and high sample throughput.

And that's only the beginning of a long list of features which could read like your own NMR wishlist:

- 47-kG Nb-Ti superconducting magnet with 50-mm bore
- 25 liters liquid He dewar capacity; 3-month refill interval
- 35 liters liquid N_2 dewar capacity; 14-day refill interval (45 days with optional refrigerator)
- 5- and 10-mm samples standard; other sample sizes optional
- Broadband probes covering 20-80 MHz and 188-212 MHz ranges
- Flexible mix/match RF system with fixed-frequency sources such as ^{1}H, ^{13}C, ^{19}F, and ^{31}P
- Compatible with RF synthesizer for broadband multi-nuclear operation
- 50-kHz spectral widths with quadrature phase detection
- Automatic ^{2}H internal field/frequency stabilization with exclusive AutoLock™ circuit
- ^{1}H homo/heteronuclear decoupler for a wide variety of gated modes
- Programmable 32K CPU for data processing and multi-tasking
- Independent 32-bit parallel processor with dedicated random-access memory for spectrometer control and data acquisition
- Built-in I/O devices include solid-state keyboard; 5M-word moving-head disk with dual platter (one removable); high resolution raster scan storage/display oscilloscope; 32-column line printer; 500 x 240 mm X-Y recorder.

If you would like the balance of the features to compare with your wishlist, write Varian Associates, Inc., Box D-070,611 Hansen Way, Palo Alto, CA 94303.

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Phone: (713) 783-1800

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Bldg. 2, Suite 230
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Phone: (206) 454-2910

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UNIVERSITÉ PARIS VII

ITODYS

INSTITUT DE TOPOLOGIE ET DE DYNAMIQUE DES SYSTEMES
1, rue Guy de la Brosse - 75005 PARIS - Tél. : 336 25.25, poste 36-15

LABORATOIRE DE CHIMIE
ORGANIQUE PHYSIQUE

J.-E. DUBOIS, *Directeur*

Paris, February 7th, 1979

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

Dear Dr. Shapiro,

We wish to report several modifications in the PG 100 software package for a Jeol PFT 100 Fourier transform NMR spectrometer interfaced with a Jeol JEC 100 computer. Apart from minor practical changes, the main improvements concern Nuclear Overhauser Effect (NOE) measurements and automatic relaxation time measurements. The revised software package requires 12K core memory words instead of the 8K words for the initial PG 100 (although the modifications require less than 4K words, only 4K or 8K word extensions are available for the computer).

Two-Block Accumulation

$^{13}C-\{^{1}H\}$ NOE measurements require great spectrometer stability, especially in the case of signal accumulation over a long period of time. Spectrometer instability effects can be cancelled by alternately accumulating, in two different parts of the memory, the complete decoupled FID and the gate-decoupled FID (1). Thus, odd-numbered FID's are accumulated in block 1 of the memory, and even-numbered FID's in block 2. The required pulse sequence is programmed using the 16-word sub-program in the PG 100 package (cf. below). This modification makes it possible to perform accurate measurements of the difference between two spectra or of the ratio of peak intensities for any kind of differential spectroscopy.

Base-Line Adjustment by Phase Correction

When measuring NOE using peak areas, the integration base-line level is critical, especially for broad lines. Since peak areas greatly depend upon base-line level and phase correction, and since, in the case of a noisy spec-

trum, peak area measurements can be highly uncertain, we have included a routine in which the average value of the two mean noise levels on each side of a given peak is used to compute the peak area. This is done by adjusting the two phase correction parameters until the two base-line levels are equal (perfect phase correction).

Automatic Relaxation Time Measurement

The initial automatic relaxation time measurement routine (using peak intensities) has been extended to the peak areas. Peak integration limits and integration base-line level are entered separately for each peak. Furthermore, a Carr-Purcell or Carr-Purcell-Meiboom-Gill sequence, where the number of π pulses is automatically varied (up to 20 different values) and the last half-echo is digitalized, has been added to the automatic T_2 relaxation time measurement routine.

Two-Parameter Exponential Least-Square Fitting

It has been shown (2) that non-linear exponential curve-fitting gives more accurate results for T_1 (or T_2) measurements than the classical linear fitting. As uncertainty on the values of the thermal equilibrium magnetization, M_0, is the main cause of error in T_1 determination (2d), M_0 is treated as an unknown parameter. A two-parameter exponential least-square fitting routine computes optimized M_0 and T_1 or (T_2) values of variables M and T, in order to minimize the sum of the square of the residuals, S :

$$S = \sum_{i=1}^{n} \{M(A - B \exp(-\frac{t_i}{T})) - M_i\}^2$$

in the following cases :

1) inversion-recovery (A = 1, B = 2)
2) saturation-recovery (A = 1, B = 1)
3) fast inversion recovery (A = 1, B = 2 exp $(-\frac{t_r}{T_1})$, where t_r is the repetition time
4) Freeman-Hill modified inversion recovery (A = 0, B = - 2)
5) T_2 measurement (A = 0, B = - 1).

For a given value of T, S has a single maximum when M = M (T). Therefore, replacing M by M (T) in determining S leads to a one-parameter minimization problem. The root of the equation $\frac{dS}{dT} = 0$ is sought by a dichotomous algorithm in an interval chosen by the user. This routine makes it possible to suppress any given data. Peak height and peak area computation is sequential.

Pulse Sequence Capabilities

In the initial software, a 16-word sub-program allows the user to build pulse sequences. Now, there is a further possibility to store 8 different sub-programs of this kind in order to have quick access to pulse sequences not included in the initial software.

PG 100 owners interested in this improved software package can contact us for further details.

Sincerely yours,

J.P. Lemaire B. Tiffon B. Ancian

REFERENCES

1 - a) R.K. Harris and R.H. Newman, J.Magn.Reson., 24, 449 (1976) ;
b) R. Richards and K. Wüthrich, ibid., 30, 147 (1978).
2 - a) R. Gerhards and W. Dietrich, ibid., 23, 21 (1976) ;
b) M. Sass and D. Ziessow, ibid., 25, 263 (1977) ;
c) J. Kowalewski, G.C. Levy, L.F. Johnson and K. Palmer, ibid., 26, 533 (1977).
d) A.H. Brunetti, ibid., 28, 289 (1977).
e) T.K. Leipert and D.W. Marquardt, ibid., 24, 181 (1976).

246-29 **IWAN N. STRANSKI-INSTITUT**
für Physikalische und Theoretische Chemie
der Technischen Universität Berlin
Prof. Dr. D. Ziessow

Berlin, den February 12, 1979
Tel.: (030) 314- 4958
Az.:

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Straße des 17. Juni 112
Ernst-Reuter-Haus
~~1 Berlin 10~~
~~Ernst-Reuter-Platz~~
~~Telefunken-Haus~~

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

Title: Dynamic Range in Hadamard Spectroscopy

Dear Professor Shapiro:

Some time ago Hadamard NMR Spectroscopy was proposed as an alternative[1] method to achieve broadband excitation and detection of NMR lines. With respect to the dynamic range problem, it was taken as an advantage that a non-decaying Hadamard signal seemed to be better adapted for digitization than a decaying FID signal since the optimum total signal power per given time is the same. Later this was questioned and arguments were given that the proposed dynamic range advantage did not hold.[2]

We still favour our earlier ideas and would like to support our view by means of a digital simulation. Fig. 1 shows the calculated Hadamard and pulse responses as well as the corresponding spectrum. In the case of the doublet, the time function was multiplied by 1/200 in order to simulate the situation of two C-13 satellites of a proton line. After multiplication the doublet time function was added to the singlet time function for both the Hadamard signal and the FID signal. The maximum number of the time function was in both cases 32.767 which is the maximum number in a 16 bit computer. The 32.767-FID signal was fouriertransformed and is displayed in the bottom trace of Fig. 2 in order to demonstrate the error resulting from the limited word length of the computer. The process of digitization was simulated by multiplying both the Hadamard and the pulse response time function with a factor such that the maximum number was 1.000, 500, and 250 (corresponding to an A/D resolution of ± 10, 9, 8 bit). This does not represent the actual A/D conversion with respect to the round-off process (100,4; 100,6 yields in our case 100;100, in actual practice, however, 100;101). We feel, however, that the resulting inaccuracy should be the same in the Hadamard and the pulse case. Fig. 2 depicts the resulting satellite spectra for the 10, 9, 8 bit A/D conversion. In the Hadamard case, the time function is first subjected to a Hadamard transform; the resulting FID type time function was treated in the same way as the pulse response time function.

It seems to be clear from these pictures that in the Hadamard case the dynamic range problem (weak signals besides a very strong one) is somewhat relaxed.

Sincerely yours,

Dieter Ziessow

1) R. Kaiser, J.Magn.Res. 15, 44-63 (1974)
D. Ziessow and B. Blümich, Ber.Bunsenges., 1169-1179 (1974)

2) J. W. Cooper, in Topics in C-13 NMR Spectroscopy, Vol. 2, Ed. G.C.Levy, Wiley (1976)
J. W. Cooper, in Transform Techniques in Chemistry, Ed. P. R. Griffiths, Heyden (1978)

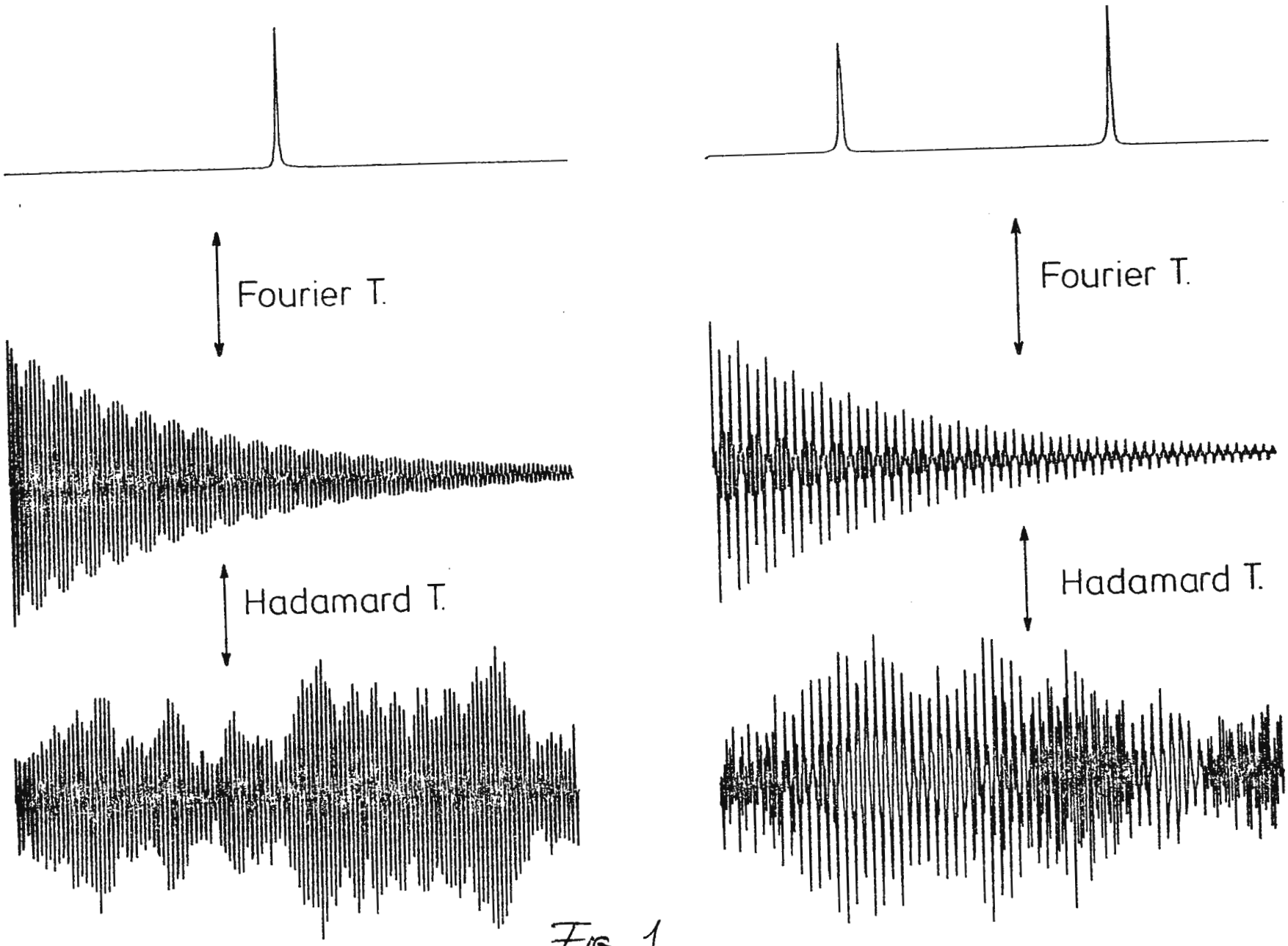


FIG. 1

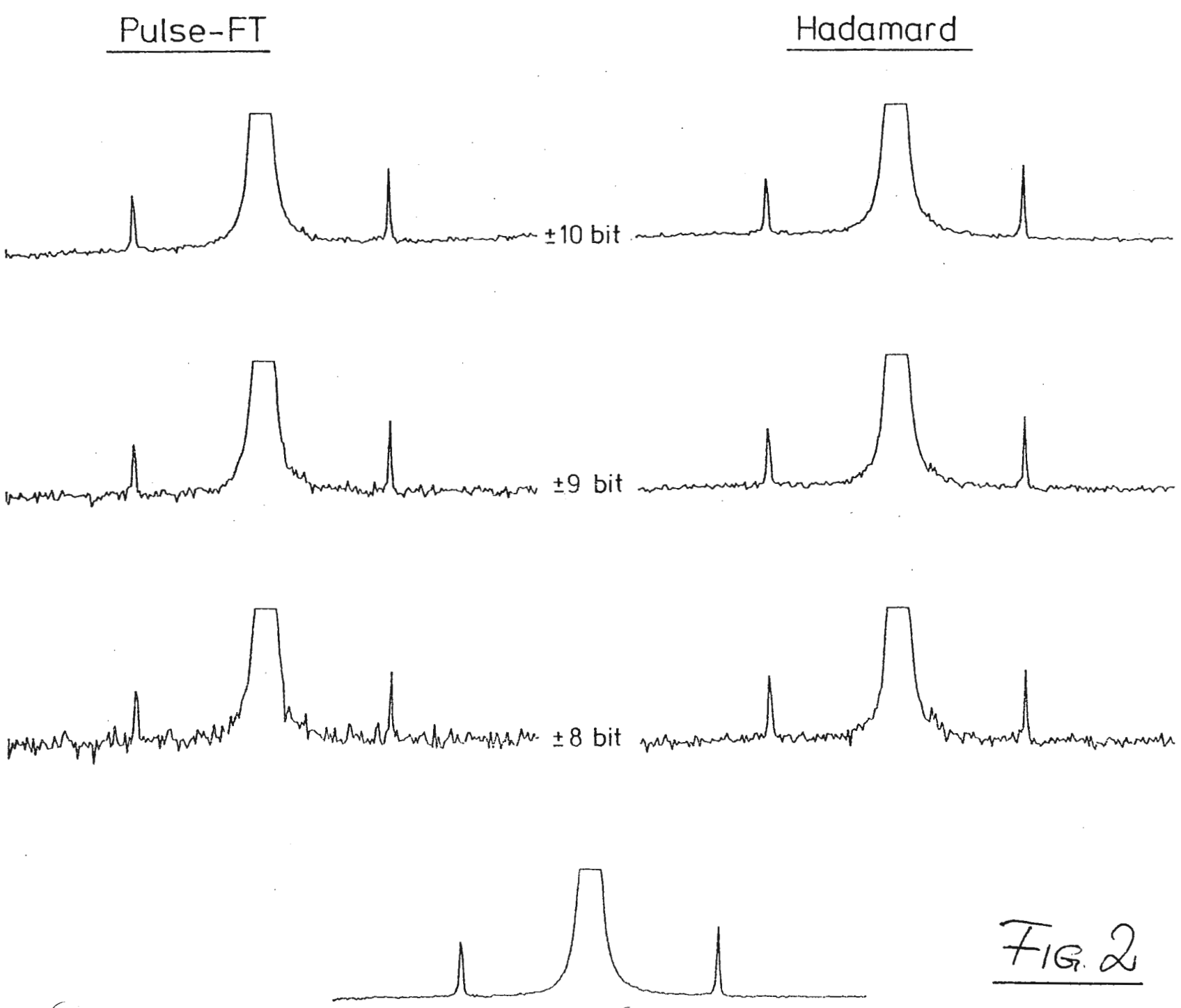


FIG. 2

The University of Alabama in Birmingham
Comprehensive Cancer Center
205/934-5077

February 7, 1979

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

Dear DR. Shapiro:

A postdoctoral position is available in our laboratory for a recent Ph.D. with experience in nmr spectroscopy interested in developing nmr techniques for delineating the solution conformation of peptides. The project will employ the neurohypophyseal hormones, oxytocin and vasopressin, as the principal models. The project will stress multiple resonance experiments (e.g., NOE and transfer of saturation) and paramagnetic probe techniques. Available instrumentation includes Bruker WH-400, CXP-270 and HX-90 spectrometers.

The preferred starting date is February - June, 1979. Please have appropriate candidates contact me.

Sincerely yours,

Jerry D. Glickson, Ph.D.
Director, Cancer Center,
NMR Core Facility

JDG/tc

cc

UNIVERSITY OF DELAWARE
NEWARK, DELAWARE
19711

DEPARTMENT OF CHEMISTRY

February 13, 1979

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

Dear Dr. Shapiro:

With regard to the last letter, I felt such information would be interesting and useful to those persons doing multiple pulse NMR of polymer species. But, perhaps, it's better to let people learn of it in J. Chem. Phys.

One parameter which is of some use in characterizing molecular motion in ordered phases is T_{1D}, the relaxation time for the dipolar energy. Recently, we have studied this parameter as a function of temperature for three different samples of polypropylene, each having been characterized by DSC, IR and viscosity as to its tacticity, glass transition and percent crystallinity. The data are shown in the accompanying figure. Both actactic samples show a marked change in T_{1D} around the glass transition temperature. The noncrystalline sample, APP(1), shows no Jeener echo at temperatures much above the glass transition. The 20% crystalline sample, APP, shows a break in T_{1D} at the glass transition temperature but, at high temperatures, Jeener echoes are still observed. The highly crystalline isotactic sample has a somewhat longer dipolar relaxation time than either actactic sample. There is a drop in T_{1D} with temperature as one approaches the melting point. To see if these relaxation times are associated with only part of the sample at higher temperatures, we did spin counting at selected temperatures on the APP sample. Somewhat to our surprise, this experiment suggested that we see the same number of spins above T_g as we do below T_g.

Please credit this to the account of the Blue Hen NMR Complex.

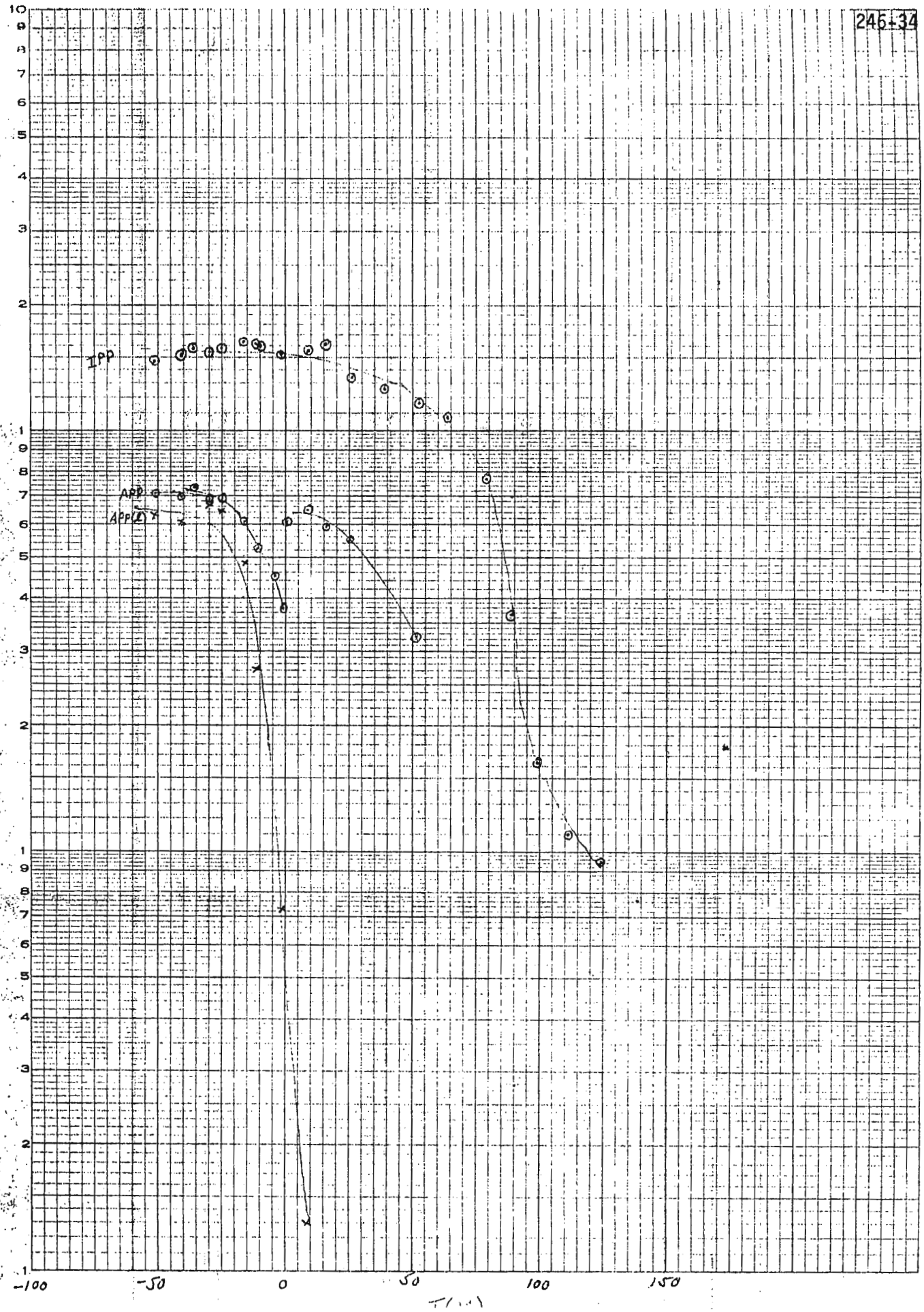
Yours truly,

Cecil Dybowski

Cecil R. Dybowski
Assistant Professor of Chemistry

sr

Enclosure



CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

February 16, 1979

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

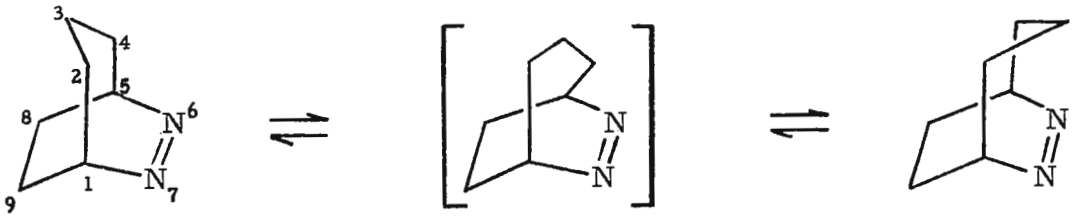
JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

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

Conformational Equilibria in Bicyclic Azoalkanes

Dear Barry,

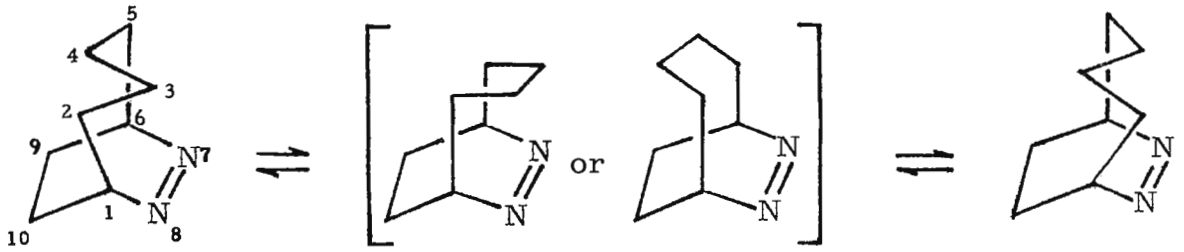
Recently we have investigated the temperature-dependent ^{13}C NMR spectra of 6,7-diazabicyclo[3. 2. 2]non-6-ene (I) and its homolog, 7,8-diazabicyclo-[4. 2. 2]dec-7-ene (II). [1] Not unexpectedly, the barrier to ring inversion in I is very low, and only at -155°C in dimethylether/$CFCl_2H$ at 25. 2 MHz is broadening observed of three of the four (C_S symmetry) signals, namely the ones corresponding to C2, 4, C3 and C8, 9 (see Table). This behavior is indicative of slowing of the ring flipping in I on the NMR time scale, and



Ia Ic Ib

for an equilibrium at -155°C which is not strongly biased towards one side. The activation barrier is likely to result from a transition state in which the C1,2 and C4,5 bonds are not fully aligned, but C1, C2 and C3 lie in one plane. In this transition state, total eclipsing of the hydrogens on C2, C3 and C4 is avoided and the boat conformation of the quasi-cyclohexene becomes skewed.

The ^{13}C spectrum of II, on the other hand, is temperature-dependent between ca. -70° and -120°C. At -122°C, all four carbon signals (C_S symmetry) observed up to -60°C are duplicated, indicating a frozen isodynamic system (see Table). We believe that the eight signals can be assigned to the racemic mixture of IIa and IIb (C_1 symmetry) which slowly interconvert at -122°C on the NMR time scale.



IIa IIc IId IIb

This assignment is supported by calculations on cyclooctane[2] and by the assumption that the π family can be treated as a 1,4-bridged cyclooctane. Anet and Krane[2] calculated the relative energies for the transition state for the BC ⇌ TBC equilibrium to be 3.3, the boat (B) 11.2, and the chair (C) 7.5 kcal/mol. These values indicate that IIa (a bridged TS of the BC ⇌ TBC interconversion) is lower in energy than IIc (a bridged C) or IId (a bridged B) by a few kcal/mol. Assuming that the nonbonded interaction between H_2 (C3,4) and H_2 (C9,10) is less favorable (IId) than the corresponding one between H_2 (C3,4) and N7,8 (IIc), IIc appears to be the likely transition state in the racemization of II. The calculated energy[2] for the transition state of the TBC ⇌ C process is 7.5 kcal/mol in close (and maybe accidental agreement) with the observed value for II. The observed $\Delta G^{\ddagger}$ value for the ring inversion in cyclooctane[3] is 8.1 and in 1,1-difluorocyclooctane[4] it is 7.5 kcal/mol.

Table. ^{13}C Chemical Shifts (25.2 MHz) of I and II in Solvent Mixtures and at Different Temperatures.

Compound	Solvent mixture	Temp., °C	C1,5 C1,6	C2,4 C2,5	C8,9 C9,10	C3 C3,4
I	CS_2/CD_3COCD_3	ambient	62.6	25.9	19.3	22.6
II	CH_3OCH_3/CCl_2FH	-68	62.2	23.6	19.6	32.5
II	CH_3OCH_3/CCl_2FH	-122	61.2 62.5	22.6 23.3	17.1 21.5	29.8 34.2

Best wishes,

Rainer Dyllick-Brenzinger

John D. Roberts

1. We thank Dr. Henrik Olsen of ETH Zurich for supplying us with samples of I and II.

2. F.A.L. Anet and J. Krane, Tetrahedron Lett., 5029 (1973) and references to older calculations therein.
3. F.A.L. Anet and J.S. Hartman, J. Am. Chem. Soc., 85, 1204 (1963).
4. J.E. Anderson, E.S. Glazer, D.L. Griffith, R. Knorr, and J.D. Roberts, J. Am. Chem. Soc., 91, 1386 (1969).

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19174

School of Medicine G3

DEPARTMENT OF
BIOCHEMISTRY AND BIOPHYSICS

14-February-1979

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

Dear Barry,

I want to sell the Varian HR-220, 220 MHz, FT NMR spectrometer here at the Middle Atlantic NMR facility. The instrument is equipped for the for observing only protons. The sensitivity is 100/1 S/N for 1% ethylbenzene, the resolution 0.5 Hz, and the spinning sidebands are less than 0.1%. The instrument is equipped with a Varian 620I, 16K computer, a cassette drive for program and data storage, a programmable Fluke frequency synthesizer, field and frequency sweep in the CW mode, a homonuclear lock and variable temperature control. The room temperature field shim coils were updated by Varian to provide z^1, z^2, z^3, z^4, x, y, xy, xz, yz, and $x^2 - y^2$ gradient corrections.

The magnet dewar needs repair. One of the internal supports broke so that part of the helium canister touches the nitrogen canister. Consequently there is a very high liquid helium boiloff rate. Varian informally estimated that the dewar could be repaired for about $4,000. Alternatively, the magnet could be fitted with a modern dewar by Oxford instruments for about $14,000. (See the Dec 1978 TAMU Newsletter, p. 48). This would lower the operating cost by a factor of five to six.

I will also consider selling the console, magnet and data systems seperately. Interested parties may contact me at 215-243-6396.

Sincerely yours,

George G. McDonald

George G. McDonald

Laboratorium
für anorganische Chemie
Eidg. Technische Hochschule
Zürich

Dr. P. S. Pregosin

8006 Zürich, Universitätstrasse 6

February 15, 1979

246-38

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

Dear Professor Shapiro,

The increasing interest in metal complexes of phosphine ligands as homogeneous catalyst has spurred interest in their $^{31}P\{^{1}H\}$ NMR spectra. Since there is relatively little known about ^{31}P spin lattice relaxation in metal complexes we have measured T_1 values for some trans-$PdCl_2P_2$ derivatives, P = a tertiary phosphine, and show these values below. The relaxation is predominantly dipolar $[^{31}P - {}^{1}H)$ as indicated by the NOE values. A full report will appear in Helv. Chim. Acta shortly. Please credit this contribution to the account of L. M. Venanzi.

Very truly yours

Paul Pregosin

P. S. Pregosin

Complex	T_1*	NOE*, η
$PdCl_2(PEt_3)_2$	9.5	0.97
$PdCl_2(PPr^n_3)_2$	6.3	1.07
$PdCl_2(PBu^n_3)_2$	4.3	1.14
$PdCl_2(PCy_3)_2$	3.6	1.21

* For $CDCl_3$ solutions at 303^{o}.

246-39

Department of Chemistry

YORK UNIVERSITY

FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW, ONTARIO M3J 1P3

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

Dear Professor Shaprio:

i) Metal Interactions in Peptides

ii) NMR parts for sale

We have recently been looking at interactions of metal ions with small peptides. The metal peptide derivatives were originally being made for X-ray work but inadvertently strayed into an nmr Tube during crystallization. As an example, we have looked at the interaction between Ni^{2+} and Thyrotropin Releasing Factor (<Glu-His-Pro-NH_2). Not surprisingly, we find that small amounts of nickel ion broaden out the histidyl ring carbon signals (this has been observed by others eg. I.C.P. Smith at NRC, Ottawa who warns against using Nickel syringe needles etc. in preparations of related hormone solutions). Next the β and α-carbon of the histidyl residue broaden and vanish. Then at 0.5 Ni : 1.0 TRF the propyl δ-carbon and carbonyl carbon begin to broaden. This we did not expect, tending to anticipate some interaction with the glutanyl residue. We also do not know why the δ-C and the C=O group which are on opposite sides on the ring are affected. Dilution tends to restore the sharpness of the peaks indicating both a labile and relatively weak interaction with the Ni^{2+}. Work continues. We have also obtained Anrhenius plots of T_1 versus temperature for the unmetallated hormane. From the slopes of these plots we suspect intermolecular hydrogen bonding centered at the pyroglutamyl end of the molecule. Perhaps this is why Ni stays away from this end!

Subject to reasonable offers we have the following equipment which is becoming redundant to our needs:

One HA-100 NMR with proton variable temperature and ^{19}F crystals. (Solid state power supply & superstabilizer)

One CFT-20 variable temperature 5 mm proton probe assembly.

Sincerely yours,

Clive Holloway

C.E. Holloway
Associate Professor
416-667-2308

Texas A&M University N-M-R Newsletter

Policies and Practical Considerations

(Revised Version of 1 March 1979)

1. Policy: The TAMU NMR Newsletter is envisaged as a means for the rapid exchange of information between active workers in the field of nuclear magnetic resonance. As such, it will serve its purpose best if the participants impart whatever they feel will be of interest to their colleagues, and inquire concerning whatever matters interest them. Since the participant is clearly the best judge of what he considers interesting, our first statement of policy is "We print anything". (This is usually followed by the mental reservation "that won't land us in jail".) Virtually no editorial functions are performed, although I feel the time has come when contributions dealing with the likes of how to clean spectrometer cooling coils, still another discovery of non-equivalent methylene protons, etc., should not be considered adequate. The TAMU NMR Newsletter is not, and will not become, a journal. We merely reproduce and disseminate exactly what is sent in. Foreign participants should not feel obliged to render their contributions in English.

2. Finances, Subscriptions and Advertising: The Newsletter is wholly self-supporting, and depends for its funds on advertising, donations and individual subscriptions, for which the rate of $70.00 per year for a single subscription is now charged. A 50% academic or personal discount is available. Organizations and individuals are also invited to consider becoming a Contributor or Sponsor of the Newsletter and to have their organization's name appear in the appropriate list in each month's Newsletter, as well as the satisfaction of knowing they are helping keep this non-profit Newsletter in a solvent configuration. We will be happy to provide further details to anyone interested.

A major, indeed essential, source of funding to support the Newsletter is advertising. We earnestly solicit present and potential participants of the Newsletter to seek advertising from their company or institution. Our rates are modest and the need is great. Please inquire for all details.

3. Participation is the prime requisite for receiving the TAMU NMR Newsletter; in order to receive the Newsletter, you must make at least occasional contributions to its contents. We feel that we have to be ruthless in this connection and the following schedule is in effect: Eight months after your last contribution you will receive a "Reminder" letter. If no contribution is then forthcoming ten months after your last contribution, you will receive the "Ultimatium" letter, and then the next issue will be your last. If you are dropped from the mailing list, you can be reinstated by sending a contribution, and you will receive back issues (as available) and forthcoming issues at the rate of nine per contribution. Frequent contributions are encouraged, but no "advance credit" can be obtained for these. In cases of joint authorship, either contributor, but not both, may be credited - please indicate to whose account credit should be given.

PLEASE NOTE: A subject of concern to several present and potential TAMU NMR Newsletter participants, as well as to ourselves, is whether the Newsletter ought to contain material which either appears essentially simultaneously in the formal literature (or is presented at a meeting) or is definitely scheduled to appear very shortly (i.e., within a few weeks) after it would appear in the Newsletter. Our attitude is that a TAMU NMR Newsletter contribution should not duplicate, summarize or abstract material which has been published or which will appear in the formal literature within a small number of weeks of the Newsletter account. On the other hand, let it be firmly emphasized that if the appearance in a journal is several months away, a brief account (as an abstract with or without a "Preprint Available" notice, a separate informal account, a selection of material from the manuscript, or what have you) sent in to the TAMU NMR Newsletter fulfills one of the very functions which we feel this Newsletter should provide. We trust that a participant will in each case himself apply the criterion of whether or not his contribution will communicate some subject matter to the Newsletter audience before they could read it elsewhere.

4. Public Quotation: Public quotation of Newsletter contents in print or in a formal talk at a meeting, etc., is expressly forbidden (except as follows), and reference to the TAMU NMR Newsletter by name in the scientific literature is never permissible. We remind you that in order to quote results or use material from the Newsletter, it is necessary, in each individual case, to obtain the prior permission of the author in question and then to refer to the material quoted as a "Private Communication".

If your copy of the Newsletter is shared with other readers, it is your obligation as the actual recipient of the Newsletter to see that these other readers of your copy are acquainted with and abide by the statements of policy and practical considerations.

5. Practical Considerations:

a) All contributions to the TAMU NMR Newsletter should be sent to the undersigned and will always be included in the next issue if received before the deadline dates, which appear in each issue.

b) Contributions should be on the minimum (NOTE!!!!) number of 8½ x 11" (21 x 27.5 cm) pages and printed on one side only. Margins should be between 2 and 3 cm on all sides - *PLEASE* observe these limits. Black ink, typing, drawings, etc., essential. We are not equipped to deal with large size pieces of paper - e.g., A-60 charts.

Please conserve space by avoiding double spacing (except where necessary), ultra-wide margins, half-filled pages, etc. In general, please plan and construct your contribution so as to fill the minimum number of pages needed. On the other hand, drawings and spectra lose both eye-appeal and utility when they are too small. Only in very rare and absolutely necessary circumstances will a contribution in excess of three pages - including drawings, figures and references - be accepted. Economic necessity forces this policy.

Since reproductions of various kinds do not themselves reproduce too well, contributors are urged to submit their photographic originals to us (if the size does not exceed 8½ x 11"), and we will be happy to return these if requested. Some law of physics says that photographic reproductions of fuzzy or blurred originals never come out less fuzzy or blurred.

c) Please provide short titles of all topics of your contributions, as they will ensure accuracy in preparing the title-page index.

d) Please do not send in manuscripts, theses, books, etc., and ask us to be your consciences in selecting what should and shouldn't go into the Newsletter.

6. Suggestions: They are always welcome.

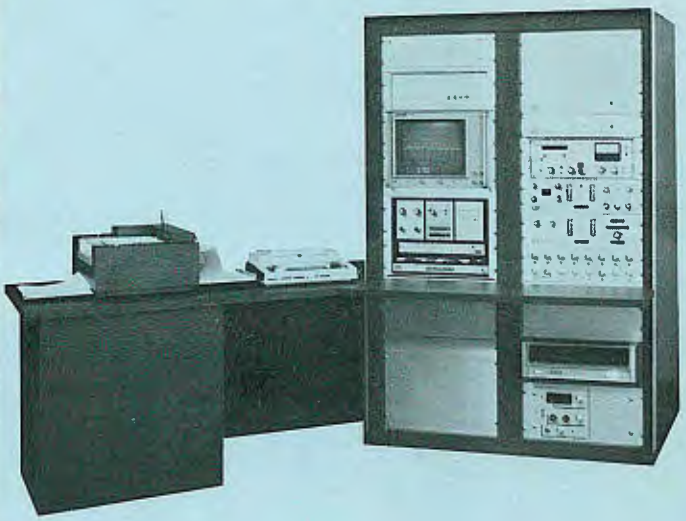
B. L. Shapiro
1 March 1979

Address for all Contributions and Inquiries:

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

(Phone: [713]845-6944)

NT-150 A WIDE-BORE, FT-NMR SYSTEM FROM NICOLET



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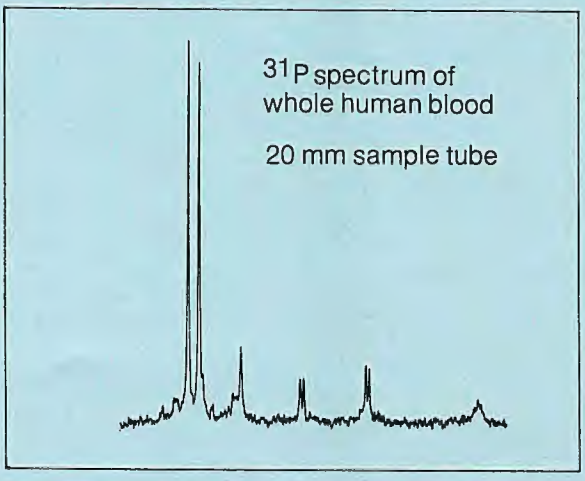

For more information or to discuss your applications, please telephone or write.

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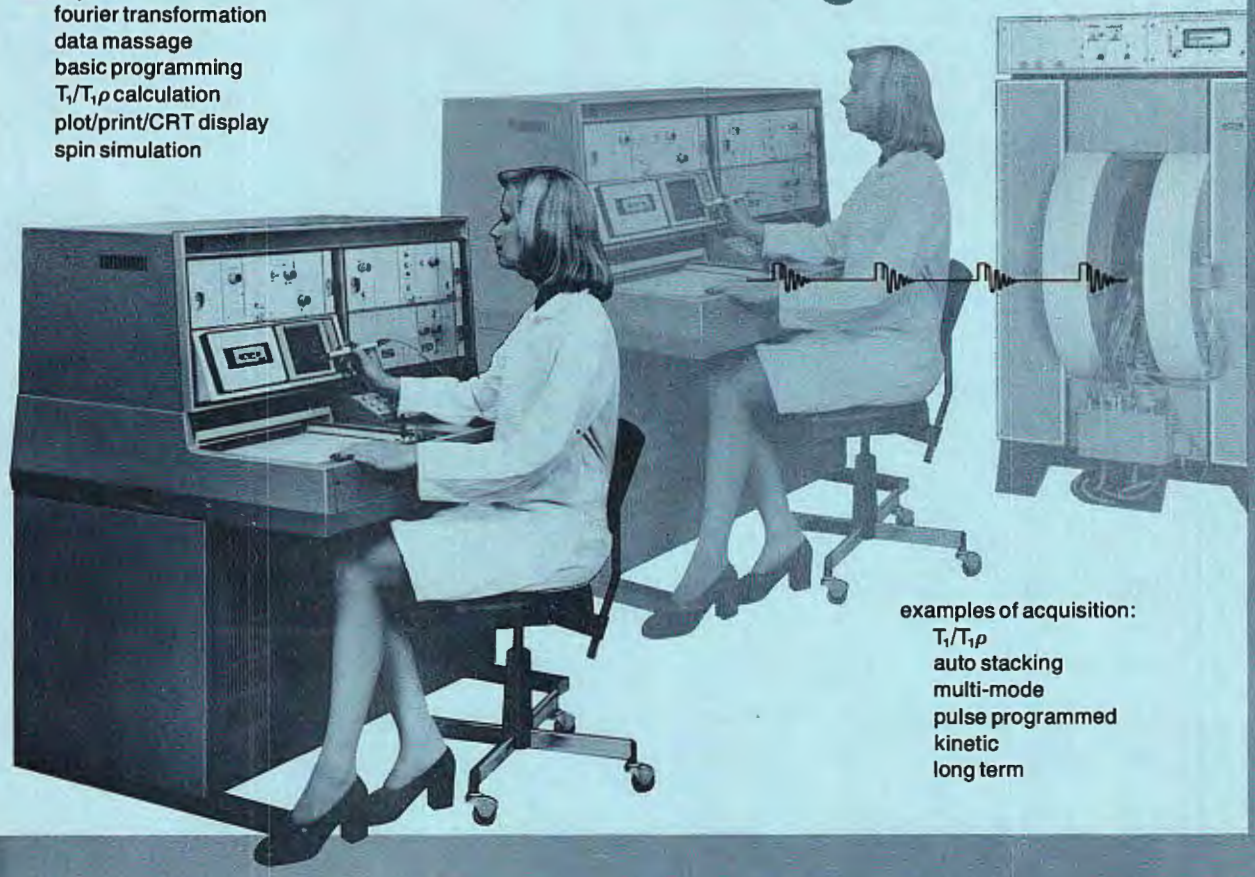

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