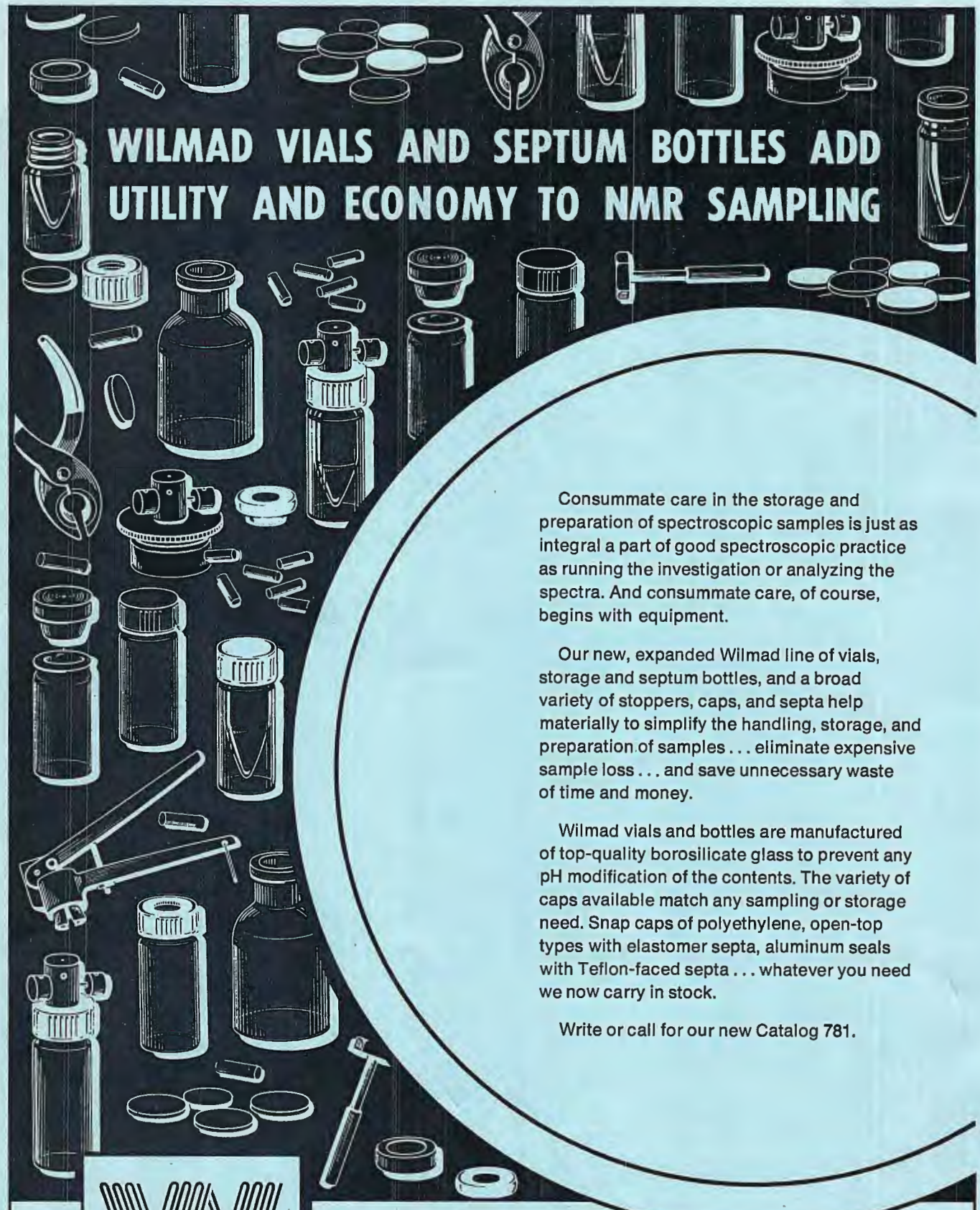
TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 283

April, 1982



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DEADLINE DATES: No. 284 3 May 1982
No. 285 7 June 1982

All Newsletter Correspondence, Etc., Should be Addressed To:

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 283

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

9 DEC 81

Dear Barry

MAGNETIC RELAXATION IN HETEROGENEOUS SYSTEMS

Glass bead dispersions have often been used as models to determine the mechanism of proton transverse relaxation in heterogeneous systems. Fung and McGaughy[1] have recently drawn attention to possible discrepancies in previous interpretations. We would like to report here new measurements on these systems.

Transverse relaxation rates (T_2^{-1}) have been measured as a function of nmr frequency and C.P.G.M. pulse separation, tcp, for normal water dispersions and dispersions in which water has been replaced by other solvents (e.g. acetone, chloroform, and butan-1,4-diol). The objective of the work was to determine the contribution of diffusion through field gradients caused by bulk magnetic susceptibility effects to the T_2 mechanism. The solvents butan-1,4-diol, chloroform, were chosen mainly because χ is close to the value for water, while their interaction with the glass surface is much less.

Measurements were carried out on a Bruker 322S spectrometer operating at 16-60 MHz. The dispersions were prepared by addition of the liquids to the beads (size distribution ca 10-60μm) in the nmr tube, followed by agitation. All samples contained 6% by weight of the liquids.

The T_2 decays for water (fig. 1) were non-exponential and independent of both tcp, the 180° pulse separation, and H_o, the applied magnetic field. The time taken for the magnetisation to decay to $1/e$th of its maximum intensity at $t = 0$, T_{2eff}, is given to demonstrate that diffusion through magnetic field gradients makes no significant contribution to T_2 in this system. For the other fluids, if surface effects are important, e.g. solvent/surface H-bonding we would expect T_2 values in the order: water < butan-1,4-diol < chloroform ≃ acetone, while a mechanism involving diffusion of solvent molecules across field susceptibility gradients between particles would, on the basis of the usual equation:

$$M(t) = M_o \exp[(-t/T_2)+(-\gamma^2 G^2 D n t^3 cp/12)]$$

and known diffusion coefficients put T_2 values in the order:

acetone ≃ chloroform < water << butan-1,4-diol.

Magnetisation decays for the three solvents - acetone, chloroform and butan-1,4-diol were also non-exponential (examples in figure 2) with the measured T_{2eff} values in the sequence:

water < butan-1,4-diol < acetone ≃ chloroform

This is the order we expect if surface effects are important as the T_2 mechanism. However, for acetone and chloroform a dependence of T_{2eff} on tcp is detected for longer pulse separations, this being much weaker at 16 MHz than at 60 MHz. Thus, diffusion through magnetic field inhomogeneities due to magnetic susceptibility effects is important for non-interacting solvents with long T_2 values at high frequencies.

In considering the relevance of these results for studies on colloidal systems generally, two factors are important: First, few species undergo as rapid self-diffusion as chloroform or acetone since other molecules are larger. Secondly, most practical dispersions are diamagnetic, hence the magnitude of ($\chi vs - \chi vm$) will be reduced by a factor of four or more over the present system. Therefore the susceptibility mechanism is unlikely to be important for most systems, with the exception of measurements made at very high frequencies and temperatures or for long T_2 values. This contribution can easily be detected by its nmr frequency dependence.

References

1. B.M. Fung and T.W. McGaughy, J.Magn.Resonance, 43, 316 (1981).
2. J.S. Murday and R.M. Cotts, J.Chem.Phys., 53, 4724 (1970).
3. D.W. McCall, D.C. Douglass and E.W. Anderson, Ber.Bunsenges Phys Chem, 67, 336 (1963).
4. D.E. O'Reilly, J.Chem.Phys, 49, 5416 (1968).

Yours sincerely

K Rendall J W Rockliffe E G Smith G J T Tiddy

FIG. 1.

SEMI-LOG PLOT OF THE TRANSVERSE MAGNETISATION OF PROTONS IN WATER-GLASS BEAD DISPERSIONS AS A FUNCTION OF TIME FOR SEVERAL PULSE SPACINGS (t_{cp}) AT THREE EXPERIMENTAL FREQUENCIES.

60 MHz t_{cp} = ○ - 200 μsec, ◐ - 1 msec, ● - 4 msec.
30 MHz t_{cp} = △ - 200 μsec, ▲ - 1 msec, ▲ - 4 msec.
16 MHz t_{cp} = □ - 200 μsec, ◧ - 1 msec, ■ - 4 msec.

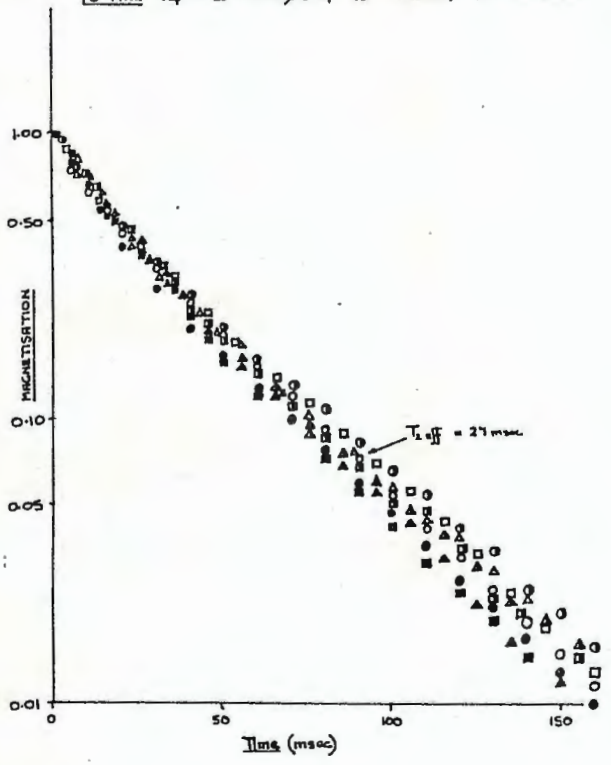
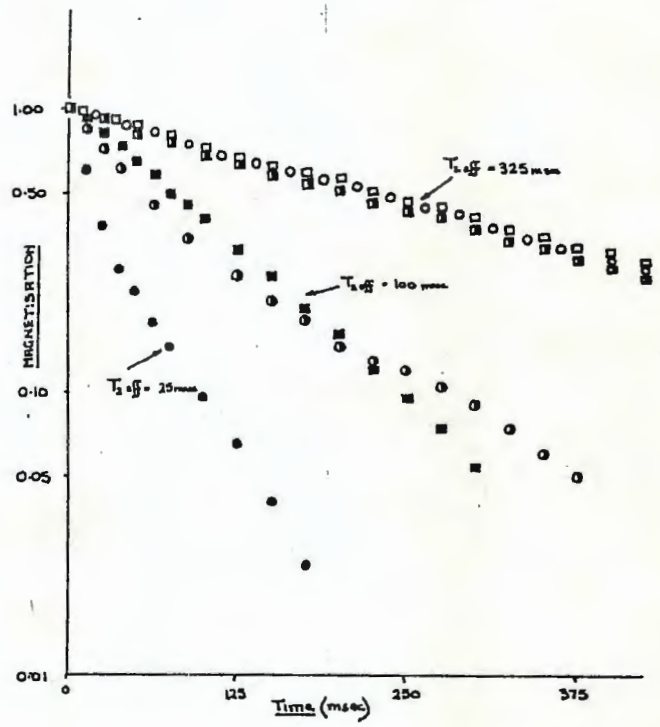


FIG. 2.

SEMI-LOG PLOT OF THE TRANSVERSE MAGNETISATION OF PROTONS IN CHLOROFORM-GLASS BEAD DISPERSIONS AS A FUNCTION OF TIME FOR SEVERAL PULSE SPACINGS (t_{cp}) AT TWO EXPERIMENTAL FREQUENCIES.

60 MHz t_{cp} = ○ - 200 μsec, ◐ - 1 msec, ● - 4 msec.
16 MHz t_{cp} = □ - 200 μsec, ◧ - 1 msec, ■ - 4 msec.



283-3

AMHERST COLLEGE
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Department of Chemistry
Telephone 413-542-2342

February 25, 1982

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

Deuterium NMR Studies of Bile Salt-Lipid Mixed Micelles

Dear Barry:

We have recently initiated a ^2H relaxation study (in collaboration with Barry Sears and Bill Curatolo at M.I.T.) of selectively deuterated lipids solubilized in bile salt micelles. Mixtures of these substances with cholesterol are excellent models for intestinal bile contents, though the dynamic state of the lipid bilayer in mixed micelles has been the subject of some controversy. As for other bilayer systems in which acyl chain motions are correlated, we find a characteristic plateau for both linewidth (T_2) and T_1 values along most of the saturated lipid chain (see figure below). ^2H T_1's at positions 2, 6, and 10 are anomalously short, indicating that tight packing in the mixed micelles may slow the rate of segmental motions. In addition, both T_1 and T_2 processes are probably influenced by slow motions (perpendicular tumbling, collective bilayer modes, and/or overall aggregate tumbling); we find $T_1 > T_2$ at each molecular site and over a substantial range of temperatures. The nature of the various motional contributions, as well as order parameters for each C-D bond, should be revealed by field-dependent relaxation studies--so we'll be running up the spectrometer time until our supply of semi-log paper gives out!

Best regards,

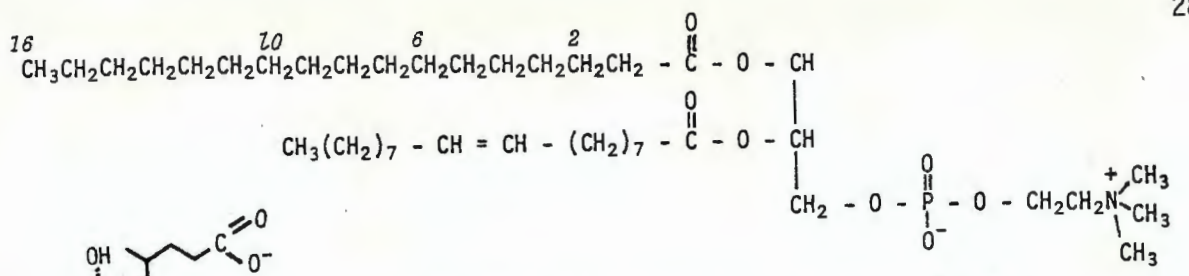
Ruth

Ruth E. Stark
Assistant Professor of Chemistry

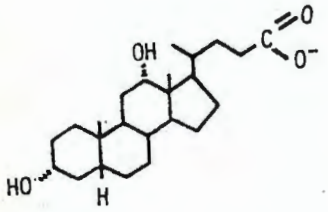
Joanne L. Manstein

Joanne L. Manstein

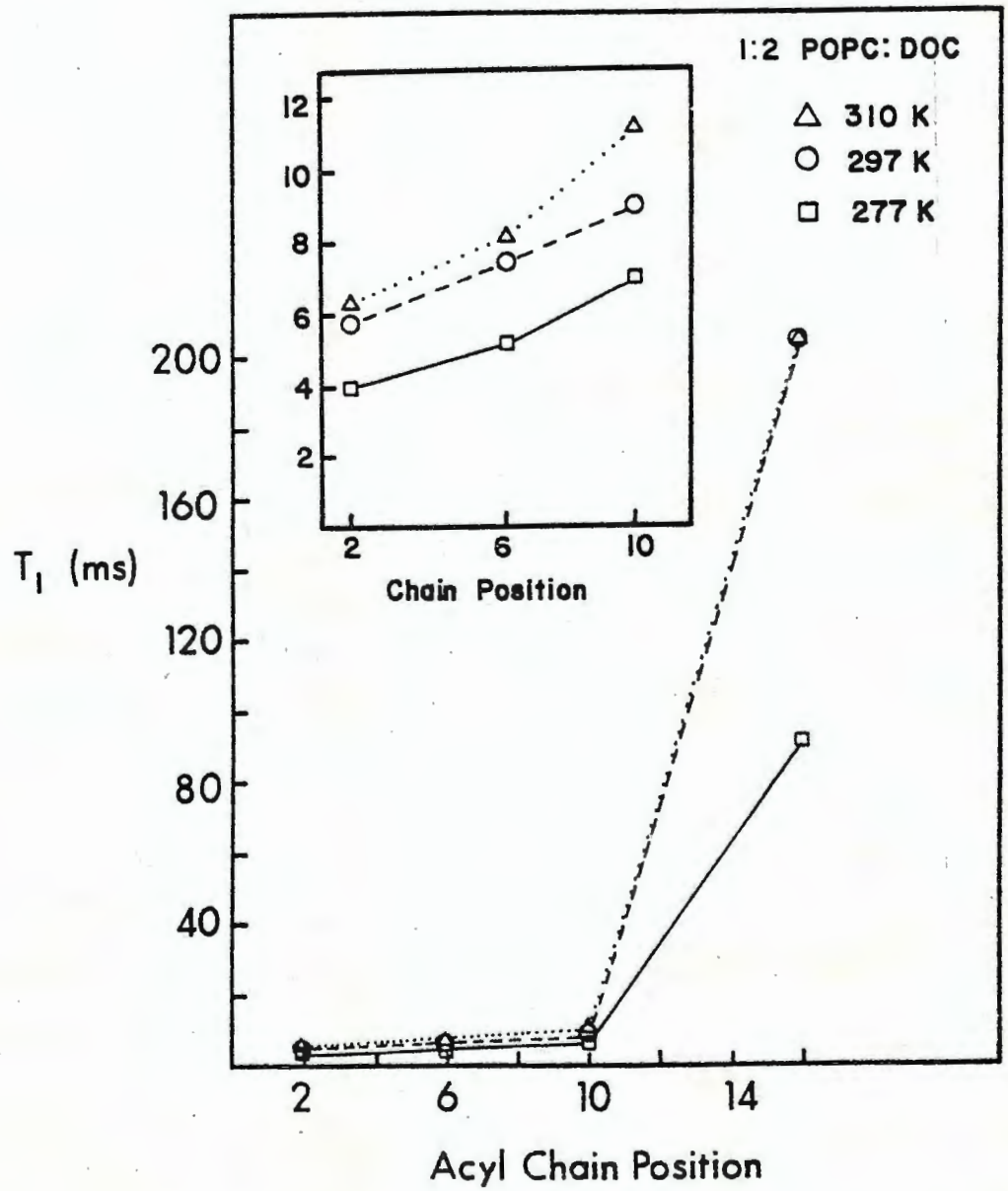
RES/gtc



1-palmitoyl-2-oleyl-*sn*-glycero-3-phosphorylcholine
(POPC)



DEOXYCHOLATE (DOC)



^2H T_1's as a function of chain position for 1:2 POPC:DOC mixtures at three temperatures. Solutions were typically 25 mM in lipid; the data was acquired with a JEOL FX-100Q spectrometer operating at 15.29 MHz and 24°C. T_1 differences among 2, 6, and 10 positions are small but reproducible.

283-5

Eidgenössische
Technische Hochschule Zürich

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ETH-Zentrum
Durchwahlnummer 01 / 256 43 68
Telefonzentrale 01 / 256 22 11

February 23/1982

0430

Professor B.L. Shapiro
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Texas 77843 USA

PETITION FOR OBEDIENCE TO LAW

Dear Barry,

In most countries of the civilized world there are binding laws governing the use of physical units. Similar to other countries, the Swiss law on measurements forces us to exclusively use SI units:

Bundesgesetz über das Messwesen

(Vom 9. Juni 1977)

Die Bundesversammlung der Schweizerischen Eidgenossenschaft,

gestützt auf die Artikel 31 bis Absatz 2 und 40 der Bundesverfassung,

nach Einsicht in eine Botschaft des Bundesrates vom 9. Januar 1976 [1],

beschliesst:

Erstes Kapitel: Gegenstand

Art. 1

Dieses Gesetz ordnet auf dem Gebiet des Messwesens:

a. die in der Schweiz verbindlichen Masseinheiten;

b. die Pflicht zur Verwendung der gesetzlichen Einheiten;

c. die Typenzulassung und Eichung der Messmittel, die in Handel und Verkehr sowie im Dienst der Gesundheit und der öffentlichen Sicherheit verwendet werden;

d. die Pflicht, in Handel und Verkehr Mengen und Preise anzugeben;

e. die Durchführung von Forschungs- und Entwicklungsarbeiten;

f. die Aufgaben der Kantone.

Zweites Kapitel: Masseinheiten

Art. 2

Gesetzliche Einheiten

[1] Die gesetzlichen Masseinheiten sind:

a. die in Artikel 3 aufgeführten Basiseinheiten des internationalen Einheiten-Systems (Système international d'Unités SI);

[1] BBl 1976 I 345

Siebtes Kapitel: Strafbestimmungen

Art. 21

Unerlaubte Messmittel

Wer geeichte Messmittel fälscht,

wer vorsätzlich oder fahrlässig Messmittel benützt, die der Zulassung oder Eichpflicht unterliegen, aber nicht zugelassen oder nicht vorschriftsgemäss geeicht sind,

wer vorsätzlich oder fahrlässig eichpflichtige Messmittel, welche die gesetzlich festgelegten Fehlergrenzen überschreiten, benützt,

wird, sofern kein schwererer Tatbestand erfüllt ist, mit Haft oder mit Busse bestraft.

Art. 22

Missachtung der Vorschriften über Mengen- und Preisangaben

Wer vorsätzlich oder fahrlässig falsche Mengenangaben macht,

wer die nach Artikel 11 vorgeschriebenen Angaben von Mengen und Preisen unterlässt oder

wer vorverpackte Güter, die den Füllmengenvorschriften nicht entsprechen, in Verkehr bringt,

wird, sofern kein schwererer Straftatbestand erfüllt ist, mit Haft oder mit Busse bis zu 20 000 Franken bestraft.

fine up to 10'000 $

imprisonment

Art. 23

Widerhandlungen im Geschäftsbetrieb

[1] Wird eine Widerhandlung beim Besorgen der Angelegenheiten einer juristischen Person, Kollektiv- oder Kommanditgesellschaft, Einzelfirma oder Personengesamtheit ohne Rechtspersönlichkeit oder sonst in Ausübung geschäftlicher oder dienstlicher Verrichtungen für einen andern begangen, so sind die Strafbestimmungen auf diejenigen natürlichen Personen anwendbar, welche die Tat verübt haben.

[2] Der Geschäftsherr oder Arbeitgeber, Auftraggeber oder Vertretene, der es vorsätzlich oder fahrlässig in Verletzung einer Rechtspflicht unterlässt, eine Wider-

Nevertheless most NMR spectroscopists still stick to the old fashioned and outdated cgs-Gauss system and are not even aware of the deadly crime they commit. I would like to petition for obedience to law to save the members of the NMR community from possible imprisonment and heavy fines.

The systematic use of SI units has only very few consequences in NMR which I would like to summarize in the following.

1. It is the magnetic induction $\vec{B}$ (measured in Tesla) and not the magnetic field $\vec{H}$ which enters into most equations relevant to magnetic resonance. The energy of a molecular moment μ is given by

$$E = -\vec{\mu}\,\vec{B} \ .$$

The susceptibility χ is defined by the relation

$$\vec{B} = \mu_o (1 + \chi^{SI})\,\vec{H}$$

with the magnetic field constant $\mu_o = 4\pi \cdot 10^{-7}\ \frac{Vs}{Am}$. Note that the susceptibility χ is different in SI and cgs-Gauss units

$$\chi^{SI} = 4\pi\,\chi^{cgs} \ .$$

2. The dipole-dipole interaction Hamiltonian includes an additional factor $\mu_o/4\pi$:

$$H_{Dk\ell} = \frac{\mu_o}{4\pi}\ \frac{\gamma_k \gamma_\ell \hbar^2}{r_{k\ell}^3}\ \{\vec{I}_k \vec{I}_\ell - 3\ \frac{(\vec{I}_k \vec{r}_{k\ell})\ (\vec{I}_\ell \vec{r}_{k\ell})}{r_{k\ell}^2}\} \ .$$

Note that $\mu_o/4\pi = 10^{-7}$! Obviously this factor enters then into all equations involving the dipolar interaction. For example the second moment of a homonuclear spin system requires an additional factor $(\mu_o/4\pi)^2$ in comparison with cgs-Gauss units:

$$M_2 = (\frac{\mu_o}{4\pi})^2\ \frac{3}{4}\gamma^4 \hbar^2\ I(I+1)\ \sum_{k\neq i}\ \frac{(1 - 3\cos^2\vartheta_{jk})^2}{r_{jk}^6} \ .$$

The longitudinal relaxation rate T_1^{-1} induced by dipolar interaction also includes such a factor:

$$T_1^{-1} = (\frac{\mu_o}{4\pi})^2\ \hbar^2\ \gamma_I^2\ \gamma_S^2\ r_{IS}^{-6}\ \tau_c \ .$$

3. The gyromagnetic ratio of an electric angular momentum is

$$\gamma^{SI} = \frac{-e}{2m_e} \quad , \qquad \gamma^{cgs} = \frac{-e}{2m_e c} \quad .$$

This influences the equations for chemical shifts, e.g.:

Lamb shift:

$$\sigma^{SI} = \frac{\mu_o e^2}{3m_e} \int_0^\infty r\rho(r)\,dr \quad , \qquad \sigma^{cgs} = \frac{4\pi e^2}{3m_e c^2} \int_0^\infty r\,\rho(r)\,dr \quad ,$$

Ring current shift:

$$\sigma^{SI} = -\frac{\mu_o}{4\pi} \frac{e^2}{2m_e} \frac{a^2}{r^3} \quad , \qquad \sigma^{cgs} = -\frac{1}{c^2} \frac{e^2}{2m_e} \frac{a^2}{r^3} \quad .$$

4. That calories should be used exclusively by historians is likely to be wellknown by now.

It is certainly one of the noble duties of editors of journals (including the TAMU-Letter) to warn innocent authors of the great danger inherent in violations of the indisputable public laws.

Best regards.

Sincerely yours,

Richard R. Ernst

Richard -

1. *I was unaware that editors have "noble duties" or that our authors are "innocent".*
2. *Since when are public laws "indisputable"?*
3. *Does it follow that as an accessory to many such violations, may I no longer dream of a safe visit to your beautiful country? (You have even made me worry about possible Texas-Switzerland extradition laws.)*
4. *You are probably yourself suspect for your many associations with known law-breakers. Submit one case of Lindt Bittersweet chocolate bars per month x 2.628 x 10^6 s^{-1}, or I'll send copies of all your past Newsletter contributions to your government.*

Barry

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Villeurbanne, le 22 Février 1982

Professeur B.L. SHAPIRO
TEXAS A & M UNIVERSITY
College of Science
College Station
TEXAS 77843

Water relaxation time in COLZA pollen

Cher Dr SHAPIRO,

Les biologistes savent que la viabilité du pollen maintenu à température et hygrométrie constante est nulle au bout de 10 jours ; il faut entendre par là que sur 800 graines de pollen, il n'en reste pas une seule de "vivante".

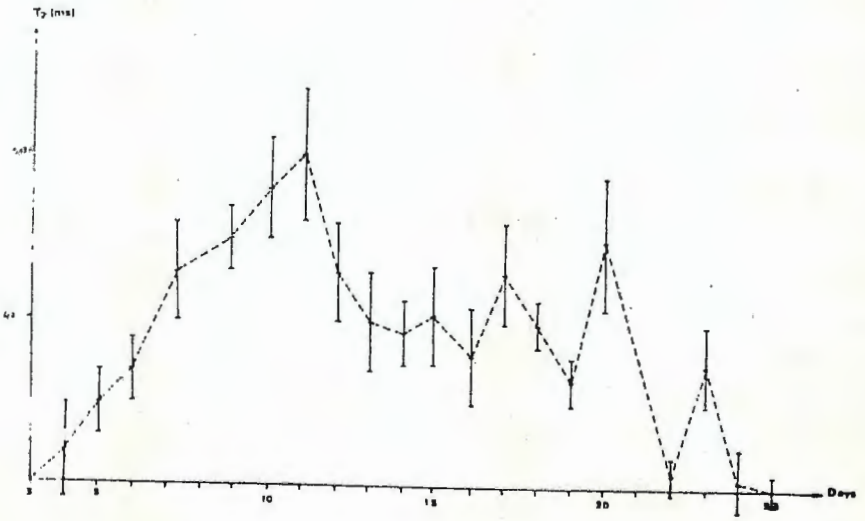
Disposer d'une méthode pour tester la viabilité d'un échantillon est de première importance en biologie.

Il a paru intéressant de suivre l'évolution au cours du temps de la relaxation spin-spin par la méthode des échos de Carr et Purcell. On observe une exponentielle unique avec tout d'abord une augmentation de T_2 suivie d'une diminution ; au delà de 15 jours T_2 reste constant sauf variation de l'humidité ambiante.

Il semble donc que des mesures de T_2 puissent constituer le test recherché par les biologistes.

Cordialement.

J.C. DUPLAN J. DELMAU C. DUMAS



STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

STANFORD MAGNETIC RESONANCE LABORATORY

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

March 1, 1982

Dr. Barry L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77483

Dear Barry,

Mapping Relaxation Fits

The analysis of NMR relaxation in proteins traditionally requires use of a specific model --- e.g. wobble-on-a-cone --- before calculation of motional correlation times. An alternative approach which we are actively pursuing is to search over a number of motions and a range of motional frequencies and amplitudes for fits to experimental relaxation data (1-3).

Past searches were carried out on the campus IBM computer and generated massive output. With current Reaganomics, we decided to teach our Nicolet 1180 computers to behave like the big IBM, and simultaneously mitigate the output problem by adding a grid map to code the errors of fit (σ^2).

The attached figure shows output for a test case and a set of 90 MHz ^{13}C relaxation data for a resolved αCH line of a protein, assuming pure dipolar relaxation by the directly bonded proton. We consider here the case where relaxation is due to three independent motions, λ_1, λ_2, and λ_3. λ_1 is taken as the overall tumbling rate of the protein. The program is set to search λ_2 and λ_3 values (typically 10^7-10^{12} Hz), calculate theoretical T_1, T_2, and NOE and calculate errors of fit. An error magnitude map is consequently constructed as a coded function of λ_2 and λ_3 to allow fits to be visualized.

With the caveat that experimental T_1, T_2, and NOE are probably only good to 10%, it became rapidly clear that there is no one unique answer. Instead, a family of fits typically cluster into regions. When $\alpha^2<10^{-3}$, the calculated and experimental parameters are effectively indistinguishable. The best fits for the test occur with $\lambda_2 \simeq 10^9$ Hz and $\lambda_3 \simeq 10^{10}$ Hz (or vice versa). The lack of unique fits is also observed when using specific models (4).

The resolved α-CH line was analyzed using $\lambda_1 = 1.25 \times 10^8$ Hz (τ_c = 8 nsec) for the protein tumbling. The grid map reveals the best fits to cluster about $\lambda_2 \simeq 10^7$ Hz and $\lambda_3 \simeq 10^{10}$ Hz (or vice versa).

Sincerely yours,

Anthony Ribeiro David Wemmer Oleg Jardetzky

1. TAMU Newsletter 259 29 (1980).
2. O. Jardetzky, Acc. Chem. Res. 14 291 (1981).
3. A. Ribeiro et al, J. Amer. Chem. Soc. 102 4040 (1980).
4. O. Jardetzky, in: NMR and Biochemistry, S.J. Opella and P. Lu (eds.), Marcel Dekker, Inc., NY (1979).

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 2.290E-1          1.519E-1          1.604E0          2.9851E-8
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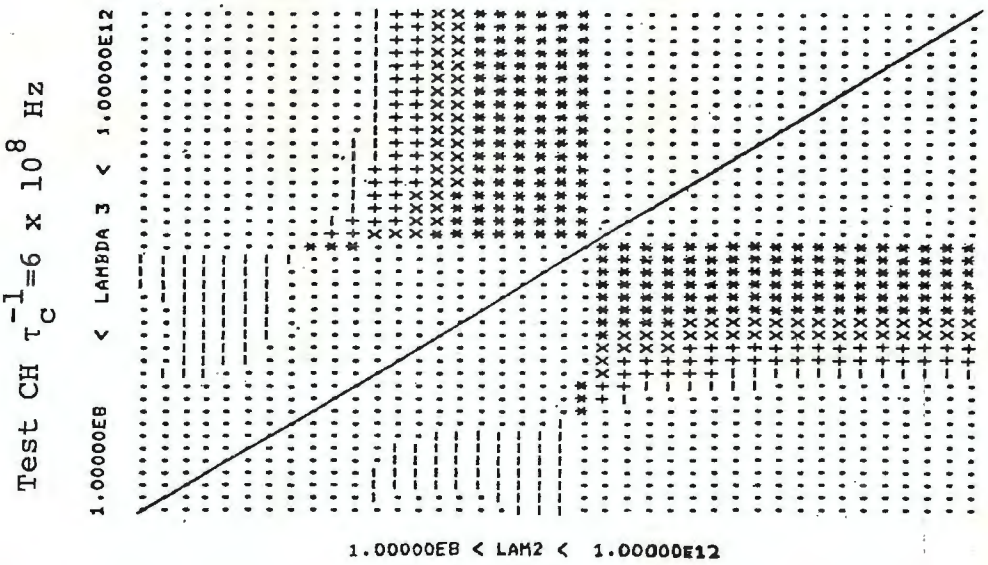

σ^2 Error code: $1>\sigma^2>0.1$, dash; $0.1>\sigma^2>0.01$, plus; $0.01>\sigma^2>0.001$, cross; $0.001>\sigma^2$, star.

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1.25E8      1.99E7     2.51E10      8.841E-1    8.453E-2   3.129E-2
 4.119E-1          1.999E-2          1.179E0          2.2354E-8

1.25E8      2.51E7     1.00E10      8.785E-1    1.082E-1   1.316E-2
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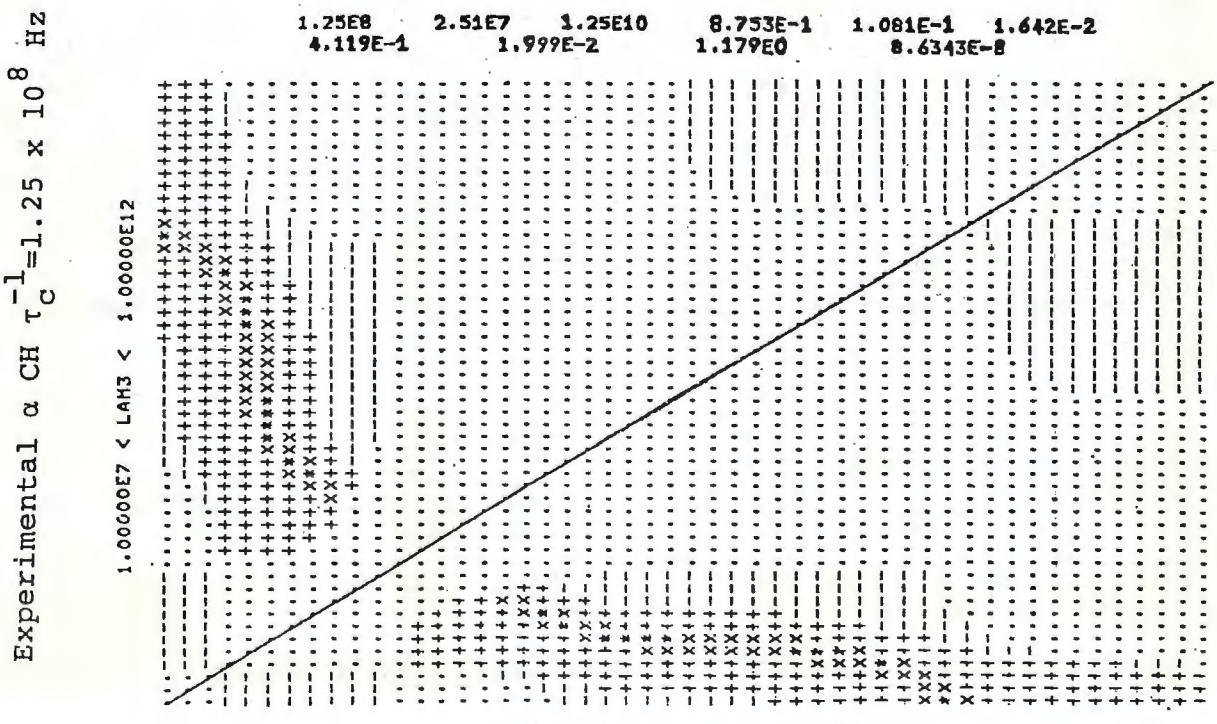

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SAN FRANCISCO, CALIFORNIA 94143

March 1, 1982

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

Re: A Tale With a Twist--^{31}P NMR Relaxation of Supercoiled (Closed Duplex) DNA

Dear Barry:

We have been carrying out the first NMR experiments on intact plasmid DNA in closed duplex, supercoiled form, as well as the circular and linear forms. The particular plasmid studied was pIns36 (7200 base pairs long), which is derived from plasmid pBR322 but contains a subcloned 2800 base pair DNA fragment (human insulin gene). The ^{31}P relaxation parameters for aqueous solutions of the supercoiled, nicked circular, and linear forms of pIns36 at 40.5MHz, 25° are summarized below:

	T_1(s)	T_2(s)	NOE
linear	2.4 ± 0.2	0.019 ± 0.003	1.3 ± 0.1
circular	2.5 ± 0.2	0.25 ± 0.07	1.4 ± 0.15
supercoiled	1.64 ± 0.15	1.17 ± 0.10	1.45 ± 0.18

The results for the linear form are in accord with our earlier studies of much shorter (~700 base pair) DNA fragments (1,2), supporting our suggestion that the motional properties of double-stranded DNA longer than about one persistence length (~180 base pairs) are similar and independent of polymer length.

The T_1 and NOE values for all three forms are consistent with the existence of a subnanosecond internal motion of the phosphorus. Most striking, however, are the order of magnitude changes in T_2 going from the linear to the circular and then to the supercoiled forms. These oft-repeated measurements cannot be fully rationalized by differences in the radius of gyration of each form. Analysis of the results for the linear form indicate a slower, isotropic motion with a correlation time of 0.86μs in agreement with our earlier studies on shorter fragments; this can most logically be ascribed to bending motions. We suggest that the T_2 values can be explained by increased effective frequency of bending motions for the closed DNA forms due to an excess of conformational energy; coupling to higher-frequency torsional motions may also occur.

Sincerely,

Tom

Thomas L. James
Associate Professor of Chemistry
and Pharmaceutical Chemistry

Peter Bendel

Orgad Laub

TLJ:bw

(1) P.H. Bolton and T.L. James, J. Phys. Chem. 83, 3359 (1979); J. Am. Chem. Soc. 102, 25 (1980).

(2) J.W. Keppers and T.L. James, J. Am. Chem. Soc. 104, Feb. (1982).

JEOL GX REPORT #1

THE plexus DATA SYSTEM

PLEXUS: An interwoven network of parts or elements in a system.

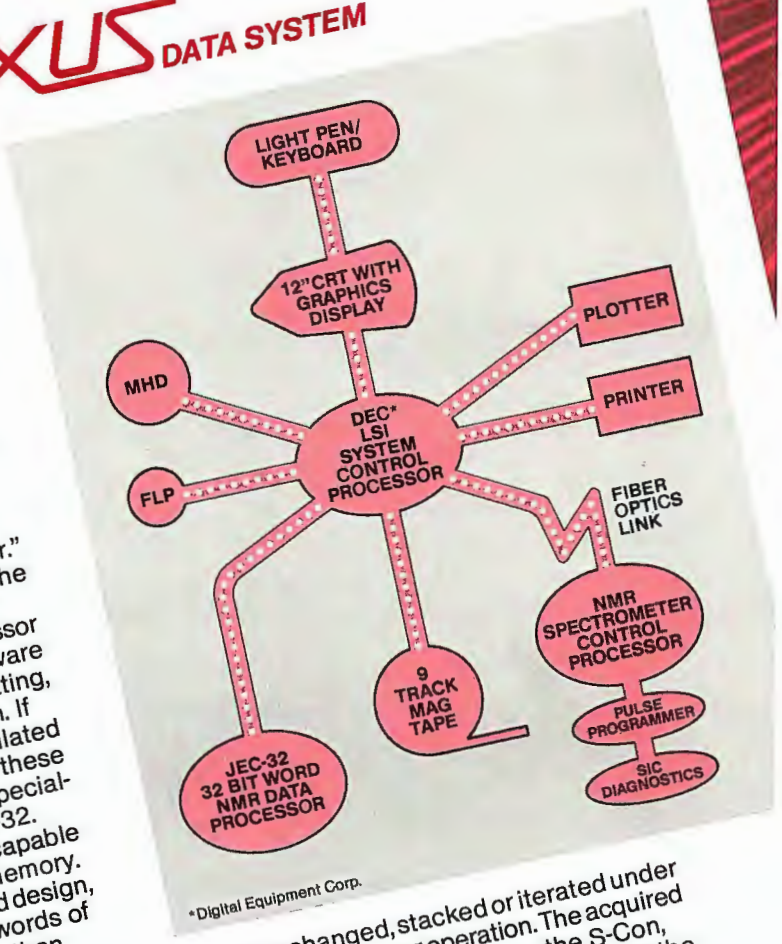
There is no better way to describe the data processing philosophy incorporated into the GX-400/500 FT-NMR spectrometers. To accommodate the increased demands placed on an FT-NMR data system, the PLEXUS data system deviates from the usual single computer approach. A multi-computer network using distributed processing software is employed to achieve trend setting levels of performance for speed, efficiency, and flexibility.

The center of the PLEXUS data system is the Digital LSI "system control processor." All interaction between the operator and the spectrometer pass through this hub. Job assignments are determined by this processor and distributed to the appropriate hardware for execution, for example; printing, plotting, disc storage or spectrometer operation. If actual data is to be acquired or manipulated (Fourier transformation, phasing, etc.) these jobs are assigned to a second, highly specialized "NMR data processor," the JEC-32.

The JEC-32 is a 32-bit computer, capable of accommodating 256K words of memory. Because of its unique and specialized design, fast Fourier transformations of 8K words of data (32 bit words) are done in less than 3 seconds! The real value of this amazingly fast FFT time can be appreciated more fully when considering large data sets, especially 2-dimensional FFT, where transform times are decreased dramatically, making 2-D NMR a much more practical and efficient experiment.

The spectrometer system is made complete by total computer control over all spectrometer functions by the PLEXUS data system. Through the "system control processor" and "spectrometer control processor," PLEXUS totally controls all spectrometer variables, including lock offset, lock phase, lock level, receiver gain and all irradiation and observation phases allowing any NMR parameter to be changed, stacked or iterated under unattended computer operation. The acquired experimental data is sent from the S-Con, over distortion-free fiber optics cables, to the JEC-32 where data treatment is carried out.

A further benefit of the PLEXUS concept is the SIC diagnostics (Status Integrity Check) which monitors all of the spectrometer hardware through status registers located on each board. Valuable service information concerning NMR hardware and computer components can then be extracted directly from the GX spectrometer or remotely.



*Digital Equipment Corp.

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201—272-8820

University of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building,
295 Cathedral Street, Glasgow G1 1XL Tel: 041-552 4400

PB/MAS

4th March, 1982

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

Dear Barry,

Impurity in CD_3CN ^{13}C n.m.r. Data Base

Our latest news is that we have acquired a Bruker WH-250, and in doing so have mortgaged the Department for several years to come. We reckoned that the financial situation could only get worse (a prediction subsequently borne out) and it was a case of now or never!

So far we are just getting used to its potentialities. As part of an ongoing project (cf. J.C.S. Perkin II, 1981, 1616), it is being used by Dr. Colin Suckling for studies on the interaction of aromatic substrates and surfactant molecules. At the concentrations necessary for these studies we ran into a problem in connection with the solvent CD_3CN being used. One batch of this material manufactured by C.E.A. in France had some 0.03% of alkyl alcohol present! In ordinary use this amount of impurity might easily have gone unrecognized if not unnoticed, but in the WH-250, the spectrum led to instant identification. For these experiments its presence is very worrying.

The work on the ^{13}C - n.m.r. data base mentioned in our last letter is progressing. The programs for entering data and retrieving it have been written, and the data base itself contains some 3000 entries mostly collected from the readily accessible compilations and reviews. Once data is to hand entering it into the file is fairly quick using our graphics screen, as can be judged from the fact that these 3000 entries were made in just over 1 month.

Kind regards,

Yours sincerely,

Peter.

Peter Bladon

283-15

THE UNIVERSITY OF WINNIPEG
WINNIPEG, CANADA R3B 2E9

March 1, 1982

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

Dear Barry:

Mercury-199 Relaxation at 9.4 Tesla.

While on sabbatical at the University of Guelph, Bob Lenkinski, Charlie Rodger and I measured ^{199}Hg spin-lattice relaxation times in several mercury (II) compounds at applied fields of 5.875 T and 9.40 T.

Compound	B_o	$T_1(^{199}Hg)$
$Hg(CN)_2$	9.40 T	0.063s
	5.875	0.184
$K_2Hg(CN)_4$	9.40	> 6.5
	5.875	7.0 ± 0.4
$Hg(CH_3)_2$	9.40	0.148
	5.875	0.308
$Hg(CH_2C_6H_5)_2$	9.40	0.036
	5.875	0.087
$HgCl_2$	9.50	0.113
	5.875	0.281

With the exception of tetrahedral ions such as $Hg(CN)_4^{2-}$ or $HgCl_4^{2-}$ the T_1's of all compounds are short for a spin ½ nucleus (less than 0.15s at 9.40 T), and field dependent. For the two-coordinate mercury (II) compounds, the ratio T_1 (5.875)/T_1 (9.40 T) is generally within experimental error of 2.56, the value expected for chemical shielding anistropy relaxation. The CSA mechanism also dominates in diphenylmercury at B_o= 7.05 T (1). The ratio of T_1's measured for $(CH_3)_2Hg$ is 2.1 ± 0.2 indicating that mechanisms other than CSA (probably spin rotation (21)) make a slight contribution to the rate of relaxation in this molecule.

In large molecules, with rotational correlation times greater than 10^{-9}s, it may be difficult to observe ^{199}Hg resonances because of their large linewidth at high fields ($B_o \simeq$ 9.4T) if the mercury is essentially two coordinate. Low field ^{199}Hg nmr studies might be preferable for such molecules.

Yours sincerely,

Rod

Rod Wasylishen
Associate Professor
Department of Chemistry

RW/er

References:

1. D.G. Gillies, L.P. Blaauw, G.R. Hays, R. Huis and A.D.H. Clague, J. Magn. Reson, 42, 420 (1981).

2. M.A. Sens, N.K. Wilson, P.D. Ellis and J.F. Odom, J. Magn. Reson. 19, 323 (1975).

3. C.R. Lassigne and E.J. Wells, Can. J. Chem. 55, 1303 (1977).

283-17

ROCHE

3 March 1982

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

Roche Products Limited · PO Box 8 · Welwyn Garden City · Hertfordshire AL7 3AY
Telephone Welwyn Garden 28128 *Telex 262098 ROCHEW*

Expanding the Karplus curve and a fast ring inversion

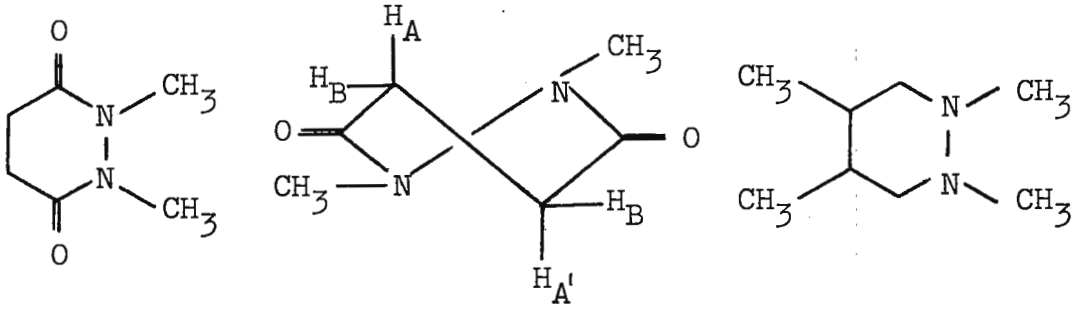
Dear Barry

Your barrage of reminders caught us between instruments, in that our new narrow bore WM-300 was delivered on Christmas Eve, and is now at the stage where we are striving to achieve the excellent sensitivity (95:1 on 0.1% Etbenzene) and resolution (0.05Hz) achieved by the Swiss engineer during commissioning.After a euphoric tour through the Periodic Table (^{15}N, ^{17}O, ^{2}H, ^{23}Na, ^{29}Si, ^{31}P and ^{19}F) we have come down to earth and already solved several long standing problems.

We were interested in freezing out the conformational equilibrium in the six-membered ring (I). The conformation of this compound in the crystal is a twist boat (II) with the CH_2-CH_2 fragment perfectly staggered[1]. Because we had evidence from other compounds of this type that the trans diaxial vicinal coupling constant is enormous (up to 15.0Hz) in fixed twist boat conformations of this ring system it was of interest to try to freeze out the parent compound (I) and analyse the AA' BB' spectrum at low temperatures. Unfortunately the ^{1}H spectrum obstinately remained as two sharp singlets, just starting to broaden at the lowest temperature reached (-120°C) before the solution precipitated.

In this ring inversion the two amide planes have to pass each other about the N-N axis. Clearly this process has a much lower energy barrier than in the corresponding hexahydropyridazine e.g. (III) where slow synchronous nitrogen inversion was shown to take place[2].

I hope this contribution involving the work of Ian Whitcombe and Phil Gilbert, though incomplete at this stage, reinstates us for a while.



(I) (II) (III)

1. T Otterson and U Sorensen, Acta. Chem. Scand. 1977, A31, 808-812.
2. J E Anderson and J M Lehn, Bull. Soc. Chim. France, 1966, 2402.

With best wishes.

Yours sincerely

Jon.

Dr W A Thomas

WAT/PS

283-19

TELEPHONE
345 1844

TELEGRAMS
UNIMELB PARKVILLE

University of Melbourne

DEPARTMENT OF ORGANIC CHEMISTRY *Parkville, Victoria 3052*

4th March, 1982

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

Dear Professor Shapiro,

Over the past few years we have been involved in a systematic investigation of the variation of ^{13}C chemical shifts with increasing electron demand in dialkylaryl carbocations. Deviations in plots of the cationic carbon shifts δc^+ against Hammett σ^+ constants were found to be due to inappropriate σ constants. Thus, in collaboration with H. C. Brown and M. Periasamy at Purdue University, we have developed two new sigma constants, σ^{c^+} for correlation of cationic carbon shifts and $\sigma^{\alpha c^+}$ for correlation of alpha carbon shifts. When applied to representative series of acyclic, cyclic and polycyclic cations excellent linear correlations are realized.

On the other hand, plots for the cationic carbons of 2-aryl-2-norbornyl cations against σ^{c^+} deviate from linearity for the electron withdrawing substituents, which has been previously interpreted by others as due to the onset of σ-bridging in these cations. We have now shown that similar deviations occur in the plots for a variety of other cations where σ-bridging is either impossible or highly unlikely. Thus 3-aryl-3-nortricyclyl, 1-aryl-1-cyclopropylethyl, 2-aryl-exo(and endo)5,6-trimethylenenorbornyl and benzhydryl cations all show very similar if not identical plots to that for 2-aryl-2-norbornyl cations (Fig.).

We can thus conclude that deviations from linearity in such plots cannot be used as evidence for nonclassical character (σ-bridging) in carbocations. This is the subject of a manuscript currently under review.

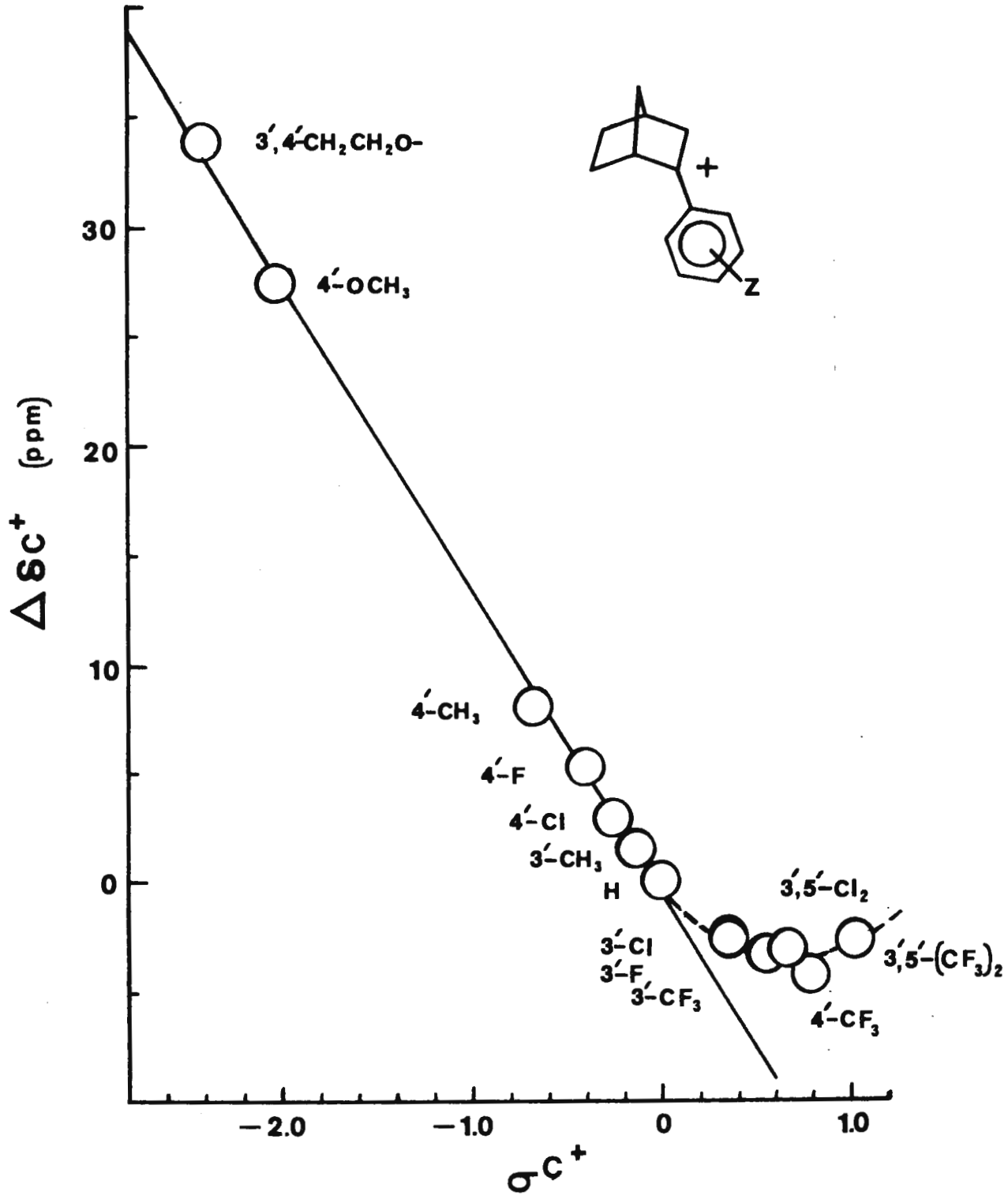
Yours sincerely,

D. P. Kelly

DPK:EC

D. P. Kelly.

Title: ^{13}C Chemical Shift Hammett Plots for Dialkylaryl Carbocations.


3′,4′-CH2CH2O-
4′-OCH3
4′-CH3
4′-F
4′-Cl
3′-CH3
H
3′-Cl
3′-F
3′-CF3
3′,5′-Cl2
3′,5′-(CF3)2
4′-CF3
+
Z
Δδc+ (ppm)
30
20
10
0
−2.0
−1.0
0
1.0
qC+

283-21

February 4, 1982

Major Analytical Instruments Facility
Chemistry Department
Case Western Reserve University
Cleveland, Ohio, 44106

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

APT for XL-100 Users

Dear Dr. Shapiro,

The Attached Proton Test (APT) program (the poor man's 2-D J coupled routine), described in TAMUNMR newsletter no. 273, appealed to us as a very useful tool, but we were disappointed that a version was not available for XL-100 users. Taking matters into our hands, we have modified an E level program to allow us to run APT by flagging in the necessary 180° pulses (including the second refocussing pulse) and delays (in the millisecond range). This program can run normal and gated decoupled acquisitions as well, in fact, it has become our resident standard program. It can not run two pulse routines without echo detection (refocussing). For anyone interested, we have it available on cassette tape and will provide copies on tapes sent to us.

Please credit this contribution to Dr. Ritchey's subscription.

Yours,

Nicholas Baldwin

P.S. The appropriate documentation will included with the program copies.

Varian announces the new XL-300

Supercon FT NMR Spectrometer

For immediate information call Bob Sheldon, Varian NMR Product Manager, in Palo Alto, California, at (415) 493-4000, ext. 3047. **For literature** contact Varian Instrument Group, D-070, 611 Hansen Way, Palo Alto, CA 94303, (408) 734-5370, ext. 415. For a Varian **representative** to call on you, please contact the Varian Sales Office nearest you.

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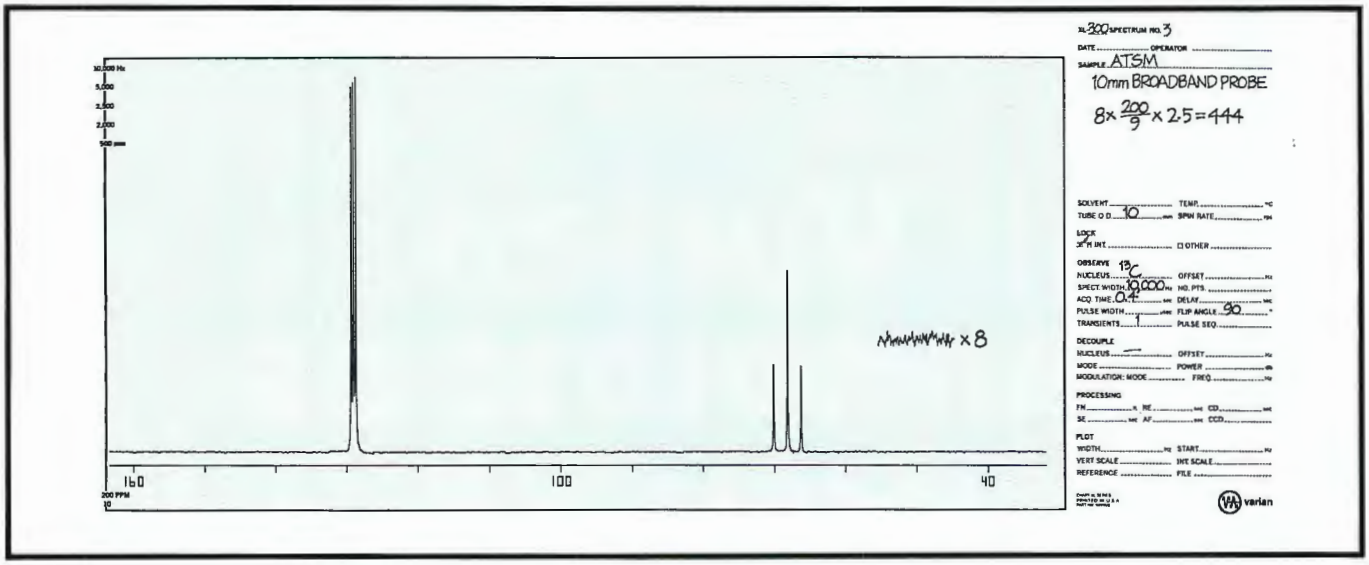
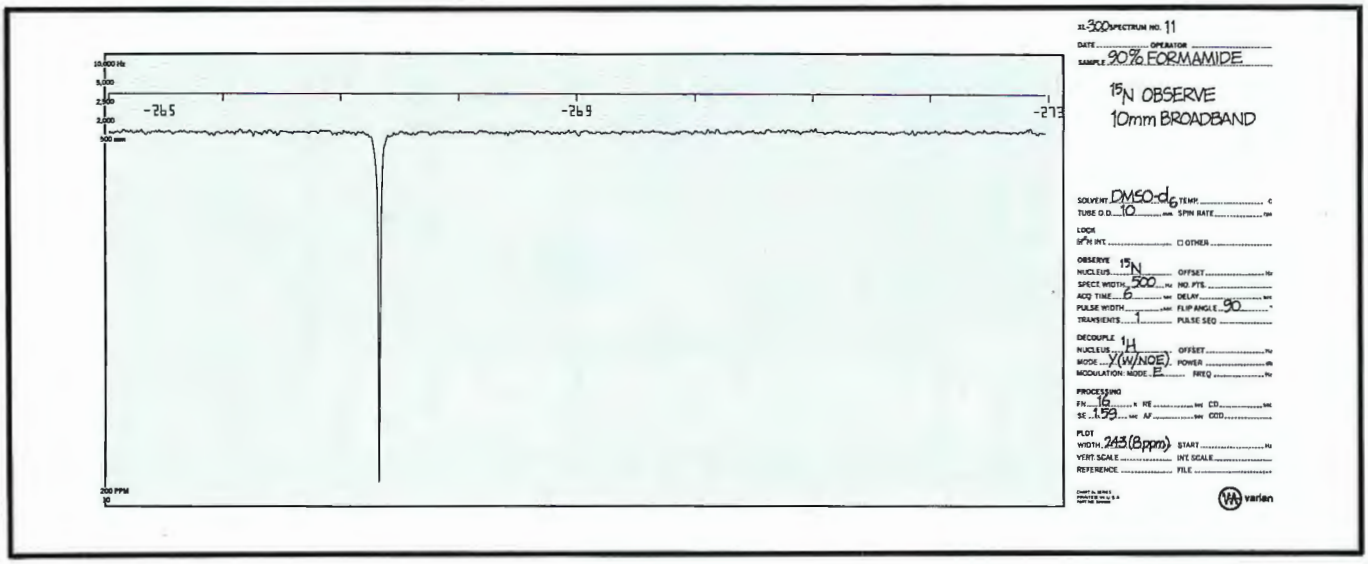
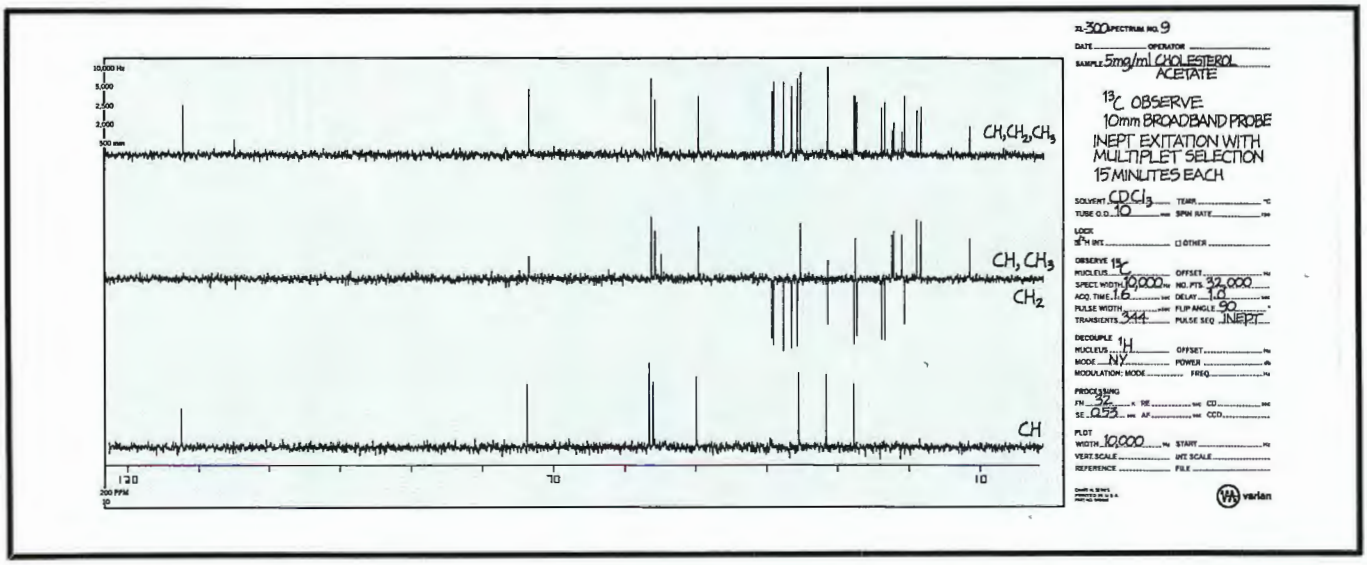
Some of the exciting results the XL-300 delivers...







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TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS
DEPARTMENT OF CHEMISTRY

March 15, 1982

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

Dear Barry:

1) $^4J_{HF}$ = 70.6 Hz in 1-Fluorobicyclo[1.1.1]pentane.

2) $^5J(N\text{-}C_\alpha\text{-}C(O)\text{-}N\text{-}C_\alpha\text{-}H)$ Again: Paradox lost.

Recent results indicate that simple-minded theory can be quite useful in suggesting experimental measurements, and in explaining apparently contradictory results.

We were prompted by the results of Ern Della and coworkers [J. Am. Chem. Soc. 103, 4131 (1981)] for $^{13}C\text{-}^{19}F$ coupling constants to perform INDO-FPT MO calculations on the series of 1-fluorobicycloalkanes. The calculated values followed the experimental trends, but we were particularly intrigued by the calculated value of 72.1 Hz for the $^4J_{HF}$ in the 1-fluorobicyclo[1.1.1]pentane, and wrote to Ern suggesting that he attempt to measure this number. After cleaning the sample up, the ^{19}F spectrum yielded a clean doublet of septets and the former splitting was 70.6 Hz in quite good agreement with the calculated value! Steve Walter measured some of the more difficult coupling constants in the bicycloalkane series using two-dimensional techniques on the WM-250.

Steve and I commented previously in the LETTERS [261, 26 (1980); 272, 21 (1981)] on the disparity between the calculated MO and the experimental results for the signs of the long range cis and trans $^5J(H\text{-}C_\alpha\text{-}C(O)\text{-}N\text{-}C_\alpha\text{-}H)$ in cyclo-[Gly-Tyr] and cyclo-[Gly-Phgly]. Clearly, the calculated results conform to some hypothetical "gas phase" molecule, whereas the measurements were made with D_2O as solvent, and yielded positive signs for both the cis and trans coupling constants. On repeating the MO calculation for cyclo-[Gly-Gly] with ten associated water molecules, the calculated cis and trans coupling constants were both positive in agreement with the experimental results!

Sincerely yours,

Mike

Mike Barfield

283-25

National Research Council Canada
Conseil national de recherches Canada

Division of Biological Sciences
Division des sciences biologiques

File Référence

12 February 1982

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

Dear Professor Shapiro:

PHANTOM QUADRATURE IMAGES ENCOUNTERED WHEN ACQUIRING AND PROCESSING DATA WITH DIFFERENT COMPUTERS

Several months ago we described in TAMU No. 277 the interfacing of a Nicolet 1280 computer with the Bruker ASPECT-2000 computer in our CXP-300 spectrometer. This distributed processing system has proven to be extremely flexible, and it has greatly enhanced our data analysis capabilities. Due to practical considerations, such as computing speed and limited access to the spectrometer computer in a multi-user environment, we have found our distributed processing system to be much more efficient than would be an improved software package for the ASPECT computer, e.g. time-sharing facilities. As we discussed previously, it was very easy to interface the Nicolet computer to the Bruker computer, and this link allows us to process the data collected on the CXP-300 with the Nicolet 1280. We have discovered only one problem with this arrangement, one that we thought would be of special interest to anyone wishing to process data collected on a Bruker spectrometer using non-Bruker software.

The symptoms of the problem are shown in Figure 1; a properly phased, image-free spectrum (top) generated using Bruker software appears to have a frequency-dependent phase error and frequency-dependent images when the same time-domain data are Fourier transformed (bottom) using Nicolet software, or other standard Fourier transform routines. The origin of this problem is in the manner in which quadrature NMR data are acquired on Bruker and Nicolet spectrometers. The most

Ottawa, Canada
K1A 0R6

straightforward method of quadrature detection is to sample the two outputs of the phase-sensitive detector (PSD) simultaneously, using two sample-and-hold circuits, and digitize the analog signals so that they may be handled by the computer as true complex numbers. This is the method used by Nicolet in their spectrometers. Data collected in this fashion can be processed, i.e. Fourier transformed and phase-corrected, using standard software routines. An alternate method for implementing quadrature detection involves using a single sample-and-hold circuit such that the two outputs of the PSDs are multiplexed and sampled alternately in time. This is the technique used in Bruker spectrometers. If data collected in the Bruker format are Fourier transformed using Bruker software, then spectra such as the top of Figure 1 are obtained. However, if the same time domain data are transformed using a standard complex Fourier algorithm, such as the Nicolet software, the bottom spectrum of Figure 1 results. The problem arises from the fact that the two channels of Bruker data do not form true complex pairs. The Bruker software compensates for this fact by using a very clever trick devised by Redfield and Kunz (J. Magn. Res. 19, 250 (1975)). This trick involves storing the real and imaginary time-domain data in alternate memory locations (i.e. Re,Im,Re,Im,...) and (prior to the Fourier transform, or during acquisition) inverting every other pair of points (i.e. Re,Im,-Re,-Im,Re,Im,-Re,-Im,...). The data are then transformed as if they were single phase data only; thus there are twice as many (real) data points as there were complex pairs acquired. The trick in effect moves the transmitter frequency from the middle to one end of the spectrum, in which case only single-phase data are necessary to give the proper, image-free spectrum.

In order to process the Bruker data properly using the Nicolet NMR software, it was necessary for us to add an assembly language routine to the software which implemented the so-called "Redfield trick". When this was done, identical spectra were obtained on the two computers.

In closing, we would like to comment that the use of two sample-and-hold circuits, as in the Nicolet system, yielding true complex data, gives the NMR spectroscopist much more processing flexibility than does the alternate sampling used by Bruker. For example, simultaneous sampling allows one to apply zero-order phase corrections to the time-domain data, which is useful in some types of experiments, especially when the signal-to-noise ratio, or spectrometer design, does not allow one to set the reference phase of the PSD properly.

283-27

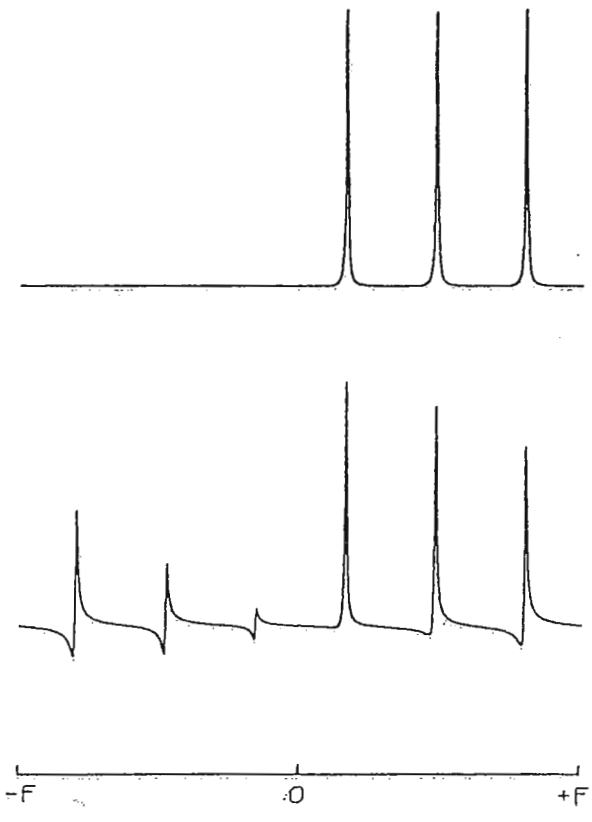
Prof. Bernard L. Shapiro

12 February 1982

Please credit this contribution to the NRC account in Dr. Ian Smith's name.

Sincerely yours,

Mark Rance R. Andrew Byrd



BRUKER Instruments, Inc.
MANNING PARK
BILLERICA, MASSACHUSETTS 01821
(617) 667-9580

March 23, 1982

Dr. B. L. Shapiro
TAMUNMR Newsletter
Texas A & M University
College of Science
College Station, TX 77843

"Quaderly Report"

Dear Barry:

In response to the letter by Byrd and Rance, I wanted to point out that it is indeed possible to sample and hold quadrature points alternately or simultaneously using the Aspect-2000.

In the first case, the FT command would be used to transform the data and in the second the FC (Forward Complex) command would be used.

Either way that you choose to process quadrature data you must also do some other shuffling: if you sample sequentially you must perform the point negation trick of Redfield and Kunz, and if you sample simultaneously you must interchange quadrants 1 and 4 and quadrants 2 and 3 in the transformed data.

We chose the former method and others have chosen the latter, but there is no substantial difference between them and a 1-bit software change would allow Bruker acquisition routines to perform the other way.

Sincerely,

Jim

James W. Cooper, Ph.D.
Vice President
Software Development

JWC/c

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19104

Department of Chemistry

March 10, 1982

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

^{13}C NMR of Crystalline Phenylalanine

Dear Dr. Shapiro:

Several recent solid-state ^{2}H NMR studies of d_5 ring-labelled crystalline phenylalanine (Phe) samples give somewhat conflicting results. Gall et al. [JACS 103, 5039 (1981)] and Rice et al. [Biomolecular Stereodynamics II 255 (1981)] showed that Phe crystallized from water at neutral pH has some of the molecules undergoing rapid 180° ring flips about the C_β -Cγ bond axis and some without large amplitude ring motions on the 10^6 Hz timescale determined by the ^{2}H quadrupole interaction. Rice et al. also showed that Phe·HCl and Kinsey et al. [JBC 256, 9028 (1981)] showed that Phe crystallized from ethanol/water are immobile in the same NMR experiment. The aromatic region of the high resolution ^{13}C NMR spectra of these crystalline Phe samples are presented in the Figure of this letter. Interpretation of these data add significantly to the ^{2}H NMR data in explaining the properties of the various solid Phe samples.

Phe crystallized from water at neutral pH gives spectrum A by cross-polarization. By contrast, the spectrum resulting from rapid $\pi/2$ pulses at the ^{13}C resonance frequency has only two lines. This result is readily explained by their being two different classes of molecules; one of which undergoes 180° ring flips and the other of which is rigid on the ~ 10^2 Hz timsecale determined by isotropic chemical shift differences. Not only are these classes of molecules dynamically different as reflected in the short T_1's for the δ and ε sites and the chemical shift averaging for these same sites, but they are environmentally different by having distinguishing chemical shifts. This same sample has two resolved C_β resonances, also indicating two different types of molecular environments. These ^{13}C isotropic chemical shift data are in complete agreement with the analysis of the ^{2}H data for the parallel samples.

Phe crystallized from ethanol/water gives a different but equally complex aromatic ^{13}C spectral region as shown in B. Rapid pulsing of these ^{13}C resonances gives no signals. There are probably two different types of phenylalanine molecules in this sample based upon the two resolved γ and two (partially) resolved ζ resonances that are rigid on the ~ 10^2 Hz timescale. This is also in agreement with the finding of rigid rings on the 10^6 Hz timescale of the ^{2}H NMR experiment. The most unusual aromatic ^{13}C

spectrum is C for Phe·HCl where there are two sharp lines corresponding to the γ and ζ carbons and a broad resonance corresponding to the δ and ε sites. This spectrum suggests that the aromatic rings are undergoing 180° flips on a timescale comparable to the chemical shift difference between the respective δ and ε sites, probably on the order of 10^2 Hz resulting in an intermediate exchange situation. This type of sample gives a rigid ^2H quadrupole powder pattern. Therefore the Phe·HCl rings bracket the timescale for motions; since they are rigid on the ^2H NMR 10^6 Hz timescale but in intermediate exchange on the ^{13}C NMR 10^2 Hz timescale. Apparently there is only one type of molecule present in the Phe HCl samples based on the single γ and ζ resonances.

Clearly, the structural and dynamical properties of phenylalanine in the crystalline states are complex. By combining the ^{13}C isotropic chemical shift NMR data and ^2H quadrupole NMR data a consistent and detailed picture of the dynamics of the molecules emerges.

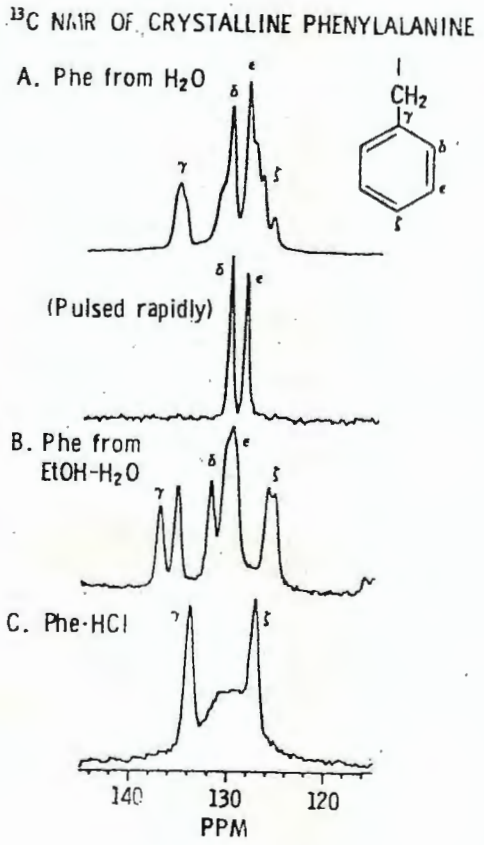


Figure Legend : Aromatic regions of ^{13}C NMR spectra of Phe samples crystallized under the described conditions conditions. All were obtained at 63 MHz with a 2.0 mT decoupling field and magic angle sample spinning at 3.9 kHz on a homebuilt spectrometer.

Michael Frey

Stanley J. Opella
Associate Professor of Chemistry

283-31

1880 Kodak 1980

A 100-year start on tomorrow

March 4, 1982

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

Implementation of Levitt-Freeman Decoupling and a Comparison of Other Decoupling Schemes

Dear Professor Shapiro:

Spin decoupling has once again been stirring the thoughts of NMR spectroscopists! A most notable advance is the scheme proposed recently by Levitt and Freeman,[1] using composite pulses. We have been able to implement this scheme readily by writing a simple program for our Nicolet 293B pulse programmer. The routine uses a conditional jump instruction which tests the Nicolet computer sweep output to determine when an FID is being acquired. We tried out the method, both on our home-built 200 MHz wide-bore system[2] in the Kodak Research Laboratories and on the Nicolet 200 MHz instrument at the Kodak Park Industrial Laboratory. Some results obtained on the latter instrument are shown in Fig. 1.

A sample of 20% crotonaldehyde in acetone-d_6 in a 12 mm tube was used. The proton irradiation frequency was ~6 ppm to low field of TMS. The effectiveness of various decoupling schemes was assessed by the sum of the four peak heights. Our conclusions are summarized as follows:

a) The Nicolet modulation and the Levitt-Freeman method yield comparable results when 6.5 watts of bilevel decoupling are used.
b) When the power was reduced to 1.8 watts, the effectiveness of the Nicolet modulation scheme decreased and could not be improved by changing the modulation frequency. The results are shown in Fig. 1a. However, the effectiveness of the Levitt-Freeman method remained the same as obtained with 6.5 watts (Fig. 1b).
c) Our comparison of a variety of modulation schemes at low power (1.8 watts), each with optimized parameters, is summarized in the following rank ordering of decoupling methods.

	Method	Relative Effectiveness
1.	Levitt-Freeman	1.00
2.	Square wave (100 MHz modulation)	0.74
3.	"Dykstra" (386 Hz modulation) (see TAMU NMR Newsletter, December 1981)	0.68

Professor B. L. Shapiro

4.	Nicolet bilevel 4-phase modulation (1.8 W/1.8 W; 150 Hz)	0.62
5.	Pseudo-random noise (optimum 10-bit sequence 2000 Hz clock)	<0.43

We feel that Levitt-Freeman decoupling is very appropriate when high-decoupling r.f. power is undesirable (e.g., dielectric heating). We use the method routinely to obtain spectra of aqueous ionic solutions of biopolymers, such as gelatin, contained in 20 mm sample tubes. Details of the implementation of the Levitt-Freeman decoupling for users of Nicolet software with a 293B pulse programmer are available upon request.

Please credit this contribution to the subscription of the Kodak Research Laboratories.

Sincerely,

N. Zumbulyadis

NZ:SG:EJP:JW:KK:eca

Nicholas Zumbulyadis

Stanley Gross

Stanley Gross

Research Laboratories

Emily J. Pleau

J. Whitefield

James Whitefield

Ken Keymel

Ken Keymel

Industrial Laboratory

References

1. M. H. Levitt and R. Freeman, J. Magn. Reson., 43, 502(1981).
2. S. Gross and N. Zumbulyadis, to appear in Rev. Sci. Instrum.; May 1982.

283-33

CROTONALDEHYDE 20 PERCENT
IN ACETONE

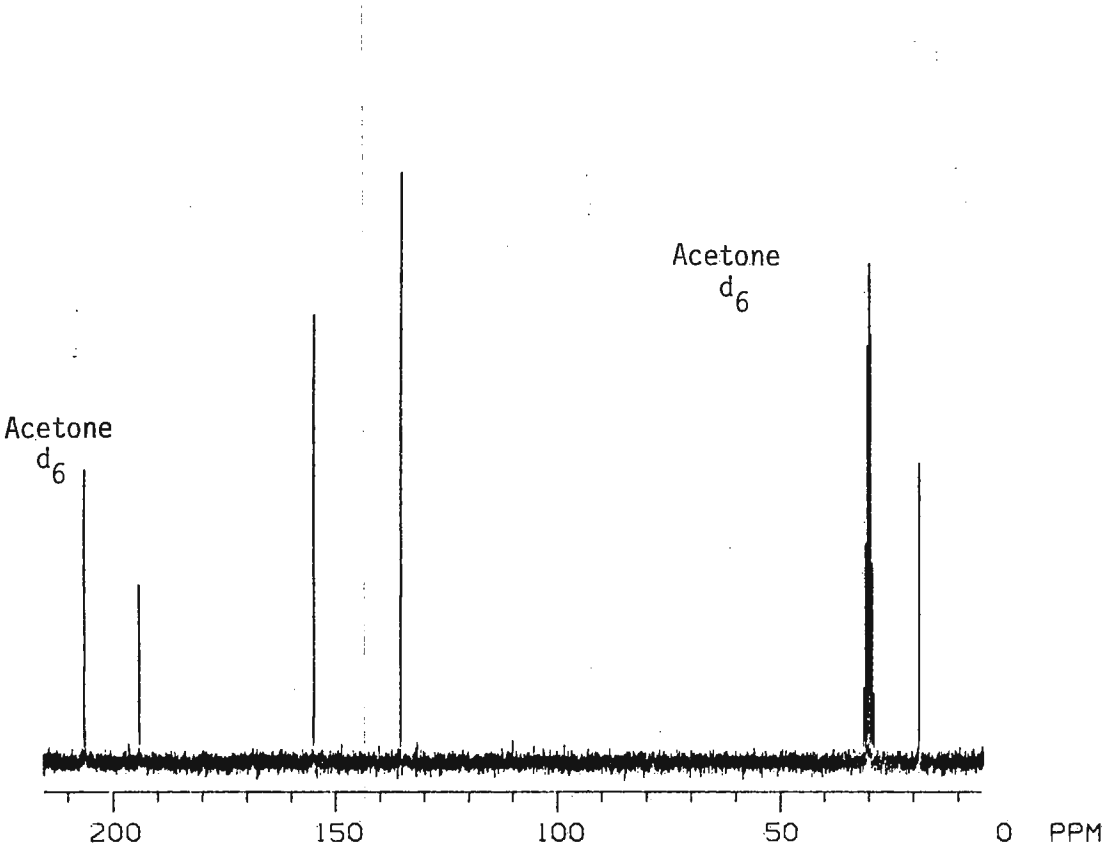


Fig. 1A

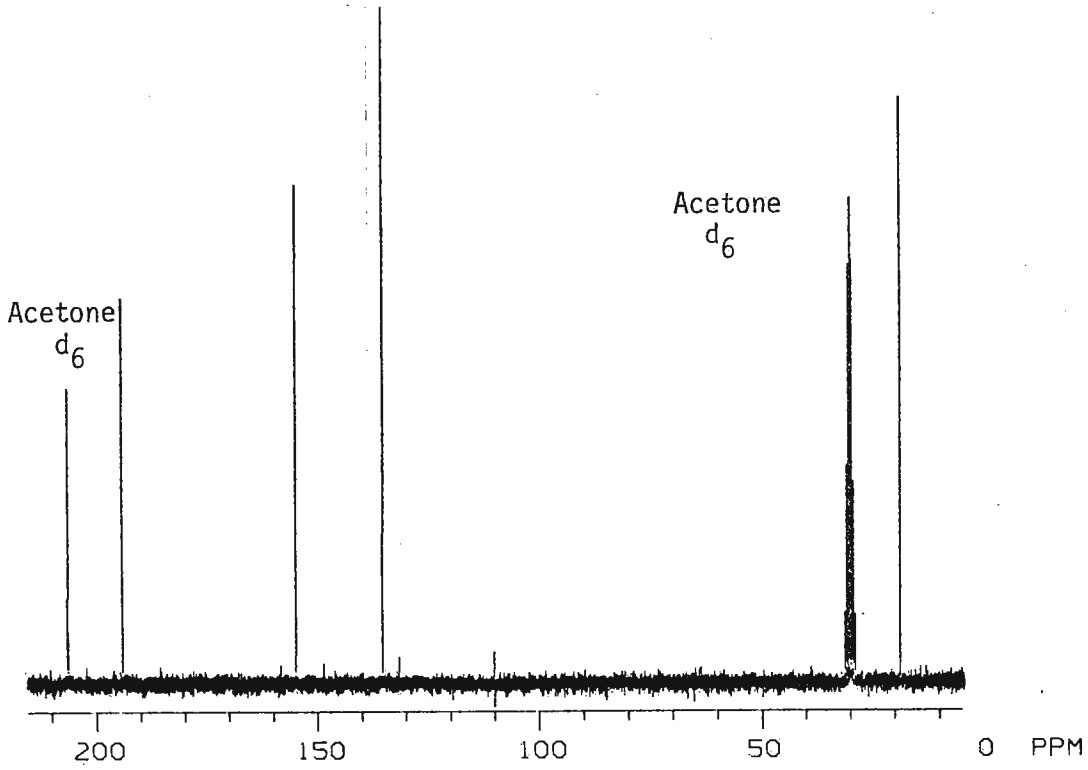


Fig. 1B

UNIVERSITY OF SOUTH FLORIDA
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DEPARTMENT OF CHEMISTRY
TAMPA, FLORIDA 33620

15 March 1982

EFFECT OF LANTHANIDE SHIFT REAGENTS ON COUPLING CONSTANTS

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

Dear Barry:

Over the last few years we have amassed quite a collection of data on the interaction of various substrates with $Eu(fod)_3$. Recently we have begun to sort out some of the other information which is buried among the lanthanide induced shifts -- for example, the effect of complexation on coupling constants. Although geminal coupling constants can vary by 1-2 Hz [B.L. Shapiro, M.D. Johnston, Jr., and R.L.R. Towns, J. Am. Chem. Soc., 94, 4381 (1972)], the question of vicinal coupling is still unresolved.

We have therefore extracted coupling constants from a number of spectra. The large number of spectra obtained in each shift reagent run allows a statistical analysis of the data, and the Table summarizes linear regression analyses of the observed coupling constant vs. the fraction of substrate that is complexed. (The bound fractions were calculated by a complete analysis of all shift and concentration data). It would be unreasonable to claim that the coupling constants of the free and complexed substrates are identical. Nevertheless, the data for these compounds suggest that any change is within experimental error of zero -- even where J is conformationally dependent.

Vicinal Coupling Constants as a Function of Complexation with $Eu(fod)_3$.

Compound[a]	Entry	Slope ± SD	intercept ± SD	SD(J)	N
$CH_3-\overset{O}{\overset{\|}{C}}-\underline{CH_2}-\overset{CH_3}{\overset{\|}{CH}}-CH_3$	043	0.27 ± 0.14	6.71 ± 0.11	0.14	17
	087	0.07 ± 0.14	7.16 ± 0.11	0.15	17
	104	-0.57 ± 0.47	7.40 ± 0.33	0.35	21
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\overset{\|}{CH}}-\underline{CH_3}$	043	0.26 ± 0.09	6.45 ± 0.08	0.12	24
	087	0.22 ± 0.14	6.76 ± 0.20	0.21	23
	104	0.12 ± 0.16	6.52 ± 0.13	0.26	25
$CH_3-\overset{O}{\overset{\|}{C}}-\underline{CH_2}-CH_2-CH_3$	039	0.08 ± 0.12	6.98 ± 0.10	0.16	22
	098	0.24 ± 0.15	6.96 ± 0.12	0.24	25
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\underline{CH}-CH_3$	039	0.19 ± 0.14	6.99 ± 0.11	0.22	24
	098	0.24 ± 0.14	7.00 ± 0.12	0.23	25

[a] The hydrogen for which the coupling constant was measured is underlined.

Sincerely,

Douglas J. Raber Milton D. Johnston, Jr.

283-35

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

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

JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

March 4, 1982

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

Deuterium Isotope Effects on ^{13}C NMR of Cyclopropyl and Cyclobutyl Derivatives

Dear Barry,

As part of a study by the Saunders deuterium isotope-shift perturbation technique of the carbocations formed from cyclopropylmethyl and cyclobutyl derivatives, we synthesized several deuterium-substituted cyclobutyl and cyclopropyl derivatives. In view of the current flurry of interest by TAMUNMR subscribers in intrinsic deterium isotope effects on carbon-13 shifts, we report in Table I several of such isotope effects. The spectra were taken at 125.76 MHz on our Bruker WM-500 spectrometer which has proven to be an invaluable asset to our research generally. All of the shifts reported are relative to the respective unlabeled compounds as internal standards.

The isotope shifts we have obtained are not particularly unusual, except for the two stereospecific phenylcyclopropanes where there is a 0.04-ppm greater shift for the ^{13}CHD when the deuterium is cis to the phenyl than when it is trans.

With all good wishes,

Sincerely yours,

William J. Brittain

William J. Brittain

Jack

John D. Roberts

Table I. The effect of deuterium substitution upon ^{13}C NMR chemical shifts[a] at 125.7 MHz.

Compound[b]	$\Delta\delta$, ppm[c]				$^1J_{CD}$, Hz			
	C1	C2	C3	C4	C1	C2	C3	C4
3*Z*-***d***-2,2-dichloro-1-phenylcyclopropane	0.00		-0.31					
3*E*-***d***-2,2-dichloro-1-phenylcyclopropane	0.00		-0.31					
2*E*,2*Z*,3*Z*-d_3-1-phenylcyclopropane	-0.30	-0.72	-0.53			24	25	
2*E*,2*Z*,3*E*-d_3-1-phenylcyclopropane	-0.30	-0.72	-0.49			25	25	
2*E*,2*Z*,3*E*-d_3-cyclopropanecarboxylic acid	-0.27	-0.67	-0.43					
2*E*,2*Z*,3*E*-d_3-cyclopropylmethanol	-0.29	-0.66	-0.48	-0.08			24	
cyclopropyl-1,1-d_2-methanol	-0.18			-0.77				21
1,2*E*-d_2-cyclobutanol	-0.57	-0.45	-0.15	-0.15	22	21		[d]
2,2,4,4-d_4-cyclobutanol	-0.36	-0.72	-0.13	-0.72		20		20

[a] Chemical shifts are $\pm$ 0.01 ppm. [b] C1, C2 and C3 refer to cyclopropyl group, and C4 is the exocyclic carbon. [c] Negative values correspond to an upfield isotopic shift, [d] $^2J_{CD}$ = 1.7 Hz.

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Durchwahl 740 - 4390/4400

March 7, 1982

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

U S A

Still More on $^{2}H/^{1}H$ Isotope Effects $^{n}\Delta$ on ^{13}C Chemical Shifts!

Dear Barry,

following our observation of negative (downfield) intrinsic $^{2}H/^{1}H$-isotope effects on carbon-13 chemical shifts [1], we have studied a number of unsaturated systems. The results obtained clearly indicate that negative shifts are observed for situations where hyperconjugative interactions are involved and where these interactions are perturbed by the introduction of a C-D for a C-H bond. To our knowledge Maciel [2] was the first to discuss secondary $^{2}H/^{1}H$ isotpe effects on ^{13}C chemical shifts in these terms. At this time (1966), however, the available instrumentation and field strength were quite limited and did not allow to measure small shift changes. This situation has now changed.

Using toluene as the classical test case, we find the data summarized in Table 1. We assume that the para-carbon (C-4) is the best indicator

Table 1. $^{2}H/^{1}H$ Isotope Effects on ^{13}C Chemical Shifts in Toluene, Ethylbenzene, and Cumene (in parts per billion, ppb); exp. error ±0.2 ppb; positive values are shielding effects

Ø-R	C-1	C-2,6	C-3,5	C-4	C-α	C-ß
R = $-CD_3$	+104.9	- 1.6	0	-12.1	+826.5	---
$-CHD_2$	+ 69.2	- 1.1	0	- 8.0	+550.8	---
$-CH_2D$	+ 34.1	- 0.2	0	- 3.9	+275.5	---
$-CHDCH_3$	+ 29.3	+ 2.0	0	- 2.1	+349.1	+ 81.1
$-CD(CH_3)_2$	+ 29.6	+14.3	0	0	+434.4	+109.4

for the hyperconjugative mechanism since the conventional (inductive?) through-bond effect is already zero at the meta-position (C-3,5). In the ortho-position (C-2,6) the observed effect is the sum of the hyperconjugative shift and a conventional positive contribution. Accordingly, smaller negative values are observed. The Table also shows data for ethylbenzene and cumene deuterated at the α-position. Here, for steric reasons we expect the C-D bond to occupy increasingly a position less favorable for hyperconjugation. As a consequence, the ortho-effect is now increasingly positive and the para-effect decreases and finally vanishes.

Best regards from

J. Wesener H. Günther

[1] R. Aydin, H. Günther, J.Am.Chem.Soc. 103, 1301 (1981).
[2] G. E. Maciel, P. D. Ellis, D. C. Hofer, J.Phys.Chem. 71, 2160 (1967).

G. D. R. M.

GRUPPO DI DISCUSSIONE PER LE RISONANZE MAGNETICHE

Segreteria:Dr.F.Podo,Istituto Superiore di Sanita',Rome,Italy

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

February 25th, 1982

Dear Professor Shapiro:

An International Summer School entitled "Advances in NMR of Biological Systems", organized by the International Society of Magnetic Resonance, the Italian Discussion Group on Magnetic Resonance (GDRM) and the Universita' della Calabria, will be held in Italy from June 28 to July 6, 1982.
The school will take place in the beautiful Convento dei Maestri Artigiani, Rende (Cosenza), Universita' della Calabria.
Organizing Committee: F. Conti (University of Rome) - Chairman; P. Bucci (University of Calabria); G. Chidichimo (University of Calabria); M. Delfini (C.N.R., Padua); F. Podo (Istituto Superiore di Sanita', Rome); P.A. Temussi (University of Naples); M.Terenzi (University of Calabria).
The school will consist of lectures, discussion groups and round tables.
The following topics will be covered: Pulse Fourier Transform NMR spectroscopy and advanced techniques - Molecular dynamics - Hydrogen bonding - Determination of peptide and protein conformation - Less receptive nuclei in biological systems - NMR in membranes, cells, tissues, organs - NMR Imaging.

Preliminary list of speakers: E.R.Andrew (Nottingham); P.T.Beall (Houston); I.D.Campbell (Oxford); P. Cozzone (Marseille); J.W. Doane (Kent); R.R. Ernst (Zürich); S.Fermandjan (Saclay); D. Fiat (Chicago); S. Forsèn (Lund); W. Gibbons (Madison); D. Hoult (Bethesda); O. Jardetzky (Stanford); P.C.Lauterbur (New York); M. Pintar (Waterloo); H. Rüterjans (Munster); R. Shulman (Yale); C.P. Slichter (Urbana); K. Wüthrich (Zürich), and Members of the Organizing Committee.

The number of the participants will be limited to 70. Registration fee for the school is 200 S. Accomodation full board at the Convento (9 days) is 150 S.

Information and registration: G. Chidichimo or M. Delfini, Dipartimento di Chimica, Universita' della Calabria, I-87030, Arcavacata di Rende (Cosenza), tel.0984/839321, telex: UNICAL 800044.

Thank you. With all my best personal regards.

Sincerely yours,

G. D. R. M.
GRUPPO DI DISCUSSIONE PER
LE RISONANZE MAGNETICHE
IL SEGRETARIO
(F. Podo)
Franca Podo
and Members of the Organizing Committee

283-39

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V/RÉF.

N/RÉF. GJB/gf

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

Geneva, 10th March 1982

Dear Professor Shapiro,

In response to your note of March 1st, 1982, please find here after abstracts of papers accepted for publication in the near future :

1. Etude de la viscosité et de la coagulation de solutions aqueuses de fibrinogène par dispersion de la relaxation protonique.
   G.J. Béné, B. Borcard, S. Conti, P. Descouts, A. Dupanloup, E. Hiltbrand et P. Magnin
   Helv. Phys. Acta (1981), 54, 48-51

   Abstract

   Measurements of relaxation times T_1 and T_2 of the water protons in fibrinogen solutions of concentrations between 2 and 16 g/ℓ were made over a large domain of Larmor frequencies (2 KHz $\leq \nu_o \leq$ 100 MHz). The results show a strong relation between the relaxation times and the viscosity of the solutions, more particularly for T_2 measured in the earth's field, in agreement with theoretical predictions. Analysis of this kind permits a simple interpretation of the dynamics of the coagulation.

2. Identification and dosing of meconium in the amniotic fluid (A.F.) by means of the nuclear magnetism.
   B. Borcard, E. Hiltbrand, P. Magnin and G.J. Béné, Section de Physique de l'Université de Genève, Suisse
   A. Briguet, J.C. Duplan, J. Delmau, UER Physique
   S. Guibaud, M. Bonnet, Laboratoire de Biochimie, Hôpital de la Croix-Rousse, Université de Lyon I, France
   M. Dumont, J.F. Fara, Clinique obstétrique, Hôpital de la Croix-Rousse, Université de Lyon I, France
   Physiol. chem. and Phys. (1982)

./.

To Prof. B.L. Shapiro, Department of Chemistry
College Station, Texas, USA
Geneva, 10th March 1982

Abstract

Measurements of T_2 at 23.5 Koe or 0.5 oe on solvent water in meconium polluted A.F. give reliable information :
- characteristic of concentration of meconium in A.F.;
- with very small extracted samples at 23.5 Koe ($\sim$0.1 cm^3) or possibly in situ at 0.5 oe;
- without any handling of samples (filtration, centrifugation, dilution) as in spectrophotometric method;
- obtainable in a short time (smaller than half an hour)

This variation of T_2 is mainly due to mucopolysaccharides (80 % of meconium). Measurements were made on calibrated solutions of meconium in normal A.F. and in isotonic fluid.

3. Proton NMR-relaxation dispersion in meconium solutions and healthy amniotic fluid : possible applications to medical diagnosis.
G.J. Béné, B. Borcard, E. Hiltbrand, P. Magnin, Section de Physique de l'Université de Genève, Suisse
V. Graf, F. Noack, Physikalisches Institut der Universität Stuttgart, Stuttgart, Germany. Z. für Natur. (1982)

Abstract

In order to show that for a possible application in medical diagnosis NMR-relaxation experiments at low Larmor frequencies ($\nu_o \leq 20$KHz) are more sensitive than the up to now done high field measurements in the MHz-range, we present dispersion curves (ν_o = 50 Hz to 50 MHz) of the proton longitudinal relaxation time T_1 and values of the transversal relaxation time T_2 for the example of amniotic fluids. Only for Larmor frequencies below $\simeq$ 100 kHz the relaxation times for healthy amniotic fluid and pathological meconium solutions are significantly different, whereas at high Larmor frequencies, i.e. in the conventional MHz-range, the observed changes are rather small.

Yours sincerely,

Professor G.J. BENE

283-41

INSTITUT FÜR PHYSIK DER UNIVERSITÄT BASEL
EXPERIMENTELLE KERNPHYSIK
Klingelbergstrasse 82, Telefon 061 - 44 22 80
Prof. Dr. P. Diehl

CH - 4056 Basel (Schweiz) 15 March, 1982

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

Measurement of liquid crystal diamagnetic susceptibility anisotropy by ^{1}H-NMR-spectroscopy

Dear Barry

About a year ago C.L. Khetrapal and A.C. Kunwar suggested the use of mixed liquid crystals with opposite sign of the diamagnetic susceptibility anisotropy for the measurement of chemical shifts anisotropy. [TAMUN 268, 10, 1981; Mol. Cryst. Liq.Cryst. 72, 13, 1981; Chem. Phys. Lett. 82, 170 1981]. This method is based on the fact that at a certain critical concentration the optic axis of the liquid crystal mixture rotates by 90 degrees, i.e. from a parallel (with respect to the applied field) to a perpendicular orientation or vice versa depending upon the direction from which the critical point is approached.

We are suggesting the use of this critical point for the measurement of the anisotropy of the liquid crystal dimagnetic susceptibility. [To be published in Chem. Phys. Lett.]. Actually at the critical point the macroscopic diamagnetic anisotropy of the mixture is zero and if we assume that the anisotropy is additive, as are e.g. specific polarisation and refractions of non-polar compounds, we can write at the critical point (p_c):

$p_c \cdot \Delta\chi_m$ (Liqu. Cryst. A) + $(1-p_c) \cdot \Delta\chi_m$ (Liqu. Cryst. B)= 0

Here p_c is the mole fraction and $\Delta\chi_m$ are the products

$$\Delta\chi_m = S(\text{Liqu. Cryst.}) \cdot \Delta\chi_a$$

with $\Delta\chi_a$ = molecular susceptibility anisotropy.

With a known $\Delta\chi_m$ for one liquid crystal as a basis we can now determine $\Delta\chi_m$ of different liquid crystals by detecting the critical point of axis rotation and measuring mole fractions.

We have applied this method to several mixtures and found that the results agree within approximately 5% with results of different methods. These results also confirm the additivity of effects.

Yours sincerely

Peter Diehl Jukka Jokisaari

283-43

IWAN N. STRANSKI-INSTITUT
für Physikalische und Theoretische Chemie
der Technischen Universität Berlin

Berlin, den March 17th 1982
Tel.: (030) 314-
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Ernst-Reuter-Haus

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Ernst-Reuter-Platz 7
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Professor Bernard L. Shapiro,
Chemistry Department,
Texas A and M University,
College Station,
Texas 77843, USA

Dear Barry,

"Skyline Projections in Two-Dimensional NMR Spectroscopy"

Cross-sections and projections are of great value for the rapid display of the relevant information in 2D NMR spectra. It is common practise to use integral projections which have been defined by Nagayama et al.(1). Along a chosen direction the signal intensities of the 2D spectrum are integrated and the various sums are plotted as a function of frequency. The resulting 1D spectrum thus incorporates all signals of the 2D frequency plane. In some cases, however, positive and negative signals cancel so that the integral projection may look deceptively simple. One prominent example is given in 2D-J-resolved spectroscopy where the so-called "phase-twist" line shape causes the 45° integral projections to be zero. This artefact may be alleviated by using the absolute-mode 2D spectrum for integration at the expense of severe broadening and distortions for overlapping resonance lines.

A remedy is to obtain integral projections from 2D spectra where the phase twist has been removed by either additional measurement (2-4) or additional data treatment ("pseudo echo", ref.5).

Particularly in cases of decent signal-to-noise ratio, the much attended integral projection faces a powerful but yet neglected alternative. Instead of defining a projection as the sum of signals along a given direction, it may be defined in terms of the shadow cast by an object in the sun light. Thus the skyline of the 2D spectrum determines the projected spectrum. These projections are therefore called skyline projections.

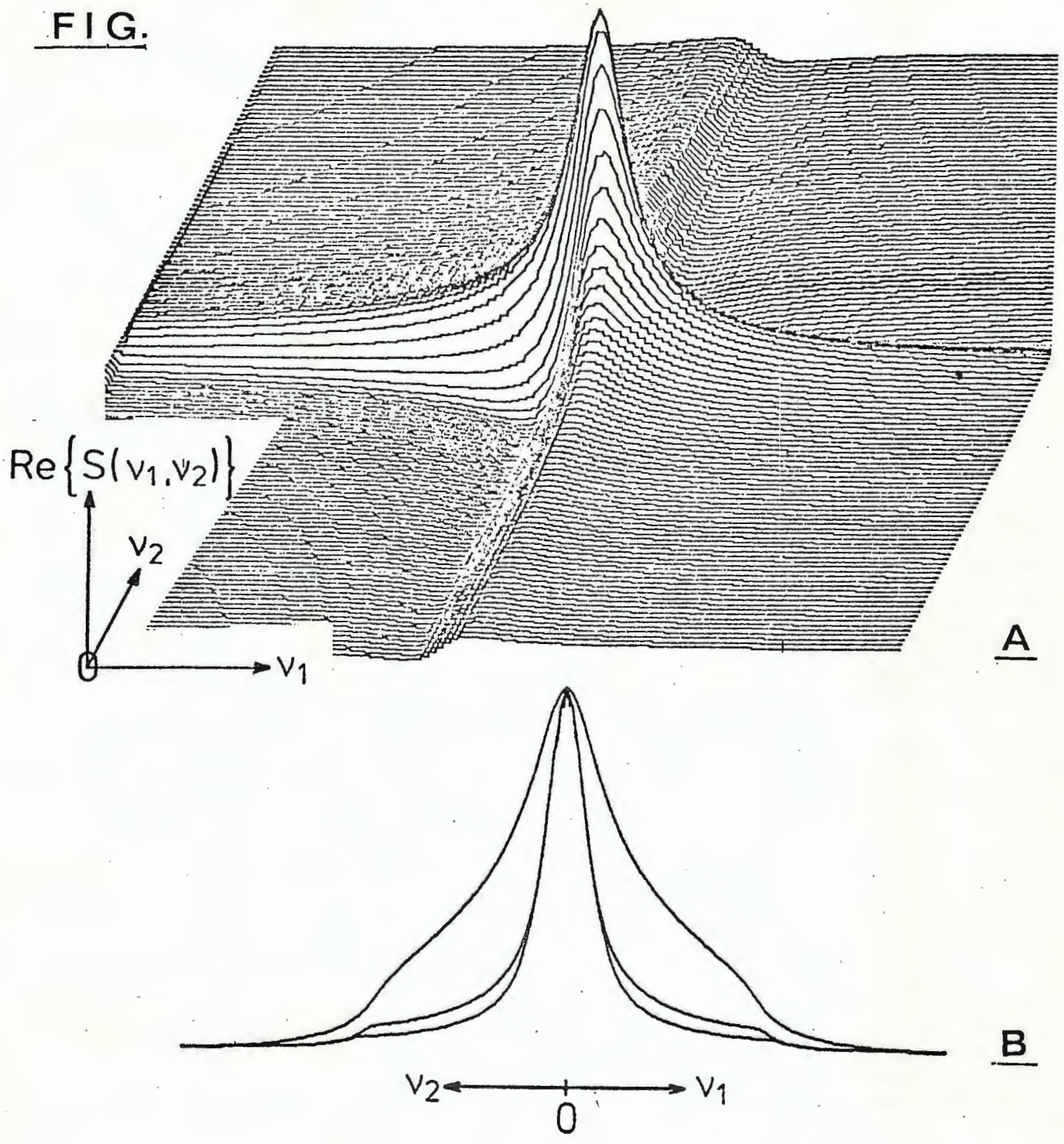
The Figure shows the typical phase-twist line shape(a) and the integral and skyline projections at 45°. The inner lineshape is a skyline projection of both the positive and the magnitude of the negative values of the spectrum ($|\mathrm{Re}\{S(\omega_1,\omega_2)\}|$, absolute real mode skyline). The slightly broader lineshape in the middle is the skyline projection of the magnitude spectrum $|S(\omega_1,\omega_2)|$ which may be used for spectra with phase error. The outer lineshape eventually results from the integral projection of the magnitude spectrum. These lineshapes demonstrate the superior resolution of the skyline projections. Since no integration is applied, the peak heights in a skyline projection are in general not a measure of the signal intensities.

Best regards,

Bernhard Blümich

Dieter Ziessow

FIG.



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2) P. Bachmann, W.P. Aue, L. Müller, and R.R. Ernst, J. Magn. Reson. 28, 29 (197)
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4) A. Bax, A.F. Mehlkopf, and J. Smidt, J. Magn. Reson. 35, 373 (1979)
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283-45

Varian / 611 Hansen Way / Palo Alto / California 94303 / U.S.A.
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varian

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

March 23, 1982

^{15}N NATURAL ABUNDANCE OF POLYPEPTIDES ON THE XL-300

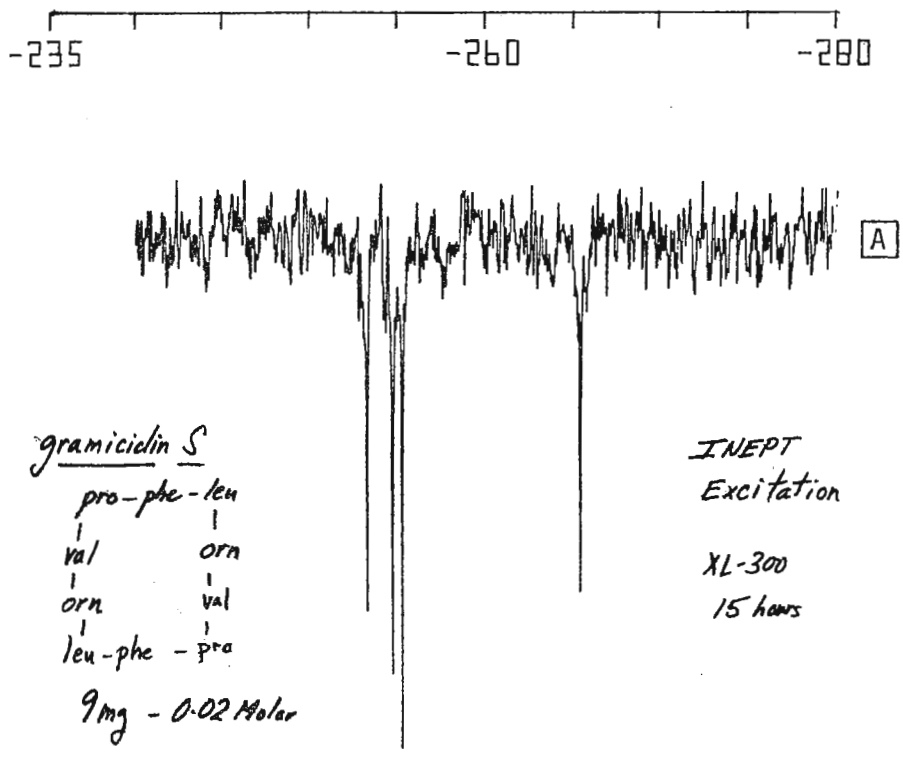
Dear Barry:

We've been exploring the utility and limitations of ^{15}N NMR of polypeptides and have obtained some interesting results lately on the XL-300 at 30 MHz. The higher field and improved probe technology can now permit using solutions in the range of 10 millimolar. Even small amounts can be studied, for example the 9 mg sample of gramicidin S (Spectrum A). This 0.02 molar solution was run in a 5 mm broadband probe on the XL-300 for 15 hours. Obviously a 4 hour run would be adequate.

Another polypeptide which presents interesting demands on spectral interpretation is angiotension II. The NOE spectrum (B) resulted from an overnight run on a 0.056 molar solution in a 10 mm broadband probe. The protonated $-NH_3^+$ terminal nitrogen gives rise to the high-field signal, while the NH_2's are just visible in the center of the spectrum. Four resonances at lower field represent the six amide nitrogens (see expansion D). The proline and histidine resonances were not observed due to unfavorable T_1/NOE.

The INEPT polarization transfer pulse sequence is very valuable for ^{15}N NMR and it was used to produce C-D. Spectrum C was obtained after setting the refocussing delay for exciting only NH resonances. Note that the guandino NH of arginine now is much stronger. Spectrum B' was obtained under conditions for NH down, NH_2 up, confirming the arginine NH_2 assignment.

INEPT ^{15}N spectra are dramatically affected by the lability of the protons bonded to the nitrogens. Note that the $-NH_3^+$ resonance is completely absent from the INEPT spectra while strong in the NOE spectrum. No histidine resonances are observed as well. Proton exchange destroys the coherence of the proton magnetization during the polarization transfer process. For $J \sim 90$ Hz the various delays in the pulse sequence add up to $\sim$11 ms so that exchange lifetimes must be significantly longer than this to permit effective polarization transfer and subsequent detection. The two arginine NH_2's actually integrate to about the same as one amide NH when delays were set to have all peaks upright.



See you at the ENC,

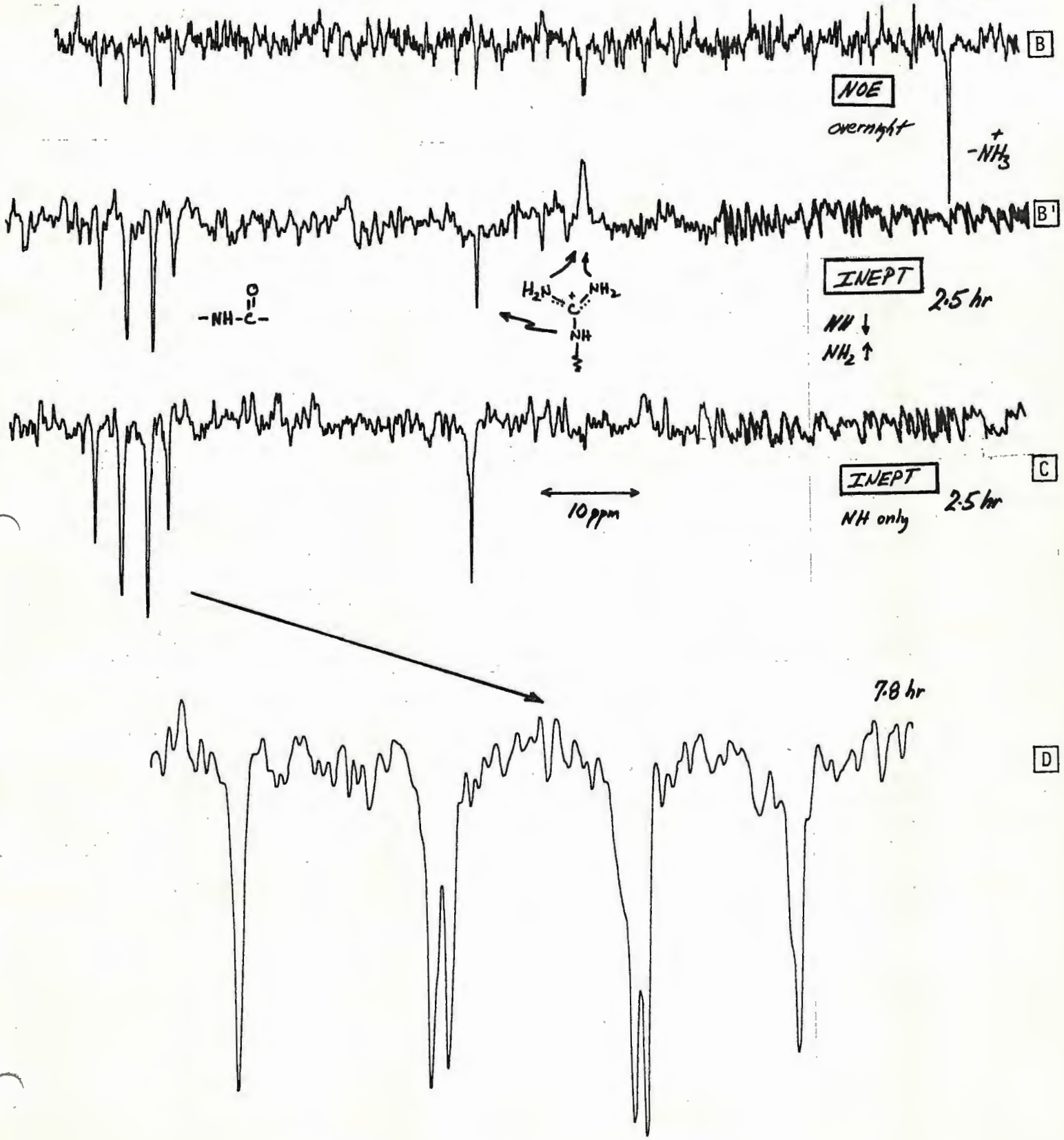
George A. Gray
NMR Applications Laboratory
Varian Instrument Division

^{15}N Observe 10 mm Broadband Probe

XL-300

0.056 M Angiotensin II

Asp-Arg-Val-Tyr-Ile-HisT-Pro-Phe



Columbia University in the City of New York | *New York, N.Y. 10027*

DEPARTMENT OF CHEMISTRY Havemeyer Hall

March 24, 1982

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

Folding in Jeener Spectra

Dear Professor Shapiro:

Now that I am settled at Columbia I should like to resume my subscription to TAMU NMR Newsletter. In the hope that you will accept pretty pictures instead of science, I offer this contribution.

One of the perennial problems in FT NMR is the recognition of peaks which have been "folded" (or aliased) from outside the spectral width. So what about folding in 2-D NMR? The mind boggles!

The effect of folding in homonuclear 2-D J spectra have been elegantly demonstrated recently (1). However, the temptation to reduce the spectral width may be even greater for the 2-D autocorrelation experiment (2). Some preliminary data are shown here.

The upper autocorrelation map shows the aliphatic part of a 512 x 1K data-matrix. The width of the plot is 1KHz in both dimensions. The spectral width in both dimensions was 2KHz (at 300 MHz) in order to cover all the proton resonances. Note that the olefinic region containing 3 protons is not shown. The data was acquired with quadrature in both dimensions without delay before acquisition (COSY).

The lower autocorrelation map was recorded with delay before acquisition (SECSY) and shows the same region. The matrix size was reduced to 256 by 512, all of which is displayed here. The sweep width in F_2 was reduced to 1KHz. Notice that the cross-peaks (filled in black) denoting coupling between the aliphatic and olefinic region appear in an unambiguous position, from which the location of two of the olefinic protons can be determined. However these cross-peaks are not actually folded, since they fall within both the spectral widths. A more troublesome situation can be found at the high field end of the map. Here the other olefinic proton and its associated cross-peaks are both folded in.

At present, I am busy having fun folding spectra of DBPA about every conceivable axis.

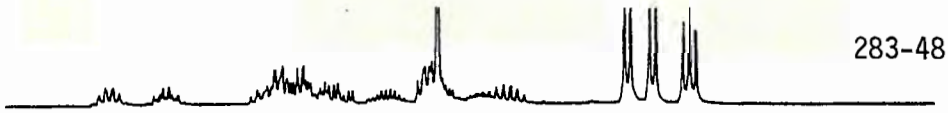
King regards,

Chris Turner

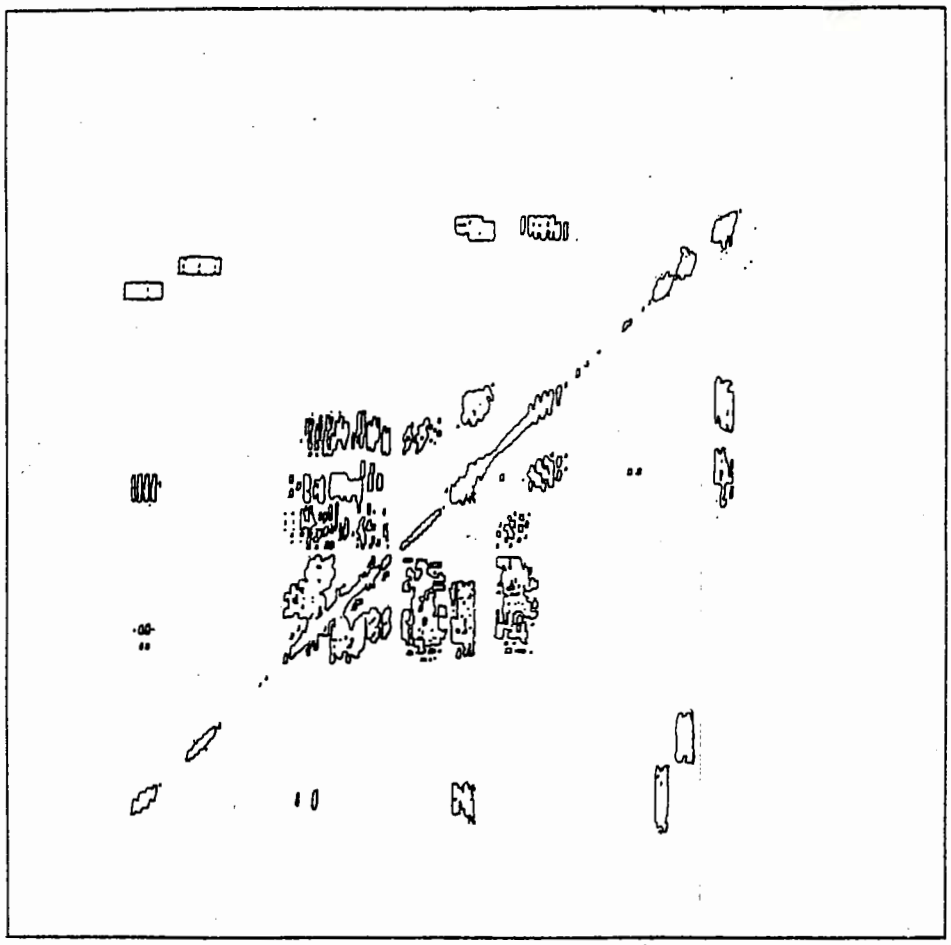
C. J. Turner

1) G. Wider et al. J. Magn. Reson., 42, 73 (1981)
2) A. Bax et al. J. Magn. Reson., 42, 164 (1981)

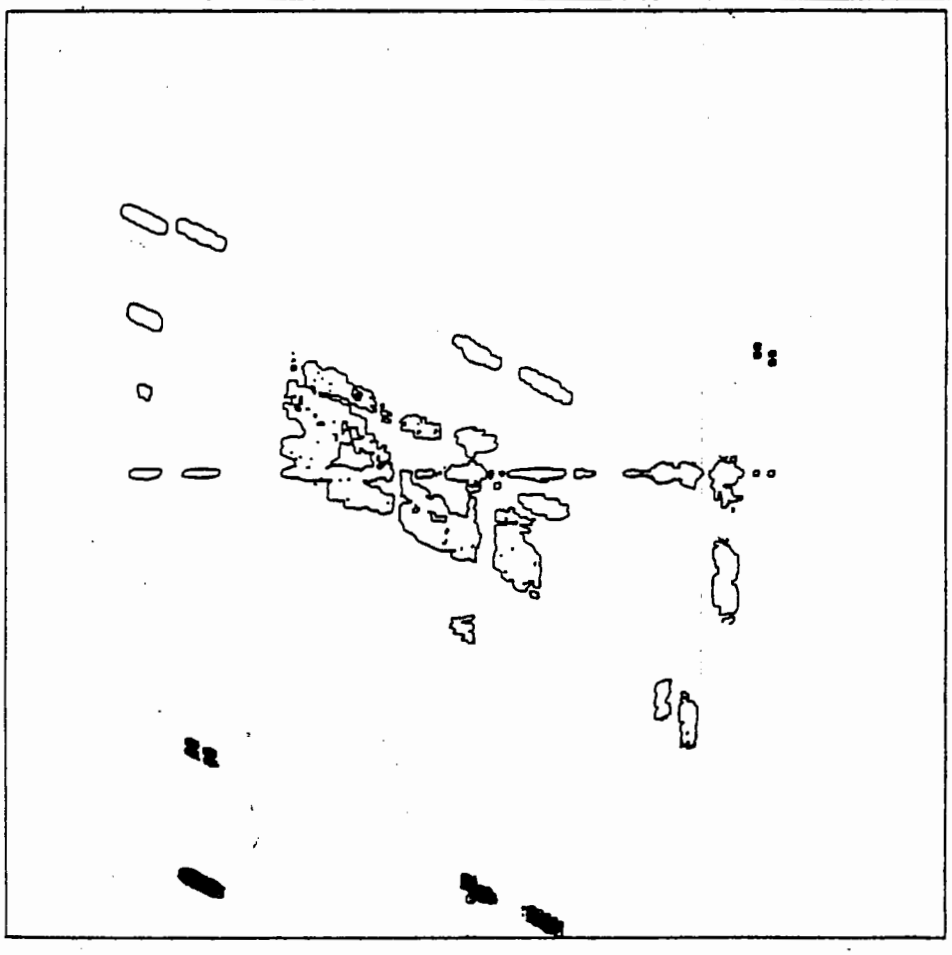
a)



b)



c)



283-49

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

March 30, 1982

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

TMA As A ^{1}H Chemical Shift Reference

Dear Dr. Shapiro:

We would like to caution your readers concerning the use of TMA, $[N(CH_3)_4^+]$, as a chemical shift reference when comparing shifts in aqueous solutions of different ionic strength.

A change in ionic strength affects the magnitude of the bulk magnetic susceptibility of the sample and should cause equal chemical shifts (on an absolute scale) for all components of the solution and no change in relative shifts. The change in the chemical shift of TMA appears to differ from that of the sample as a whole. The accompanying table shows $\delta_{(CH_3)_4N^+}$ and δ_{CH_3CN} in solutions of increasing ionic strength in an unlocked, stable magnetic field. The ionic strength, μ, is due to a mixture of organic and inorganic salts. The difference between the shifts, or the shift of TMA relative to acetonitrile, is plotted vs. μ. Although our experience using these references indicates that δ_{TMA} is variable rather than δ_{CH_3CN}, we are making further measurements to verify the chemical shift stability of CH_3CN over a large range of ionic strength.

Please credit this letter to the subscription of William C. Hutton.

Yours sincerely,

Eileen M. Stephens

Eileen M. Stephens

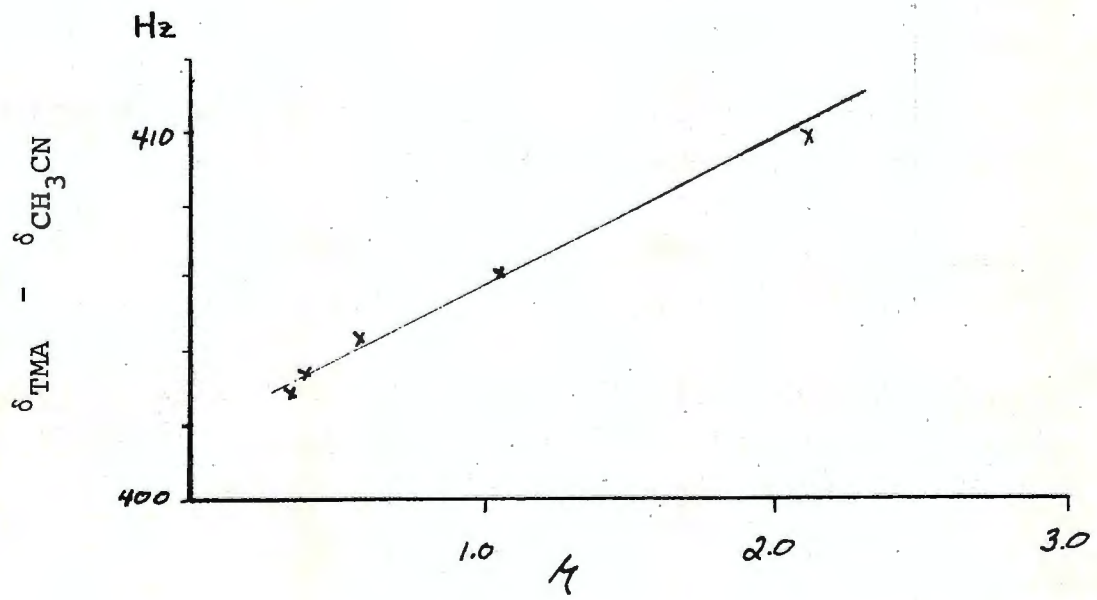
Sook-Hui Kim

Sook-Hui Kim

EMS:ttn

Ionic Strength	Hz at 8.45T*	
Moles/ℓ	$\delta_{(C\underline{H}_3)_4N^+}$	$\delta_{C\underline{H}_3CN}$
0.328	1240.54	837.69
0.383	1237.25	833.83
0.571	1231.20	826.82
1.052	1210.58	804.38
2.100	1159.34	749.53

*Drift rate less than 1 Hz/hr.



283-51

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Prof. SHAPIRO
Chemistry Department
Texas A and M University

COLLEGE STATION
Texas 77843
USA

N./Réf. 82 03 121 CB/MCH
V./Réf.

Wissembourg, le March 15, 1982

^{15}N NMR : Remember long range couplings !

Non protonated ^{15}N Nitrogens are very difficult to detect via direct observation because of very long relaxation time (Pyridine : 85 seconds, acetonitrile : 90 seconds) associated with diabolic NOE values, generally around - 1.

A rapid look to the literature furnishes the proof of long range $^{n}J_{15N-H}$ couplings ($n > 1$) for such nitrogen atoms (1), the obvious starting point for INEPT experiments.

The attached spectra are self speaking and do show that ^{15}N NMR could be used routinely for such systems.

Spectrum a : acetonitrile, pure liquid, 16 scans. $^{3}J_{15N-H}$ = 1,7 Hz. Repetition time : 6 seconds ; Scale : 1 Hz/cm.

Spectrum b : Pyridine (30/70, v/v in $CDCl_3$), 1 000 scans. $^{2}J_{15N-\alpha H}$ = 10,5 Hz Repetition time : 6 seconds, the $^{3}J_{15N-\beta H}$ = 1,5 Hz is clearly visible ; scale : 2,5 Hz/cm. Triplets separation : 2 x $J_{15N-\alpha H}$.

.../...

Spectrum c : a real structural problem from a cooperation with Prof. K. Vrieze and Dr G. Van Koten, U. of Amsterdam. Compound is shown in the insert. Solution : 200 mg in 3 ml of CD_3OD. Repetition time : 2 seconds. Overnight run, average driving INEPT coupling : 5 Hz. Reference : $MeNO_2$ 50/50 in $CDCl_3$. A crystal structure of the parent compound with R = H shows two sets of imine-pyridine nitrogens (2). One with a long (N^1_{im}, N^1_{py})-Ag bonding interaction (2.43 Å), a second one with a short (N^2_{im}, N^2_{Py})-Ag bonding interaction (2.24 Å). This solid state situation is not averaged out in solution as shown by the ^{15}N spectrum where one clearly distinguishes the two kinds of N_{im} and N_{py} nitrogens (N^1, N^2) with two different chemical shifts and $^1J_{Ag-15N}$ couplings reflecting unambiguously the different ^{15}N-Ag bonding distances.

By the way, we found the ^1H non decoupled INEPT sequence more powerful in these problems, compared to the ^1H decoupled one, (try to calculate the optimum refocalizing time to switch the decoupler on in situation C !).

Best regards,

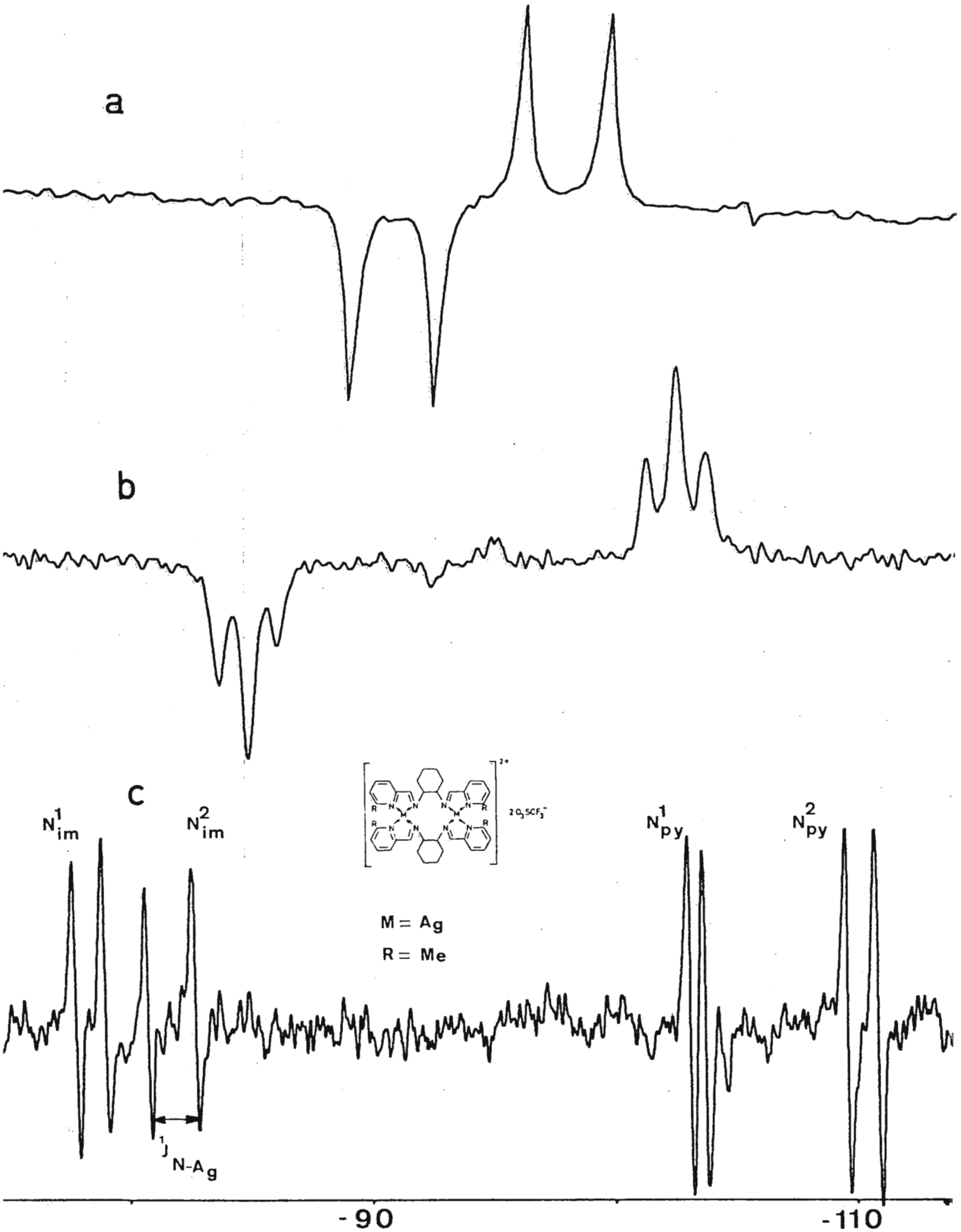
C. BREVARD

R. SCHIMPF

(1) "Nitrogen 15 Nuclear Magnetic Resonance". G.C. Levy, R.L. Lichter, Wiley-Intersciences. 1979. Chapter 4, page 115-119.

(2) G.C. Van Stein, H. Van der Poel, G. Van Koten, A.L. Spek, A.J.M. Duisenberg, P.S. Pregosin, J.C.S. Chem. Commun 1016 (1980).

(3) ^{15}N frequency : 25,3 MHz. Spectrometer : WM 250. 10 mm tube.


a
b
c
N^1_{im}
N^2_{im}
N^1_{py}
N^2_{py}
$^1J_{N-Ag}$
M = Ag
R = Me
$2O_3SCF_3^-$
-90
-110

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CASE WESTERN RESERVE UNIVERSITY • CLEVELAND, OHIO 44106

March 3, 1982

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

Dear Barry!

I am enclosing a contribution for the News Letter and an announcement of our January Clearence Sale - as usual, I'm just a little late. If you glance over the list of items, it is clear that most of these are in great demand. Thus, one should buy now (before they're gone) and figure out a use for them later!

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I hope I don't get killed in the STAMPEDE!

Bill

William M. Ritchey
(216-368-3668)

283-57

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BYRON H. ARISON, PH.D
SENIOR INVESTIGATOR
DEPARTMENT OF BIOPHYSICS

TELEPHONE (201) 574-6746
(201) 574-5394

March 31, 1982

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

Dear Barry:

Accurate Determination of the Degree of Racemization
Accompanying Peptide Syntheses in the Sub 1% Range

A fundamental criterion for judging a new sequence for peptide synthesis is the degree of racemization accompanying the procedure. It is not unusual to detect the presence of approximately 2% of an unwanted racemate by standard NMR measurements. While this may be adequate for many applications, a higher sensitivity would be desirable in multistep syntheses where the accumulated racemization even at 2% per step might be unacceptable. It is possible in favorable cases to improve the NMR threshold of detectability by well over an order of magnitude by using the ^{13}C satellites of an analytical signal as internal reference peaks. Since these are exactly 0.55% of the parent resonance they are ideally suited for quantitative analyses in the 0.1-1.0% range. In the present example which involves a new method for the preparation of protected N-alkyl amino acids, the ^{13}C satellite method was used in conjunction with the chiral shift reagent $Eu(hfbc)_3$.

Initial studies with the racemate at 300 MHz had indicated that a separation of 20-40 Hz of the enantiomeric methoxyls could be achieved in the presence of roughly 0.3-0.5 molar equivalent of lanthanide. Trace A in the accompanying figure shows the methoxyl region of L-N^{α}-methyl-O-benzyl serine methyl ester in the presence of 0.4 molar equivalent of $Eu(hfbc)_3$. The ^{13}C satellites of the methoxyl appear at 3.46δ and 3.96δ. Trace B illustrates the effect of adding a few microliters of lanthanide treated D-isomer. It is evident from the comparison of A and B that any racemization that may accompany this synthetic sequence is less than the detectability limit which is estimated at 0.06-0.07% based on the signal-to-noise ratio of the ^{13}C satellite peak at 3.46δ.

The foregoing is to be part of a forthcoming paper in J. Org. Chem. by R. Freidinger et al.

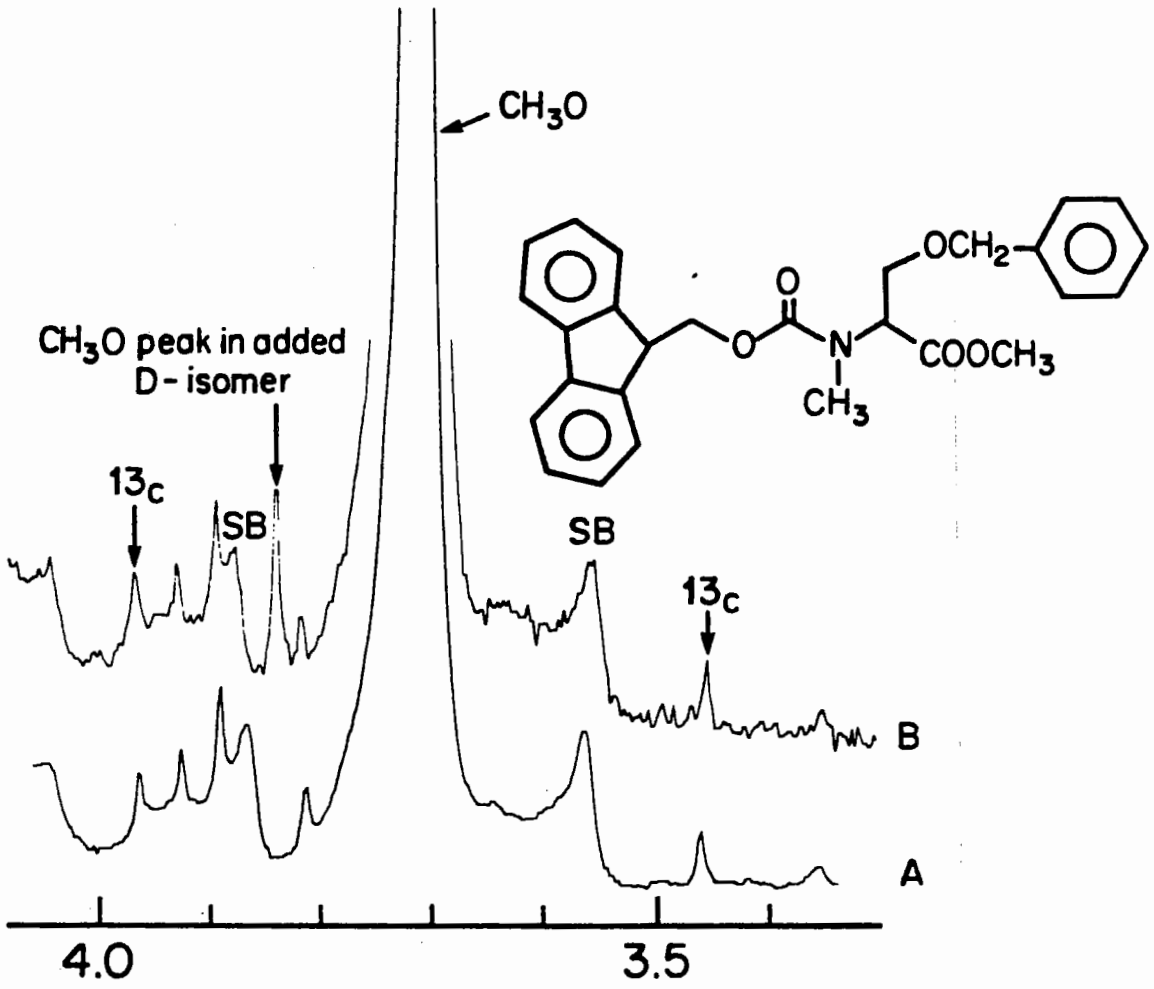
Sincerely yours,

Byron

Byron H. Arison

/oah

Attachment



A: 300 MHz trace of methoxyl region of L-isomer in presence of 0.4 molar equivalent of $Eu(hfbc)_3$

B: L-isomer plus small amount of lanthanide treated D-isomer

283-59

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA 93106

March 30, 1982

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

Fluorine Spectrum of Myoglobin

Dear Barry:

Researchers in biological chemistry have taken advantage of the fact that many microorganisms will incorporate fluorinated amino acids present in their diet into their proteins. The fluorine nmr spectra of these materials are usually spread over 6-12 p.p.m. and are often highly resolved, making possible detailed structural studies of such proteins. It was demonstrated over 20 years ago that the rabbit can do the same trick but as yet we are unaware of any attempts to observe fluorine spectra with proteins from this animal. We have raised several New Zealand white rabbits on a diet containing 0.3% D,L-p-fluorophenylalanine and are now in the process of examining their proteins. The Figure below shows the fluorine spectrum of myoglobin isolated from one such animal. Amino acid analyses of related systems indicate that about 3% of the phenylalanine in this molecule has been replaced by the fluoro analog. Ignoring the minor peaks for the present, the spectrum suggests the presence of 8 phenylalanines

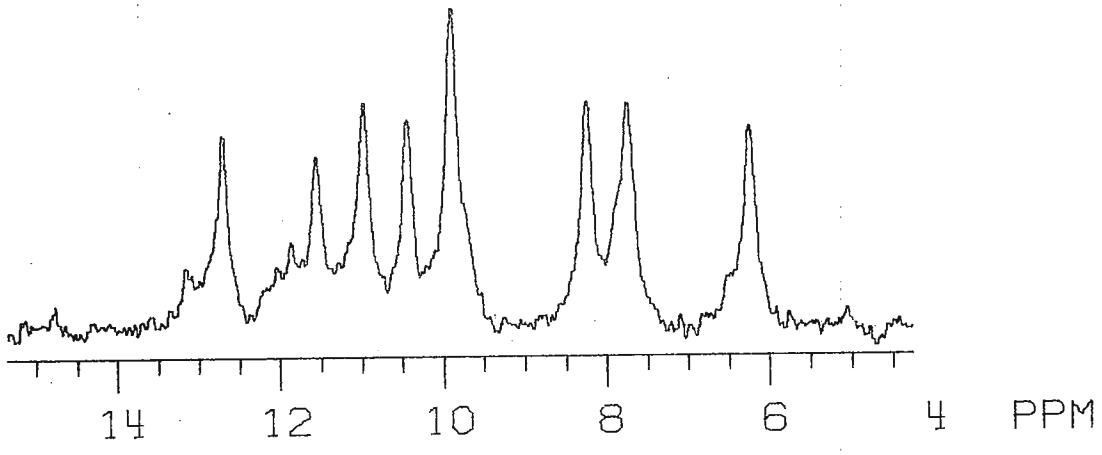

Figure 1. Fluorine nmr spectrum of p-fluorophenylalanine-containing rabbit cyanometmyoglobin, obtained at 282 MHz and 25°. The protein concentration was about 0.7 mM but only about 3% of any phenylalanine position is fluorinated.

in the sequence. Experiments are underway to provide assignments of these signals to particular phenylalanine positions in the sequence and, when these are available, rather detailed studies of the structural changes that accompany binding of oxygen should be possible.

Our results so far suggest that the proteins of mammals obliging enough to eat fluorinated amino acids may well have interesting fluorine nmr spectra.

Sincerely yours,

R. A. Nieman

Tom

J. T. Gerig

HERCULES INCORPORATED

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February 26, 1982

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

Dear Dr. Shapiro:

USED ^{1}H NMR WANTED

The PFW division of Hercules, located in Middletown, New York, is seeking a used CW NMR for routine spectra. The instrument should be operable and in reasonable condition, and preferably located in the Eastern half of the U.S. The following equipment would be suitable: T-60, EM 360-390, A-60 (D model preferred if in good condition), R-12, R-32 or comparable instruments.

Persons interested should contact Mike Karras or Brian Byrne at (914) 343-1900, Ext. 316.

Sincerely,

Walter J. Freeman

Walter J. Freeman
Research Scientist
Analytical Division

283-61

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March 2, 1982

Professor B.C. Shapiro
Texas A&M NMR Newsletter
Department of Chemistry
Texas A&M University
College Station, Texas 77483

re: Position available

Dear Professor Shapiro,

We have a position available in our final test group. The successful applicant will be handsomely compensated for testing and trouble-shooting nmr spectrometers. Electronics experience and a familiarity with nmr spectroscopy are required.

Interested applicants should send resumes to my attention, to the address below.

Sincerely yours,

Stephen E. Ulrich

Stephen E. Ulrich
Test Manager
NICOLET MAGNETICS

SEU/dly

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March 26, 1982

Dr. Bernard L. Shapiro
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Sincerely,

Michael Reinhold

Michael Reinhold, Ph.D.
Product Manager

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283-63

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March 12, 1982

Professor Barry Shapiro
Texas A & M University
College Station, Texas 77843

Dear Professor Shapiro:

Our laboratory is presently engaged in a variety of projects that involve NMR techniques. Among them are the following: (1) A study of the mechanism of RNA polymerase, as modified by different metal ions, (2) the interaction of metal ions with DNA and RNA, (3) the interconversion of DNA conformers - we have recently discovered a series of reversible consecutive DNA transformations, and (4) age changes in the metabolism of tissues, organs and whole animals. One of my coworkers on these studies will leave at the end of the summer, and I want to replace him with someone who is interested in the types of studies that we are carrying out and who is well-trained in NMR spectroscopy. Some experience in biochemical preparations would be helpful, but not essential - general intellectual and laboratory skills are more important.

The applicant would be considered for an NIH staff fellowship, if he is a U.S. citizen, or an NIH visiting fellowship, if he is not. Visiting fellows are paid $16,000 per year immediately after obtaining the doctorate, somewhat more with greater experience. Staff fellowships start at $17,000 and can go as high as $32,955, as warranted by experience.

If you know of suitable candidates, please let me know about them or have them contact me directly.

Sincerely yours,

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

GLE/alh

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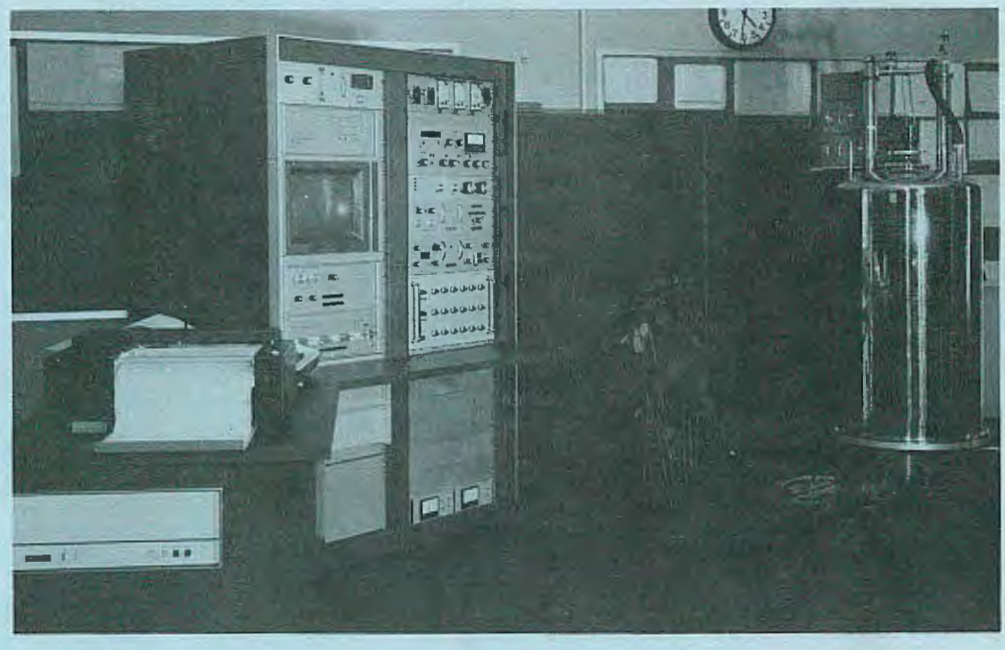

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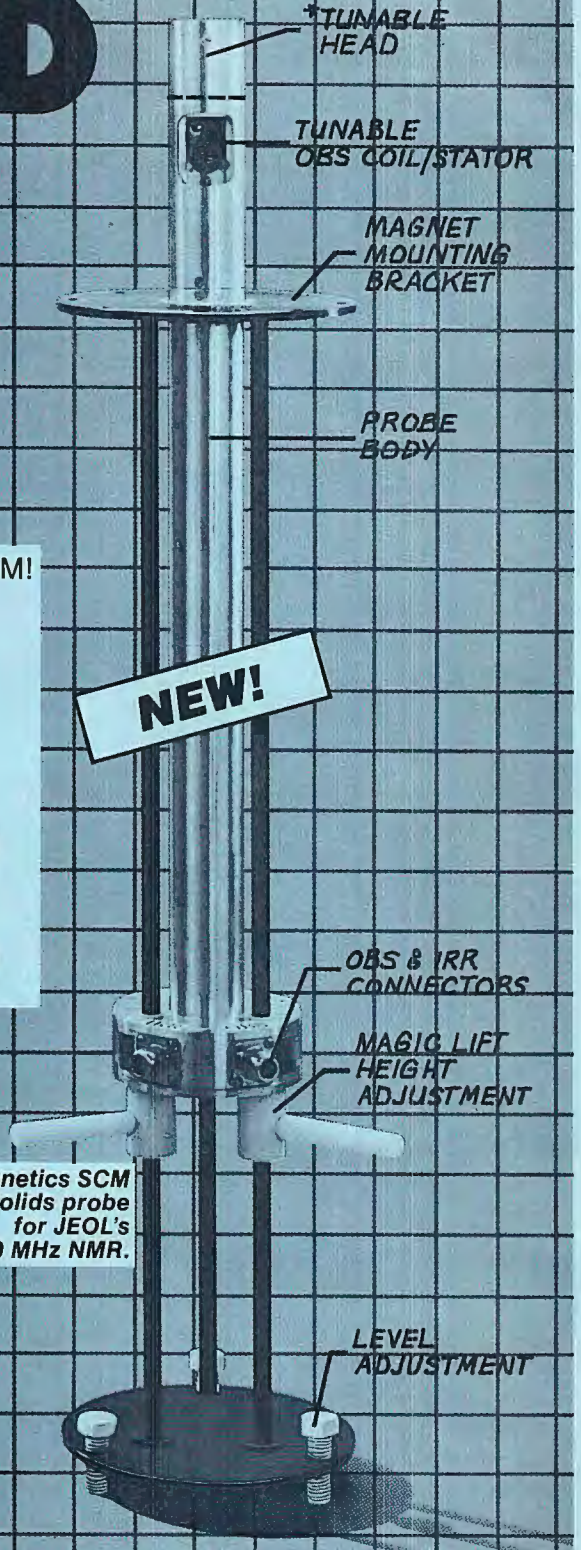

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