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NMR
NEWSLETTER

No. **284**

May, 1982

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DEADLINE DATES: No. 285   7 June 1982
                  No. 286   5 July 1982

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

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

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February 17, 1982

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

Dear Dr. Shapiro:

We have recently added a circuit to our Bruker CXP 180 that has greatly reduced a problem that we have had with pulse feed through. Although the CXP is equipped with a receiver blanking circuit it proved to be inadequate, because of a D.C. level change that occurred during blanking. This would result in a pulse whose duration would be greatly extended by the low pass filter.

We were able to solve this problem by adding the sample and hold circuits shown below between the receiver and the filter. When this circuit was in the sample mode (switch closed) the output followed the input and the device had no affect. When the circuit was in the hold mode (switch open) the output remained at the input level present just prior to the switch opening. Thus, the signal was blanked while no level change occurred at the filter input. This circuit has proved to be very effective at reducing problems from pulse feed through while having no apparent negetive affects.

Please credit this contribution to Dr. Robert Kleps' account.

Sincerely yours,

Mike Mutaw

MM:kam

Enclosure
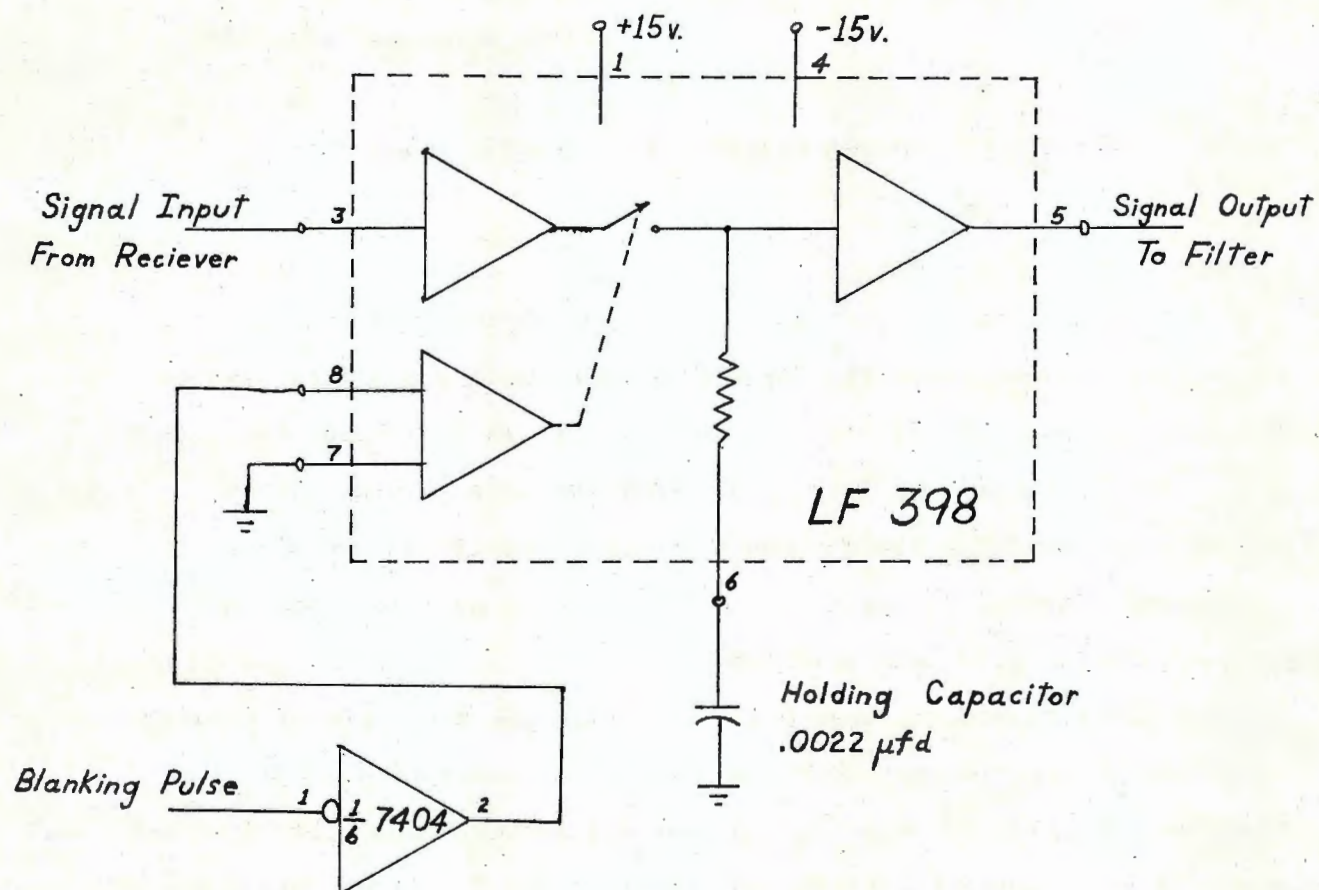
Sample and Hold for Reciever Blanking

C. N. R.
Centro di Studio per le
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Istituto di Chimica del Politecnico
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Tel 230845-6-7-8-9

February 24/1982

Professor B. L. Shapiro

Department of Chemistry

Texas A&M University

College Station, Texas 77843

Conformation of Dibenzo-p-dioxin Oriented in a Nematic Phase.

Dear Barry,
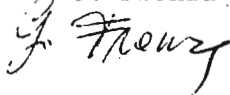
It is known that certain halogenated derivatives of dibenzo-p-dioxin possess extreme toxycity. For this reason, such a tricyclic system has been extensively studied, both in solution and in the solid state, mainly to determine the angle of folding, ϕ, about the axis joining the two heteroatoms. In the solid state dibenzo-p-dioxin resulted to be planar within the experimental errors, while has been found puckered from the dipole moment data in benzene solution.

We have investigated the possibility to determine the angle of folding by using the NMR spectroscopy in liquid crystal solvents (Phase IV). The calculations were done for the rigid planar and for the bent structures and the deviations between the experimental and computed D_{ij} values are reported in the Table along with the experimental data. An ispection of the Table shows that the deviations for the inter-ring D_{ij} values are larger for the planar than for the bent conformation, clearly indicating that the molecule is puckered. A value of $165.6 \pm 2°$ was obtained for the angle of folding, in excellent agreement with that determined from the dipole moment data (163.8°).

The full paper will appear in the Journal of the Chemical Society, Perkin Transactions II.

Sincerely yours
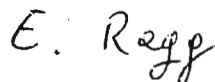
G. Fronza   R. Mondelli   E. Ragg
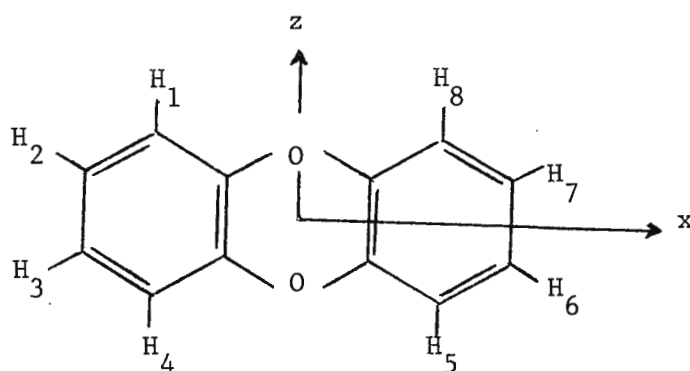
Table. Experimental and computed data of dibenzo-p-dioxin dissolved in Phase IV.

Parameter	Experimental value	$D_{calc} - D_{exp}$ (folded conformation)	$D_{calc} - D_{exp}$ (planar conformation)
D_{12} (Hz)	-1559.16 ± 0.03	0.00	0.01
D_{13}	-52.43 ± 0.04	0.01	0.01
D_{14}	48.01 ± 0.13	0.00	0.00
D_{15}	-42.35 ± 0.13	-0.22	-1.70
D_{16}	-55.15 ± 0.04	-0.05	-0.94
D_{17}	-102.15 ± 0.01	-0.01	-0.82
D_{18}	-348.37 ± 0.13	-0.02	2.34
D_{23}	391.68 ± 0.13	0.01	-0.01
D_{26}	-40.29 ± 0.13	0.30	-0.63
D_{27}	-48.99 ± 0.13	0.43	-0.64
$\nu_1 - \nu_2$ (Hz)	26.10 ± 0.25		
wtrms (Hz)		0.072	0.655
S_{xx} [a]		0.29741 ± 0.00018	0.28889 ± 0.00015
S_{zz} [a]		-0.04982 ± 0.00001	-0.04982 ± 0.00001
ϕ° [b]		$165.6 \pm 2°$	$180°$

a) $r_{23} = 2.481$ Å (assumed)

b) Angle of folding defined as the dihedral angle between the two aromatic rings.

EX**X**ON RESEARCH AND ENGINEERING COMPANY

ANALYTICAL AND INFORMATION DIVISION
J. K. PATTERSON
Director

March 17, 1982

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

Dear Barry:

Title: ^{15}N Chemical Shifts of Cobalt(III) – Amino Acid Complexes

As part of a collaborative effort to characterize transition metal–amino acid complexes, we have determined ^{15}N chemical shifts of several series of cobalt(III) complexes at the natural–abundance level of the isotope. The ability to observe resonances, even on our aging JEOL PFT–100 spectrometer, affords access to larger ranges of compounds than heretofore has been possible, because of limited availability of suitably enriched materials.

The table gives results for complexes of the type λ–cis (NO$_2$)–trans (NH$_2$)–[Co(NO$_2$)$_2$(Am)$_2$]$^{(+/-)}$, (AmH = amino acid). Single lines were observed for distinct nitrogens, with linewidths of 5–10 Hz. In all cases, coordination with cobalt(III) induces a shielding of 24–42 ppm compared with the protonated amino acids. It is interesting that the one β–amino acid, which forms a weaker, six–membered chelate ring, displays a smaller coordination shift than the α–amino acids, which form stronger, five–membered chelates with cobalt(III). However, the variations in Δ_C among the α–amino acids are more difficult to explain. The lysine and arginine results demonstrate that binding sites in more complicated amino acids are easily identified.

More detailed discussion of these results will appear shortly in Inorganic Chimica Acta. The complexes were prepared and characterized by M. B. Čelap, M. J. Malinar, and P. N. Radivojša.

The letterhead indicates only where I am currently spending part of my sabbatical, nothing more!

Regards,

Nenad Juranić RC

Nenad Juranić
Visiting Fulbright Scholar
University of Belgrade

Bob

Robert L. Lichter
Professor of Chemistry
Hunter College

/pjs

Table ^{15}N Chemical Shifts of Aminocarboxylato Ligands Coordinated in λ-cis(NO$_2$)- trans(NH$_2$)-[Co(NO$_2$)$_2$(Am)$_2$]$^{(-/+)}$ Complexes and Corresponding Protonated Amino Acids[a]

Amino Acid	Coordinated	Protonated	Δ^{b}_{c}
Glycine	-10.8	30.9	-41.7
S-Aminobutyric acid	-4.0	30.0	-34.0
S-Valine	-1.5	37.3	-38.8
S-Leucine	1.8	42.9	-41.1
S-Isoleucine	0.0	38.9	-38.9
S-Phenylalanine	3.6	40.8	-37.2
S-Proline	18.6	54.6	36.0
S-Methionine	4.7	39.1	-34.4
S-Lysine	5.0	42.6 (α-NH$_3^+$)	-37.6
	33.4	35.6 (ε-NH$_3^+$)	-2.2
S-Arginine	8.2	42.8 (α-NH$_3^+$)	-34.6
	75.9	74.1 (NH$_2 \rightleftarrows$ NH$_3^+$)	1.8
	89.2	86.6 (-NH-)	2.6
β-Alanine	9.8	34.2	-24.4

a) In ppm from anhydrous liquid ammonia.   Positive sign indicates a shift to lower shielding.

b) Defined as the difference in ^{15}N chemical shifts between coordinated aminocarboxylato ligand and protonated amino acid.

University of Nottingham

Department of Chemistry

Professor of Inorganic Chemistry
J. J. Turner

UNIVERSITY PARK NOTTINGHAM NG7 2RD
TEL NOTTINGHAM 56101

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

26 April 1982

Dear Professor Shapiro,

Drastic Chemical Shift Changes on Dilution of $Pb(OAc)_2$ Solutions

Aqueous solutions of lead(II) acetate exhibit very large changes in lead-207 chemical shift on dilution. At concentrations in the range 1.0-0.25 M, the chemical shift varies little, decreasing from -1337 to -1429 ppm (relative to tetramethyllead as zero), but at concentrations of less than 0.1 M, the shift moves rapidly to higher field, reaching a value of -1956 ppm at a concentration of 0.01 M. These observations are readily interpreted in terms of the well-established equilibrium:

$$Pb(OAc)_2(aq) \quad + \quad H_2O \quad \rightleftharpoons \quad Pb(OAc)(aq)^+ \quad + \quad OAc^-$$
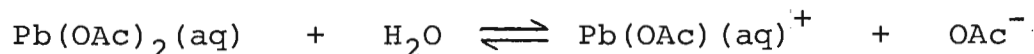
Computer simulation of this rapidly exchanging system yields calculated values of -1202 ppm for the cationic aquo species $Pb(OAc)(aq)^+$ and -2299 ppm for the neutral $Pb(OAc)_2(aq)$ species. with the equilibrium constant $\underline{k}$ having a value of 0.013 mol. at 25°.

Please credit this contribution to the account of Dr. Harold Booth of this Department.

Yours sincerely,

Philip G. Harrison

Are you aware of any existing
well-proven commercial NMR spectrometer,
capable of doing:

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CANADA

Title: $^1J_{C-H}$ in <u>syn</u> and <u>anti</u> Carbonyl Derivatives.

April 14, 1982

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

Dear Barry:

We have just completed (with Monique Bresse) an examination of the effect of configuration on the value for $^1J_{C-H}$ in oximes, hydrazones and imines. This became possible through the availability of <u>syn</u> isomers (6) via alkylation of the lithiated intermediate as in [1].
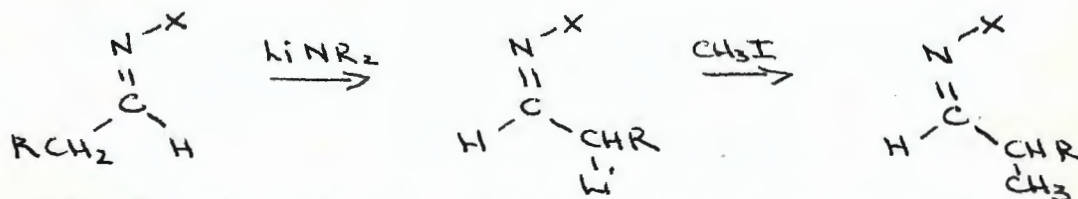
Table I presents the theoretical data in the literature and the four values currently on record. Table II presents our data which clearly shows A) $^1J_{syn} > {}^1J_{anti}$ and B) little resemblance to theoretical predictions.

The significance of the consistently greater $^1J_{syn}$ values lies in its use for assignment of configuration. For example, the two measured values for the pivalaldehyde imines in Table 2 are a strong indication of the <u>anti</u> configuration. Our paper on this topic should appear shortly.

Yours sincerely

Bob

RRF:cmg

Robert R. Fraser.

TABLE 1. Calculated Values for $^1J_{C-H}$ in $R_2C=N-X$

Compound	$^1J_{syn}$	$^1J_{anti}$	Reference
H, OH — C=N — H	186	167	(1)
CH₃, OH — C=N — H and anti	141	131	(5)
	183	122	(3)
	182	160	(1)
	(177)[a]	(163)	(2)
C₂H₅, OH — C=N — H and anti	178	157	(1)
(CH₃)₂CH, OH — C=H — H and anti	(174)[a]	(162)	(4)
H, NH₂ — C=N — H	185	176	(1)
H, H — C=N — H	183	146	(3)
	181	167	(1)
H, CH₃ — C=N — H	176	176	(1)

[a] The values appearing in brackets are values measured experimentally.

TABLE 2. Values for $^1J_{C-H}$ in Carbonyl Derivatives[a]

Compound	$^1J_{syn}$ (Hz)	$^1J_{anti}$ (Hz)
(a) <u>Oxime</u>		
$CH_3CH_2CH=N \sim OH$	173	160
(b) <u>Hydrazones</u>		
$CH_3CH_2CH=N \sim\sim N(CH_3)_2$	174(-20)[b]	155
$(CH_3)_2CHCH=N \sim\sim N(CH_3)_2$	170(-20)	154
(c) <u>Imines</u>		
$CH_3CH_2CH=N-(CH_2)_2\emptyset$	170(-35)	153
$(CH_3)_2CHCH=N-(CH_2)_2\emptyset$	171(-30) [±3][c]	154
$(CH_3)_3CCH=N\sim\sim(CH_2)_2\emptyset$		155(-18) 155
$CH_3CH_2CH=N-CH(CH_3)_2$	170(-20) [±4][c]	151(-25) 152.5
$(CH_3)_2CH-CH=NCH(CH_3)_2$	170(-50)	152
$(CH_3)_3CCH=N-CH(CH_3)_2$		150

[a] unless specified by the figure in brackets, the temperature is 25°C.

[b] temperature at which spectrum was measured appears in brackets.

[c] square brackets indicate the precision, if it exceeds ±2Hz

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5. T. Yonezawa, I. Morishima, K. Fukuta and Y. Ohmori, J. Mol. Spectrosc. <u>31</u>, 341 (1969).

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FACULTÉ DES SCIENCES
Université de Nantes
—

CHIMIE ORGANIQUE PHYSIQUE
E.R.A. : RMN et réactivité chimique
nº 315 - CNRS
—

Nantes,

le 30 mars 1982

Title : ^{2}H labelling without enrichment

Dear Barry,

In figure 1 is displayed a beautiful deuterium spectrum recorded with a well known commercial spectrometer (other interesting natural abundance ^{2}H spectra obtained with several types of spectrometers may also be found in the documentation of the competing manufacturers !). The integrals are also shown, which tend to persuade the reader that counting the deuterium atoms can be done without difficulties. Chemists interested in the structural aspect are certainly gratified with the good quality of the integral since the intensities of the deuterium signals appear to be roughly proportional to the relative numbers of deuterium atoms.

However, inspection of the natural abundance ^{2}H spectrum of commercial ethylacetate (fig. 2) should have given some trouble to the operator. Clearly the intensity of the methylene signal is greater than expected and the situation is even worst with the CH_2D CO-line, which is abnormally small with respect to that of $CH_2 DCH_2-$. A calculation of the molar fractions of the three monodeuterated species I, II, III, gives the following values.

		I	II	III
$CH_3COOCH_2CH_3$	f(i) expected	0.375	0.250	0.375
I II III	f(i) observed	0.305	0.300	0.394

In trying to find a method capable of characterizing the origin of natural products we have recently proved that spectacular differences exist in the internal distribution of deuterium at the natural abundance level (1). In fact, theses results show that ^{2}H quantitative NMR offers a powerful method for measuring selective deuterium contents $(D/H)_i$ ppm. We have therefore at our disposal a new tool for determining the origin of natural and synthetic products (2). This labelling without enrichment also provides an interesting way of investigating chemical and biochemical mechanisms (3) and we are presently very enthousiastic over the various applications of the method which can be developed.

Yours sincerely

Gérard J. Martin

Maryvonne L. Martin

(1) G.J. Martin and M.L. Martin   C.R. Acad Sci II – 293-31-1981
and Tetrahedron Letters 3525-1981

(2) G.J. Martin, M.L. Martin and F. Mabon   J. Amer. Chem. Soc. 1982

(3) G.J. Martin, M.L. Martin, F. Mabon and M.J. Michon
J.C.S. Chem. Comm. 1982

Fig. 1
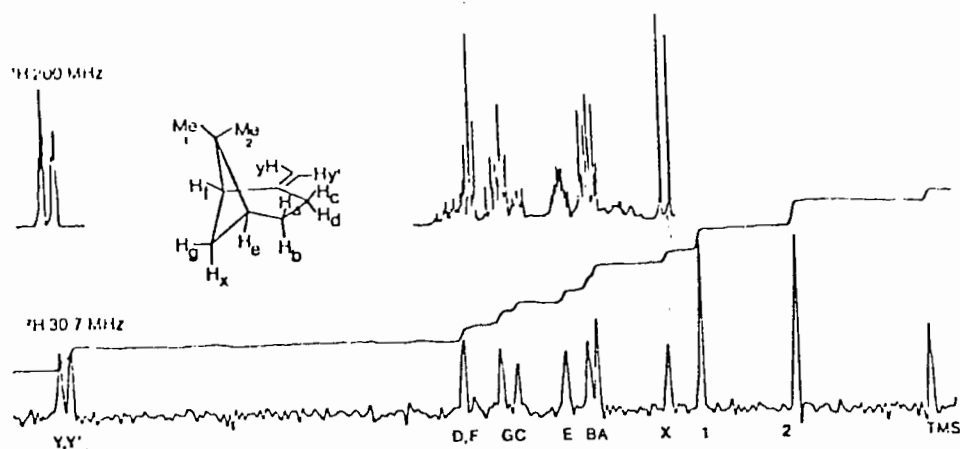
Varian document XL 200

Fig. 2
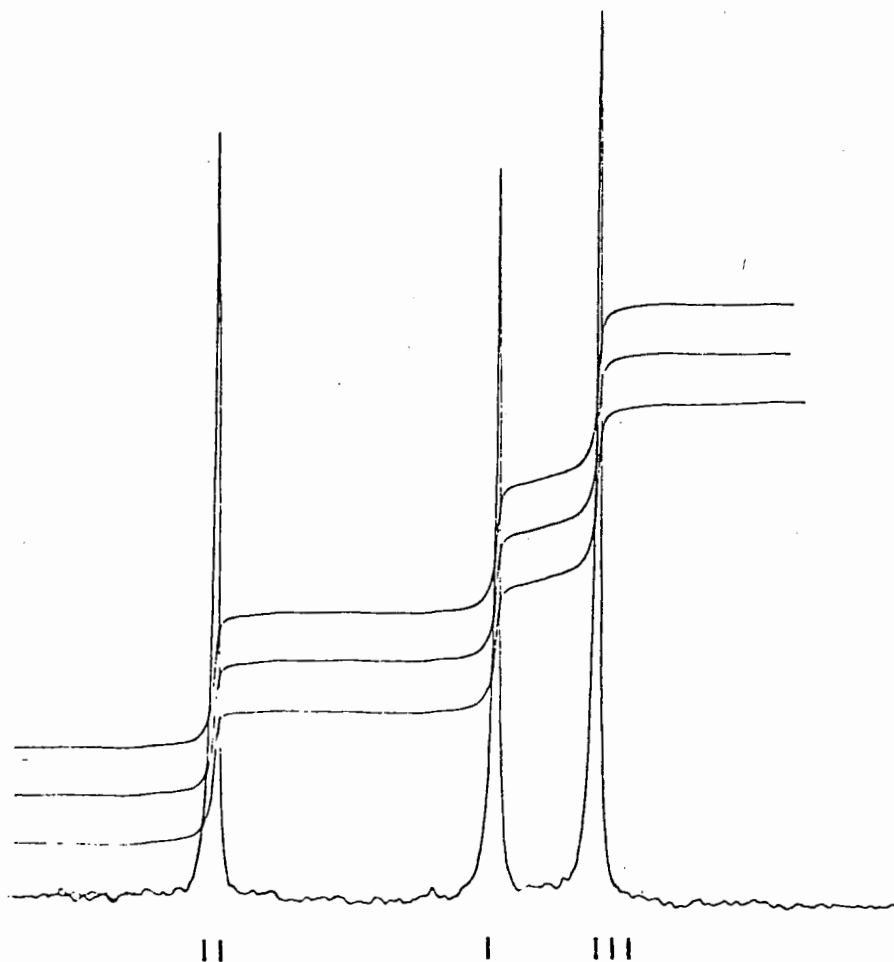
GENERAL ⊛ ELECTRIC

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RESEARCH AND

DEVELOPMENT

March 31, 1982

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

Title: ^{13}C NMR of Phthalimidines

Dear Barry:

We've recently gone back to studies that were initiated several years ago with Ron Markezich (now at Hooker Chemical) who prepared some derivatives of 3-phenyliminophthalimidine, 1. The room temperature ^{13}C spectrum of 1 clearly shows that presence of anti and syn isomers although the initial reports of the synthesis (1,2) did not mention them. At 120°C the interconversion is rapid, and when the sample is recooled to 38°C the original pattern of the spectrum appears. We are currently examining a series of derivatives to determine the steric and electronic effect of various substituents on the isomerism. The spectrum shown in the Figure was obtained on a Varian CFT-20.

Regards,

E. A. Williams   P. E. Donahue
Materials Characterization Branch
MATERIALS REACTIONS & CHARACTERIZATION
LABORATORY

1. W. Flitch and H. Peters, Angew. Chem. Int.Ed. 6, 173 (1967).

2. J. A. Elvidge and R. P. Linstead, J. Chem. Soc., 5000 (1952).

/jk
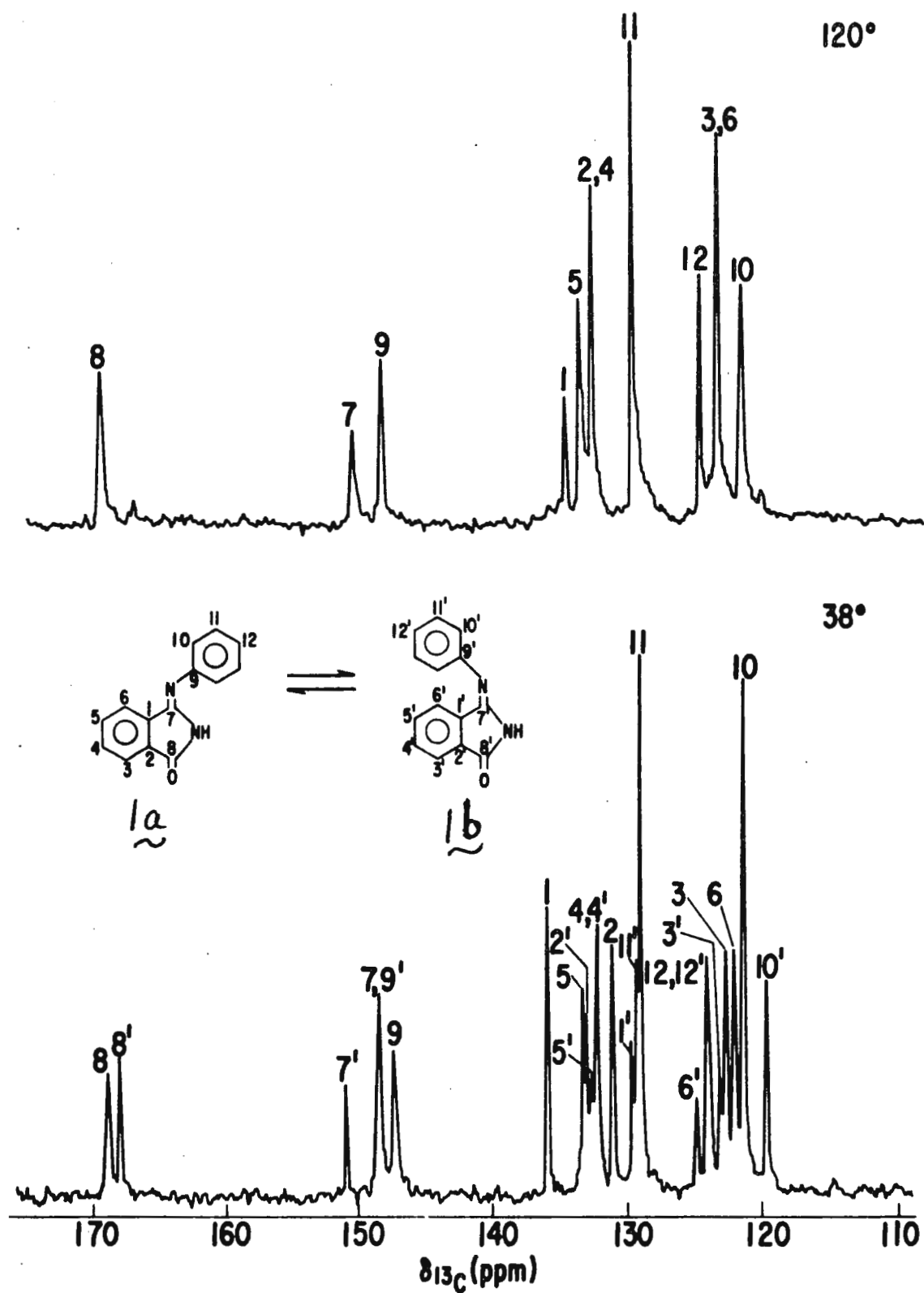
Figure 1. ^{13}C nmr spectra of 3-phenyliminophthalimidine in DMSO-d$_6$ at 38° and 120°.

ISOTOPE DEPARTMENT   מחלקת איזוטופים

Direct phone: (054) 8   (054) 8   :טלפון ישיר

Aesthetic excitation

Dear Prof. Shapiro:

The conventional method of NMR excitation, the application of a strong single-frequency radio-frequency pulse, has the defect that the rotating-frame trajectory of the magnetization vector is a simple arc, so that pictorial representations of the motion of the spins are not of much aesthetic interest. We have been studying another excitation technique which leads to more pleasing excursions of the magnetization vector. The spin system is excited by a multiple-frequency r.f. field, and under good conditions the simultaneous absorption of photons from different frequency components leads to a most aesthetically pleasing trajectory of the magnetization vector, as seen below for three-photon resonances in a spin-1/2 system, using double-frequency excitation fields with parameters shown.
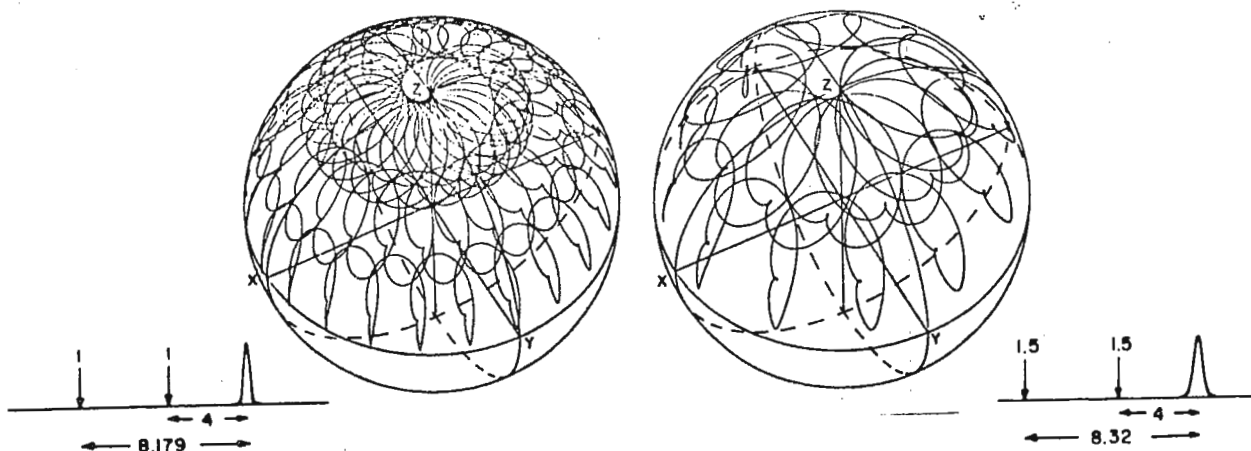
We have conducted an experimental and theoretical study of three-photon resonance in a spin-1/2 system. We have been interested principally in the strength of the effective multiphoton excitation field, the unusual phase properties of the resonances, and the remarkable spiral motion in the rotating frame which can be seen in the computer simulations above.

Aesthetic excitation of spin-1/2 is not the only use we envisage for multiphoton resonance. We anticipate that in higher spin systems multiple-quantum coherences will also appreciate the aesthetic possibilities and get excited about them too. This is now under investigation.

Malcolm Levitt,   Yuval Tsur,   Shimon Vega

Please credit this contribution to Rafi Poupko.

IN REPLY PLEASE QUOTE
REF.

THE UNIVERSITY OF NEW ENGLAND
ARMIDALE, N.S.W.
Department of Chemistry

28th April 1982

Professor B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
COLLEGE STATION, TEXAS 77843.

Dear Barry,

NMR AND RELATED CALCULATIONS ON THE HP-41C

A contribution by M.R. Willcott (TAMUNMR Newsletter, <u>262</u>, 26) finally convinced me more than a year ago to purchase an HP-41C programmable calculator. Your contributor was correct in suggesting it is nearly trivial to program a variety of useful calculations but that it costs a good deal to get the desirable extras (I would include the card reader ahead of the printer/plotter but the recently-announced cassette-tape unit would no doubt be even more desirable).

Although I have not yet completed all details of the programming, his suspicion that an NMR calculation for 4 spins could be fitted in is almost certainly correct, but may be overtaken by his statement: "the speed is not awesome." I have written a program for diagonalization of matrices up to order 6 (as required for 4 spins). Order 3 may take up to 260s, order 4 up to 520s, order 5 up to 20 min or more, and order 6 takes 30-40 min. Apart from diagonalization of the various matrices, arithmetic for the other operations is "nearly trivial" - say, 2-4 min for 4 spins - so the complete calculation would require 50 min or more. A 5-spin calculation would require several hours but the various matrices up to order 10 required as well as program instructions could not be fitted in simultaneously.

Don't misunderstand me! The HP-41C is a very powerful calculator, and the estimated 50 min or so for a 4-spin calculation is to be set off against the several minutes it would take me to go to the nearest (unoccupied) computer terminal, log in, enter the data, and give instructions to execute the program and print the results - then wait an hour or so until the printed output is delivered - when I could have done the whole job without moving from my desk!

I have also written, and make frequent use of, a program to calculate dihedral angles. Up to 10 sets of Cartesian coordinates are first entered; thereafter, a set of 4 points is specified, and the calculation takes about 35s. The program then returns for another set, and so on.

Yours, sincerely,

Noel V. Riggs

P.S. I have composed several <u>avant-garde</u> tunes using the TONE function of the HP-41C, and play them to "soothe the savage breast" in occasional moments of leisure.

DEPARTMENT OF PHYSICAL CHEMISTRY
ÅBO AKADEMI
FINLAND

April 5, 1982

Spin-spin coupling tensors and anti-tensors; Viste's principle

Dear Professor Shapiro,

We have recently been milking our "REXNMR" program[1] which calculates spin-spin coupling tensors using the relativistic equivalent of Ramsey's non-relativistic theory[2] and "REX", i.e. Relativistically parameterized Extended Hückel wave functions[3].

1. Spin-spin tensors and anti-tensors. During the course of the work[1] we were quite shocked to find that some of our tensors violated the Buckingham-Love (1970) symmetry rules. The puzzle was finally solved by ADB himself. The old rules require modification if a symmetry operation exchanges the coupled nuclei (e.g. $^2\underline{\underline{J}}(HH)$ in formaldehyde). Such a coupling "tensor" is no longer a second-rank polar tensor like the other J:s for unexchanged nuclei (e.g.$^1\underline{\underline{J}}(CO)$ in formaldehyde). The name *anti-tensor* was coined for the "exchanged" case and the new symmetry rules derived in ref. 4.

2. Viste's principle. We[5] also applied REXNMR on clusters of up to 20 atoms ($Hg_{10}Te_{10}$) of CdTe, HgTe and PbTe and verified the suspicion that the large observed[6] increase of the anisotropy of the reduced spin-spin coupling tensor, $|\Delta K|$, could be ascribed to relativistic effects. During this calculation, lo and behold, from the morass of semiempirical quantum chemistry emerged a lean and pure Principle: *Both K (if of type $s_A - s_B$ or "contact")and ΔK (if of type $s_A - p_{1/2B}$) are positive if the relevant electronic excitations are of type bonding-to-antibonding, a case likely for half-filled valence shells. If the excitations are bonding-bonding or antibonding-antibonding, both K and ΔK are negative in this simple picture.*

$$K > 0 , \Delta K > 0 \qquad\qquad K < 0 , \Delta K < 0$$

CdTe, HgTe   PbTe

3. Two possible assignments for solid state spin-spin tensors. Both our REXNMR results and the Principle would give for CdTe and HgTe $\Delta K > 0$ while the original experimental references give $\Delta K < 0$. The worse for them, because the absolute sign of the observed splitting,

$$\Delta\nu = J + D' \ (1-3 \cos^2\theta), \quad D' = D - \frac{1}{3} (J_{||} - J_{\perp}) ,$$

is unknown. In the alternative assignment of Nolle's data, $\Delta K > 0$!

The same possibility of two assignments was recently noted by
Tutunjian and Waugh[7] for a $^1\underline{J}$ (PP).

4. The observed, large variations of certain ^1J(PbC) and ^1J(PbPb)
were recently attributed[8] to a frontier-orbital effect: the varia-
tions of J as a function of substituent seem to be due to excitations
from a single MO, the highest occupied σ MO. In systems like $HC{\equiv}CPbR_3$
or $Me_3PbPbMe_3$, this MO has a node near the lead nucleus. Thus very
rapid variations of J are naturally explained.

---

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[8] P. Pyykkö, J. Organomet. Chem. (1982).

[§] On sabbatical leave from Department of Chemistry, Augustana
College, Sioux Falls, SD.

Sincerely yours,

Pekka Pyykkö

OXFORD ◐
RESEARCH SYSTEMS

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

Date   7 April 1982

Our Ref.   REG/SIE

Your Ref.

Dear Professor Shapiro,

The use of NMR to study the biochemistry of living systems has culminated in
the use of surface coils (1), TMR field profiling (2) or a combination of both (3)
for in-vivo investigations in animals and humans.

The ^{31}P spectrum presented below was obtained using the method of reference 3 from
the heart region of a 2.5 kgm rabbit with a 5.5 cm diameter surface coil and the
axial extent of the profiling field set to 3.0 cm. The measurement was carried
out at 32.5 MHz in a TMR 32 200 spectrometer.(900 scans at 2s intervals)
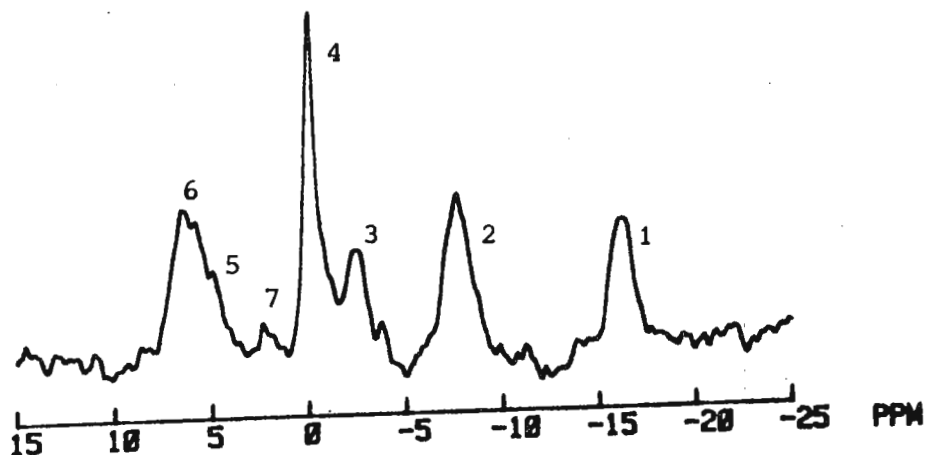
^{31}P Spectrum of the heart region of an anaesthetized rabbit

Signal assignments are 1, 2 and 3, the β-, α- and γ- phosphate, respectively of
ATP; 4, phosphocreatine; 5, inorganic phosphate; 6, sugar phosphate and a
substantial contribution from the 2,3-diphosphoglycerate in the blood; 7, phospho-
diesters. The dominant contribution in the spectrum comes from the heart although
it is likely that there will be contributions from lung and perhaps skeletal
muscle.   /.....
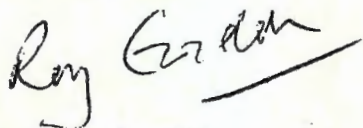
It will now be possible to carry out in-vivo, some of the types of cardiac NMR studies that have so successfully been performed on many intact but isolated preparations.

Please credit this contribution to Dr. D. Shaw's account.

Yours sincerely,

Roy Gordon

DR. R.E. GORDON

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(3) Balaban R.S., Gadian D.G., Radda G.K., Kidney International, 20, 575 (1981).

Southern Research Institute

KETTERING-MEYER LABORATORY

P. O. Box 3307-A
XQXXXXXHNXXHXXXXXXXXXXXXXXXXH
BIRMINGHAM, ALABAMA ▮▮▮ 35255
TELEPHONE   205-323-6592

April 14, 1982

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

Title: New Biochemical Finding?

Dear Barry:

Some of the most interesting NMR work we have done lately has been
in connection with a collaboration of Drs. John A. Montgomery and John
A. Secrist III, of Southern Research Institute, with Dr. Raymond L.
Blakley, of St. Jude's Children's Hospital, Memphis, in the preparation
of analogs of 2'-deoxyadenosine by an enzymatic process.

Certain analogs of 2'-deoxyadenosine have proved to have pronounced
antitumor activity in cell culture and in animals. Recently, significant
quantities of certain 2'-deoxyadenosine analogs have become available by
an enzymatic process. The enzyme, nucleoside deoxyribosyltransferase
from Lactobacillus leichmannii, has been purified and utilized to carry out
the following transformation in quantities (hundreds of milligrams to several
grams) sufficient for animal testing.

Adenine analog + thymidine ⇌ 2'-deoxyadenosine analog + thymine
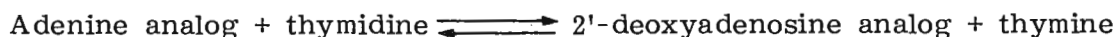
Not all adenine analogs are substrates for the enzyme, and we have supplied
Dr. Blakley with many heterocycles relating to adenine to test as substrates.
In one series of compounds, we supplied Dr. Blakley with various 8-sub-
stituted adenines. These compounds are poor substrates, but do form 2'-
deoxynucleosides slowly. The first compound that was examined was 8-
(trifluoromethyl)adenine. It reacted cleanly to produce one nucleoside,
which Dr. Blakley assumed was the standard 2'-deoxynucleoside 1a. From
the chemical behavior of 8-(trifluoromethyl)adenine and certain characteris-
tics of the new 2'-deoxynucleoside, we suspected that it might not be 1a,
but rather a nucleoside with the 2'-deoxyribose attached at a different site,
most likely the 3-position (2a). Examination of the ^{1}H-coupled ^{13}C-NMR
spectrum of the new compound established it to be 2a.

a) R = CF$_3$
b) R = Br
c) R = Cl
d) R = CH$_3$

a) R = CF$_3$
b) R = Br
c) R = Cl
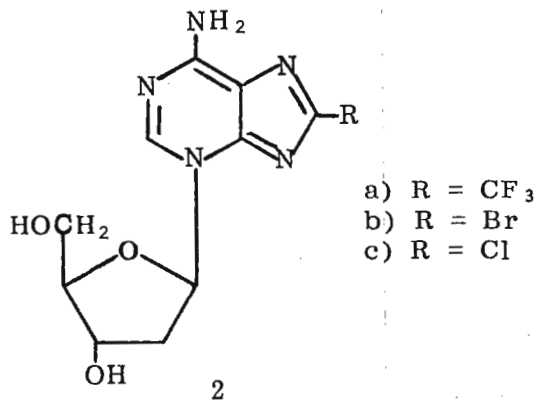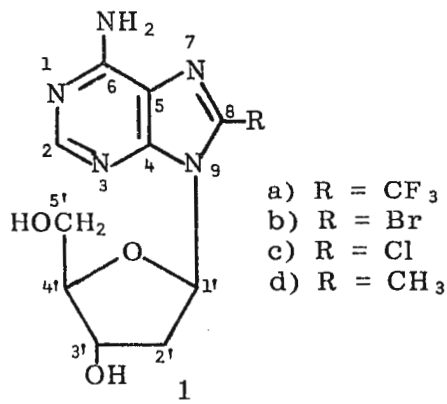
Southern Research Institute

Prof. Bernard L. Shapiro   April 14, 1982

This observation may mean that we are seeing an enzyme which can transfer a 2'-deoxyribose to a site based at least somewhat on electron densities, or that the enzyme may bind the 8-substituted compounds in a different manner for steric reasons, and thereby attach the 2'-deoxyribose at a different site, or some combination of these two explanations. The matter is still under investigation, and other possibilities exist, but if either of these explanations is correct, this observation is an important new biochemical finding. After establishment of the structure of 2a, we sent Dr. Blakley 8-bromoadenine and 8-chloroadenine. Interestingly, in these cases, two nucleosides were formed. These were established to be 1b and 2b for 8-bromoadenine and 1c and 2c for 8-chloroadenine by ^{1}H-coupled ^{13}C-NMR spectra. A key observation which suggests some sort of electronic influence is that 8-methyladenine produces only 1d. To complete the investigation the interconversions (or lack thereof) between 3- and 9-substituted 2'-deoxynucleosides in the presence of the enzyme are being examined.
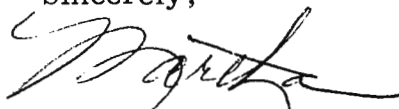
Chemical shifts of these analogs are given below.

Chemical Shift, δ_C, (DMSO-d$_6$)

Carbon	Compound					
	2a	1b	2b	1c	2c	1d
2	143.82	152.33	141.84	152.52	141.92	151.27
4	147.16	149.98	148.07	149.73	147.65	149.82
5	120.42	119.72	121.40	117.96	120.35	118.04
6	157.08	155.07	153.87	155.14	153.99	155.28
8	149.70	126.47	138.73	136.64	149.52	148.66
1'	89.63	86.34	89.70	85.13	89.66	84.41
2'	39.98	37.09	40.00	37.10	39.98	37.86
3'	70.28	71.16	70.30	71.09	70.29	71.18
4'	88.83	88.33	88.86	88.29	88.85	87.98
5'	61.23	62.11	61.30	62.08	61.29	62.12

Data on the coupling constants, and other details, will be given in a publication which is now in preparation.

Sincerely,

Martha Thorpe
Senior Chemist

MT/cpm

28 April 1982

Dear Barry,

"RRRR̄ R̄RRR̄ R̄R̄RR̄ RR̄R̄R RRRR̄ R̄R̄RR̄ R̄R̄R̄R̄ RRR̄R̄

R̄RRR̄ R̄R̄RR̄ RRR̄R̄ R̄RRR̄ R̄R̄R̄R̄ RR̄R̄R̄ RRRR̄ R̄R̄RR̄"

The title is the MLEV-64 version of a new method of broadband decoupling aimed at reducing the radiofrequency power dissipation within the NMR sample compared with the present techniques of noise decoupling, square-wave phase modulation, chirp modulation or the various elaborations of these favored by different NMR spectroscopists. The scheme is based on the use of composite spin inversion pulses (1) which can be shown to be far less sensitive to radiofrequency offset effects than conventional 180 pulses. Several possible composite pulse elements can be designed; one which we have found to be particularly successful is written:

$$R = 90(+X) \ 180(+Y) \ 90(+X)$$
$$\bar{R} = 90(-X) \ 180(-Y) \ 90(-X)$$

These two elements are linked together into a magic cycle (MLEV-4) of the form $(R \ R \ \bar{R} \ \bar{R})_n$ which is repeated continuously (2). A considerable improvement in decoupling (reduction of the residual splitting) is achieved by combining such cycles into supercycles (3), for example MLEV-16 or MLEV-64. The recipe for constructing a supercycle involves two distinct types of operation:

(a) a cyclic permutation of one element of the cycle:
$$R \ R \ \bar{R} \ \bar{R} \ \rightarrow \ \bar{R} \ R \ R \ \bar{R}$$

(b) Phase inversion of all the elements:
$$R \ R \ \bar{R} \ \bar{R} \ \rightarrow \ \bar{R} \ \bar{R} \ R \ R$$

If we call the primitive cycle C, its cyclic permutation P, its phase-inverted counterpart $\bar{C}$, and its phase-inverted cyclic permutation $\bar{P}$, then the first approximation to the next supercycle should contain C, P, $\bar{C}$, and $\bar{P}$. In some situations not all of these four forms are necessary and the redundant cycles can be discarded without degrading the effectiveness of the decoupling.

We would like to show here a practical test of the supercycle MLEV-16 using the 75 MHz carbon-13 spectrum of ethyl vanillin, chosen because of the wide range of proton shifts between CHO and CH3. The pulse programme was written on the Varian XL-300 spectrometer in the Palo Alto Applications Laboratory. Coherent off-resonance decoupling was used to calibrate the proton irradiation level, giving $\gamma B_2/2\pi = 2.0$ kHz, corresponding to one watt of input radiofrequency power.

The requirement for the speed of cycling means that we must satisfy the condition $\gamma B_2/2\pi \gg J(CH)$. One element R thus required 500 microseconds, and the 16-element supercycle was completed every 8 milliseconds. There were no intervals between radiofrequency pulses, between elements, or between cycles, the decoupler being left on continuously but subjected to the prescribed sequence of phase shifts to give MLEV-16:

$$(R\ R\ \overline{R}\ \overline{R}\quad \overline{R}\ R\ R\ \overline{R}\quad \overline{R}\ \overline{R}\ R\ R\quad R\ \overline{R}\ \overline{R}\ R)_n$$

The carbon-13 free induction decay was sampled at intervals of 62.5 microseconds giving a spectral width of 16 kHz (quadrature detection). It was convenient to have both pulsing and acquisition controlled by the same computer programme so that the two functions were synchronized, but in fact the alternative of asynchronous acquisition is perfectly feasible and can offer some practical advantages under certain circumstances.

A comparison is made in the Figure with the widely-used techniques of noise modulation (3 kHz clock rate), coherent 100 Hz square wave modulation (4), and frequency-swept square wave phase modulation. In each case the decoupler frequency was centered in the proton spectrum and the same method was used to generate the Overhauser enhancement (square wave), so that it is only the decoupling efficiency which is being tested. The two quaternary carbon resonances (Q) serve as a control, since they are little affected by the choice of techniques. Note that the CHO and CH3 responses, which have proton resonances separated by 2.5 kHz, exhibit intensity variations of more than an order of magnitude.

Yours sincerely,

Malcolm Levitt
Howard Hill
Steve Smallcombe
Bob Jones
Ray Freeman

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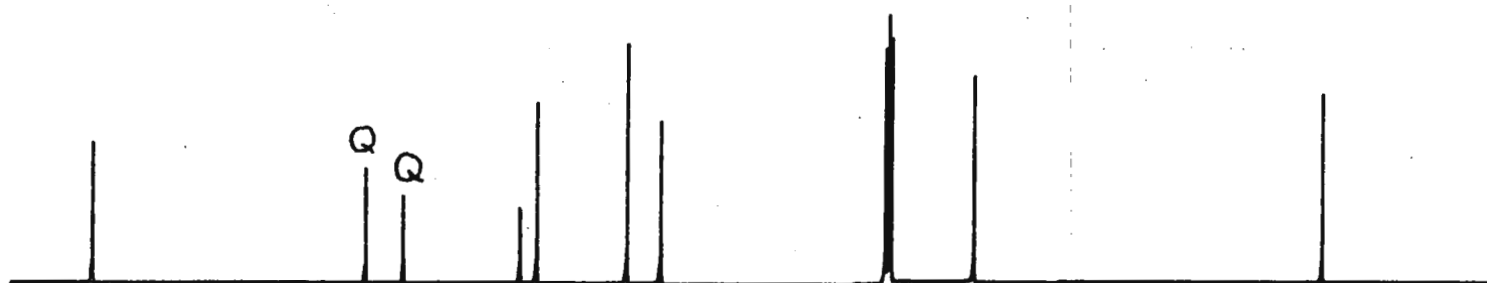
MLEV-16
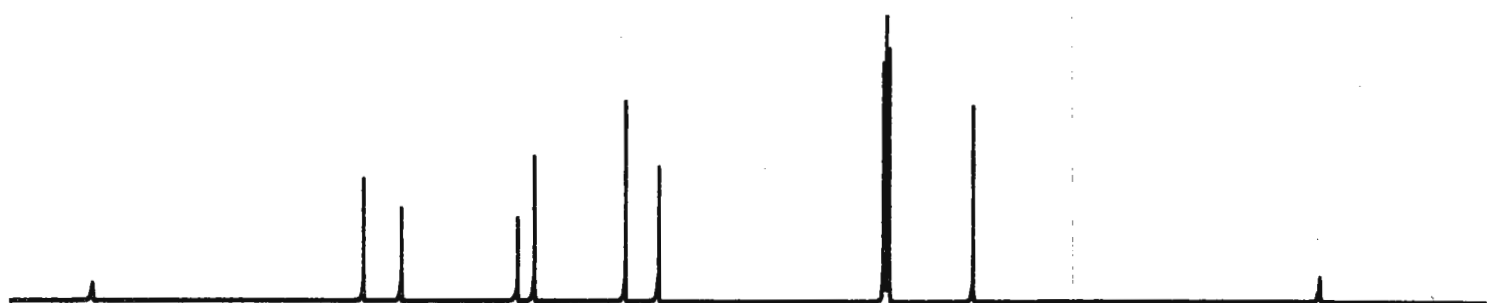
SWEPT SQUARE WAVE

SQUARE WAVE (100 HZ)

NOISE

Carnegie-Mellon University   Department of Chemistry
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213
(412) 578-3149

April 2, 1982

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

Dear Barry:

After 25 years of NMRing, we have accumulated quite a lot of equipment which is beginning to crowd us, but which we are reluctant to throw out because someone might have a use for it.   Below is a partial list. We would consider sale, swap, or outright gift.   If someone is interested, he or she should drop me a line or give me a call (412) 578-3149.

> Two Varian 12" magnets, high impedance
> Tube power supply for above
> One 250 MHz small-bore magnet, Dewar, support, probe
>   support, power supply
> Components of Varian DP-60 spectrometer
> Baldeschwieler lock-box (a genuine antique, suitable
>   for display on parlor mantel)
> Hewlett-Packard signal generator (10-450 MHz)
> Hewlett-Packard 8707A synchronizer for above
> Tektronix oscilloscope camera (C12)
> HD-60 heteronuclear spin decoupler
> Variable temperature unit Hitachi R-20

and, as they say in the ads--much, more more.

Items we would be interested in acquiring:

> General Radio 1164 Frequency Synthesizers (any condition)
> Floppy for Bruker (working)
> Pulse programmers
> Rhodium salts (for plating)
> Shim coils for Bruker large-bore magnet

I promise to write before long on field-dependent spin-spin splittings.

Sincerely,

Aksel A. Bothner-By

AAB/mmg

Yale University

DEPARTMENT OF MOLECULAR BIOPHYSICS
AND BIOCHEMISTRY

Sterling Hall of Medicine, 333 Cedar Street
P.O. Box 3333
New Haven, Connecticut 06510
(203) 43 2-3722

April 15, 1982

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

<u>In <u>vivo</u> ^{31}P NMR Investigations of Solid Tumors by TMR</u>

Dear Barry:

In order to retain, or possibly regain, my subscription to the TAMU NMR Newsletter, I will take this opportunity to inform your readers of a new area of research recently initiated in my group.

This work involves the application of ^{31}P NMR to monitor <u>in</u> <u>vivo</u> phosphorylated metabolites in solid tumors. The original and current impetus behind this work is to determine whether phosphorus metabolites could be used to characterize tumor response to radiation therapy. The rat rhabdomyosarcoma BA1112 was chosen as the tumor model because it is a transplantable tumor, isologous to an inbreed line of WAG/R$_{ij}$ rats and it elicits no demonstrable host immune response. Furthermore, the tumor groups locally at the implantation site and rarely metastasizes. The NMR instrument used for these studies is an Oxford Instruments TMR-32 spectrometer. Figure 1 shows the ^{31}P spectrum of the tumor at 32.4 MHz obtained with one-turn (20 mm dia.) surface coil. Pertinent acquisition parameters are shown on the spectrum. From the technical standpoint, disregarding tumor models and size, it is perhaps of interest to compare the resolution and sensitivity in this spectrum to the ^{31}P tumor spectrum reported by J.D. Glickson <u>et</u> <u>al</u>. in issue #281 of TAMU NMR newsletters which was obtained at a higher (2.5 times) field. Significant and reproducible changes are observed in the ^{31}P NMR spectrum in response to radiation therapy which will not be discussed here. Suffice to say that we are very encouraged with our observations to date and that we are actively pursuing this work.

With best regards,

Ian M. Armitage   Catherine T. Hunt

Figure 1.   In vivo ^{31}P NMR of Murine Rhabdomyosarcoma BA1112.

TMR-32 SPECTRUM

Nucleus	P
# Scans	512
Acq. Time	.410 S
Spec. Width	2500 Hz
Exp. Weight	10.000 Hz
C.D. Weight	200.000 Hz
C.D. Factor	.900
Pulse Length	4 uS
Delay	2.000 S

SP = Sugar Phosphates
Pi = Inorganic Phosphates
GP = Glycerol Phosphates
PCr = Phosphocreatine

OSU
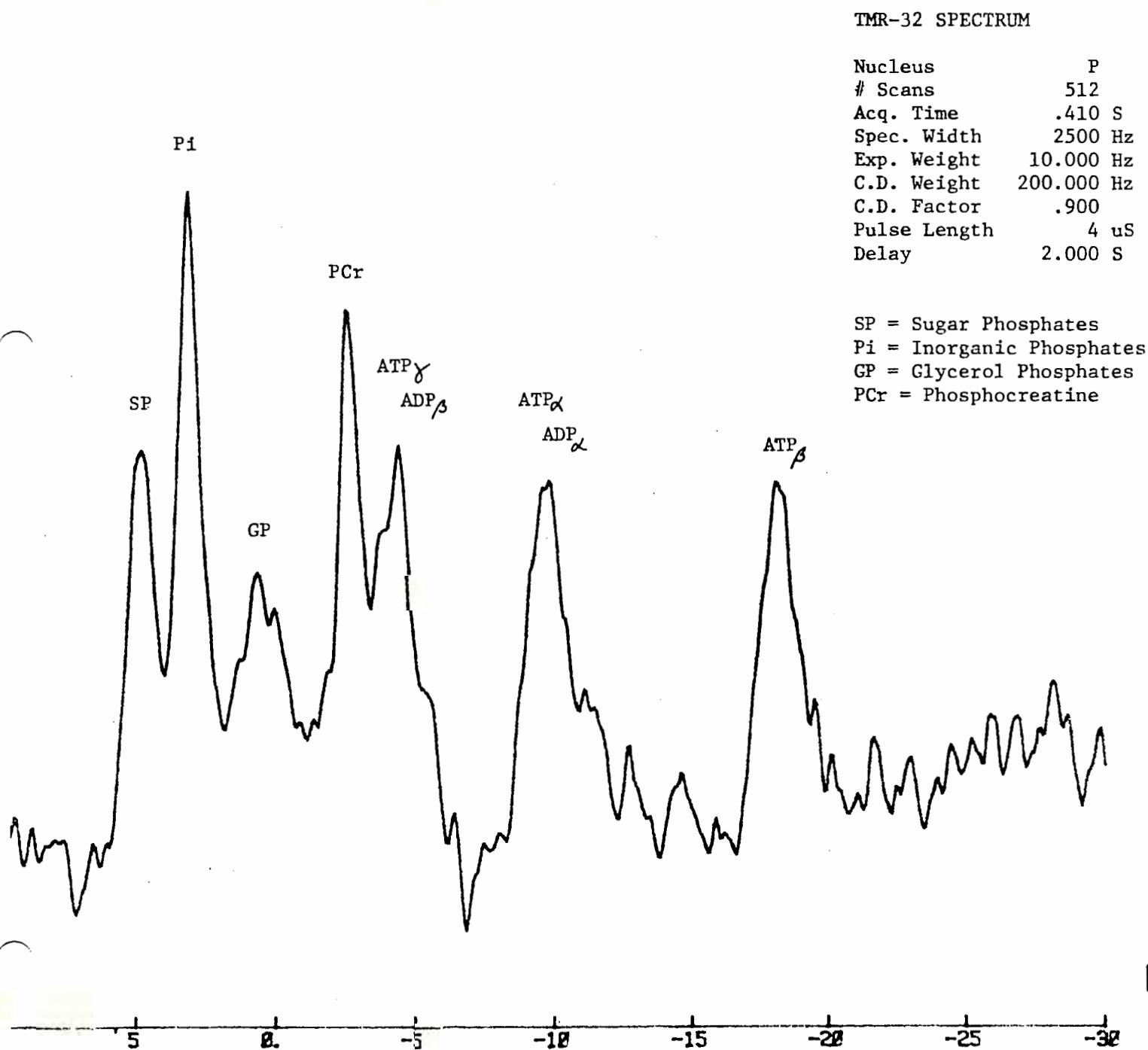
The Ohio State University

Department of Chemistry

140 West 18th Avenue
Columbus, Ohio 43210

Phone 614 422-2251

Campus Chemical Instrument Center
Alan G. Marshall, Director
(614)-422-3446
20 April, 1982

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

Two Chemical Shifts for A Single Chemical

Chemical Environment: DISPA Analysis of

^{23}Na in Sodium Laurate

Dear Barry,

One of the most fundamental axioms of experimental NMR is that nuclei with the same chemical environment must have the same Larmor frequency. However, quadrupolar nuclei of spin 3/2 (e.g., ^{23}Na, ^{35}Cl, ^{81}Br, etc.) exhibit two types of transitions with relative intensity 3:2 (see Figure 1). When extreme narrowing obtains, all single-quantum transitions have the same energy difference, but for slower motion (e.g., micelles, membranes, macromolecules and polymers), the widths and frequencies of the two types of transitions become different.[1] Although a difference in line width has been observed,[2] there are to our knowledge no reports of the corresponding "dynamic" frequency shift that must also be present.

The effect is important for at least two reasons. First, the two peaks could be misinterpreted as two distinct chemical environments (e.g., free and bound Na^+) when in fact only a single environment is present. Second, the relative positions and widths of the two peaks make possible a direct determination of rotational correlation time from a single spectrum.

Since the effect can easily be obscured by slight mis-phasing of the final spectrum, one needs some other means to demonstrate its presence. The extraordinary sensitivity of the dispersion-vs.-absorption (DISPA) plot to slight deviations from Lorentzian line shape[3] affords a simple and reliable way to visualize the small chemical shift. Figure 2 shows a ^{23}Na NMR spectrum and the corresponding DISPA plot for a milky sodium laurate/lauric acid sample. The observed experimental DISPA plot closely matches that expected for $\omega_0 \tau_C = 6.0$.

Finally, in confirmation of the DISPA result obtained from a single spectrum, the experimental response to a 180°-τ-10° pulse sequence exhibits a two-component recovery,[4] with the faster recovery corresponding to the broader signal. [The usual 180°-τ-90° pulse sequence would have mixed the recovery rates of the broad and narrow components, obscuring the desired separation.[1]]

Sincerely,

Alan G. Marshall
Professor, Chemistry and Biochemistry

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4. Marshall, A. G., Lin, T.-C., and Cottrell, C. E., to be published.

ABSORPTION

$\omega_0 \tau_c = 1.2$

$+\frac{3}{2}$

$+\frac{1}{2}$

$-\frac{1}{2}$

$-\frac{3}{2}$

FREQUENCY
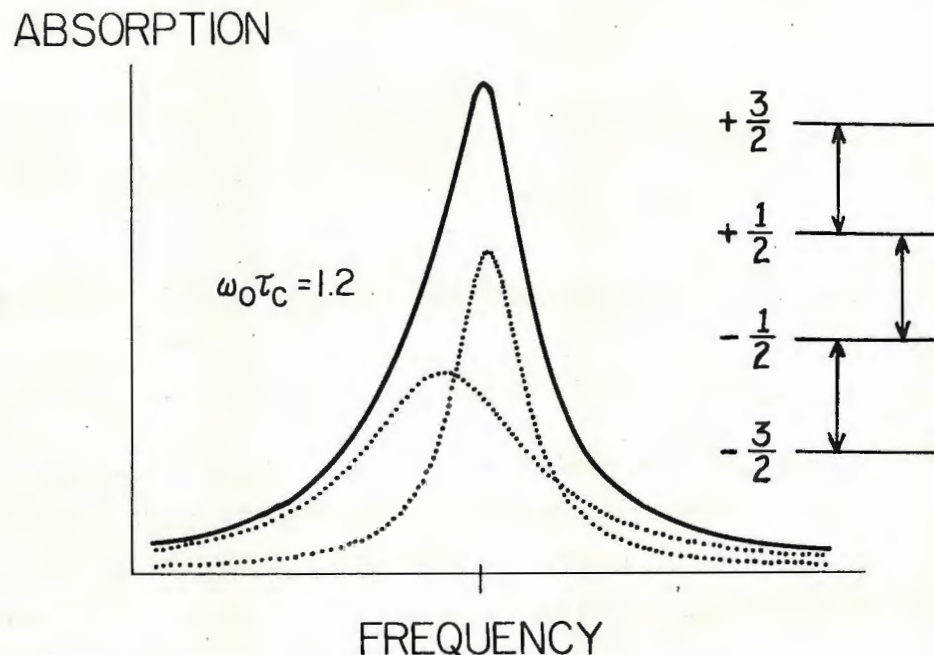
Figure 1. Energy-level diagram (right) and single-quantum NMR spectrum (left) for a spin-3/2 nucleus with rotational correlation time, $\tau_c = 1.2/\omega_0$, corresponding to about 15 nsec for ^{23}Na at 70 kGauss. Note the chemical shift difference between the broad and narrow transitions.

D

A

D

$\omega_0 \tau_c = 6.0$

A

BRUKER

LARNAP2.026
AU TPULS
DATE 16-4-82

SF   79.388
SY   110.39
O1   41100.000
SI   8192
TD   8192
SW   5000.000
HZ/PT   1.221

PW   10.0
RD   .5000
AQ   .819
RG   320
NS   256
TE   297

DE   0
PA   12
FW   6300
O2   4500.000
DP   63L PO

LB   0.000
NC   4
CX   30.00
CY   0.00
F1   2620.17
F2   2557.37
MI   0.00
HZ/CM   2.360
PPM/CM   .030
SR   2000.00

→| 10 Hz |←

Figure 2. Experimental ^{23}Na NMR spectrum for a sample of 20 mM sodium laurate, 5 mM lauric acid, and 120 mM NaCl. The DISPA plot (left) constructed from this data agrees closely with a theoretical DISPA plot (right) computed using $\omega_0 \tau_c = 6.0$.

THE ROYAL INSTITUTE OF TECHNOLOGY
DIVISION OF PHYSICAL CHEMISTRY
S-100 44 STOCKHOLM 70
SWEDEN

Cable address: Technology

Stockholm, April 21, 1982

Professor B L Shapiro
Department of Chemistry
Texas A&M University
COLLEGE STATION, Texas 77843   U S A

^{2}H Quadrupole Splittings from Lamellar Liquid Crystals Containing Nonionic Surfactants

Dear Professor Shapiro,

Recently we have been interested in the interaction between water and non-ionic surfactants with polar groups of polyethyleneoxide type. We have measured the ^{2}H quadrupole splittings from D_2O in lamellar liquid crystals in the systems $D_2O-C_{12}E_4$ and $D_2O-C_{12}E_6$ ($C_{12}E_x$ denotes the nonionic surfactant $C_{12}H_{25}-(O-CH_2-CH_2)_x-OH$). Some results are presented in Figure 1. It is seen that for the composition two water molecules/EO-group the observed splitting is much greater for the surfactant with a polar part containing few EO-groups showing that the water molecules closest to the alkyl chains are more ordered.

For $C_{12}E_4$ with two water/EO-group the splitting decreases monotonously with increasing temperature. For the other cases the splittings increases, passes through a flat maximum and decreases at the highest temperatures. These results indicate that two effects with different temperature dependence might be of importance. Higher temperature of course means increased amplitude of the thermal motions of the wate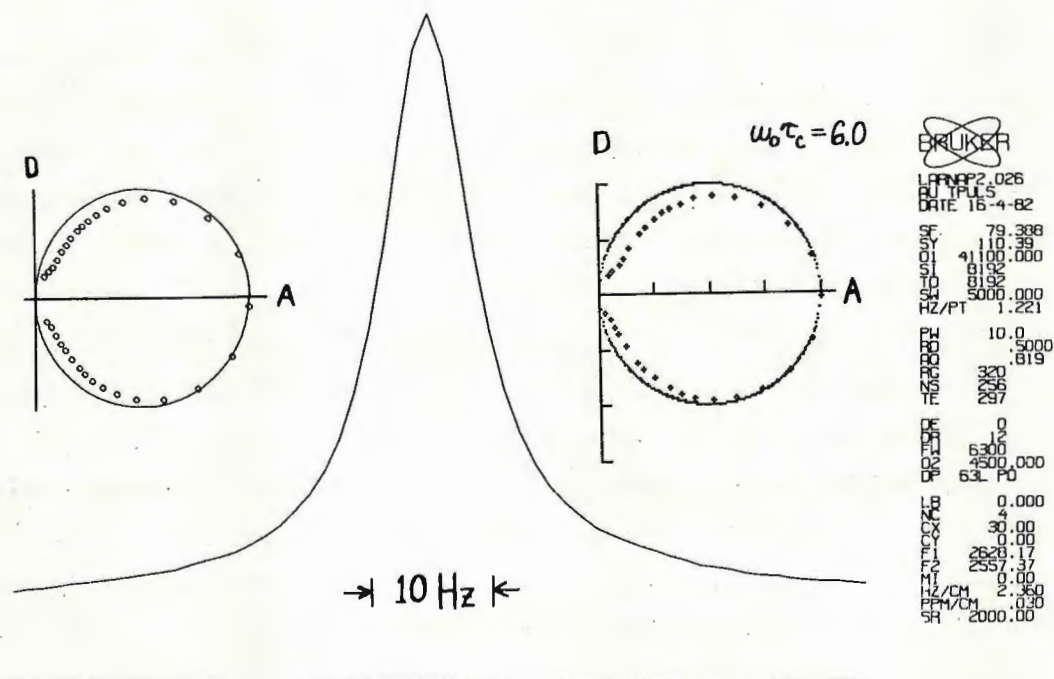r molecules. The order parameters are consequently reduced. On the other hand, the interaction between the hydrated EO-groups is repulsive at low temperature (1). The polar groups are thus forced to be rather well separated and the area/polar group is large. When the temperature is increased the interaction between the polar groups becomes less repulsive and the conformation of the polar parts of the surfactants is probably changed as the distance between the head groups is decreased. This conformation change might be the explanation to the observed increase in Δ with temperature at high water content and low temperature.

Sincerely yours

Ulf Henriksson

Tomas Klason

REFERENCES

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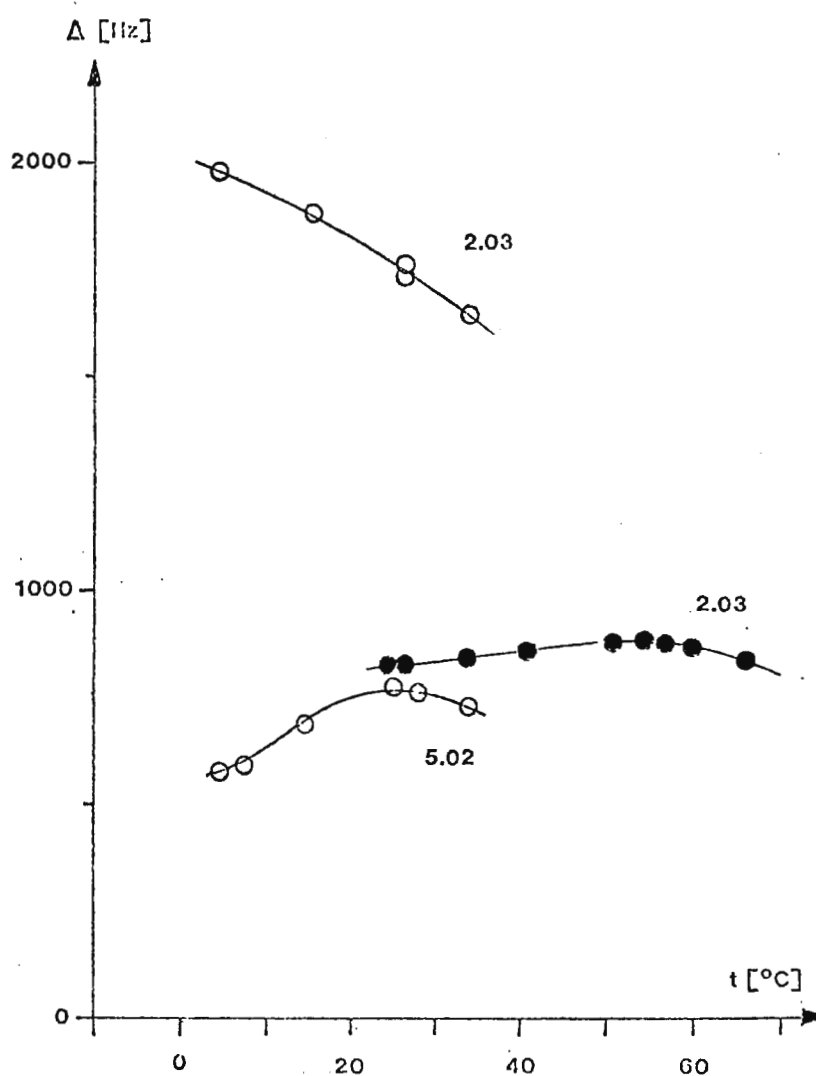
Fig. 1. ^{2}H quadrupole splittings from D_2O as function of temperature at different concentrations. The numbers in the figure are the sample composition expressed as the number of water molecules per EO-group.

o   System D_2O-$C_{12}E_4$

•   System D_2O-$C_{12}E_6$

CENTRO DE INVESTIGACION DEL IPN
APARTADO POSTAL 14-740
MEXICO 14, D. F.

DEPARTAMENTO DE QUIMICA

April 29, 1982

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

Dear Barry:

A SPT Exercise

The SPI-experiment is always a good exercise for students to get a feeling for decoupler power and frequency settings. During my course on NMR taught in the last two weeks at the UNAM and the IPN here in Mexico we therefore tried it with Dr. Joseph-Nathan's XL-100 and a sample of $CHCl_3/CDCl_3$[1]. Lack of a suitable program forced us to time the decoupler manually. It finally worked, not quite SPI but a population transfer sufficient to convince the students that Boltzmann populations can be disturbed.

$^{13}C\{^1H\}$ SPT; single pulse; frequency settings 100,061399 and 100,061608 MHz; decoupler power 33 dB.

Harald Günther
Visiting Professor

Viele Grüsse

Pedro Joseph-Nathan
Professor of Chemistry

1) K.G.R. Pachler, P.L. Wessels, J. Magn. Reson., 12, 337 (1973).

Non-Magnetic Precision Trimmer Capacitors For NMR Applications

Voltronics has developed non-magnetic trimmer capacitors for manufacturers of NMR Spectrometers. The requirement for non-magnetic properties is that in a 14,000 gauss field the capacitor must not distort the usable field by more than 1 part per 600 million. To achieve this, no materials or platings exhibiting measurable magnetism, such as stainless steel or nickel, are used. Typical magnetic susceptability is 40×10^{-6} CGS units.

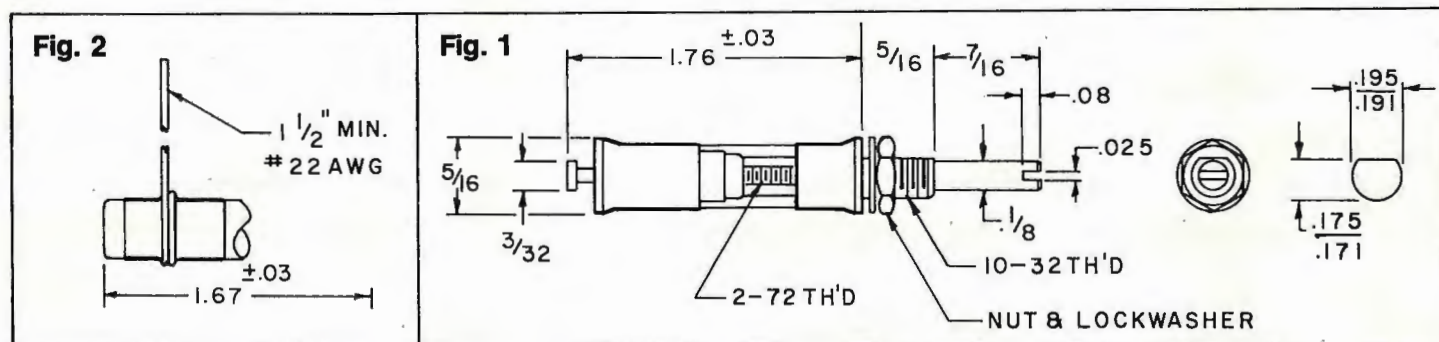The capacitors have Voltronics unique non-rotating piston design which offers 1% tuning linearity without reversals, high Q, long life, and low internal inductance. A slotted 1/8" extended shaft is provided for screwdriver or knob tuning.

Three versions are available with different dielectrics and thus different specifications as listed:

Type	Dielectric	Capacitance Tuning Range (pF)		Q at 20 MHz	DCWV	Outline
		Min.	Max.			
NMTM38GE	Annular Band Glass	1	38	500	1500	Fig. 2
NMTM120CE	Embedded Band Glass	2	120	350	1000	Fig. 1
NMQM22GE	Quartz	1	22	2000	2500	Fig. 2

Insulation Resistance:	10^6 megohms	Construction:	Non-magnetic materials
Temperature Coefficient:	-100 to +500 ppm/°C	Tuning Torque:	3 in. oz. max.
Temperature Range:	-55°C to +125°C	Life:	Stop to Stop - 1000 min.
Withstanding Voltage:	Twice D.C.W.V.	Resolution:	Over 50 usable turns

Notes:
1. The embedded band glass (Fig. 1) has a metal end cap with a turret terminal rather than the rounded seal end of the others. (Fig. 2)
2. No rating is given for RF voltage since we cannot test at high RF voltages at the use frequencies. However, the quartz dielectric should be by far the best, the annular glass next, and the embedded band style the worst since its inner dielectric is only 0.0035" thick.

Prices	Part No.	2-4	5-9	10-24	25-49	
	NMTM38GE	$69.00	$65.00	$60.00	$54.00	Consult factory for larger quantities
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DELFT UNIVERSITY OF TECHNOLOGY
Laboratory of Organic Chemistry

Julianalaan 136
2628 BL DELFT
The Netherlands

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

U.S.A.

Delft, April 22, 1982

Dear Professor Shapiro,

We would like to mention two examples of the use of chiral lanthanide shift reagents in structural analysis.

1. Recently, we have synthesized cis- and trans-2,5-diallyloxy-2,5-dihydrofuran (1 and 2, respectively). The cis/trans configuration

has been determined with the aid of a chiral lanthanide shift reagent. The trans compound 2 has two enantiomers, whereas the cis compound 1 is not chiral. However, compound 1 contains enantiotopic nuclei, which may become anisochronous in a chiral environment.

Upon addition of the chiral lanthanide shift reagent tris(3-heptafluoro-butyryl-d-camphorato)europium(III), we observed in the 200 MHz ^{1}H NMR spectra of both compounds a splitting of the $H_{2,5}$ and $H_{3,4}$ resonances. For one of the compounds the splitting was less pronounced, but that one showed, in addition, an AB pattern for $H_{3,4}$. These ^{1}H NMR data unambiguously show that the latter compound is the cis-isomer 1. The coupling constant observed ($J_{H_3H_4}$) was identical with that obtained from an analysis of ^{13}C satellites.
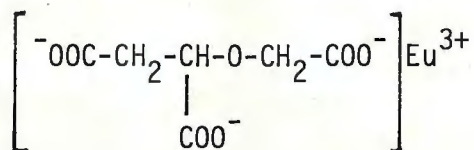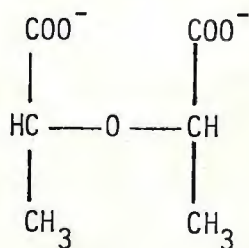
2. For the analysis of some polycarboxylic acids, we have employed a new chiral lanthanide shift reagent for aqueous solution viz. europium(III) (S-)-(carboxymethoxy)succinate ($\underline{3}$). This compound is easily accessible

$$\left[\begin{array}{c} {}^-OOC-CH_2-\underset{\underset{COO^-}{|}}{CH}-O-CH_2-COO^- \end{array} \right] Eu^{3+}$$
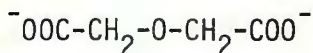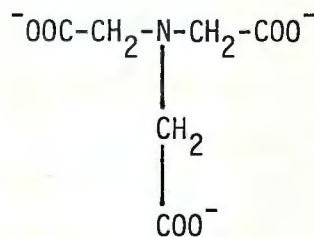
$\underline{3}$

via a 3-step synthesis. It is a solid and can be easily handled. Until now, with the use of $\underline{3}$, we were able to observe spectral resolution of the two enantiomers in racemic oxydilactate ($\underline{4}$) and of the enantiotopic protons of the CH_2 groups of the prochiral compounds oxydiacetate ($\underline{5}$) and nitrilotriacetate ($\underline{6}$). Further investigations on the applicability of this chiral lanthanide shift reagent are in progress.
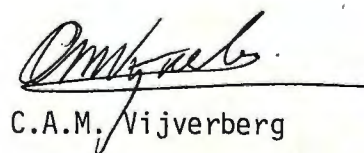
$$\underset{CH_3}{\overset{COO^-}{|}} \quad \underset{CH_3}{\overset{COO^-}{|}}$$
$$HC-O-CH$$

$$\underline{4}$$

$${}^-OOC-CH_2-O-CH_2-COO^-$$

$$\underline{5}$$

$${}^-OOC-CH_2-\underset{\underset{COO^-}{\underset{|}{CH_2}}}{N}-CH_2-COO^-$$

$$\underline{6}$$

Sincerely yours,

M.S. Nieuwenhuizen

C.A.M. Vijverberg

J.A. Peters

A.P.G. Kieboom

H. van Bekkum

ETH
EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE
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Laboratorium für anorg. Chemie

April 29, 1982

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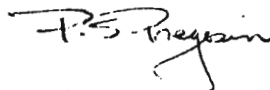CH-8092 Zürich

PD Dr. P. S. Pregosin

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

Dear Professor Shapiro,

One of the advantages of ^{195}Pt NMR (and metal NMR in general) is that the spectra are normally quite simple. This tends to become tedious in that one spectrum looks just like another. We were therefore somewhat refreshed by the ^{195}Pt{^{1}H} spectrum of trans-[PtBr(C$_6$F$_5$)(PEt$_3$)$_2$] shown attached. The two ^{31}P spins and all of the ^{19}F atoms couple to the metal (even though the p-F atom is five bonds away). Further, since the lines are reasonably sharp ($\Delta\nu_{1/2} < 5$ Hz) it would seem that T_2^* is not adversely affected by the quadrupolar halogen.

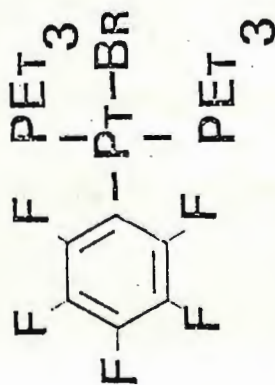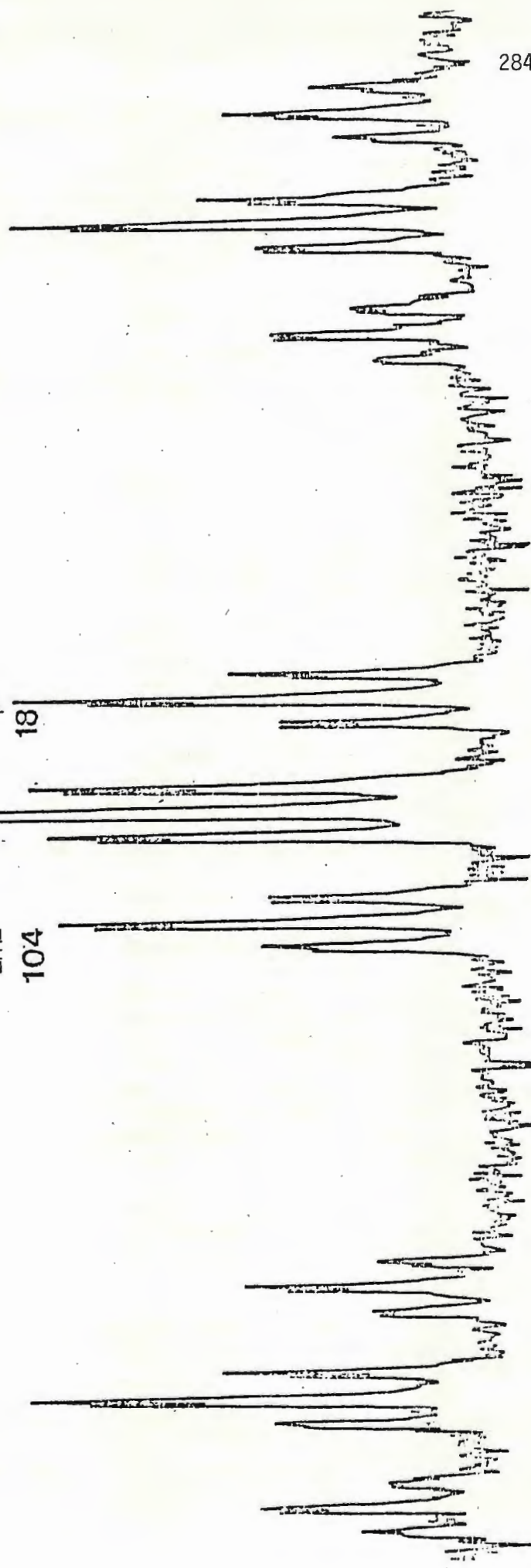Please credit this contribution to the account of Prof. L. M. Venanzi.

Sincerely

P. S. Pregosin

Suggested title: ^{195}Pt NMR Spectrum of [PtBr(C$_6$F$_5$)(PEt$_3$)$_2$]

284-44

^{195}Pt NMR

$\delta = -.4507$

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38041 GRENOBLE CEDEX , France

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

USA

GRENOBLE, LE 23 Avril 1982

Dear Professor Shapiro,

I am looking for a position starting in September 1982 in either Physics or Physical Chemistry or Biophysics.

In 1977 I graduated with a PhD from the University of Grenoble. My PhD deals with relative molecular motions in polyatomic liquids as studied by Intermolecular Dipolar Nuclear Spin Relaxation.

After my PhD studies, I worked on various topics :

1) ground state configuration of arrays of spins ;

2) relativistic band structure calculations of crytals ;

3) Intermolecular Dipolar Nuclear Spin Relaxation as a powerful tool for studying the coupling between the local distribution of the molecules and their dynamics, both in 3-D polyatomic liquids and in adsorbed or inter-calated 2-D polyatomic fluids. I have dealt with fluids of non reactive and reactive molecules. I have developed several models considering both continuous diffusional Brownian motions and finite jumps motions, and based on effective two-particules diffusion equations. I have also performed Monte-Carlo simula-tions of these fluids. I have applied my models to various actual systems.

The principal papers which have been or will be published under topics 2) and 3) constitute my These of State Doctorate (DSc). As you know, the These of State Doctorate is the second dissertation in the French academic system.

I have a Master degree in Pure Mathematics. I taught Applied Mathematics and Physics at both undergraduate and graduate levels.

In summary I am a theorist strongly interested in studying actual systems and in cooperating with an experimental group.
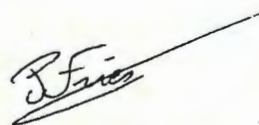
I note the references of some of my last papers :

[1] Comment on nuclear spin relaxation by translational diffusion in liquids : effects of the eccentricity of the nuclei. (E. BELORIZKY, P.H. FRIES). J. Phys. C. Solid State Phys. 14 (1981) L 521.

[2] Effects of eccentricity on nuclear magnetic relaxation by intermolecular dipole-dipole interactions : ^{13}C relaxation of neopentane. (J.P. ALBRAND, M.C. TAIEB, P.H. FRIES, E. BELORIZKY). J. Chem. Phys. 75 (5) (1er Sept. 1981) 2141.

[3] NMR study of a polyatomic physisorbed fluid (P.H. FRIES). Journal de Physique 42 (1981) L 513.

[4] Dipolar nuclear spin relaxation in liquids and plane fluids undergoing chemical reactions. (P.H. FRIES). Submitted to Molecular Physics.

Should you require further information about my scientific career, I shall send you an updated and detailed curriculum vitae and the names of references.

Thank you in advance for advising me about positions that might be available.

Pascal H. FRIES

UNIVERSITY OF CALIFORNIA, DAVIS

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DEPARTMENT OF CHEMISTRY   DAVIS, CALIFORNIA 95616

April 14, 1982

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

RE: Postdoctoral Position Available

Dear Barry:

There will be several postdoctoral positions open in our laboratory during the next eight months. Starting dates as early as July 7 can be accomodated. Our work invovles primarily high field nmr spectroscopy of biopolymers. Hence some experience in nmr spectroscopy would be essential and experience with proteins useful but not necessary.

Our current work focuses on the solution structure and dyanmics of hemoproteins using a variety of isotope labeled hemes. Deuterium nmr of labeled side chains as indicators of internal mobility has shown particular promise, and we are now getting involved in NOE studies of C-13 labels incorporated into the porphyrin skeleton. We are also continuing our study of the dynamic stability of hemoproteins using saturation transfer to exchangeable protons in the protein interior.

Our equipment is excellent, the Nicolet WB-200 is completely multinuclear from 6 to 200 MHz for 12 and 20 mm samples, our Nicolet 360 (also 55 MHz D-2 and 90 MHz C-13) has been upgraded with a 1200 Data System and 293B pulse programmer, and in three weeks we will take delivery of a Nicolet 500 (with 80 MHz D-2). The NT-360 and -500 have compu-shim. Preliminary checkout at Nicolet revealed 0.1% ethyl benzene S/N ~250, so we should be able to obtain excellent S/N with essentially no sample!

Stipends for these positions run between $13,000 and $16,000 depending on qualifications, and include the usual health care fringe benefits. Appointments are for one year and are renewable by mutual consent. Those interested should please send me a curriculum vitae and arrange to have forwarded two letters of reference at their earliest convenience. UCD is an affirmative action-equal opportunity employer.

Sincerely,

Gerd N. La Mar
Professor of Chemistry
Co-director, UCD NMR Facility

GNL/kht

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• Simplified control of spectrometer operations and parameters by using easy keyboard commands.
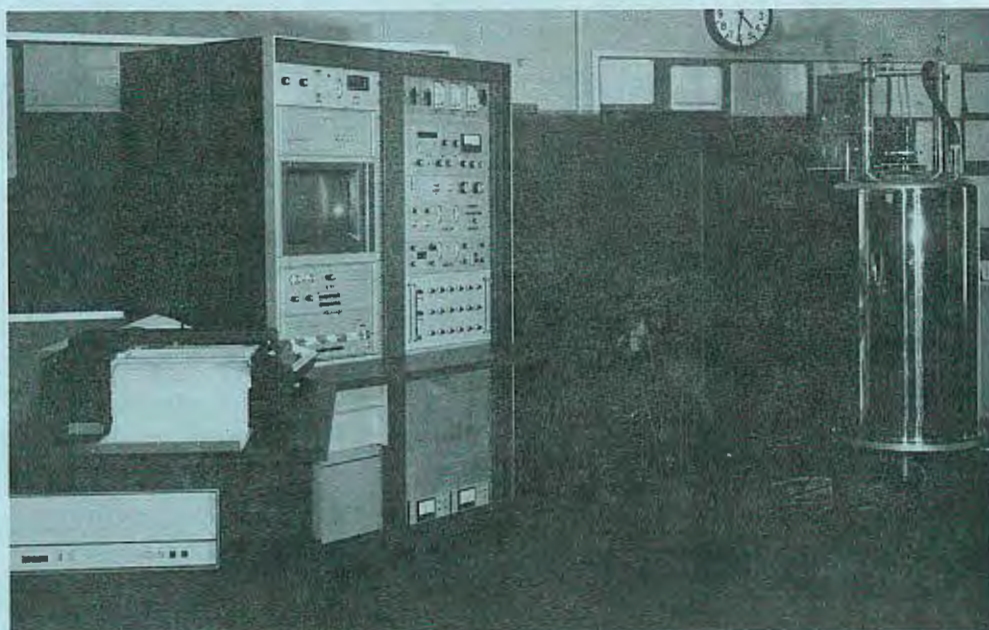
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• Automated T_1 and T_2 measurements.

• Chemical dynamics studies.

• Temperature-programmed experiments.

• ^{31}P experiments on living organs.

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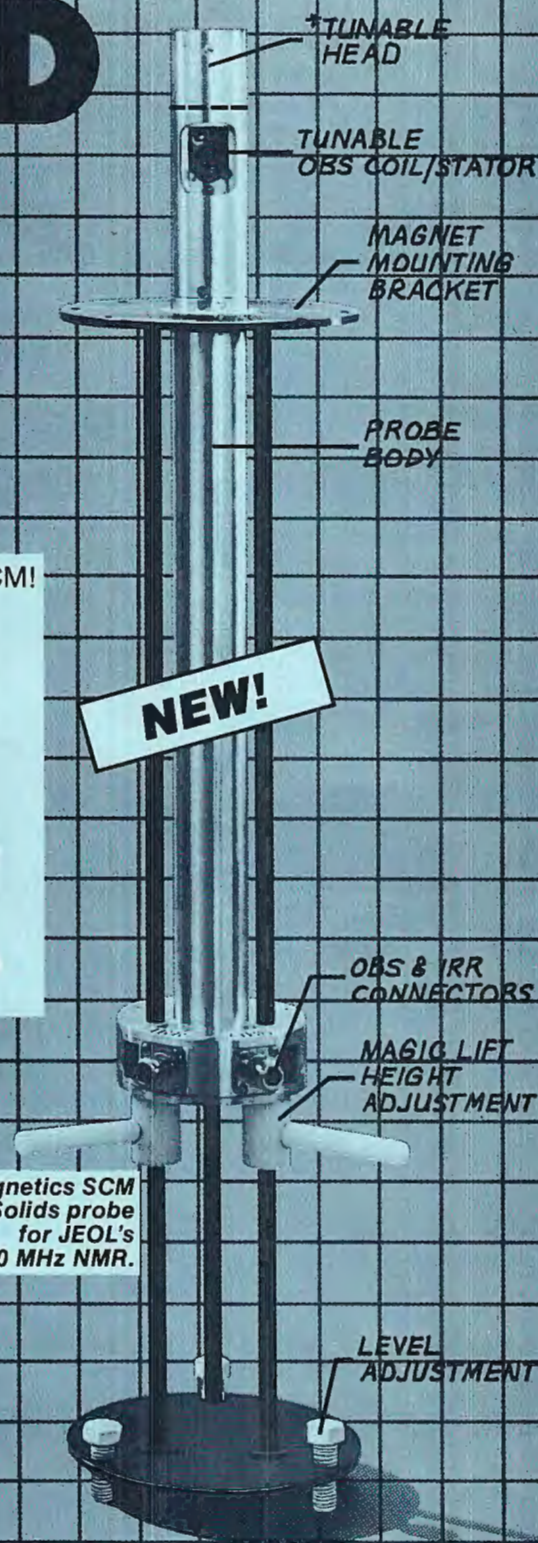Telephone: 415-969-2076