Texas A & M University N – M – R Newsletter

No. 180

September, 1973

All Newsletter correspondence, etc. should be addressed to:

SPONSORS:

Abbott Laboratories
Bruker Scientific, Inc.
Digilab, Inc.
JEOL, Inc.
The Lilly Research Laboratories, Eli Lilly and Company
The Monsanto Company
Unilever Research (U.K.)

CONTRIBUTORS:

The British Petroleum Co., Ltd. (England)
Eastman Kodak Company
International Business Machines Corporation
Dr. R. Kosfeld, Abt. Kernresonanz, Inst. f. Phys. Chemie, TH Aachen (Germany)
The Perkin-Elmer Company
The Procter & Gamble Company, Miami Valley Laboratories
Shell Development Company
Thompson-Packard, Inc.
Union Carbide Corporation

ADVERTISERS:

Glaxo

Glaxo Research Ltd, Greenford, Middlesex

Telephone: 01-422 3434
Telegrams: Glaxotha, London
Telex: 22134
Code: New Standard, Bentleys

5th June, 1973

Dear Professor Shapiro,   Please address reply to:

Manual cycling of A60 nmr spectrometer

Our rebuilt, 1962-vintage, A60 nmr spectrometer (cf. Texas AMU NMR Newsletter, 1971, (152), 8) continues to give good service, but it has become extremely sensitive to magnet cycling. When the machine is switched on, e.g., after an electrical power failure, the setting of the curvature control is usually off-scale, beyond either the top or bottom end of the potentiometer. This fault can sometimes be corrected by turning the magnet field control to the extreme ends of its range for one or two minutes, or if the magnet is over-cycled (i.e., curvature control setting is off-scale at the lower end), by switching the machine off for a few minutes. However, if the magnet is under-cycled (i.e., setting is off-scale at the top end), conventional cycling is too extreme, and inevitably sends the curvature control off-scale at the bottom end.

We have fitted a manual cycling control to cope with this problem. The control can be operated to give any desired cycling time, however short; the normal cycling timer is set for about 20 seconds with the current increase minimised, thus allowing the valve heaters to warm up slightly with the H.T. off.

Two ordinary button-type micro-switches in a push-button holder were wired with one switch (normally open) connected (cf. Varian drawing No. 87-102-706, A964) as shown below, and the second switch (normally closed) connected in series with the H.T. primary fuse (F404): the latter switch turns off the H.T. when increased field current is applied. The 1000 Ω resistor may be varied to suit the particular machine: when its value is small the current increase will be greater. The switches are mounted near the cycling timer thus ensuring that electrical leads are short.
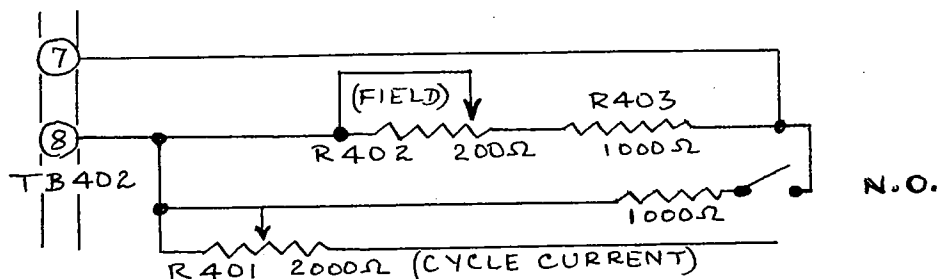
We have replaced the USA3 D.C. amplifier in our HA100 spectrometer by a solid-state unit designed and built by our electronics engineer, Mr. P.C.W. Loughery. He is providing modified units that will be suitable for use in our A60, A60D and HA100 spectrometers.

Dr. J. E. Page   Dr. R.A. Fletton   Mr. G.F.H. Green

NATIONAL CHEMICAL RESEARCH LABORATORY

OF THE SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

Telephone 74-6011 Telegrams NAVORSCHEM

<u>Air Mail</u>

P.O. Box 395

OUR FILE   YOUR FILE   **PRETORIA**

60/6 – Pach.

Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
<u>COLLEGE STATION</u>
Texas 77843
U.S.A.

Dear Prof. Shapiro,

^{13}C CONTACT AND PSEUDOCONTACT LIS

Montaudo's letter (TAMUNN 177-1), citing our work, conveniently provides a topic for our contribution.

We believe the anomalies in the ^{13}C LIS of quinoline, (first available to TAMUNN 162-4 readers only, and then to the general public Tet. letters 4033, 1972) are indeed due to contact shift.

We have extended the previous investigation (Eu and Pr LSRs) to some other $Ln(dpm)_3$ complexes Nd, <u>Gd</u>, Dy, Ho, Er and Yb. $La(dpm)_3$ at the same maximum concentration caused no detectable shifts.

Line broadening made the determination of Gd ^{13}C LIS difficult, (and impossible for ^1H : see Solomon and Bloembergen's equation) but substantial contact shifts were observed with this reagent.

An analysis was made of the ^1H and ^{13}C LIS produced by all the above $Ln(dpm)_3$ complexes except for Gd on the assumptions.

1 The $Ln(dpm)_3$-substrate geometry is identical for all.

2 The ratios of spin densities (R_i) at the substrate nuclei are identical in each Ln-substrate system, and for C nuclei equal to those observed with Gd.

Expressing the shift of the ith nucleus with Ln as :-

$$S_i^{Ln} = W^{Ln}G_i + V^{Ln}R_i$$

Where R_i is the ratio of spin densities, and G_i the McConnell-Robertson geometric term, the analysis gave W^{Ln} and V^{Ln} for each lanthanide.

W^{Ln}, measures of the relative pseudocontact shifting powers are in good agreement with those calculated by Bleaney[1]. The V^{Ln}, the measures of the contact shifting powers are interesting in that they are smaller in the second half of the series than would be expected for a straight correlation with $\langle S_z \rangle$. The signs of V^{Ln} are the same as $\langle S_z \rangle$ except for Dy where the contact shift is too small a proportion of the LIS for the analysis to give meaningful results.

There appears to be some other property which overlays the $\langle S_z \rangle$ relationship, in the $Ln(dpm)_3$ complexes; this we believe is the degree of covalency in the Ln-quinoline bond. Justification for this can be found in a paper by Boeyens[2] where several properties of $Ln(dpm)_3$ complexes are correlated with bonding.

	W	Bleaney[1]	V	$-\langle S_z \rangle$[3]
Pr	−12.9	−11.0	−4.3	− 3.0
Nd	− 6.3	− 4.2	−4.1	− 4.5
Eu	+ 8.3	+ 4.0	+7.4	+10.7
Dy	−100	−100	−3.0	+28.5
Ho	−30.4	− 39	+1.8	+22.6
Er	+31.3	+ 33	+8.0	+15.4
Yb	+21.5	+ 22	+4.0	+ 2.6

1   B. Bleaney, _J. Magn. Res._, 1972, **8**, 91.

2   J.C.A. Boeyens, _J. Chem. Phys._, 1971, **54**, 75.

3   R.M. Golding and M.P. Halton, _Aust. J. Chem._, 1972, **25**, 2577.

Yours sincerely,

A.A. Chalmers
SENIOR RESEARCH OFFICER

K. Pachler
SENIOR CHIEF RESEARCH OFFICER

ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT MAINZ
LEHRSTUHL III
Prof. Dr. H. Ringsdorf
Dr. G. Montaudo

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

CAN LIS BE USED IN CONFORMATIONAL ANALYSIS ?

Although out of town for a while(Mainz is refreshin gly cooler than Catania in the summer),I wish to entratain your audience on our continuing Lanthanide Induced Shifts work.

We have performed a computer simulation of the observed LIS for a number of α,β -unsaturated aldehydes(14), ketones(8),esters(4),and amides(8).
We are also mad enough to claim that the results allow to estimate the population ratio between the s-cis and s-trans conformers in these compounds. Aldehydes,in agreement with previous literature, are found predominantly in the s-trans form. Ketones and esters are found to exist as mixtures of the two forms, while the s-cis form predominates in amides.

We have also obtained population data for some 2-carbonyl derivatives of furan and thiophene,which are known to be very controversial at the present.

Due to the general agreement of our results with estimates from other techniques,and also because of the internal consistency of our data,we are willing to propose that the LIS method may be use to estimate the s-cis/s-trans population ratio for this class of compounds.

ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT MAINZ
LEHRSTUHL III
Prof. Dr. H. Ringsdorf

D 65 MAINZ, den
Johann-Joachim-Becher-Weg 18-20
Ruf 171
Bei Durchwahl: 17873
oder 17886
Postfach 3980

I am well aware that this claim is likely to stir some nasty comments! As matter of fact,many seem to be lieve that the ligand will necessarily affect the conformational equilibrium of every system.

Our results show that this is not the case at least for the important class of compounds studied.
The Ld location in the complex corresponds always to a "strain free" situation, so that internal molecular adjustements(as changes in the population ratio between the conformers) are not needed to equilibrate the system.

A detailed report of our findinngs and methods will appear in the JACS (November).

Sincerely,

GIORGIO MONTAUDO

7 August 1973

Dear Dr. Montaudo:

I believe.

Yours sincerely,

B. L. Shapiro

RICE UNIVERSITY

HOUSTON, TEXAS

77001

DEPARTMENT OF CHEMISTRY   August 3, 1973

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

RE: Postdoctoral and Technician NMR Openings

Dear Barry:

On September 1, I will formally leave Rice University to join the faculty at Michigan State University. There will be two job openings generated at Michigan State.
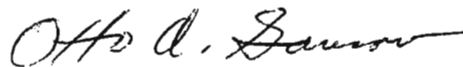
Postdoctoral: I wish to hire a postdoc to do research with me. The nmr research facilities at Michigan State University consist of, at present, seven nmr spectrometers, including a superconducting NMR facility, wide line instruments, an HA-100 and other more routine instruments. Additionally, the Bruker HFX-90 with its superb Fourier transform and multinuclear facility is moving to Michigan State University also. The ideal applicant could either be someone steeped in nmr lore, or a synthetic-inorganic-organometallic chemist with a desire to learn nmr. This is, of course, a pure research and not a service position. If anyone is interested, send a resume to me, at Rice University before September 1, 1973; at Michigan State University after that.

Technician: The Department of Chemistry at Michigan State University wishes to hire a technician whose primary responsibility will be routine maintenance and sample running service on the Bruker HFX-90 NMR. More detailed information may be obtained by writing:

> Dr. R. E. Miller
> Department of Chemistry
> Michigan State University
> East Lansing, Michigan 48123

Some chemical experience is desirable.

Sincerely,

Otto A. Gansow
Assistant Professor of Chemistry

OAG:ka

"The New Resolution"

After frequently adjusting the resolution of Varian NMR machines one soon realises there are too many controls. With a little experimentation it is soon found that only four of these controls are necessary and the remainder are not necessary.

The following controls are necessary X, Y, Z and CURV and the remainder are set at their zero current readings and never used. The X, Y, Z and CURV controls are adjusted with the sample non spinning while observing the lock signal on the oscilloscope. The controls are at first adjusted for a maximum peak height and then a check made that the signal collapses down the centre of the scope when the X and Y controls are offset. If this does not occur the position of probe is adjusted in the magnet gap until a position is found where the signal collapses in a vertical direction.

Next the instrument is "locked on" with a spinning sample and the Y and CURV controls adjusted in the following manner:- first they are adjusted for a maximum lock signal, then one is offset slightly and the other re-adjusted for a maximum lock signal, repeat this procedure until no further improvement can be obtained. Then stop the sample spinning and controls X and Z are adjusted for an optimum lock signal.

This procedure for adjusting the Y and CURV controls while spinning and the X and Z controls non spinning is carried out alternately until no further improvement can be obtained.

During the routine operation of the instrument only the offsetting procedure for Y and CURV controls need be carried out to keep the instrument at its peak of performance. Always use the lowest possible HI and the highest possible lock gain at all times. Also always use filtered and degassed samples in thin wall tubes for best resolution.

The procedure has been used for two years on a Varian HA100 andXL100/15 and no difficulties have been experienced with obtaining superb resolution.

Mr. P.W. Haylett,
NMR Technician.

University of East Anglia
England

31st July, 1973.

H/E

Instrument Division Research D299.   August 3rd 1973

Professor B. L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station,
Texas 77843.   "Loch Ness Monster; change of address"

                                   Water
Sehr geehrter Herr Professor, wie geht-es ?
                                  ^
        You will at once recognize this as an attempt to measure out
the absolute minimum of information necessary to keep the blue note
from becoming acidic.

        At some time or other, many of us fall into the trap of
claiming that two nuclei are "not coupled" or have a "zero" coupling
constant, when all we really know is that the J-splitting is totally
obscured by the instrumental line width.   Fortunately this is an
academic point for almost all NMR purposes, at least until someone else
runs the same spectrum under much higher resolution.   Spin echo work
is a notable exception.   If a homonuclear J-splitting is well-resolved,
spectra derived by Fourier transformation of an echo at the end of an
interrupted Carr-Purcell sequence, exhibit a progressive phase modulation
of the lines as a function of the length of the sequence.   The phase
modulation of different multiplet components is symmetrical about the
multiplet center; in a doublet for example, the two components rotate
their phase angles in opposite senses.   In contrast, if there is an
unresolved doublet, interference between the two phase modulated
components results in an amplitude modulation at a frequency J/2 Hz.

        Proton spectra derived from spin echoes from 2,4,5-trichloro-
nitrobenzene have a small (0.4 Hz) para coupling which shows this:
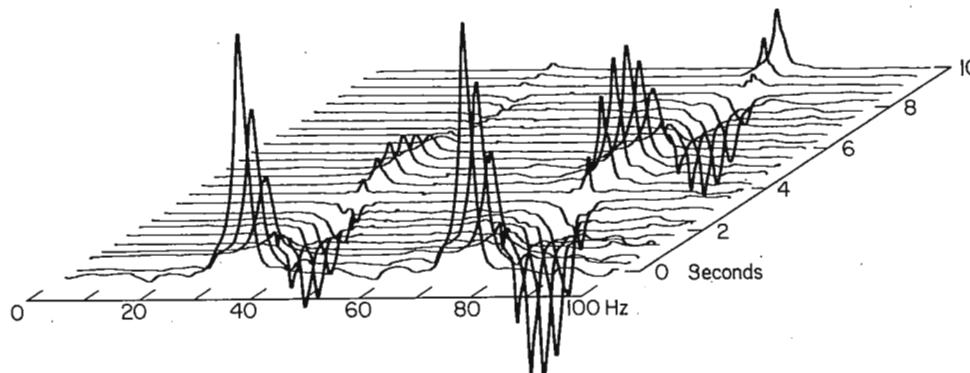
The serpentine effect has been emphasized by recording the spectra with
a chisel point felt pen.   There is a lot more about spin-spin relaxation
in a research report (No. 104) of which a few reprints are still available.

        From October 1st 1973, my new address will be:
                    Physical Chemistry Laboratory,
                    South Parks Road,
                    Oxford, England.

I would very much like to remain a contributor to your excellent Newsletter.
                                   Kindest regards,

                                   Ray

                                   Ray Freeman

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO   SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY
REVELLE COLLEGE

POST OFFICE BOX 109
LA JOLLA, CALIFORNIA   92037
August 8, 1073

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

Dear Barry,

Your nasty pink letter arrived while we were hard at work
trying to prevent you from missing your putts because of air-
craft intruding into the airspace over Torrey Pines Golf Course!!
We think you ought to be more grateful in the future. You can
rest easy, though, it appears that that international airport
will not go in.

Now, since our ancient Varian magnet power supply is down
- hopefully temporarily - we are confined to gedanken experiments:
Suppose we have a perfectly homogeneous H_o and two sets of spins A
and B, chemically shifted (but same γ) and with no scalar coup-
ling. Suppose further that the only relaxation mechanism is intra-
molecular dipolar interaction modulated by isotropic molecular
tumbling.

After a non-selective 180° pulse the recovery of each line
will be a single exponential with rate constant $R_1 = 1/T_1 =
3/2 \gamma^4 \hbar^2 \tau_d / r_{AB}^6$. The single exponential and the factor $3/2$ arise
because both A and B are inverted.

After a 90° pulse we record a free induction decay of this
perfect system and obtain a spectrum by Fourier transformation.
The lineshape function can be evaluated explicitly in closed
form for this simple case. In the physically reasonable limit
that the chemical shift is larger than the relaxation rate, the
FID consists of two decaying cosine functions, one for each type
of spin, both decaying at a rate $R_2 = 1/T_2 = \gamma^4 \hbar^2 \tau_d / r_{AB}^6$. That
is, to a very high degree of approximation each line in the spec-
trum is a Lorentzian with width $1/\pi T_2$ Hz.

Thus we have a case of single exponential recovery for the
usual T_1 experiment, single exponential decay following a 90°
pulse, no complicated multiple pulse trains, and well-defined
parameters T_1 and T_2, with $T_2 > T_1$, by a factor of $3/2$.

If T_1 is a measure of the lifetime of a spin in a given
energy state, the uncertainty principle in its usual form says
that the minimum width of a spectral line is $1/\pi T_1$. When our
magnet is working we can actually measure "T_2" > "T_1" - though
not from a single 90°!!

We are, of course, not violating the uncertainty principle
in such measurements, but the correct explanation is left to the
reader.

Best Regards

Bob & Gitte

Bob and Gitte Vold

the Nicolet 1020A is a time averaging system for magnetic resonance spectrometers that gives you results like these:

The Nicolet 1020A is an easy-to-use time averaging system combining unique data processing capabilities with extremely useful display and readout routines.

Using a normalized signal averaging method, the 1020A presents a true average on its built-in 5" CRT display. The complete spectrum (or any expanded portion of it) is continuously displayed throughout the averaging process.

Thumbwheel switches select sweep times from 60 milliseconds to 1,999 seconds for a 2048-word sweep with 4-digit accuracy. The 1020A can provide sweep current to the spectrometer and can compensate for spectrometer field drift when using the Field Stabilization mode. The calibrated sweep widths are front panel selected and can be matched to any spectrometer.

The analog-to-digital converter (ADC) resolution is 12 bits (one part in 4096) for sweep times over 1 second and 9 bits (one part in 512) for sweep times less than 1 second.

Total memory capacity is 2048 words, 24 bits long. The upper 12 bits store the final average while the lower 12 may be used to store the integral. Averaged spectra may be stored in halves of memory and added to or subtracted from one another.

Digital integration is built-in and does not destroy the original spectrum thus allowing simultaneous display of spectrum and integral. Baseline correction can be accomplished during display of the integral to assure optimal results.

Another unique display feature is the ability to expand the displayed spectrum in both the X and Y axes by factors of 2 up to a total expansion of 64 times. (Typical expansion examples are shown to the right). In addition to this analog display a simultaneous numerical display shows the amplitude and address values of any data point selected by a moveable electronic cursor.

Write or call collect for complete details or to arrange a demonstration in your laboratory.

NICOLET INSTRUMENT CORPORATION
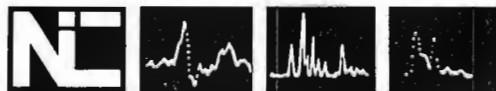
5225 Verona Road, Madison, Wisconsin 53711
Phone 608/271-3333 TWX: 910-286-2713
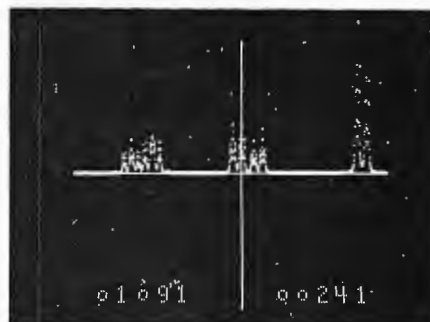
1. Averaged spectrum of 2-butyl-1, 2-dihydropyridene with spectrum expanded on amplitude scale by a factor of 2.

2. Integral of Figure 1 averaged spectrum.
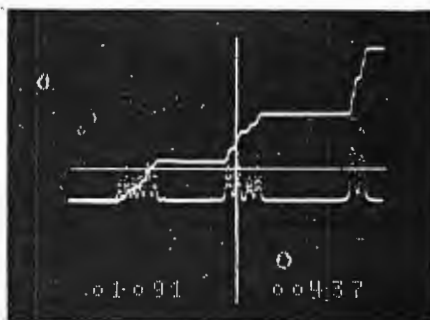
3. Figure 1 spectrum and Figure 2 integral displayed simultaneously.

4. Averaged spectrum expanded by a factor of 4 on both the amplitude scale and the frequency scale.

5. Integral of Figure 4 averaged spectrum.

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

August 14, 1973

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

Subject: Software for Nicolet Systems

Dear Barry:

We have written a small routine for use with FT systems which will
shift the spectrum right or left one or more channels as desired.
The channels at the end from which the shifting was done are cleared
to zero; it is not a circular shift. There are two versions available:
one for the PDP 8/E (EAE) - 1074 combination, a second for the Nicolet
1080. Source tapes are available on request, if the demand is not too
large.

Yours truly,

Rolf B. Johannesen
Inorganic Chemistry Section

University of Waterloo

Waterloo, Ontario, Canada

Faculty of Science
Department of Chemistry

August 8, 1973.

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

Dear Barry,

We have further investigated the large "oxygen" effect on relaxation times of the aqueous Thallium (I)-205 nucleus and carried the oxygen pressure to 5 atmospheres. The enclosed graph shows some typical results. The effect is absent or very much smaller for aqueous $(CH_3)_2Tl^+$ ions but it increases by a considerable factor for Tl(I) solutions in methanol. The increased solubility of oxygen in methanol can account for a bigger effect of oxygen in this solvent but there is a solvent effect since the increase in linear slope is not in the ratio of oxygen solubilities, but less. The huge oxygen effect is absent (much smaller) for the Pb-207 in the aqueous Pb^{++} ion.

From crude gas solubility measurements we determine that within an error of ±10% there is no enhanced solubility of oxygen in aqueous Tl(I) solutions. There is no chemical shift change with oxygen pressure to our limit of detection ~1 Hz. These facts argue strongly against a real complex between Tl(I) and molecular oxygen but support the idea of considerable penetration of the very loose solvation sphere of Tl(I). We have done a fairly comprehensive survey of aqueous thallium NMR and are surprised that these exceptional effects did not come to light before. The relaxation rates in the absence of oxygen are determined by a transient spin-rotation interaction and the same applies to Pb-207 (II) in aqueous solution.

Since Tl(I) is isomorphic with K(I) in many enzyme systems the strong oxygen effect should have real practical use in biological systems.

All best wishes - Please associate this contribution with Dr. Sai On Chan as co-worker.

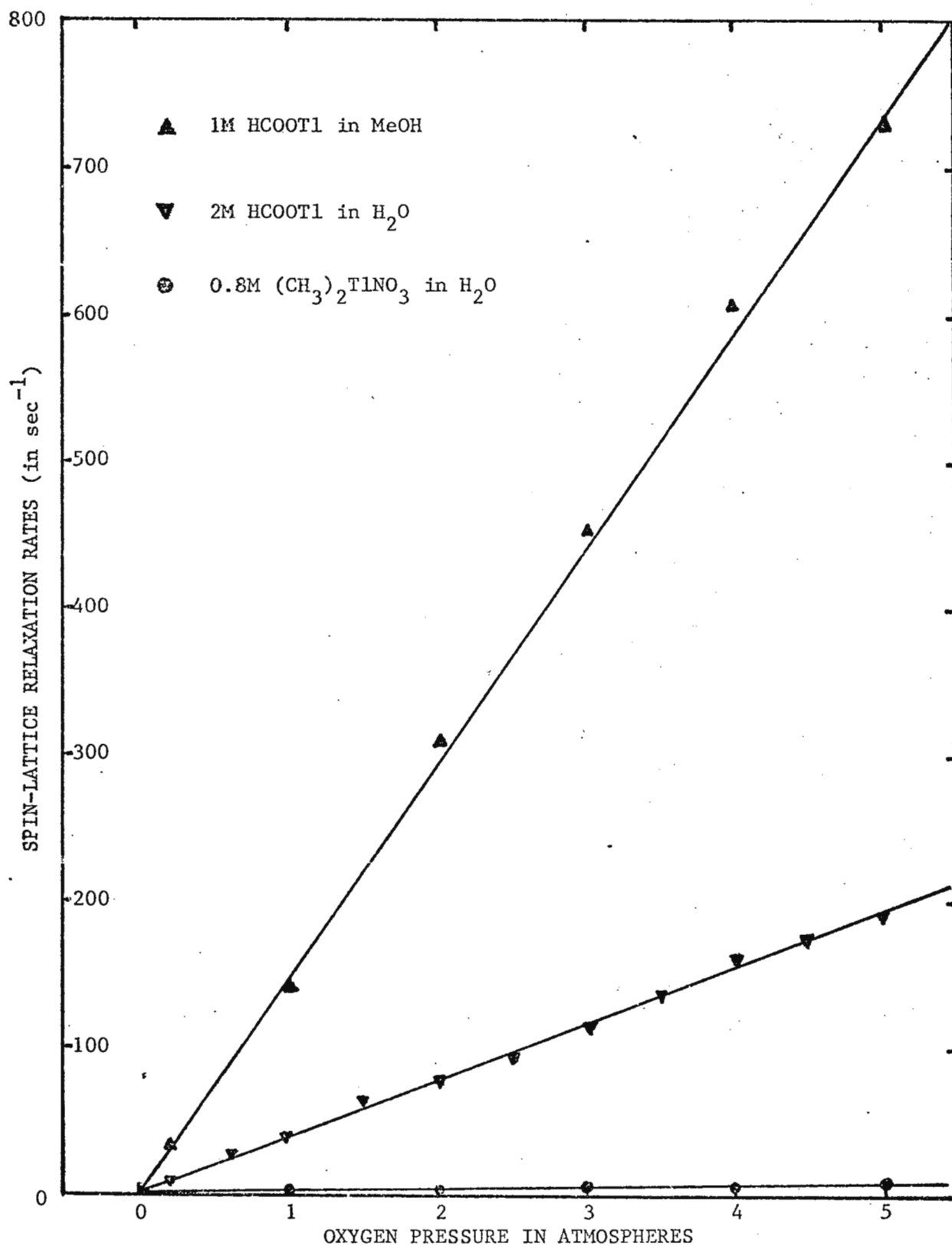Sincerely,

L.W. Reeves.

LWR/ta
Encl.

Fig. 3. Spin-lattice Relaxation Rates vs Oxygen Pressure.

August 10, 1973

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

Dear Barry:

Subject: Lanthanide Induced Shifts with Organic Cations

In the course of studying the cationic dye, 1,1'-diethyl-2,2'-cyanine chloride (pseudoisocyanine), we required some means of simplifying the complicated aromatic pmr band. Although the literature contained no example of a LIS effect with organic cations (in this case, one which possessed no typical liganding group, such as OH, $-NH_2$,-COOH, etc.), we hoped it could, in fact, be observed with this class of compounds, and, therefore, examined $CDCl_3$ solution of the dye in the presence of $Eu(fod)_3$.

For 3 x 10^{-3} $\underline{M}$ solutions of the dye chloride, induced shifts (to lower applied field) were found for each proton type and, for R $\approx$ 1.0, were on the order of -2 ppm. The low dye solubility required $\approx$3000 pulses for good S/N with our FT system. Solutions of the same dye with varied anions (Cl^-,Br^-, I^-, $SO_4^=$) showed that the induced shift, $\Delta\delta$, depends upon the anion. This is shown in Table I in which $\Delta\delta$ decreases in the order $SO_4^=$, $Cl^- > Br^- > I^-$. This, together with the absence of a "classical" coordinating substituent, leads us to conclude that cation interaction with the lanthamide ion occurs in the "outer" sphere by ion-pairing with the anion which complexes the lanthamide in the primary coordination sphere.

Induced shifts were also observed with N-ethylquinolinium Cl^- and with tetraethylammonium Cl^-. In the latter case, $\Delta\delta$ was -3.86 and -7.52 ppm for the $-CH_3$ and $-CH_2-$ protons, respectively, when R = 2.3 equivalents.

Preliminary studies indicate that the stability constants for these outer coordination sphere lanthanide complexes may compare quite favorably and perhaps exceed values found, for example, with ketones.

Dr. Bernard L. Shapiro
August 10, 1973

An account of this work is due to appear in Chem. Comm.

With best regards,

Yours sincerely,

Philip I. Rose
Chemistry Division
Research Laboratories

Richard E. Graves
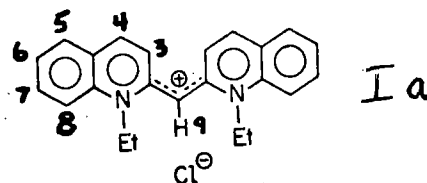Chemistry Division
Research Laboratories

PIR:pff

Ia

Table I

Eu(FOD)₃ induced shift of methyl resonances
at R = 2 for various pseudoisocyanine dyes
in CDCl₃[a]

Dye	Anion	Methyl $\Delta\delta$, ppm[b]
(Ia)	Cl⁻	-1.7
(Ib)	Br⁻	-0.71
(Ic)	I⁻	-0.30
(Id)	SO₄⁼	-1.72[c]

[a][dye] = 3 x 10⁻³ $\underline{M}$. All shifts are referenced to internal TMS.
[b]The chemical shift of the methyl resonance in the absence of Eu(FOD)₃ was -1.68 ±0.01 ppm for (Ia-d).
[c][dye] = 5 x 10⁻⁴ $\underline{M}$.

ORGANISCH CHEMISCH LABORATORIUM
DER RIJKSUNIVERSITEIT TE UTRECHT
CROESESTRAAT 79   UTRECHT, August 8, 1973
POSTGIRO 65985 - TEL. 8 23 11

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

Dear Professor Shapiro:

Title: ^{31}P-Ag coupling constants and ^{31}P chemical shifts of

$[Ag(PBu_3)_n]BF_4$ with n=1-4

The ^{31}P NMR spectra of some silver-phosphine complexes have been measured as a function of temperature and relative ligand concentration. At room temperature a solution of $Ag[P(C_4H_9)_3]_4BF_4$ in CH_2Cl_2 shows a single, somewhat broadened resonance in the ^{31}P NMR spectrum. No silver-phosphorus coupling is then observed.

$[^{107}Ag: I=\frac{1}{2}$, natural abundance 51.35%; $^{109}Ag: I=\frac{1}{2}$, natural abundance 48.65%; $\gamma^{107}Ag/\gamma^{109}Ag=0.87]$.

Clearly the phosphorus atom exchanges between the free state and coordinated sites on different acceptor atoms:

$$Ag[PBu_3]_n \quad \leftarrow \quad \rightarrow \quad Ag[PBu_3]_{n-1} + PBu_3$$
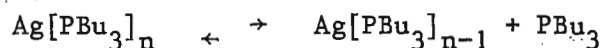
At lower temperatures a P-Ag coupling becomes apparent and at $-80^{o}C$ the obtained spectra consist of sharp resonance lines with each phosphorus resonance split into four lines, of nearly equal intensity, because of the different P-^{107}Ag and P-^{109}Ag couplings. The solution of $Ag[PBu_3]_4BF_4$ in CH_2Cl_2 shows in the nmr spectrum at $-80^{o}C$ the presence of more than one species.

Titration of $AgBF_4$ with PBu_3 in CH_2Cl_2 provides a method to observe separately the four possible $Ag[PBu_3]_nBF_4$ complexes, with n=1-4. Coupling constants and ^{31}P chemical shifts of these complexes are given in the table.

From a detailed nmr study of this spectrum the four dissociation constants and the exchange rates may be obtained.

Considering the ^{31}P chemical shifts, which are at low field from the free PBu$_3$, there is a smooth decrease in the shift difference between the shifts of the complexed and free PBu$_3$ with increasing n.

The coupling constants ^{1}J31$_{P-Ag}$ decrease smoothly with increasing n.

Lucken et al.[1] derived for symmetric complexes of type MP$_n$ the following equation for $^1J_{P-M}$:

$$^1J_{P-M} = -\gamma_P \gamma_M \; \frac{\hbar}{2\pi} \; \frac{256\pi^2}{9} \; \beta^2 |S_P(0)|^2 |S_M(0)|^2 \times \frac{1}{^3\Delta E_{\psi\psi*}}$$

$$\times - \frac{a^2(1-a^2)}{n} \; \alpha^2$$

in which a^2 is a measure of the participation of the metal s-orbital in the metal-ligand bond and α^2 is the s character of the phosphorus hybrid orbital. Assuming all factors except a^2 and α^2 to be more or less constant we may write
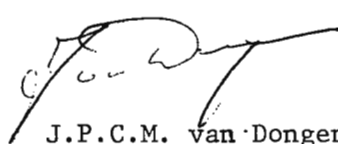
$$^1J_{P-M} = K/n \; . \; a^2(1-a^2)\alpha^2$$

In the table are given the values $n \times {}^1J_{P-Ag}$. For n=2-4 there is only a small decrease of this value, indicating only minor changes in a^2 and/or α^2. For n=1 the value of $n \times {}^1J_{P-Ag}$ is much smaller than expected from the trend for n=2-4. This may be due to a relatively large, abrupt change of α^2 arising from polymeric structures of the complex such as
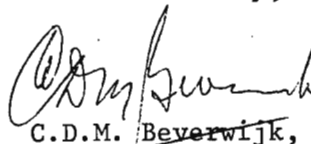
Ag — P → Ag — P →

in which the phosphorus atom is five coordinated. This assumption is supported by the observation that in the 1:1 complex the nmr lines are much broader than in the other complexes whereas it is reasonable to expect that the dissociation constant will be much smaller for the 1:1 complex than for the other complexes. The trend in the chemical shifts may be rationalized in terms of bond rehybridization of the silver atom and the silver-phosphorus bond lengths.
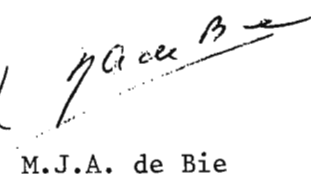
Yours sincerely,

J.P.C.M. van Dongen, C.D.M. Beverwijk, M.J.A. de Bie

Reference

E.A.C. Lucken, K. Noack and D.F.W. Williams, J. Chem. Soc. A, 1967, 148

Table: ^{31}P-data^a for the $Ag(PBu_3)_n BF_4$ complexes at $-80^\circ C$

n	$\delta^{31}P$	$J31_{P-107Ag}$	$J31_{P-109Ag}$	$n \times J31_{P-109Ag}$
PBu_3 (internal)	2.08			
1	35.40	759	874	874
2	32.91	470	542	1084
3	26.63	304	351	1053
4	15.50	219	251	1004

a. chemical shifts in ppm relative to external PBu_3; coupling constants in Hz

Gesellschaft für Molekularbiologische Forschung mbH

D-3301 Stöckheim über Braunschweig, West-Germany
Mascheroder Weg 1

Telefon (0531) 7008-1 — Telex 9-52667

Bahnstation: Expreßgut Braunschweig Hbf
Stückgut Braunschweig HGbf

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

AA'XX'Z Analysis

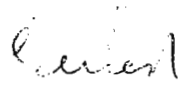| Ihr Zeichen	Ihre Nachricht vom	Unser Zeichen	Tel. Durchwahl:	Datum
	6/8/73 (blue)	Dr.EL/Dr.DNL/UH	7008 . . 222	August 14th, 1973
	8/6/72 (red)			

Dear Barry,

As you know, we are just getting settled at our new location. In the process of tidying up our old work we have written up some of our older research. One paper is dealing with an optimized scheme for the total ^{19}F analysis of pentafluorobenzenes. Tickling experiments have been devised which give the maximum of information for the minimum number of experiments, that is, two. Computer iteration is required for parameter refinement only. The results of one such experiment is presented below:
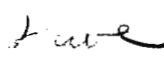
Final parameters from the analysis of pentafluorophenylthiocyanate (Hz); ω's are measured upfield from dichloro tetrafluorocyclobutene.

$J_{23,56}$	$J_{24,46}$	$J_{25,36}$	J_{26}	$J_{34,45}$	J_{35}
-21.76	4.89	7.71	-7.21	-19.61	-0.80

$\omega_{2,6}$	$\omega_{3,5}$	ω_4	rms error
1161.62	3874.25	2733.02	0.03

Sincerely yours,

Ernest Lustig   David N. Lincoln

80-20
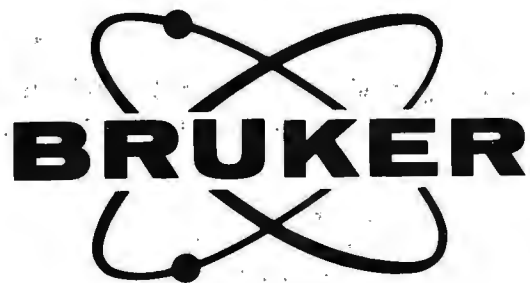
BRUKER

Variable Frequency Nuclear Resonance Pulse Spectrometer

Spin Echo

Fourier Transform

PFP Technique

Double Resonance

NQR

Ferro-Ferri-NMR

SXP 2-200

UNIVERSITY OF LONDON KING'S COLLEGE

TEL: OI-836 5454   STRAND LONDON WC2R 2LS

DEPARTMENT OF CHEMISTRY   10th August, 1973.

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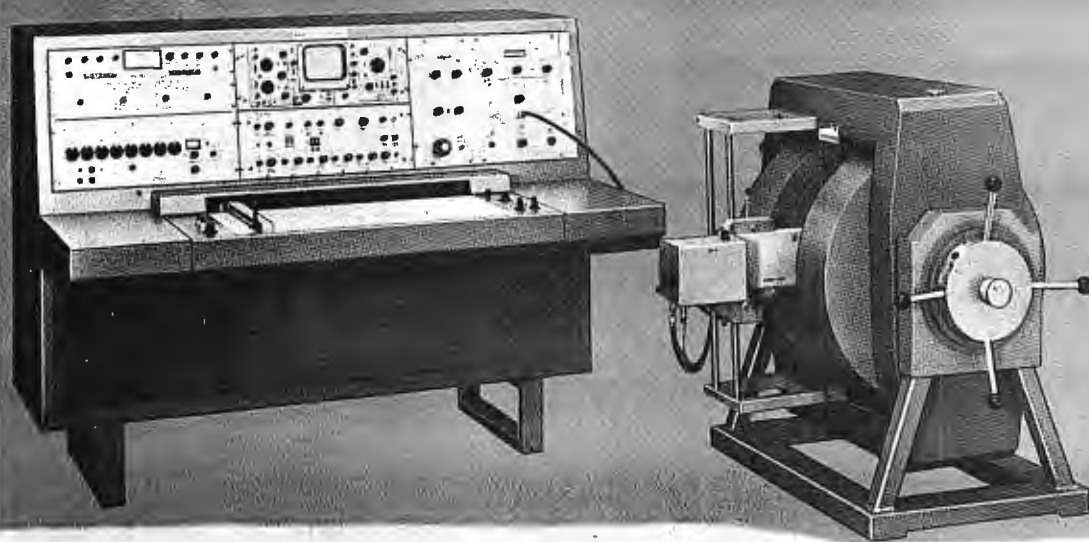Department of Chemistry,
Texas A and M University,
College Station,
Texas 77843,
U.S.A.

Dear Professor Shapiro,

Substituent σ^+ values by ^{13}C nmr.

A simple calculation reveals that I should receive another forty two of your blue letters before retirement so there is still a chance we shall beat you to the draw!

Subsequent to our observations of the ^1H spectra [1], we have utilised occasional spare hours on our Brüker HFX 90 to record the ^{13}C spectra of a series of benzylidene malononitriles (Ia,b).
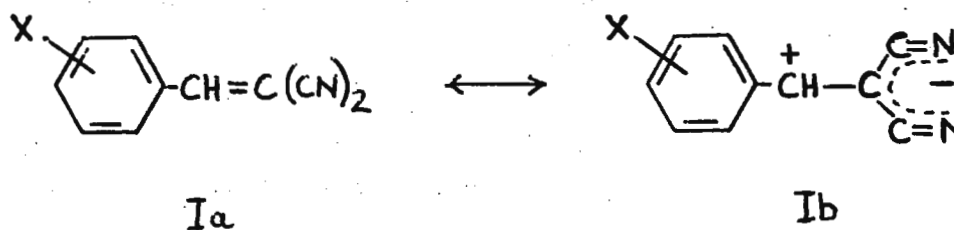
A complete analysis of the spectra will be reported elsewhere but chemical shifts of the α- and β-carbons of the 2,2 -dicyanovinyl group are shown in the Table.

SUBSTITUTED BENZYLIDENE MALONONITRILES

^{13}C Chemical Shifts (ppm w.r.t. ext. CS_2) in Acetone

SUBSTITUENT X	δ (ppm from CS_2)		σ^+	σ
	α- CARBON	β - CARBON		
p-N $(CH_3)_2$	34.5	121.8	-1.7	-0.83
p-OH	33.0 (29.3)†	115.8	-0.92	-0.37
p-CH_3O-	33.7 (28.5)†	115.5	-0.78	-0.27
p-CH_3	32.5	111.9	-0.31	-0.17
H	32.0	110.2	0	0
p-Cl	33.2	109.3	0.11	0.23
p-Br	33.4	109.6	0.15	0.23
p-CN	33.8	106.6	0.66	0.66
m-NO_2	31.7	106.9	0.67	0.71
p-NO_2	34.1	105.9	0.79	0.78

† two signals were observed in the region of 30 ppm which have not as yet, been finally assigned.

The chemical shift of the β-carbon varies over 15.9 ppm and shows an excellent correlation with the σ^+ values of the phenyl substituents (r = 0.996). The correlation with σ (r = 0.962) was markedly inferior and the results indicate that in essence, the substituents serve to stabilise (or destabilise) the positive charge on the α - carbon, formally represented by canonical form Ib. There is of course, little doubt that Ib makes a substantial

contribution to the hybrid[2] and this is reinforced by the observation
that the chemical shifts of all the β-carbons are substantially
shielded in comparison to normal olefinic carbons[3]. The α-carbon
of I is correspondingly deshielded and appears for all compounds,
within a remarkably narrow field width (see Table). The technique
appears to be a useful method of determining σ^+ values.

All spectra were recorded using acetone (+ 10% $(CD_3)_2CO$ for the
lock) as solvent with proton decoupling and a Nicolet Fourier
transform system.

Yours sincerely,

Dennis Hall.

Tamar Posner.

T. POSNER.   C. D. HALL.

1.   R.L. Powell, T. Posner and C.D. Hall, Tamun News, No. 170 p.38 (1972).
2.   S. Patai and Z Rappoport, "The Chemistry of Alkenes" p.469 Wiley (1964).
3.   E.W. Randall, Chemistry in Britain, Vol. 7, 371 (1971).

UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO   SANTA BARBARA • SANTA CRUZ

SCHOOL OF PHARMACY   SAN FRANCISCO, CALIFORNIA   94122
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

August 13, 1973

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

Dear Barry,

Roger Cooke and I have been preparing a review on the properties of water
in biological systems. In the course of this, we were impressed with
recent NMR (1) and dielectric (2) work which suggests that aqueous protein
solutions contain three different water environments. These environments
can be described by the rotational correlation time of the water molecules
for which we find:

Type I Water : $\tau c \sim 3\text{--}10 \times 10^{-12}$ sec.
Type II Water : $\tau c \sim 10^{-9}$ to 10^{-10} sec.
Type III Water: $\tau c \sim \tau c$ of macromolecules or $\geq 10^{-8}$ sec.

The relative concentrations are approximately 1: .1 : .001 for a 20%
protein solution. In brief, Type I water represents most of the water
molecules in such a solution and has often been called "bulk" water. Its
rotational and other properties are very similar to those of normal liquid
water. Type II water has frequently been referred to as "bound water".
These water molecules are thought of as forming a hydration "shell" one or
two molecules deep surrounding the protein. Type III water is held more
firmly and could be considered as "irrotationally bound water". Only a few
water molecules/protein molecule are held in this manner.

The NMR consequences of this model are interesting. If we assume fast
exchange, the observed T_1 for the water will be dominated by the Type II
molecules at frequencies above 1MHz and by Type III molecules at low
frequencies, say 10^4Hz. On the other hand, Tz for the system will always
be dominated by Type III molecules at any observing frequency. Some calcu-
lations for a particular choice of τc's is given in the Table. We are look-
ing into the temperature dependence and $T_{1\rho}$ behavior of such a model.

Reader comments, pro and con, would be much appreciated.

Best wishes,

I.D. Kuntz

IDK:dc

Calculation of NMR Relaxation Times (T_1, T_2) for a 20% Protein Solution using the model outlined in text.

Type of Water	τ_c (sec)	Intrinsic Relax. Time. 100 MHz (msec)		Contribution to System $1/T_1 (sec^{-1})$		$1/T_2 (sec^{-1})$	
		T_1	T_2	100MHz	1MHz	100MHz	1MHz
Type 1	3×10^{-12}	6700	6700	.13	.13	.13	.13
Type II	10^{-9}	40	25	2.51	5.53	4.07	5.53
Type III	10^{-6}	17000	.06	0	0.47	16.59	16.64
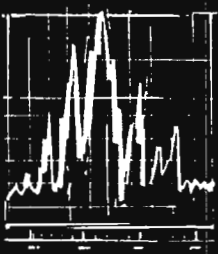
Calculated relaxation times and rates for the total solution:

	T_1 (msec)	T_2	$1/T_{1(sec^{-1})}$	$1/T_2$
100 MHz	379	48	2.64	20.16
1 MHz	163	45	6.13	22.30

References:

1. S.H. Koenig and W.E. Schillinger. J. Biol. Chem. 244, 3283, 1969.

2. S. Harvey and P. Hoekstra. J. Phys. Chem. 76, 2987, 1972.

Compounds labeled with stable isotopes. From Merck...

DEUTERIUM

Alcohols
Aldehydes
Ketones
Carboxylic Acids
Aliphatic Hydrocarbons
Aromatic Hydrocarbons

(partial list only)

CARBON 13

Acetates
Iodides
Cyanides
Glycine
Acetylene
Benzene-(ul)
Carbon Tetrachloride

(partial list only)

NITROGEN 15

Ammonium Chloride
Nitrogen Gas
Urea
Sodium Nitrate
Aspartic Acid
Glycine

(partial list only)

LABELED BIOCHEMICALS

D-Glucose-(ul)-^{13}C
Thymine-^{13}C
Amino Acid Mixture -(ul)-D or ^{13}C
Sugar Mixture -(ul)-D or ^{13}C
Glycine-D or ^{13}C
Acetates-D or ^{13}C
L-Methionine-D or ^{13}C
L-Aspartic Acid-^{15}N

(partial list only)

NMR PRODUCTS

NMR Solvents
NMR Standards
NMR Shift Reagents and Ligands

We make and stock over 500 different compounds labeled with stable isotopes.

And that's not the end of it... In fact by the time you read this we will have a couple more.
Write to us, for everything from chloroform to tris-(1, 1, 1, 2,2,3,3-heptafluoro-7,7-dimethyl-d$_6$-4,6-octanedione-d$_3$) -europium (III), for the most complete range of isotopically labeled compounds available anywhere. We probably have what you're looking for—at "going after your business" prices!

MERCK & CO., Inc. ISOTOPES

U.S.A. Merck Chemical Division, 111 Central Avenue Teterboro, N.J. 07608
Merck Chemical Division, 4545 Oleatha Avenue St. Louis, Mo. 63116

CANADA Merck Sharp & Dohme Canada Limited, Isotope Division P.O. Box 899, Pointe Claire, Dorval 700, Quebec.

Building 2, Room 108   August 16, 1973

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

Dear Barry:

Fourier Transform NMR of Exchanging Chemical Systems

In this letter we wish to show that the transient and steady
state solutions of the modified Bloch equations describing the
response of a spin system undergoing chemical exchange between
two non-equivalent sites form a Fourier transform pair.

The Bloch equations describing the motion of x, y component of
magnetization in the rotating frame as modified to include
chemical exchange are given by (1):

$$dG_A/dt + \alpha_A \ G_A = -i\gamma H_1 \ M_{OA} + T_B^{-1} \ G_B - T_A^{-1} \ G_A \qquad (1)$$

$$dG_B/dt + \alpha_B \ G_B = -i\gamma H_1 \ M_{OB} + T_A^{-1} \ G_A - T_B^{-1} \ G_B \qquad (2)$$

where $\alpha_A = T_{2A}^{-1} - i(\omega_A - \omega_{rf})$, $\alpha_B = T_{2B}^{-1} - i(\omega_B - \omega_{rf})$,

$G_A = u_A + iv_A$, $G_B = u_B + iv_B$, and T_A and T_B

are lifetimes in states A and B respectively. Other symbols
have their usual meaning. The continuous wave response is
obtained by setting $dG_A/dt = dG_B/dt = 0$ which yields (2):

$$G = G_A + G_B$$

$$= -i\gamma H_1 M_o \ [T_A + T_B + T_A T_B(\alpha_A P_B + \alpha_B P_B)]/[(1 + \alpha_A T_A)(1 + \alpha_B T_B)-1]$$

Professor Bernard L. Shapiro
August 16, 1973

where $p_A = T_A/(T_A + T_B)$, $p_B = T_B/(T_A + T_B)$

$M_{OA} = p_A M_0$, $M_{OB} = p_B M_0$

ω_{rf} is the variable frequency.

The free induction signal is obtained by solving the Bloch
equations setting $H_1 = 0$ which yield,

$$dG_A/dt + (\alpha_A + T_A^{-1}) \, G_A - T_B^{-1}G_B = 0$$

$$dG_B/dt + (\alpha_B + T_B^{-1}) \, G_B - T_A^{-1}G_A = 0.$$

On solving the differential equations, we get

$$G = G_A + G_B = C_1 e^{\Lambda_1 t} + C_2 e^{\Lambda_2 t}$$

where C's are complex constants to be determined by initial
conditions and

$$\Lambda_1, \Lambda_2 = [-(\alpha_A + \alpha_B + T_A^{-1} + T_B^{-1}) \pm \{(\alpha_A + T_A^{-1} - \alpha_B - T_B^{-1})^2 + 4T_A^{-1}T_B^{-1}\}^{\frac{1}{2}}]/2$$

Immediately after a $\pi/2$ pulse along the x-axis $M_x = 0$, $M_y = M_0$.

Therefore,

$$(G)_{t=0} = iM_0 \ , \ (dG/dt)_{t=0} = -iM_0 \ (p_A \, \alpha_A + p_B \, \alpha_B)$$

These initial conditions yield

$$C_1 = -iM_0 \ (\Lambda_2 + p_A\alpha_A + p_B\alpha_B)/(\Lambda_1 - \Lambda_2)$$

$$C_2 = iM_0 \ (\Lambda_1 + p_A\alpha_A + p_B\alpha_B)/(\Lambda_1 - \Lambda_2)$$

The Fourier transform, S, of the free induction decay signal is
given by:

$$S = \int_0^\infty Ge^{-i(\omega-\omega_{rf})t} dt$$

$$= - \frac{C_1}{\Lambda_1 - i(\omega-\omega_{rf})} - \frac{C_2}{\Lambda_2 - i(\omega-\omega_{rf})}$$

Professor Bernard L. Shapiro
August 16, 1973

Substituting values of C_1 and C_2, we obtain, after simple algebraic manipulations and redefining α_A and α_B as:

$$\alpha_A = T_{2A}^{-1} + i(\omega_A - \omega) \quad , \quad \alpha_B = T_{2B}^{-1} + i(\omega_B - \omega)$$

(ω is the variable frequency. ω_{rf} is fixed and is the pulse carrier frequency.)

$$S = iM_0[T_A + T_B + T_A T_B(\alpha_A p_B + \alpha_B p_A)]/[(1 + \alpha_A T_A)(1 + \alpha_B T_B) - 1]$$

which is the same as the continuous wave response.

FT and CW proton NMR spectra have been obtained for trimethylamine in H_2O at several pH values. These spectra are shown in the accompanying figure; CW spectra on the right; pH increases from top to bottom. The methyl doublet collapses to a singlet as pH increases, due to exchange of the NH proton. The observed line shapes seem to be equivalent within experimental error. FT and CW spectra were obtained on a Varian HR 220, and both spectra for a given pH were obtained within ten minutes.
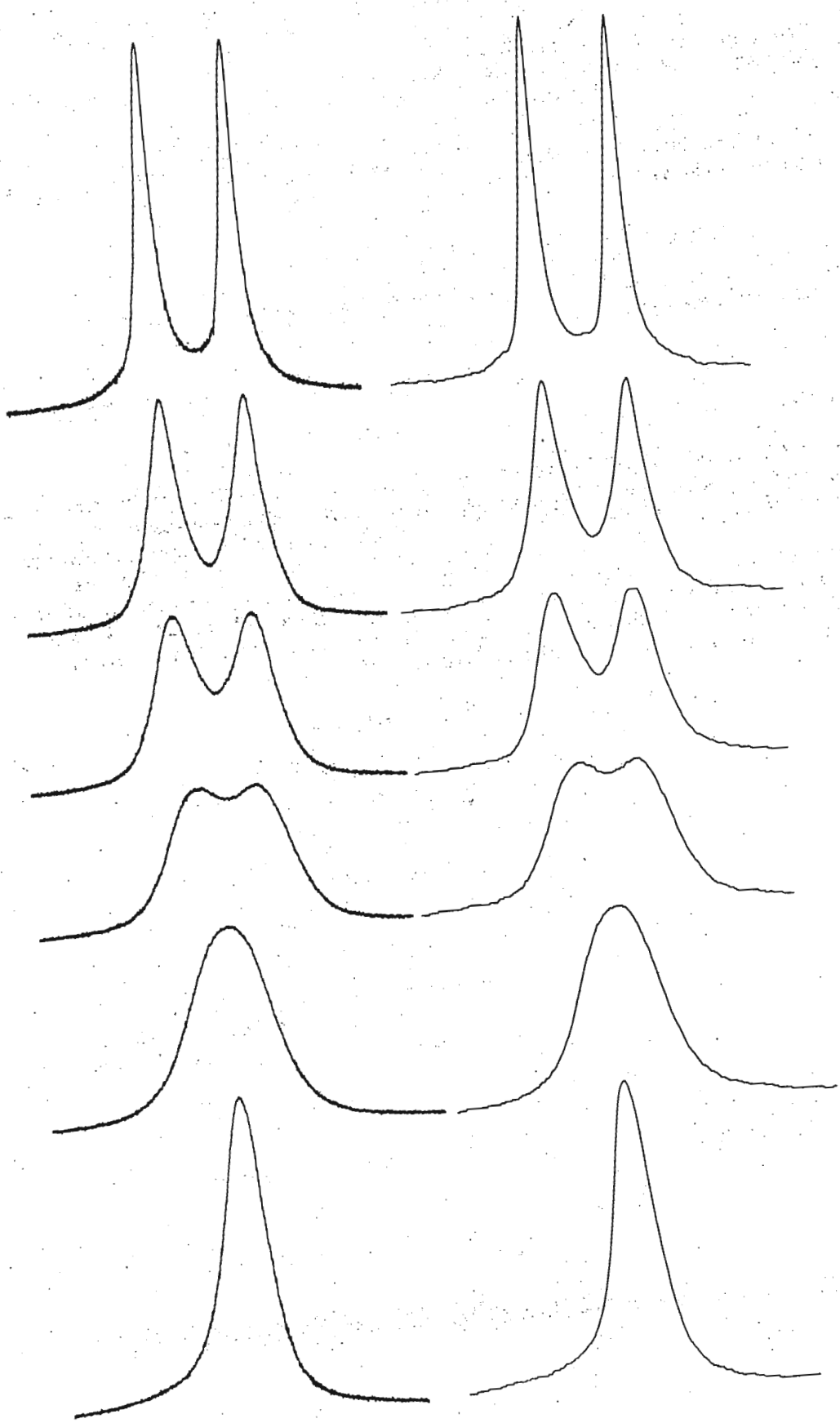
Yours sincerely,

R. K. Gupta

T. Phil Pitner

R. E. Wasylishen

Laboratory of Chemical Physics
National Institute of Arthritis,
 Metabolism and Digestive Diseases

Reference

1. M. S. Gutowsky and A. Saika, J. Chem. Phys. 21, 1688 (1953).

16 August 1973

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

Dear Barry,

An amusing NMR spectrum

In reply to your blue and pink notices which arrived here virtually simultaneously, and greeted me on my return from abroad, let me report the following, with a promise of more during the coming year. The request for funds will be handled by our office in due course.

In the course of some studies on WF_6 derivatives Henry Selig of Jerusalem and I came upon the multiplet
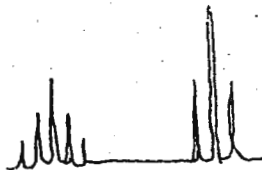
fluorine spectrum which corresponds to a highly unusual A_2X_4 structure

with J = 80 cps and δ = 480 cps = 4.8 ppm with $J_{183W-F} \sim 50$ cps. The

best interpretation we tentatively give to this is a stable $WF_6 \cdot$

CH_3CN complex, the 2:4 structure of which can only be speculated upon.

I would like to know if anyone besides Brinkman is currently working on such W

derivatives.

With best regards.

Yours sincerely,

Jeremy I. Musher
Belfer Graduate School of Science
Yeshiva University

cc: Henry Selig, Hebrew University

THE UNIVERSITY OF NORTH CAROLINA
AT
CHAPEL HILL
27514

DEPARTMENT OF CHEMISTRY

August 13, 1973

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

Title: The Alignment of $CH_3C(CD_3)_3$ in a Nematic Phase

Dear Barry:

I have returned from leave to find a pile of colored notices from TAMNMRNL. We are doing more light scattering and less magnetic resonance as time goes on, but resonances do occasionally occur. Perhaps the tidbit below will give me a reprieve.

Dr. I-yuan Wei has been synthesizing selectively deuterated compounds for use in our studies of tunneling at low temperatures. For example he has prepared CH_2DCN for comparison with CH_3CN. Our calculations indicate that tunneling should lead to a quite different NMR line shape from that predicted for rapid rotation for the $-CH_2D$ group. This point has not yet been confirmed. Dr. Wei has also synthesized a d_9-neopentane, $CH_3C(CD_3)_3$. He finds that the high-resolution ^{1}H spectrum of this compound dissolved in a mixture of butyl p-(p-ethoxyphenoxycarbonyl)phenyl carbonate (BEPC) and p-(p-ethoxylphenylazo)- phenyl undecylenate (EPU) at room temperature shows a triplet with a total width of about 16.5 Hz while both $(CH_3)_4C$ and $(CH_3)_4Si$ (TMS) give only broadened singlets in this solvent mixture (see Fig. 1). The deuterated compound apparently aligns to a greater extent than the nondeuterated neopentane. In contrast to this Snyder and Meiboom[1] observed triplets for neopentane and TMS in p,p'-di-n- hexyloxyazoxybenzene. We are in the process of repeating their experiment with the deuterated compound. The effect of deuterium substitution on molecular alignment in nematic phases has not previously been reported.

Sincerely,

C. S. Johnson, Jr.

CSJ:bs
1. L. C. Snyder and S. Meiboom, J. Chem. Phys. 44, 4057 (1966).

|←16.5 Hz→|

$(CD_3)_3CCH_3$ in BEPC + EPU
at room temperature

←→ 5 Hz

$(CH_3)_4C$ in BEPC + EPU
at room temperature
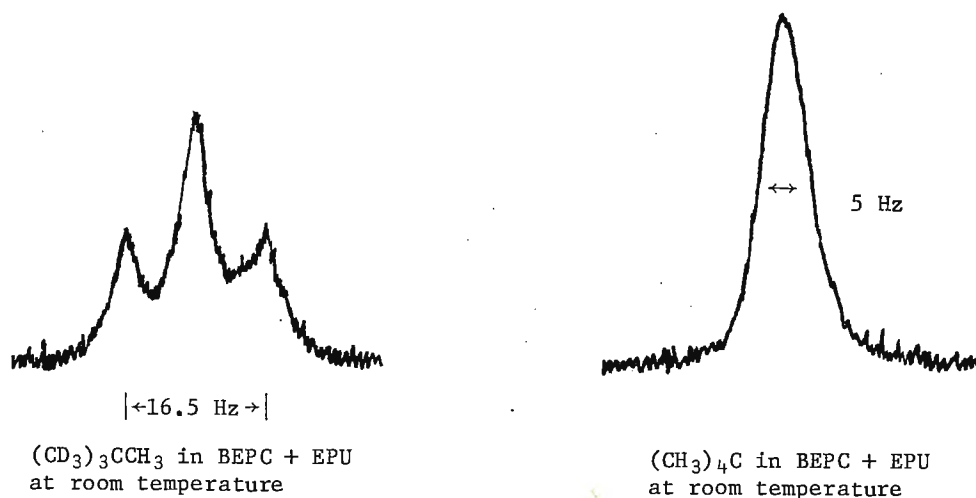
Fig. 1

University of East Anglia

From: Dr. R. K. Harris

School of Chemical Sciences
University Plain, Norwich NOR 88C
Telephone Norwich (0603) 56161
Telegraphic Address UEANOR
ENGLAND
17th August 1973

N.M.R. STUDIES OF FLUORODIAZADIPHOSPHETIDINES

Dear Barry,

We have been continuing our collaboration with Professor Schmutzler's group at Braunschweig, West Germany, by investigating the NMR spectra of diazadiphosphetidines of the form I. There are a number of interesting points involved, but there is only space here to mention a few. In many cases the spectral analyses themselves have some interest since symmetrical systems are present, and even the unsymmetrical compounds mostly give second-order spectra. We use the usual tools of sub-spectral analysis, where possible, to gain the maximum amount of information before we turn to computation, but the final results are mostly from iterative computer fitting.

$$X_{3-n}\, F_n P \diagdown \overset{\overset{\displaystyle Me}{\displaystyle N}}{\underset{\underset{\displaystyle Me}{\displaystyle N}}{}} \diagup PF_{n'}X_{3-n'}$$

I
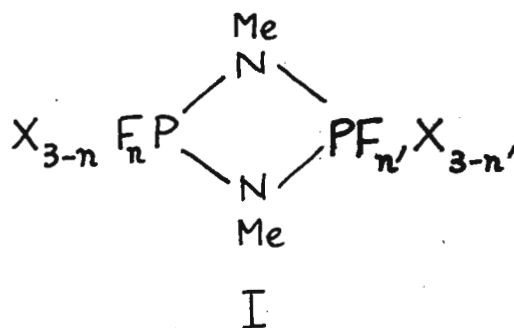
The (P,P) coupling constants, summarised in Table 1 provide some interest. They cover a wide range (a factor of 10 between the highest and the lowest) and there is clearly a strong influence from substituent electronegativity. One may devise group parameters according to the equation:

$$J_{PP} = a_P \cdot a_{P'}$$

Such parameters, given in Table 2 from results for the symmetrical compounds, show that substituent effects are non-additive (markedly so for the methyl compounds). These parameters may be used to estimate J_{PP} for the unsymmetrical compounds with success (for instance, for I, X = Me, n = 3, n' = 2, the estimated J_{PP} is 123 Hz while the observed value is 125 Hz). The existence of such parameters, correlating broadly with substituent electronegativity, suggests that the contact term may provide the dominant contribution to the coupling.

Dr. Bernard L. Shapiro   17th August 1973

In the case of compounds of the type n = n' = 2 there are compli-
cations because of the existence on the NMR timescale at low temperature
of separate <u>gauche</u> (II) and <u>trans</u> (III) isomers.

II   III
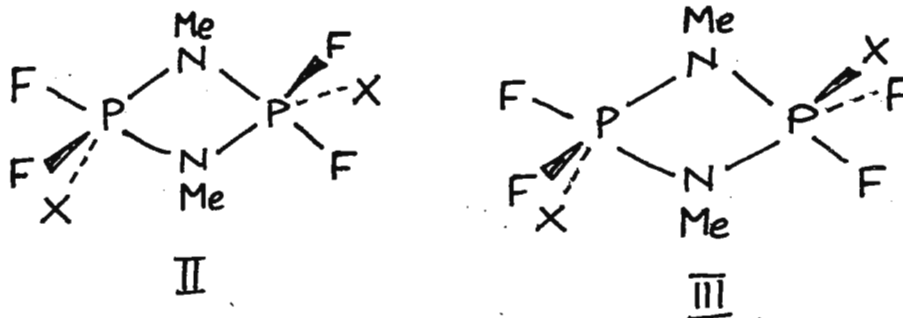
Table 3 shows that such isomers have markedly different values of J_{PP},
presumably because of geometry changes.

Other coupling constants also show a marked dependence on the
substituents and on geometry. For example, $^3J_{PF}$, which is +32 Hz for
n = n' = 3, becomes -5.5 Hz for n = n' = 1, X = Me; moreover for
X = t-Bu, n = n' = 2 $^3J_{PF}$ is +25.6 Hz for the <u>trans</u> isomer but -8.9 Hz
for the gauche isomer. There is also a pronounced effect of the axial/
equatorial nature of the fluorine nucleus involved.

We hope this brief summary of some of our results will keep us
solvent with TAMUNMR for the next nine months.

Best wishes,

R. K. Harris,   M. I. M. Wazeer,   M. Lewellyn.

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

H/W/L/R

Table 1. Values of $\left|{}^2J_{PP}\right|$ in fluorinated diazadiphosphetidines (I)

X	n	n'	$\left|J_{PP}\right|$/Hz	X	n	n'	$\left|J_{PP}\right|$/Hz
(F)	(3)	(3)	210	Cl$^+$	3	2	197
NEt$_2$	2	2	140	Cl$^+$	3	1	189
OMe	2	2	193	Cl$^+$	2	1	172
Cl$^+$	2	2	186	Cl$^+$	1	1	156
CCl$_3$	2	2	125	OMe	3	2	203
CHCl$_2$	2	2	92	OMe	2	1	181
CH$_2$Cl	2	2	78	OMe	1	1	169
CH$_3$	2	2	72	Me	3	2	125
Et	2	2	67	Me	2	1	44
t-Bu	2	2	80	Me	1	1	23
Ph	2	2	80				

$^+$Studied in collaboration with Professor Utvary (Technical University of Vienna)

Table 2. Group parameters for $\left|J_{PP}\right|$

X	F	OMe	Cl	CH$_3$
a(PF$_2$X)	14.49	13.88	13.64	8.50
a(PFX$_2$)	14.49	12.99	12.49	4.80

X	CH$_2$Cl	CHCl$_2$	CCl$_3$	Et	t-Bu	Ph	NEt$_2$
a(PF$_2$X)	8.83	9.59	11.18	8.21	8.94	8.94	11.83

Table 3. Values of $\left|{}^2J_{PP}\right|$ for the isomers of I, n = n' = 2.

X		Me	Et	Ph	t-Bu	CH$_2$Cl	CHCl$_2$	CCl$_3$
J_{PP}/Hz	gauche	54	45	51	23	62	80	100
	trans	92	85	95	94	90	100	133

Jabatan Kimia,
Universiti Malaya,
Lembah Pantai,
Kuala Lumpur,
Malaysia.

Alamat Kawat: UNIVSEL
Talipon 54361 (Samb. 248)

Dr. Soon Ng.
Department of Chemistry,
University of Malaya,
Pantai Valley,
Kuala Lumpur,
Malaysia.

Cable Address: UNIVSEL
Telephone 54361 (Ext. 248)

Bil Kami/Ref. No:

18th August 1973.

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

Dear Dr. Shapiro,

In the hydrogen bond formation between a proton donor and a base, the H-bond shift, Δ, which is the chemical shift of the bonded proton in the dimer relative to that of the free proton in the monomer, has often been assumed to be temperature independent. We have obtained the Δ values for a number of acid—base systems as a function of temperature in cyclohexane medium. The results for three systems are shown below.

Temperature Dependence of the H-Bond Shift, Δ, in Cyclohexane Medium at 60 MHz.

Acid	Base	$\Delta = f(t)$, t in $^{\circ}C$, range 7—60$^{\circ}C$.
$CHCl_3$	N,N-Di- Me-cyclohexylamine	$-0.267t + 100.9$ Hz.
$CHCl_3$	Isopropylether	$-0.0836t + 65.5$ Hz.
2,4,6-Tri-tert-butylphenol	Pyridine	$-0.467t + 175.0$ Hz.

Yours sincerely,

Soon Ng
Associate Professor of Chemistry

THE UNIVERSITY OF TEXAS AT AUSTIN

AUSTIN, TEXAS 78712

Department of Chemistry

August 21, 1973

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

Re: TAMUNMR   Title: "Diffusion in Oriented Model Membranes
by Pulsed NMR"

Dear Barry:

    Attempts to measure diffusion by pulsed NMR in model membrane
bilayer systems such as lecithin-water or oleate-water lamellar phases
have been hampered by the presence of residual dipolar interactions. The
observation of a Carr-Purcell Spin Echo (CPSE) is necessary for the simplest
diffusion measurement, and the presence of anisotoopic dipolar interactions
precludes CPSE formation.

    This note is to emphasize that bilayer systems oriented between glass
plates allow such diffusion measurements and offer broad avenues of research
into transport in model membrane systems.

    DeVries and Berendsen(1) demonstrated that the potassium oleate (KO) -
water system lamellar phase can be oriented between glass plates with the
optical axis (along the hydrocarbon chains) perpendicular to the glass plates.
They demonstrated that the line width varied as $(3 \cos^2 \Omega - 1)$ where Ω is
the angle between the optical axis and the magnetic field. This provided con-
clusive evidence that the broad NMR lines arose from incompletely averaged
dipolar interactions which have residual static interactions along the chain
direction. In particular, the line gets narrow when $\Omega = 54^{\circ}44'$, the well
known "magic angle". The free induction decay, the Fourier Transform of
the line width, thus tends to lengthen at the magic angle.(2) We have shown,
(3,4) following a suggestion from Berendsen(3), that within a few degrees of
the magic angle, a proton CPSE can be observed for KO-D_2O because the
dipolar interactions are minimized. This gives the potential to observe the
diffusion of the bilayer molecules parallel and perpendicular to the bilayer
surface by choosing the appropriate direction for the applied field gradient
in a pulsed gradient diffusion NMR experiment. McConnell and coworkers(5)
have used ESR techniques to measure diffusion of spin labels in oriented
lecithin-water systems and the small values of the diffusion coefficient they

get ($D_{//} \sim 10^{-8}$ cm^2/sec) for lecithin place stringent requirements on the pulsed gradient apparatus.

One advantage of this NMR technique over ESR is that any possible steric effects of the spin label on the membrane structure are not present. Furthermore, by studying KO-H_2O and orienting this away from the magic angle, one can see only the H_2O spin echo and thus measure H_2O diffusion under oriented conditions. Details are reported elsewhere.[4] Presumably this could be extended to studies of diffusion of other molecules in bilayer systems.

References:
1) J.J. DeVries and H.J.C. Berendsen, Nature 221, 1139 (1969).
2) G.S.T. Tiddy, Nature Phys. Sci. 230, 136 (1971).
3) E.T. Samulski, B.A. Smith, and C.G. Wade, Chem. Phys. Lett. 20, 167 (1973).
4) M. Chien, B.A. Smith, E.T. Samulski, and C.G. Wade, ACS Symposium "Ordered Fluids and Liquid Crystals", Chicago, August 1973.
5) C.J. Scandella, P. Devaux, and H.M. McConnell, Proc. Natl. Acad. Sci. (USA) 69, 2056 (1972).

Yours truly,

Chas. G. Wade
Assistant Professor
of Chemistry

USSR Academy of Sciences

SHEMYAKIN INSTITUTE FOR CHEMISTRY OF
NATURAL PRODUCTS

Ul. Vavilova, 32
Moscow V-312
USSR

August 21, 1973

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

<u>Title:</u> On the Spin-Spin
Couplings in Peptide
Fragment.

Dear Barry,

Looking for new NMR approaches to the studying of the peptide and protein spatial structure we have decided to calculate the conformational dependence of various one-, two- and three-bond spin-spin coupling constants for ^{1}H, ^{13}C and ^{15}N nuclei (total 37 constants) in the peptide fragment shown in Fig. 1.

The first step was calculation of the vicinal H-NC$^\alpha$-H proton coupling [1] and comparison with the experimental ϕ-angular dependence [2].

Here I wish to present the results for vicinal ^{1}H-C$^\alpha$C'(O)-^{15}N and ^{13}C -C$^\alpha$C'(O)-^{15}N couplings obtained in collaboration with Dr. V. Solkan.

The calculation has been performed by the finite perturbation method proposed by Prof. J.A.Pople, with the use of unrestricted Hartree-Fock molecular orbital wavefunctions in the INDO approximation.
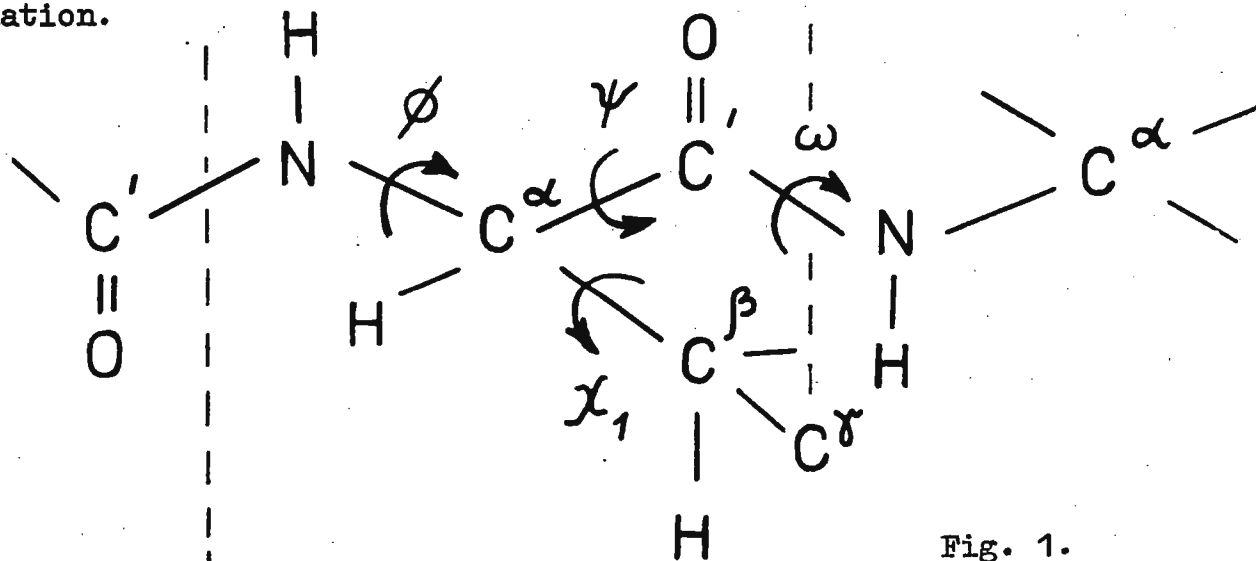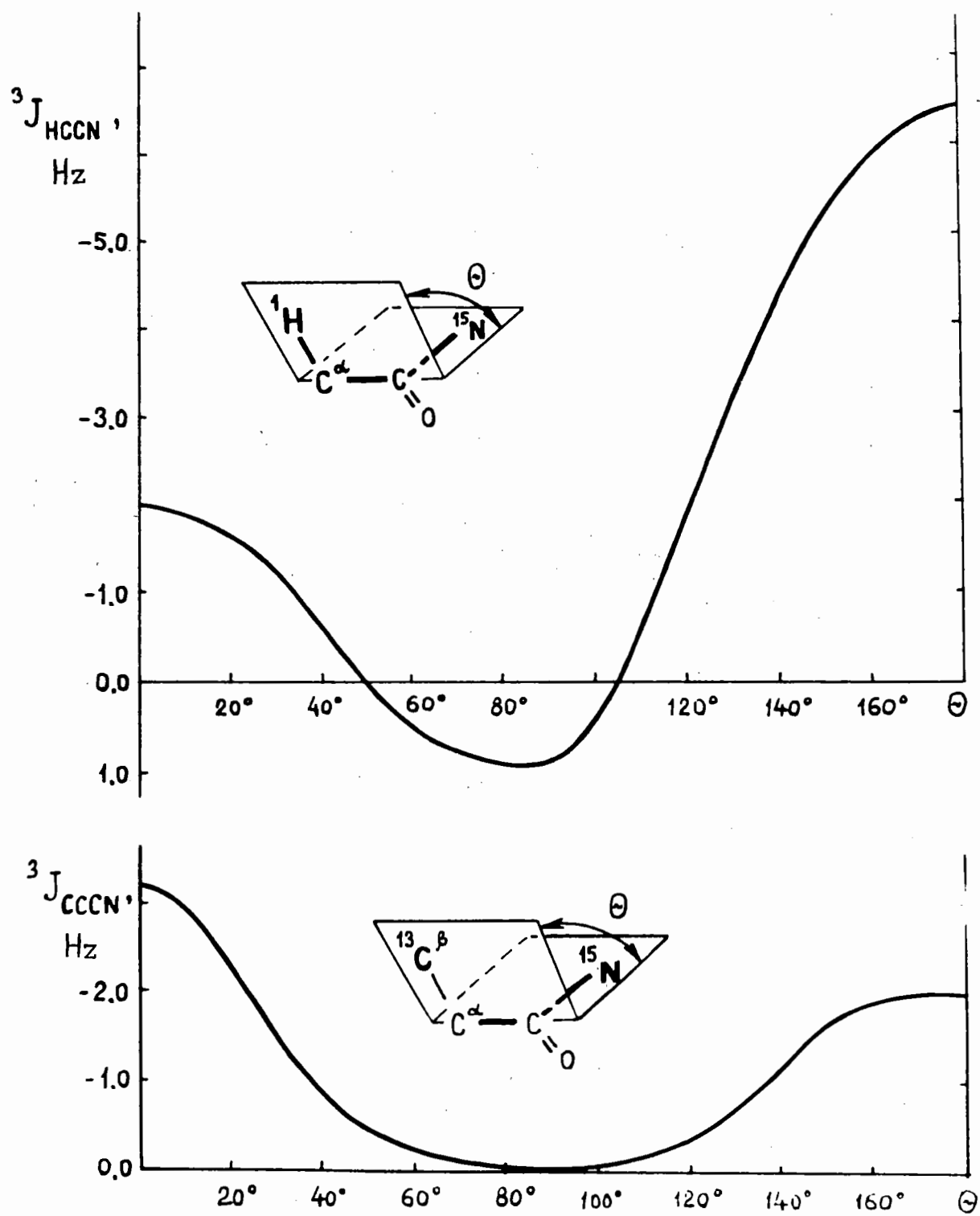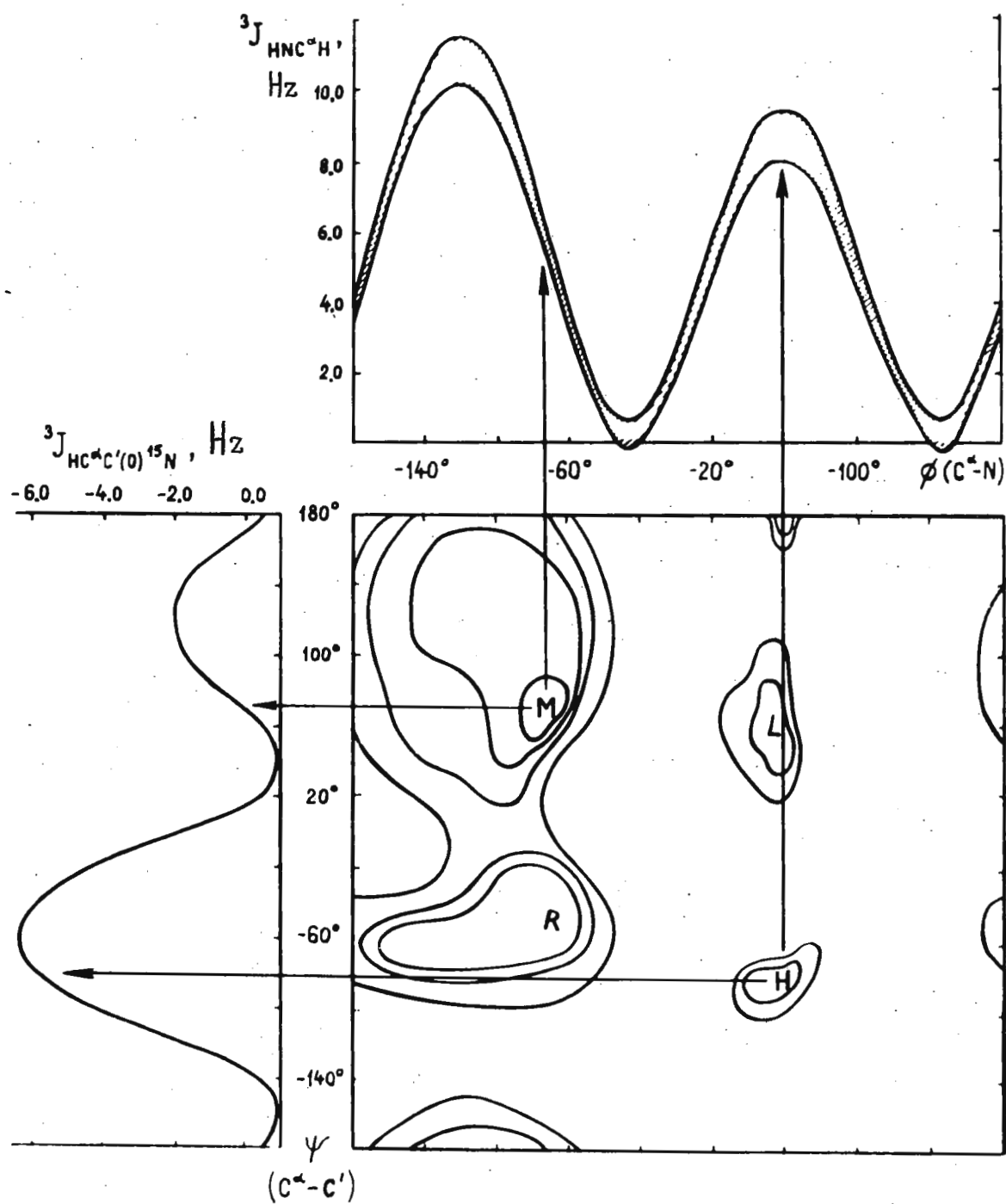

Fig. 1.

Fig. 2.

Fig. 3.

The obtained angular dependencies shown in Fig. 2 could be represented approximately by the following equations:

$$^3J(^1H-C^{\alpha}C'-^{15}N) = -4.2 \cos^2\Theta + 2.2 \cos\Theta + 0.9 \sin^2\Theta$$

$$^3J(^{13}C-C^{\alpha}C'-^{15}N) = -2.6 \cos^2\Theta - 0.6 \cos\Theta$$

The first equation is in reasonable agreement with the previous Prof. M.Barfield's calculations [3] , bearing in mind possible difference in accepted geometrical parameters for model compounds.

Both coupling constants give information on ψ angle rotation of the C^{α}-C'(O) bond of the peptide fragment. With the ϕ-angular dependence of the H-NC$^{\alpha}$-H coupling constant they could be used (after experimental checking on conformationally rigid peptides) for establishing the spatial structure of peptides and proteins (Fig.3).

The full paper is presented to Izvestiya Akademii Nauk SSSR, seriya khimicheskaya (English translation: Bulletin of the USSR Academy of Sciences, Division Chemical Society).

Truly yours,

Wladimir

V.Bystrov

REFERENCES

1. V.N.Solkan and V.F.Bystrov, Tetrahedron Letters $\vee$ *2261,* 1973 [TAMU N Newsletter 175-21] .

2. V.F.Bystrov, V.T.Ivanov, S.L.Portnova, T.A.Balashova and Yu.A.Ovchinnikov, Tetrahedron 29, 873 (1973) [TAMU NMR Newsletter 175-21] .

3. M.Berfield, TAMU NMR Newsletter 178-37.

UNIVERSITÄT DES SAARLANDES

Fachbereich 14 - Organische Chemie

Prof. Dr. H. Dürr

66 Saarbrücken, den 23.8.73

Telefon: (0681) 302.3409

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

Dear Prof. Shapiro:

CMR-Spectra of substituted Benzocyclopropenes

x-Ray structure analysis of benzocyclopropene 1 has shown that the benzene ring in this molecule is heavily distorted[1]. We therefore looked how this deformation influences the ^{13}C-spectra of compounds 1-3. Pulse Fourier Transform spectroscopy of benzocyclopropenes 1, 2 and 3, which have been prepared in our group some time ago[2], provided us with the data listed in table 1.
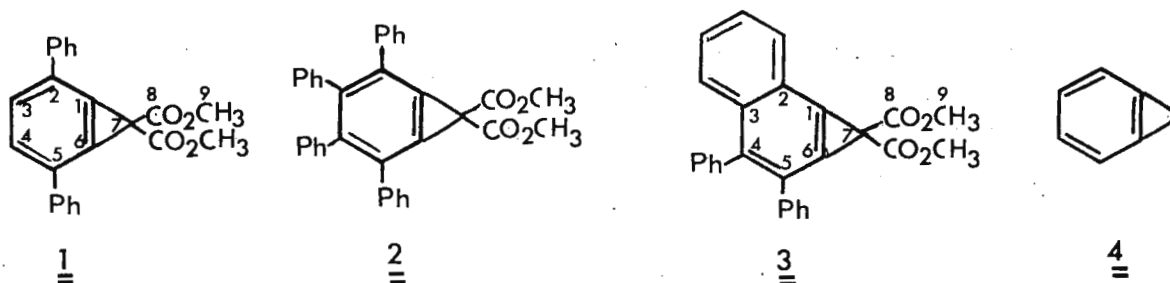

Table 1: ^{13}C-Chemical Shifts of the Benzocyclopropenes relative to TMS**.

(ppm)	1	2	3
C-1	119.3 (15)	121.1 (9)	119.5*(2)
C-2	128.3 (30)	128.3 (13)	129.6 (14)
C-3	129.4 (50)	145.5 (7)	138.5 (3)
C-4	---	---	143.4 (3)
C-5	---	---	127.5 (10)
C-6	---	---	122.5*(5)
C-7	44.9 (5)	46.6 (2)	46.8 (5)
C-8	53.1 (34)	53.2 (16)	53.0 (23)
C-9	167.7 (12)	167.8 (10)	168.3 (3)

* these assignments can also be reversed
** relative intensities in brackets

The C-atoms of the carbomethoxy group (CH_3 and $C=O$) absorb in the normal range (CH_3: 53 and $C=O$: 168 ppm). C-1 and C-6 which are equivalent in <u>1</u> and <u>2</u> are assigned to the signals at 119.3 and 121.1 ppm, respectively. In the unsymmetrical compound <u>3</u> C-6 appears at 122.1 ppm and C-1 at 119.5 ppm. The shifts of the C-1 and C-6 carbonatoms as well as δ_{C-7} show, that the

change in chemical shift is very small in going from an un-substituted cyclopropene to a benzocyclopropene system. Exept C-1 and C-7 all other benzocyclopropene carbons absorb in the normal aromatic region indicating aromatic character of the benzocyclopropene sextet. A simple correlation of $\delta_{C\,13}$

of <u>1-3</u> with charge densities calculated for <u>4</u>[3] was not observed. This is consistent with the x-ray data of <u>1</u> which demonstrate only a minor perturbation of the bond lengths of   cyclopropene by fusion with a benzene ring.

(H. Dürr)   (H. Kober)

1) <u>E. Carstensen-Oeser, B. Müller and H. Dürr</u>, Angew. Chem. <u>84</u>, 434 (1972); Intern. Ed. <u>11</u>, 422 (1972).
2) <u>H. Dürr and L. Schrader</u>, Chem. Ber. <u>103</u>, 1334 (1970).
3) <u>B. Halton</u>, private communication.

NICOLET INSTRUMENT CORPORATION
5225 Verona Road, Madison, Wisconsin 53711
Phone: 608/271-3333   TWX: 910-286-2713

August 24, 1973

Dr. B. L. Shapiro
TAMUNMR
Texas A & M University
College of Science
College Station, TX   77840

Dear Barry:

"A Nuclear Fuzz Phrase Generator"

We were trying to test out our BASIC compiler and thought that the
nmr world would probably appreciate an endless source of thesis topics.
Thus, using the "Chinese Restaurant Menu" approach (one from Column A,
one from Column B etc.) we wrote a short BASIC program to generate
random numbers and print out these valuable nmr terms. The output of
this program is on the attached page. The terrifying thing is how many
of them seem to be meaningful.

We will be glad to furnish a listing of the original BASIC program to
anyone foolish enough to ask, as it clearly has untold numbers of uses
in such diverse fields as magnetic resonance, chemical nomenclature,
Senate hearings and manuals for technical instrument salesmen.

Regards,

James W. Cooper, Ph.D.
Applications Manager

JWC:san

Enclosure

```
     1            NUCLEAR        OVERHAUSER      EFFECT
     2            SPIN           SPIN            RELAXATION
     3            NEMATIC        ENERGETIC       COUPLING
     4            NEGATIVE       INTRINSIC       ENTROPY
     5            ELECTRONIC     LATTICE         HAMILTONIAN
     6            DYNAMIC        NUCLEAR         POLARISATION
     7            HETERONUCLEAR  NOISE           PRECESSION
     8            PHASE          ALTERNATING     PULSES
     9            MAGNETIC       QUADRUPOLE      INTERACTION
    10            MOLECULAR      DIPOLE          INTERACTION
CHANGE?
? 0
NEGATIVE        OVERHAUSER     PRECESSION
MAGNETIC        ENERGETIC      POLARISATION
NEMATIC         NOISE          RELAXATION
ELECTRONIC      NOISE          RELAXATION
NEGATIVE        NOISE          PRECESSION
HETERONUCLEAR   LATTICE        PULSES
ELECTRONIC      NOISE          ENTROPY
PHASE           NOISE          HAMILTONIAN
HETERONUCLEAR   NOISE          HAMILTONIAN
MAGNETIC        ENERGETIC      PULSES
NEGATIVE        OVERHAUSER     PULSES
HETERONUCLEAR   QUADRUPOLE     EFFECT
NEMATIC         INTRINSIC      ENTROPY
PHASE           LATTICE        PULSES
DYNAMIC         INTRINSIC      INTERACTION
NUCLEAR         ALTERNATING    INTERACTION
HETERONUCLEAR   NOISE          PRECESSION
HETERONUCLEAR   NUCLEAR        COUPLING
NUCLEAR         QUADRUPOLE     ENTROPY
MAGNETIC        ALTERNATING    EFFECT
NUCLEAR         LATTICE        COUPLING
DYNAMIC         ENERGETIC      RELAXATION
HETERONUCLEAR   QUADRUPOLE     POLARISATION
DYNAMIC         LATTICE        INTERACTION
SPIN            NOISE          INTERACTION
NEGATIVE        QUADRUPOLE     POLARISATION
MAGNETIC        OVERHAUSER     EFFECT
ELECTRONIC      NUCLEAR        ENTROPY
HETERONUCLEAR   NUCLEAR        PRECESSION
SPIN            LATTICE        PRECESSION
NEGATIVE        ENERGETIC      ENTROPY
HETERONUCLEAR   ENERGETIC      INTERACTION
DYNAMIC         NUCLEAR        INTERACTION
NEGATIVE        SPIN           INTERACTION
MAGNETIC        SPIN           RELAXATION
HETERONUCLEAR   OVERHAUSER     POLARISATION
SPIN            NUCLEAR        POLARISATION
MAGNETIC        NOISE          COUPLING
NEMATIC         ENERGETIC      PRECESSION
NEMATIC         ENERGETIC      HAMILTONIAN
MAGNETIC        NOISE          EFFECT
PHASE           OVERHAUSER     HAMILTONIAN
NEMATIC         OVERHAUSER     PRECESSION
NEGATIVE        SPIN           INTERACTION
DYNAMIC         INTRINSIC      INTERACTION
ELECTRONIC      LATTICE        RELAXATION
NUCLEAR         NUCLEAR        PULSES
NEGATIVE        QUADRUPOLE     COUPLING
PHASE           OVERHAUSER     INTERACTION
DYNAMIC         INTRINSIC      RELAXATION

STOP
READY
```

Prof. Dr. Hanns Fischer

Physikalisch-Chemisches Institut
der Universität Zürich

CH-8001 Zürich   August 28, 1973
Rämistrasse 76
Telefon 01 / 32 26 20

Professor Dr. B.L. Shapiro
Texas A&M University
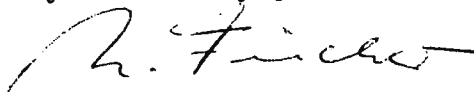College of Science

College Station, Texas 77843

U.S.A.   by Airmail

Transient Nutations in CIDNP

Dear Dr. Shapiro:

Since Torrey's work (Phys.Rev. 76, 1059 (1949)) the magnetic resonance
community is familiar with the transient nutations of a spin system
in a static magnetic field which appear after the sudden application
of a strong rf-field at or near resonance, and which reflect the
motion of the magnetization vector from its initial to its final
steady state position in the rotating frame. The same "Torrey"-oszilla-
tions are expected if the rf-field is kept at a constant high level
and the magnetization is suddenly created or destroyed at or near
resonance. This situation can be observed in CIDNP-experiments. Part a)
of the figure shows the oscillatory behavior of the v-mode emission
signal of tert.-butylchloride produced by photolysis of di-tert.-butyl
ketone in CCl_4. At the time $\oplus$ the photolysis was started, $\ominus$ de-
notes its end. Part b) shows a simulation of the transient signal
based on a solution of Bloch equations containing an additional pro-
duction term for M_Z during the period of photolysis. In CIDEP similar
effects have been noted by Fessenden (J.Chem.Phys. 58, 2501 (1973)).
Dr. G.P. Laroff and I are at present making use of the effect in
photo-modulated CIDNP-studies to discriminate true CIDNP-effects
from steady state spectra.

Very sincerely yours

Prof.Dr. Hanns Fischer

Encl.

UNIVERSITY OF CALIFORNIA, BERKELEY

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO   SANTA BARBARA • SANTA CRUZ

SPACE SCIENCES LABORATORY   BERKELEY, CALIFORNIA   94720

29 August 1973

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

Dear Professor Shapiro:

^2H, ^1H-Decoupled ^{13}C F. T. NMR on the XL-100

Recently we completed a modification (Fig. 1) of our Varian XL-100 which provides simultaneous ^1H and ^2H decoupling, while observing ^{13}C and locking on a ^7Li capillary. The motivation was primarily to observe ^2H biosynthetic incorporation in steroids unambiguously, by "switching" the $J_{^{13}C^2H}$ on and off, as an improvement on the technique reported earlier by Stothers and Tan (1). We have also used the system for collapsing ^2H solvent multiplets (e.g. DMSO-d_6) which hide a peak of interest, and foresee use of the external lock while employing microcells. Since much of the existing XL-100 circuitry could be included, the modification cost was quite low. The long-term ^{13}C resolution on the external pulsed lock is 0.5 Hz or better.

We would like to thank Bob Olsen for interrupting his 8th grade deliberations to construct the final ^2H amplifier.

Sincerely yours,

D. M. Wilson   R. W. Olsen   A. L. Burlingame

1 Stothers, J. B. and Tan, C. T. (1972) J. Amer. Chem. Soc. 94, 8581-8582.
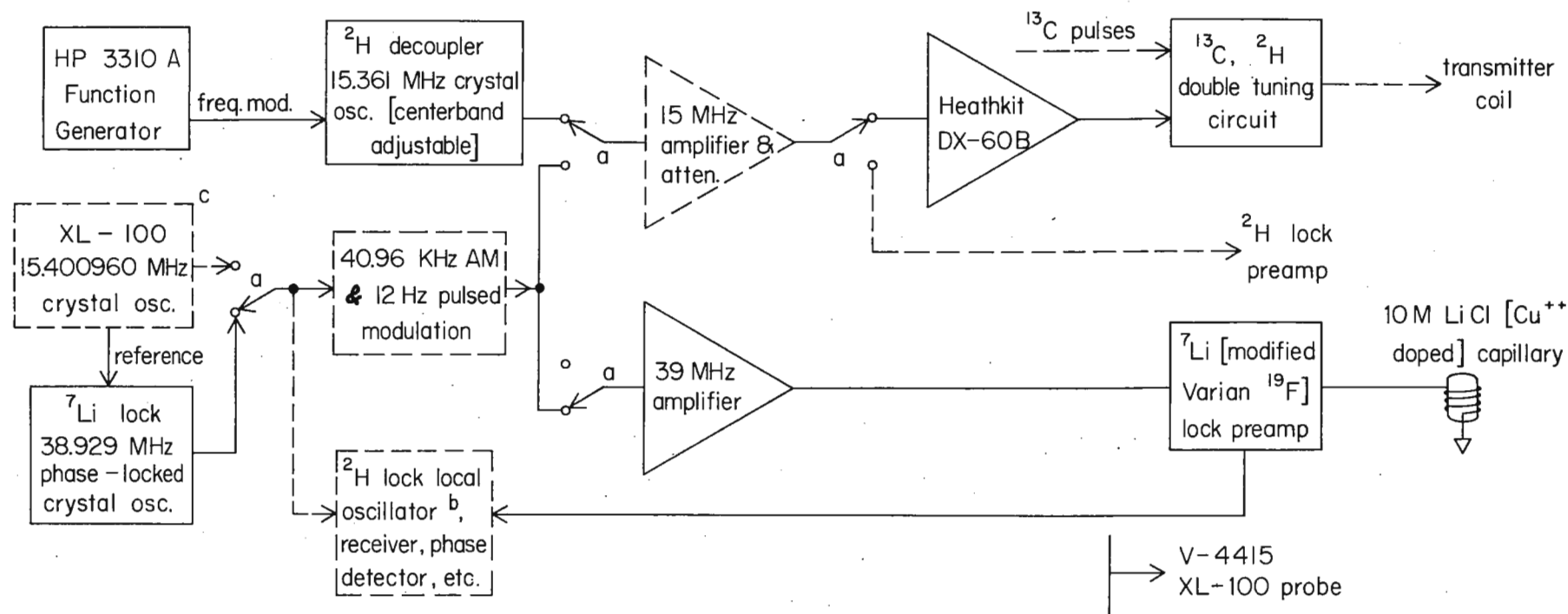
<u>Figure 1</u>

a. Relays actuated by INT-EXT switch, EXT setting shown

b. An additional 45 MHz tuned amplifier and INT-EXT relay
   was added to the XL-100 ^{2}H lock local oscillator

c. Dotted lines show already existing XL-100 circuitry

UNIVERSITY OF DENVER

UNIVERSITY PARK • DENVER, COLORADO 80210

DEPARTMENT OF CHEMISTRY / 303·753·2436

August 24, 1973

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

Dear Barry:

TITLE: Averaging of Non-Equivalent phenyl Resonances in Derivatives of Tetraphenylporphyrin.

We have been looking at the temperature dependent ^{1}H NMR of Indium porphyrins with chloride in one axial position. At room temperature the phenyl protons in Indium tetra(p-isopropylphenyl)porphyrin chloride $[In(p-iPr-TPP)Cl]$ and Indium tetra(p-trifluoromethylphenyl)porphyrin chloride $[In(p-CF_3-TPP)Cl]$ in 1,1,2,2-tetrachloroethane solution appear as an ABCD pattern and average to an apparent AB pattern at about 120° (cf. Figure). We attribute the nonequivalence of the two ortho protons and the two meta protons to restricted rotation about the meso carbon - phenyl carbon bond and the presence of chloride in one axial position with the other axial position vacant. Averaging could then be achieved either by rotation of the phenyl ring or by chloride ion exchange.

When the concentration of $In(p-iPr-TPP)Cl$ in tetrachloroethane is varied by a factor of four there is no observable change in the rate of averaging. However, when $[n-Bu_4N]Cl$ is added to a solution of $In(p-iPr-TPP)Cl$ in tetrachloroethane in a mole ratio of 0.25 moles of $[n-Bu_4N]Cl$ to 1.0 moles of $In(p-iPr-TPP)Cl$ the coalescence temperature is decreased by about 30°. When this solution is diluted by a factor of 2 or 4 the rate of averaging decreases markedly. This indicates that at

least two mechanisms of averaging are operative, based on the observed differences in concentration dependence. In the absence of added chloride ion either phenyl ring rotation or chloride exchange with dissociation as the rate determing step is consistent with our current data. Further work is underway to distinguish between these two processes. In the presence of $[n\text{-}Bu_4N]Cl$ an associative chloride ion attack is indicated.
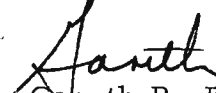
Gerd LaMar has previously observed similar effects in the $Fe(p\text{-}CH_3\text{-}TPP)Cl$ system.[1,2] Averaging of nonequivalent phenyl protons in $Fe(p\text{-}CH_3\text{-}TPP)Cl$ in the presence of $[n\text{-}Bu_4N]Cl$ was attributed to chloride ion attack. In the pure complex phenyl ring rotation was observed at higher temperatures.

Apparently in both the indium and iron chloroporphyrins at least two processes occur which effect averaging of nonequivalent phenyl protons.

Sincerely,

Sandra

Sandra S. Eaton

[signature]

Gareth R. Eaton

1. G. N. LaMar, J. Amer. Chem. Soc. 95, 1662 1973.

2. F. A. Walker and G. N. LaMar, Ann. N. Y. Acad. Sci., in press (cited in ref. 1).

Figure Caption: 100 MHz ^1H spectra of the phenyl and pyrrole resonances of $In(p\text{-}CF_3\text{-}TPP)Cl$ in 1,1,2,2-tetrachloroethane.

pyrrole-H   ortho-H   meta-H

120°

86°

65°

50°

30°

50 Hz

AUTHOR INDEX

Varian has an NMR system for every application...

for instance, the new CFT-20 for Carbon-13

Varian, world leader in magnetic resonance spectroscopy, offers a complete selection of NMR spectrometers, from low-cost instruments designed to solve the typical problems of industrial and academic laboratories to the ultimate in research systems.

EM-300X

World's lowest priced, high resolution NMR system. A really economical thermostatted 30-MHz permanent magnet system that produces highly informative spectra on a wide variety of compounds. Like higher performance proton spectrometers, it uses 5-mm samples, contains a built-in integrator, has a homogeneity adjust circuit for fast tune-up, and includes a flatbed recorder with precalibrated chart paper. Its ruggedness, small size, low weight and easy operation make it ideal for routine analyses and teaching applications.

EM-360

A legend in its own time. Reaction from hundreds of scientists who have seen it in operation has been unanimous: with its resolution (0.6 Hz), its sensitivity (18:1), and most of all, its under $11,000 price (U.S. only), the 60-MHz EM-360 is being hailed as one of the most outstanding contributions to the field of NMR to come along in years. And it's available with a lock/decoupler accessory.

T-60A

A brand new, old reliable spectrometer. The old, reliable part of the T-60A is a heritage of fine workmanship and dependability inherited from the renowned System T-60.

The brand new aspect includes a wide range of improved features—sensitivity in excess of 30:1; resolution better than 0.3 Hz; resolution stability of 0.5 Hz per day; more sweep widths; and more sweep times. Yet even with all this improved capability, the T-60A costs no more than the System T-60 before it.

CFT-20

Varian's newest instrument, the first low-priced NMR spectrometer specifically designed for ^{13}C spectroscopy. Its low impedance electromagnet is double-thermally insulated for excellent long-term stability. And the magnetic field is so homogeneous, the CFT-20 can accommodate 10-mm sample tubes for room temperature experiments and 8-mm sample tubes over the temperature range of $-80°C$ to $+200°C$. The operating console houses a keyboard for entering operating parameters and experimental commands; an oscilloscope that can display alphanumeric characters or spectral data; an X-Y plotter; and a built-in 620L-100 minicomputer with 8,192 words of memory. If that's not enough, the CFT-20 also features: internal pulsed deuterium lock; continuous wave, noise modulated and gated decoupling; Autoshim™; and a built-in read only magnetic tape cassette for loading programs. Best of all is the price: $44,500 (U.S. only) everything included.

XL-100

The industry standard. A pulsed-Fourier transform or frequency swept high resolution 23.5-kG spectrometer. It features observing capability from 7 to 100 MHz and decoupling range from 2.9 to 58 and 94 to 100 MHz for continuous wave, noise decoupling or INDOR experiments. The availability of homo- or heteronuclear internal lock on ^1H, ^{19}F, and ^2H, and external lock on ^1H and ^{19}F provides locking flexibility. Fourier transform operation, T_1 measurements, homonuclear decoupling and solvent elimination techniques are also routine XL-100 operations. The XL-100 can be tailored to meet single purpose or multi-departmental NMR needs.

SC-300 and SC-360

For the highest performance in commercially available high resolution NMR spectrometers. The SC-300 (300 MHz) and SC-360 (360 MHz) spectrometers are engineered for use in applications requiring the highest magnetic field strengths—liquid crystal, biological, biopolymer, and biochemical studies. Accessories are available for observation of other nuclei in both continuous wave and Fourier transform modes.

If you'd like more information on any of these systems, see your local Varian representative or write Varian Instrument Division, 611 Hansen Way, Palo Alto, California 94303.

varian instruments

Brand names: ANASPECT™ • CARY® • MAT • VARIAN®
VARIAN AEROGRAPH® • VARIAN TECHTRON

CFT-20