# Texas A & M University N – M – R Newsletter

**No. 144**

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All Newsletter correspondence, etc., should be addressed to:

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

# UNIVERSITY of PENNSYLVANIA

## PHILADELPHIA 19104

*The School of Medicine*

JOHNSON RESEARCH FOUNDATION
DEPARTMENT OF
BIOPHYSICS AND PHYSICAL BIOCHEMISTRY

August 10, 1970

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

Dear Professor Shapiro,

Thank you for your blue note. It is not always easy to find something relevant to the wide audience of TAMUNMRN, but I hope the following will do.

The use of Mn(II) as a paramagnetic probe for studying the binding of divalent ions to biological macromolecules is well documented. The main feature is that as a result of the binding the longitudinal proton relaxation rate (PRR) of water is usually enhanced and measurements at very low concentrations of the substance of interest are feasible. For trivalent ions, however, a suitable probe has yet to be found since the binding of Fe(III) leads to a decrease of the PRR rather than to an enhancement.

We have studied the effects of binding on the PRR due to gadolinium (III). For this preliminary investigation bovine serum albumin (BSA, M.W. 69000) was chosen since it is known to bind metal ions. It was found that bound Gd(III) is about 4.5 times more effective in relaxing the water protons than free Gd(III). It was also found (from a protein titration) that BSA has 4 binding sites for Gd(III) with a dissociation constant of approximately $5 \times 10^{-5}$ M. It appears that Gd(III) may be a very useful probe for studying the binding of trivalent ions to biological macromolecules.

Sincerely yours,

*Jacques Reuben*

Jacques Reuben

Title: Gadolinium(III) as a probe for studying binding of trivalent ions to biological macromolecules by NMR

**Glaxo**

Glaxo Research Ltd, Greenford, Middlesex

Please address reply to:

4th August, 1970.

Prof. B.L. Shapiro,
Texas A & M University,
Texas.

Dear Professor Shapiro,

### Sensitivity Test for N.M.R. Spectrometers

We are interested in comparing the sensitivities
of n.m.r. spectrometers produced by different manufacturers
and have observed that although makers normally specify the
minimum signal-to-noise ratio for a 1% (v/v) solution of
ethylbenzene in carbon tetrachloride, the conditions
specified for conducting the test vary considerably. Often,
no limit is set on the depth or volume of solution in the
spinning-tube and, hence, on the quantity of ethylbenzene.
The minimum, routinely practical, depth of solution needed
for a standard 5 mm spinning-tube varies from one instrument
to another. It is clear that the facility to use a smaller
depth of solution represents an effective increase in
sensitivity.

We suggest that a standard weight rather than a
concentration should be used in the manufacturer's
specification and, further, we believe that a crystalline
solid, which can be easily weighed, provides a better
standard than a liquid, such as ethylbenzene.

We have conducted tests on several Varian, Perkin-Elmer
and Jeolco 60 MHz spectrometers, in which we measured in the
conventional way the signal-to-noise ratio for the largest
peak of the AB quartet formed by the 21-methylene group of
a 7 mg sample of Reichstein's D diacetate ($3\beta$,21-diacetoxy-
$17\alpha$-hydroxy-$5\alpha$-pregnane-17,20-dione) dissolved in the
minimum volume of $CDCl_3$ needed to give a satisfactory
signal with the particular instrument. Standard 5 mm
spinning-tubes were used and the spectra were recorded
at a standard sweep rate of 1 Hz/sec. or at the nearest
equivalent rate; the R.F. power and filtering of each
instrument were adjusted for optimum performance.
Reichstein's D diacetate was selected, since it is readily
soluble in $CDCl_3$, gives a suitable AB quartet and, above all,
happened to be in the laboratory cupboard at the right moment.

- 2 -

We now realise that Reichstein's D diacetate is not generally available in n.m.r. laboratories and suggest that the highest peak of the methylene quartet shown by phenacetin in $CDCl_3$ solution (cf. Varian Spectrum Catalogue, 1962, No. 267) be used instead. Phenacetin is available commercially in an analytical grade; 5 mg appears to be a suitable standard quantity.

We would like to know whether other readers have had thoughts on standard sensitivity tests for commercial n.m.r. spectrometers and would like to hear of their experiences.

Yours sincerely,


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

**digital**

August 10, 1970

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

"Simplified Signal Averaging with the PDP-8/I"
Dear Barry:

With this letter I wish to start my subscription to TAMUNMR.
Bob Kurland described his instrumental set-up for $^{13}$C signal
averaging in the June issue, and I would like to describe the
computer program we developed for use with this instrumentation.

The basic method is that of computer control of the experiment
rather than of occasional interaction of two instruments. The
PDP-8/I computer has available with it an interface called
the AX-08 which contains analog to digital and digital to analog
converters (ADC's and DAC's). By loading the DAC with a number
between 1 and 512 a voltage is produced which can be used to
drive, for instance, a scope display. We used this voltage to
drive the Fluke digital frequency synthesizer, model 633A in
external sweep mode. This meant that for each input voltage there
was a discrete, reproducible frequency which could be applied
to the spectrometer.

Each time the voltage was advanced in this manner, the computer
program examined the ADC input from the spectrometer, and added
it into memory. We found that we were able to increase our S/N
markedly by sampling each of these 512 points several times (up
to 20) during each sweep. This method, known as boxcar averaging,
really amounts to 20 sub-sweeps during a single sweep. It has
been deprecated by others but we found it to be of great value
in our proton and $^{13}$C experiments.

The upshot of this instrumental method is that there is really
no difference between the spectrometer and computer sweeps as
a function of time, since they are one in the same. Thus, using
the DAC's to drive a plotter, while still connected to the
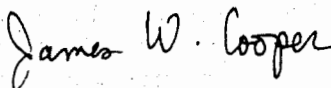
Dr. Bernard Shapiro
August 10, 1970

synthesizer, we were able to plot out the accumulated spectrum,
adjust the plotter pen to hover over any line of interest, and
read the line's exact frequency from a counter.

This method seems to be far superior to the more common approach
where the computer and spectrometer sweep concurrently, but
asynchronously, after the triggering by a sync pulse.  In this
latter method, the nonlinearity of the two sawtooth sweeps may
lead to disastrous errors in spectrum calibration.

As you can see from the letterhead, I have finished my post-doc
with Dr. Kurland and am now with Digital Equipment Corporation,
where I am still involved in this same area of work.  I'll be
glad to send further details on this method of signal acquisition
to any interested parties.

                              Sincerely,

                              James W. Cooper

                              James W. Cooper
                              Applications Programmer
                              NMR and Related Chemical Applications

JC/jb

**The University of Oklahoma       620 Parrington Oval, Room 221       Norman, Oklahoma 73069**

August 10, 1970

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

Dear Dr. Shapiro,

LINEAR FREE ENERGY CORRELATIONS OF NMR CHEMICAL SHIFT PHENOMENA

   Your pink notice catches me on the short side of completion of a study involving nmr investigation of solute-solvent interactions. In the hope of maintaining our TAMUNMR Newsletter subscription, I offer the following progress report as a pacifier:

   Some time ago (IITNMR Newsletter, 108, 2, September, 1967) we reported our observations regarding solvent effects on the nmr spectrum of 1,4,7,7-tetrachloronorbornane, (I). In particular, we observed that the appearance of the $A_4B_4$ spectrum of I in benzene was quite different from that in pyridine; the spectra have since been published, (J. Org. Chem., 34, 1109 (1969) ). Compound I possesses a pronounced molecular dipole moment ( 3.30 D ). This led us to wonder if in fact the difference between the appearance of the spectra of I obtained in these two solvents might be due to a specific solvation interaction. One might envision this as an interaction between the lone pair on the pyridine nitrogen and the positive end of the molecular dipole associated with I. This effect, of course, would be absent were pyridine replaced by benzene as solvent.

Department of
Chemistry

   Our recent work leads us to believe that the type of interaction described above is probably not responsible for the effects which we observe. In particular, we have calculated the chemical shift and coupling constant parameters ( via LAOCOON III ) for the AA'BB' spectrum of deuterium-decoupled II, below, in several monosubstituted benzene solvents, (PhX, where X = halogen, CN, NMe$_2$, NO$_2$, CF$_3$, OMe, CH$_3$, CHO, -C$\equiv$CH, CH$_2$CN).
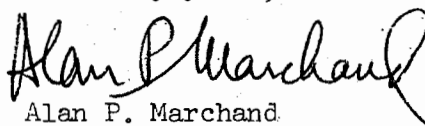
(I)                    (II)
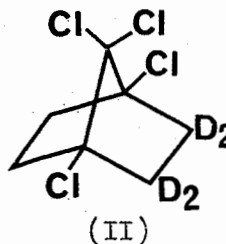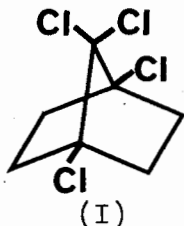
Letter to Professor B. L. Shapiro
August 10, 1970

We then attempted to correlate the difference in chemical shifts, $\Delta\delta$ , between the upfield and downfield halves of the centrosymmetric AA'BB' pattern with Hammett $\sigma$ values. Acceptable correlations have been obtained. Interestingly, electron donating substituents, X, in PhX describe one line, and electron withdrawing substituents fall on another correlation line, suggesting that fundamentally different interactions are involved in the collision complexes formed between II and these two different types of monosubstituted benzenes.

Another pertinent observation has emerged: the spectrum of II in pyridine is essentially identical to that of II in nitrobenzene! This suggests that the effect of the nitrogen atom on the spectrum of II in pyridine is due mainly to the enhanced electronegativity of nitrogen relative to carbon. (In nitrobenzene, a "ring nitrogen atom" is approximated in electronegativity by the ring carbon atom to which the highly electronegative $NO_2$ substituent is attached).

We therefore look to electronic effects (and not to lone pair- dipole association effects) to explain our original observations. Work currently in progress is aimed toward delineating the relative contribution of inductive and resonance effects of the substituent X in the solvent PhX to the overall solvent effect upon $\Delta\delta$ in the nmr spectrum of II. This work is being carried out in collaboration with Dr. Anna Segre De Angelis (Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pennsylvania, on leave from the Istituto di Chimical delle Macromolecole del C. N. R., Milan, Italy) and Dr. Arthur M. Ihrig (Department of Chemistry, Texas Christian University, Fort Worth, Texas).

Sincerely yours,

Alan P. Marchand
Associate Professor

# ARGONNE NATIONAL LABORATORY

July 31, 1970

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

## Automatic Liquid Nitrogen Delivery Line for HR-220

Dear Barry:

The Varian HR-220 NMR Spectrometer System uses a cryostat
which contains liquid helium (LHe) and liquid nitrogen (LN).
The super-conducting solenoid is immersed in LHe and the jacket
surrounding the LHe is kept filled with LN. It is desirable to
maintain a high, constant level of LN in the outer dewar to keep
the LHe loss to a minimum. An automatic LN filling system has
been designed to deliver a predetermined quantity of LN. The
system has the following operating parameters: First, an adequate
supply (160 $\ell$), available under approximately 12 lbs. pressure.
Second, adequate pressure relief valves, properly installed, to
relieve pressure built up in the transfer lines when the solenoid
valves are closed. Third, well-insulated transfer lines to
conserve LN.

The LN supply is stored at a distance of 12 feet from the
cryostat. The total length of the transfer line is approximately
22 feet. The transfer line is constructed of 3/8" stainless steel
pipe and insulated with 5/8" O.D. rubber tubing together with
5/8" x 1 5/8" polystyene type insulation. Connections from the
transfer line to the dewar are made with 1/2" x 5/8" pure gum
tubing and secured with clamps. The connection to the 160 $\ell$ LN
supply is made with 3/8" stainless steel flexible tubing and
secured with flare fittings to insure a good mechanical connection.
The problem of pressure in the transfer line after filling was
solved by using conventional pressure relief valves; one is set
at 18 lbs., and another set at 20 lbs. The two valves are mounted
on a 10 inch heat riser located near the LN supply. The other
closed loop of the transfer line is protected by the two relief
valves furnished with the instrument which are set to release at
approximately 1 lb. The thermistor probe is located as close as
possible to the dewar so the maximum length of transfer line can
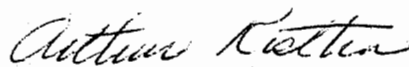be pre-cooled.

-2-

The levels of LN inside the dewar determine the points at which the system turns on and off. This is controlled by the LN sensor unit. The turn-on/off points are adjustable. When the turn-on level is reached, relay $K_1$, located in the HR-220 console, is energized. This causes relay $K_2$ to energize. The contacts of relay $K_2$ permit 110V AC to energize solenoid valves (1) and (2). These normally closed valves open and allow the LN to pre-cool the transfer line. Relay $K_3$ is energized because of the low resistance of the thermistor probe, which is located in the transfer line near solenoid valve (3). When the transfer line is cooled, and LN begins to flow, the thermistor probe causes relay $K_3$ to de-energize, which in turn causes solenoid valve (2) to close and solenoid valves (3) and (4) to open. The dewar then begins to fill with LN and this continues until the sensor unit causes relay $K_1$ to de-energize. In turn, $K_2$ de-energizes and solenoid valves (1), (3) and (4) close. Relay $K_3$ will again energize as soon as the resistance of the thermistor allows $Q_1$ to conduct sufficient current.

Timer C, energized when the system turns on, provides a timed safety factor should a malfunction such as a broken transfer line, leaky connections or lack of LN occur. If the timer times out before completion of the filling operation, its relay contacts open, causing relay $K_4$ to come on and solenoid valves (1), (2), (3), and (4) to turn off. At the same time, relay $K_4$ causes an alarm to sound. The alarm can be turned off by $S_1$ or $S_3$.

This system has been used for more than a year and has been found to be highly reliable.

Sincerely, yours,

Arthur Kostka
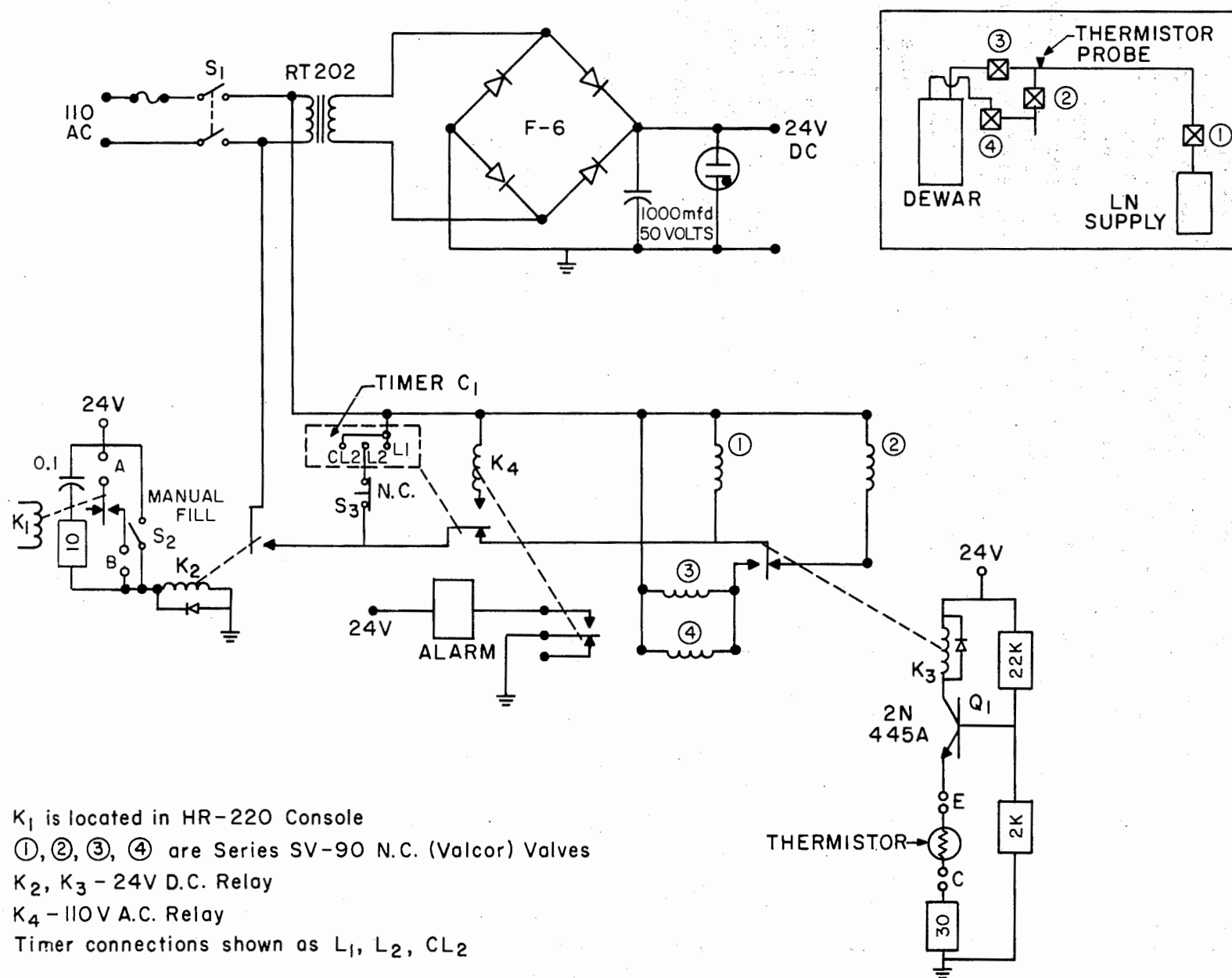Chemistry Division

AK/skj

Note: Credit to Joseph J. Katz

K₁ is located in HR-220 Console

①, ②, ③, ④ are Series SV-90 N.C. (Valcor) Valves

$K_2$, $K_3$ – 24V D.C. Relay

$K_4$ – 110V A.C. Relay

Timer connections shown as $L_1$, $L_2$, $CL_2$

RIJKSUNIVERSITEIT-GENT

**LABORATORIUM**
voor
**ORGANISCHE CHEMIE**
—

B-9000 GENT, August 10th 1970.
KRIJGSLAAN 105        Tel. (09) 22.60.95
(Belgïe · Europa)

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

TEXAS 77843.        U.S.A.

PMR features of some 1,3-dioxolanes.

Dear Barry,

We have lately been interested in some PMR features in 1,3-dioxolanes, i.e. $^2J(O_2CH_2)$. This parameter is found to depend [1,2] on the magnitude of the torsion angles between the $O(C-H)$ bonds involved and the adjacent lone electron pairs, and our aim is to trace this behaviour in pentacyclic compounds in order to obtain conformational information. Our dioxolane series is not yet worked through, but some readers might be interested in some striking features allready obtained. The table gathers some parameters, and the following is noteworthy :

1) There is a small fluctuation in $^2J(O_2CH_2)$ in 1,3-dioxolanes (1) $0 < {}^2J(O_2CH_2) < |1.2|$ cps.

2) The sign is <u>positive</u>, as follows from the <u>decrease</u> in absolute value of $^2J(O_2CH_2)$ with <u>increasing</u> polarity of the medium, causing a negative contribution [3]. There seems to exist some confusion in the literature [2,4] with respect to the sign of $^2J$ in dioxolanes, although the present result confirm the findings of Smith and Cox [3].

3) $^2J(^{13}C-H_2)$ is slightly bigger for the lowfield dioxy methylene hydrogen atom than it is for the highfield counterpart. A β-cis substituent causes a deshielding, thus $^2J(^{13}C-H_2)$ is larger for $H_c$ than for $H_t$ (1). It is clear that for a symmetric pseudorotation of the dioxolane frame work the amount of eclipsing of $H_c$ with the adjacent p lobes is equal to that of $H_t$. Therefore the phenomenon can't be explained by a preferential neighborhood [5] of the electron cloud to one of the H-atoms.



(1)

1

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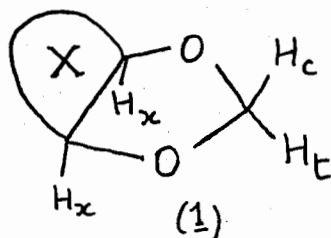
**LABORATORIUM**
voor
**ORGANISCHE CHEMIE**

GENT, August 10th 1970.

KRIJGSLAAN 105          Tel. (09) 22.60.95
(België - Europa)

.../...

4) Only the lowfield hydrogen atom $H_c$ is involved in long range coupling with $H_x$ (nmdr). This is a further example of a non-classical long-range phenomenon [6]
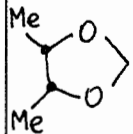
[1] Anteunis M.; Bull.Soc.Chim.Belges 75 (1966), 413.
Anteunis M. and Swaelens G.; Org. Magn. Res.; in press.
Anteunis M., Swaelens G. and Anteunis - De Ketelaere F. to be published.

[2] Cahill, R., Cookson R.C. and Crabb T.A.; Tetrah. 25 (1969), 4681.

[3] Smith S.J. and Cox R.H.; J.C.Phys. 45 (1966), 2848.

[4] Rommelaere Y. and Anteunis M.; Bull.Soc.Chim.Belges, in press.
See also Baggett N., Duxbury J.M., Foster A. and Webber J.; J.Chem.Soc. (c) 1966, 208
Inch T. and Williams N.J.; J.Chem.Soc. (c) 1970, 263.

[5] Yonezawa T. and Morishema I.; J.Mol.Spectr. 27 (1968), 210.

[6] cf. for a discussion on the controversy on the possibility for non-classical long range Anteunis M. and Schamp N.; Bull. Soc.Chim.Belges 79 (1970) 437.

[7] Rattet L., Williamson A. and Goldstein J.; J.Mol.Spectr. 26 (1968) 281.
Quoted 1.0 cps by Bunjacombe J.J., Foster A., Jones B. and Willard J.; Chem. Comm. (1965), 174.

[8] From bandwidth eventually before and after decoupling experiments or from comparison with internal reference (i.e. $CH_2Cl_2$).

Laboratory for NMR Spectroscopy.

M.J.O. ANTEUNIS

TABLE.

PMR parameters for bicyclic formal acetals, in $CCl_4$ (unless otherwise stated). $^4\tau(H_t,H_x)=0$ in all cases. Shifts in ppm from TMS (internal).

| x($\underline{1}$) | $^2\tau$ | $^4\tau(H_c \cdot H_x)$ $\delta H_c$ | $^2\tau((0)^{13}C_2-H)$ (c) $H_c$ (t) $H_t$ | $\delta H_t$ | $\delta H_x$ |
|---|---|---|---|---|---|
| 5 | 0 | 0.5 (tr) 4.90 | — | 4.53 | — |
| 6 | 1.15[7] 1.05(CDCl₃) 0.95(DMSO) | 0 5.05 | c 166.0 t 165.0 | 4.80 | 3.9 |
| 7 | 0 | 0.4[8] 5.10(CHCl₃) | c 163.8 t 161.2 | 4.73 (CHCl₃) | 4.05 (CHCl₃) |
| 8 | 0.45 0.2[8](DMSO) | 0.2[8] 4.83 | c 163.0 t 161.0 | 4.50 | 3.85 |
| 9 | 1.07 0.98(CDCl₃) 0.95(acetone-d₆) 0.80(DMSO) | 0.2[8] 4.80 | c 166.0 t 165.0 | 4.52 | 3.80 |
| 10 | 0.85 0.70(CDCl₃) 0.70(acetone-d₆) | 0.15[8] 5.0(CDCl₃) | c 164.5 t 163.0 | 4.74 (CDCl₃) | 3.99 (CDCl₃) |
| 12 | 1.10 1.00(CDCl₃) 0.95(DMF) | 0.1 4.92 | c 163.5 t 162.0 | 4.68 | 3.78 |
| Me–O / O–Me (ring) | 0.63 | <0.5 4.97 | — | 4.87 | — |

### NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201
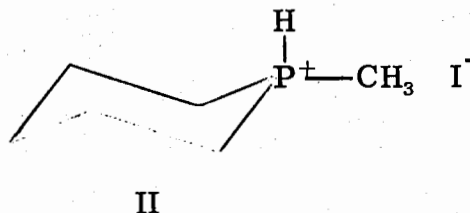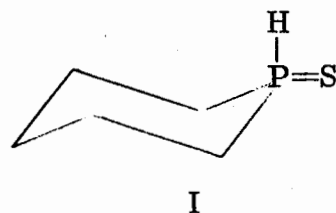
DEPARTMENT OF CHEMISTRY

August 12, 1970

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

Dear Barry:

### Conformational Studies of Phosphacyclohexanes

Continuing our studies of phosphacyclohexanes, we have prepared compounds I and II.



The splitting pattern of the proton on phosphorus was examined to determine whether the proton is axial or equatorial. In the parent compound, the corresponding proton is almost entirely axial.[1] For the sulfide I, the spectrum of the P-H proton at 90 MHz is a broad triplet independent of temperature to $-70^\circ$. We estimated the coupling constants to be $J_{aa} = 7.5$ Hz and $J_{ae} = 2.5$ Hz. These values favor the conformation for I drawn above, with the proton axial.
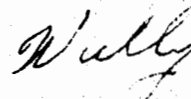
For the methiodide II, the spectrum of the P-H proton at 90 MHz with irradiation of the methyl resonances is a broad singlet. This observation is not evidence for an equatorial orientation, but arises because the axial and equatorial $\alpha$ protons have a small chemical-shift difference. For $J_{aa} = 8.0$ Hz, $J_{ae} = 2.0$ Hz, and $\Delta\nu_{ae} = 7$ Hz, the calculated spectrum is a deceptively simple singlet rather than a triplet of triplets. In the other cases, $\Delta\nu_{ae}$ is about 45 Hz, so this problem does not arise. Thus, we cannot determine the location of the P-H proton in II because of second-order effects.

Double resonance experiments on II showed that $^1J_{P-H}$ and $^2J_{P-C-H}$ have opposite signs. Since $^1J_{P-H}$ is probably positive, $^2J_{P-C-H}$ must be negative.

Sincerely yours,

Joseph B. Lambert

Wallace L. Oliver, Jr.

(1) J. B. Lambert, W. L. Oliver, Jr., and G. F. Jackson, III, Tetrahedron Lett., 2027 (1969).

DIVISION OF PHYSICAL CHEMISTRY
The Royal Institute of Technology
S-100 44   STOCKHOLM 70
Sweden
Cable address: Technology

Stockholm   August 17, 1970

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

NUCLEAR MAGNETIC RESONANCE GROUP
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70                    SWEDEN

Dear Barry:

Thank you for the reminder. I hope the equilibrium will be
restored by the following report of work carried out
together with Dr. Pinhas Lindner of this group. The short
title of our contribution is:

Water in Tendon Collagen under Tension

Tendons from male rats, about 100 days old, were assembled
in a loading device to be inserted into the spectrometer
probe under controlled tension and humidity conditions.
Prior to the measurements some of the samples were stored
for five months at 75 % relative humidity, and for 3 months
at 90 % R.H. under a constant load of 550 gr.

The tendon tension and the PMR spectra were observed at
various equilibrium water contents. The results are
exemplified in Figures 1 and 2 showing, respectively, the
variation of the tendon tension at constant length and the
corresponding width of the shifted band as functions of
the regain.

The measurements establish the existence of a structural
transition zone at about 20 % regain and a relation
between the load at constant length and the water content
of tendons expressed by the equation

$$\frac{d\sigma}{dw} = -a\sigma$$

with the solution

$$\sigma = \sigma_o \exp\left[-a(w-w_o)\right]$$

where $\sigma_o$ and $w_o$ represent respectively the initial mean stress and water content of the regain interval considered.

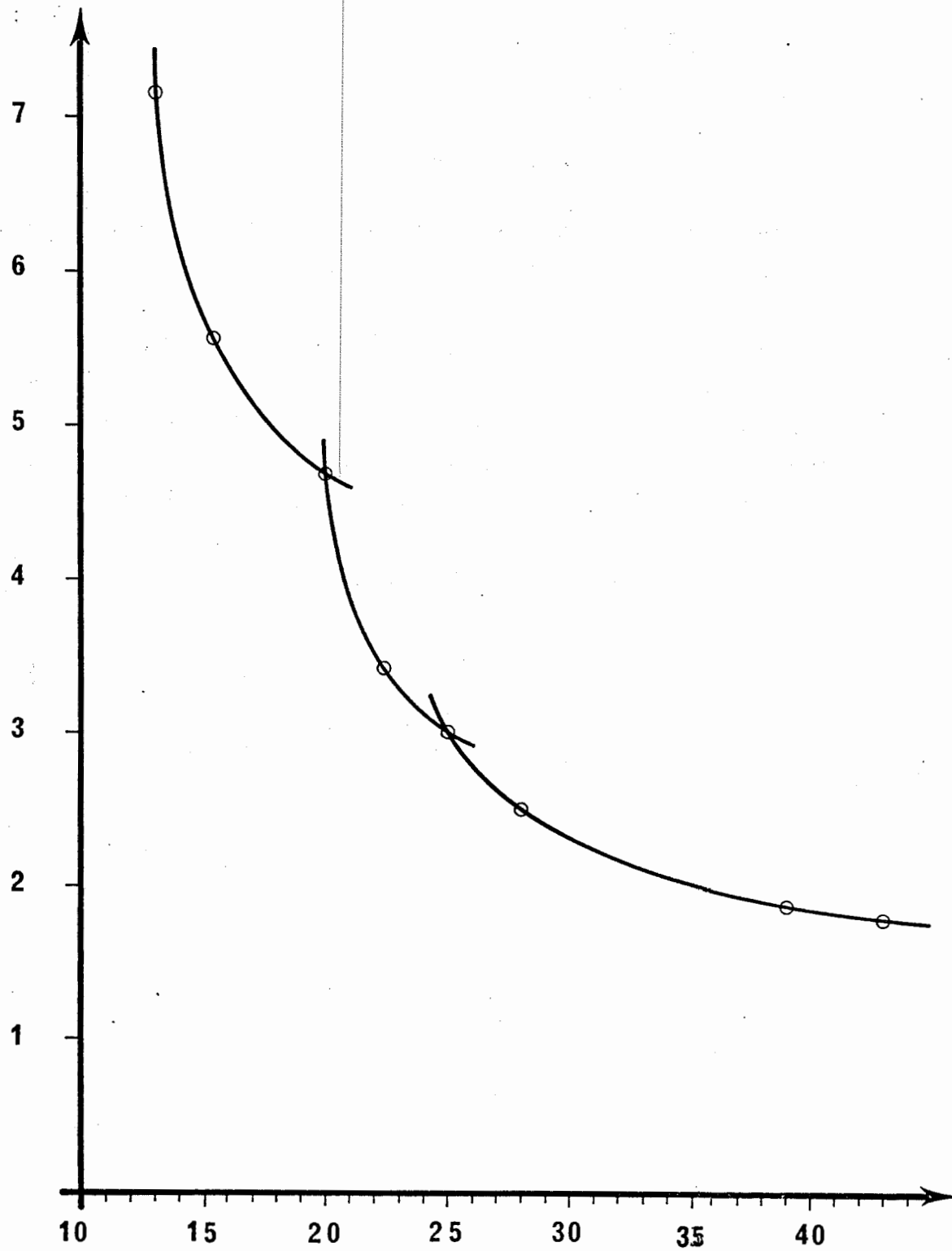These and other observations indicate that the internal water balance of the tendons plays an important role in relaxation and load redistribution processes. We would appreciate to hear from any reader interested in the function of the mucopolysaccharides in tendons.
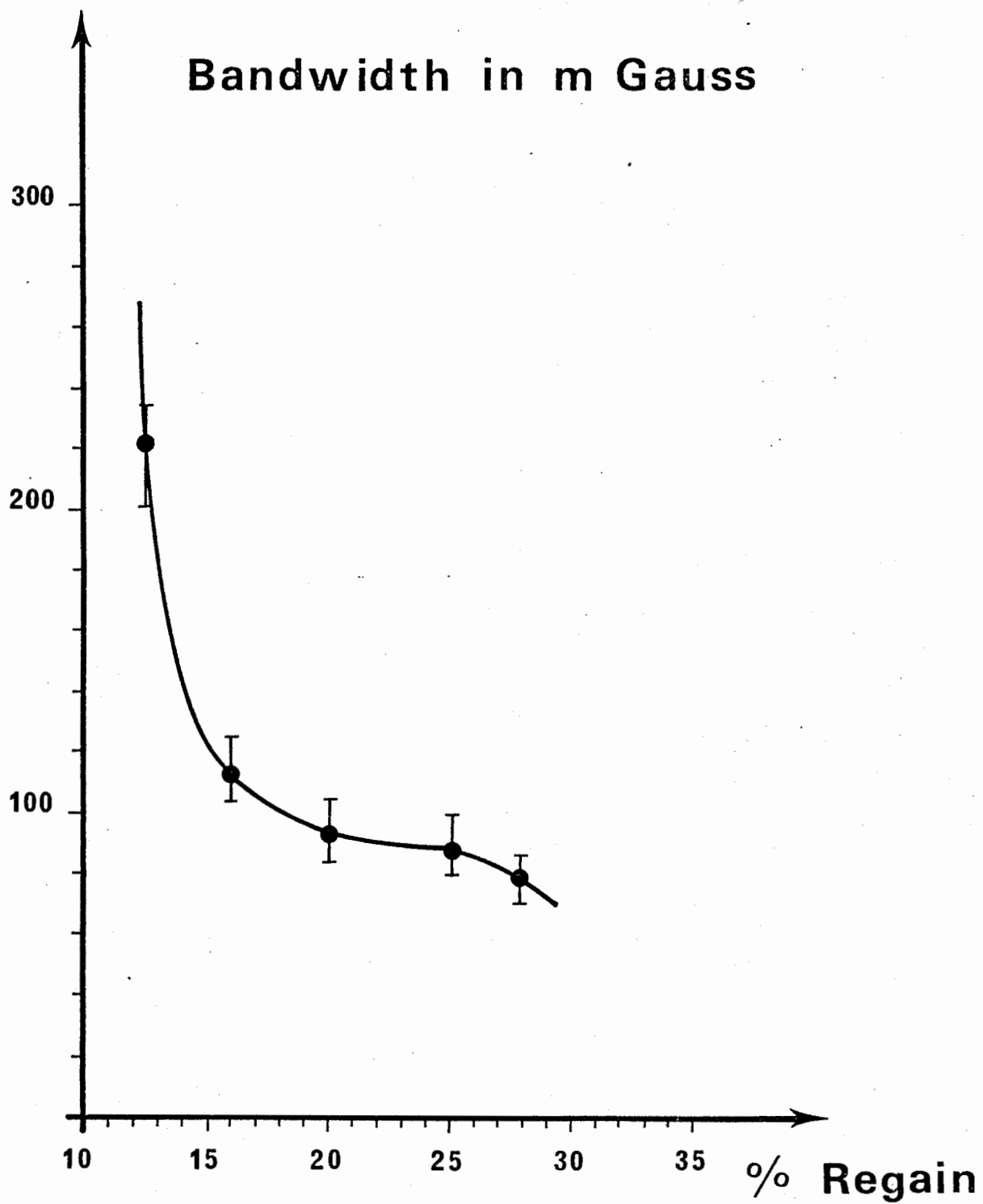
Yours Sincerely,

Erik Forslind
Professor of Chem, Phys,

**Load kg**

7

6

5

4

3

2

1

10    15    20    25    30    35    40

**% Regain**

Bandwidth in m Gauss

August 19, 1970

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

Dear Professor Shapiro:

### CONFIGURATION OF 4-ALKYLIDENE-1,2,3,4-TETRAHYDROPYRIDINES

The reaction of 4-alkylpyridine N-oxides with mercaptans in acetic anhydride yields mixtures of 2- and 3-alkylmercapto-4-alkylpyridines and a number of solid by-products which have been shown to be 4-alkyl-1,2,3,6-tetrahydropyridines 1 (1-3). A similar reaction in the presence of triethylamine affords different solid by-products which have recently been shown to be 4-alkylidene-1,2,3,4-tetrahydropyridines 2 (4,5).
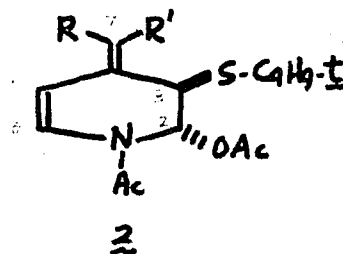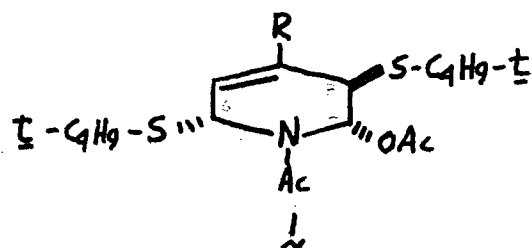


When 4-picoline or 4-isopropylpyridine N-oxide were reacted, only a single by-product (2 R=R'=H or CH$_3$) was isolated. However, when 4-ethylpyridine N-oxide was the starting material, a mixture (60:40) of two compounds resulted (2 R or R' = H or CH$_3$). Various attempts to separate this mixture have failed although a sample enriched in one isomer (~90%) was obtained by fractional crystalization. The nmr spectra were consistent with the anticipated mixture of geometric isomers. Suitable but untested rationale could be developed to assign configurations to the isomers based on the chemical shifts of the ring protons (c.f. later discussion); however, a more definitive proof was sought.

The deoxidative substitution was repeated using 4-ethylpyridine N-oxide-$\alpha,\alpha$,2,6-$d_4$ as the starting material and a mixture of tetradeuterio isomers (3 and 4) isolated.
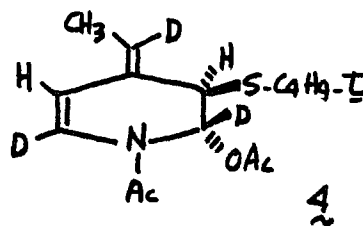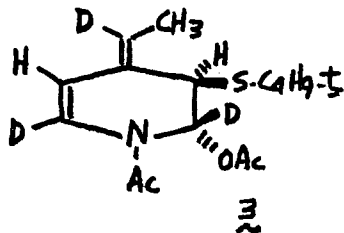


The results of a series of nuclear Overhauser effect experiments on the mixture are summarized in the table. Simultaneous irridiation of the vinyl methyls, necessitated by their similar chemical shifts, resulted in a significant increase in the integrated intensity of the resonances of H-5 major and H-3 minor and had no effect on the remaining resonances. Large intensity changes of the resonances of H-3 of both isomers resulted from irridiation of the t-C$_4$H$_9$ groups. These results require that the major isomer is 4 and the minor isomer is 3.

Dr. Bernard L. Shapiro                    -2-                    August 19, 1970

------------------------------------------------------------------------

These configurational assignments enable the chemical shift data, collected in the Table, to be rationalized.  It appears that ring protons are markedly deshielded when the methyl group is cis.  Recently, similar correlations have been made in conjugated alkadienes (6).

(1)  F.M. Hershenson and L. Bauer, J. Org. Chem., 34, 665 (1969).
(2)  F.M. Hershenson and L. Bauer, ibid., 34, 660 (1969).
(3)  R.S. Egan, F.M. Hershenson and L. Bauer, ibid., 34, 665 (1969).
(4)  B.A. Mikrut, F.M. Hershenson, K.F. King, L. Bauer, and R.S. Egan, Abstracts, 158th National Meeting, American Chemical Society, New York, Sept., 1969, No. 49.
(5)  B.A. Mikrut, Thesis, University of Illinois at the Medical Center, Sept., 1970.
(6)  C.G. Cardenas, Tetrahedron Letters, 4013 (1969).

|  | Chemical Shift $CDCl_3$ | n.O.e. % enhancement | | |
|---|---|---|---|---|
|  |  | $\{CH_3\}$ | $\{\underline{t}\text{-}C_4H_{9major}\}$ | $\{\underline{t}\text{-}C_4H_{9minor}\}$ |
| H-3$_{major}$ | 5.30 | 0 | 22.6 | 11.3 |
| H-5$_{major}$ | 5.78 | 32.4 | 0 | 0 |
| H-3$_{minor}$ | 5.54 | 20.0 | 13.6 | 14.8 |
| H-5$_{minor}$ | 5.82 | 0 | 0 | 0 |

Chemical Shifts, $C_5D_5N$ solution

|  | Major | Minor | $\Delta = \delta_{major} - \delta_{minor}$ |
|---|---|---|---|
| H-2 | 6.25 | 6.37 | -0.12 |
| H-3 | 5.48 | 6.08 | -0.60 |
| H-5 | 5.85 | ... | ... |
| H-6 | 6.76 | 6.62 | +0.14 |
| H-7 | 5.68 | ... | ... |
| $CH_3$-7 | 1.72 | 1.84 | --- |

Sincerely,

Richard S. Egan
nmr lab, D-408

vc

# CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

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

August 18, 1970

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

A General Iterative Method of Calculating Exchange-Broadened NMR Spectra

Dear Barry,

In total lineshape analyses of exchange-broadened nmr spectra, usually the line-shapes are calculated from one or more unknown parameters, and the resulting calculated spectra are compared visually to the experimental curves. The unknown parameters are adjusted and the process is repeated so as to obtain a satisfactory fit. This visual fitting can be time consuming, especially if a large number of unknown parameters are involved. We have recently been obtaining computer simulations of experimental spectra utilizing a general method which allows simultaneous optimization of several unknown parameters.

Experimental spectra are digitized by storing single or multiple scans on a CAT which is interfaced to a key punch. The calculated spectrum is adjusted to fit the experimental spectrum by a general iterative least-squares method (1) that has found wide use for normal spectral analysis. (2) In the present case, however, the amplitude of each spectral point is fitted as opposed to transition frequencies. A least-squares solution is achieved when $\phi$ defined by eq. 1 is minimized

$$\phi = \sum_{i=1}^{N} (A_i^{\exp} - A_i^{\text{calc}})^2 \qquad\qquad I$$

where $A_i^{\exp}$ and $A_i^{\text{calc}}$ are the respective experimental and calculated amplitudes of the $i$th point of the spectrum and N is the number of digitized spectral points. In general, for a given number of nuclear spins and chemical exchange sites, $A_i^{\text{calc}}$ is a function of several unknown parameters, i.e.,

$$A_i^{\text{calc}} = f_i (X_1, X_2, \cdots, X_j, \cdots )$$

where the X's refer to chemical shifts, coupling constants, rate constants, and/or relaxation times.

In each iteration, the procedure (1) involves solving eq. 2 for $\vec{X}$, the vector of corrections to the unknown parameters, $X_j$.

$$D^T \vec{A} = D^T D \vec{X} \qquad \text{II}$$

where

$$D_{ij} = \frac{\partial A_i^{calc}}{\partial X_j} \qquad \text{III}$$

and

$$\vec{A_i} = A_i^{exp} - A_i^{calc}$$

The partial derivatives in eq. 3 are estimated numerically by

$$\frac{\partial A_i^{calc}}{\partial X_j} \simeq \frac{f_i(X_1, X_2, \cdots, X_j + h, X_{j+1}, \cdots) - f_i(X_1, X_2, \cdots X_j, \cdots)}{h}$$

where the function $f_i$ is evaluated using the DNMR program (3), and h is a small increment in the $j$ th unknown.

Figure 1 shows experimental and calculated proton spectra of the t-butyl resonance in 3-chloro-2, 2, 3, 4, 4-pentamethylpentane. In the one nucleus, two-site calculation (two of the three sites are accidentally degenerate), the unknown parameters consist of one rate constant and two chemical shifts. Above the coalescence temperature, the two chemical shifts were allowed to vary in the minimization sequence, but with a constant difference. Without this restraint, convergence was not achieved.

In Figure 2, the experimental and computer-simulated proton-decoupled natural-abundance $^{13}C$ spectra of 1, 1, 3, 3-tetramethylcyclohexane are shown. The invarient peak is due to the quaternary carbon, the presence of which allows convergence while varying $T_2^*$. The exchange-broadened peaks are due to the methyl carbons and the other resonances are not shown. The other unknown parameters in the one nucleus, three-site calculations were the rate constant for conformational inversion, the three chemical shifts, and the population of the quaternary site. The latter parameter permits taking into account differences in Overhauser enhancement of methyl vs. quaternary carbons. Again, the chemical-shift differences between the two exchanging sites was held constant for spectra above the coalescence temperature.

Initial values of the unknown parameters were estimated from the experimental spectra and convergence was rapid. Five or less iterations were necessary for each spectrum in Figures 1 and 2.

The principal advantage of this general method is the small time expenditure required for accurate, total lineshape analyses.

Yours sincerely,

Bruce L. Hawkins      John D. Roberts

(1)    W. C. Hamilton, "Statistics in Physical Science", The Ronald Press Co.,
       New York, 1964, p. 150.

(2)    S. M. Castellano and A. A. Bothner-By, "Computer Programs for Chemistry",
       D. T. Detar, Ed., Vol. I, W. A. Benjamin, Inc., 1968, pp. 10-39.
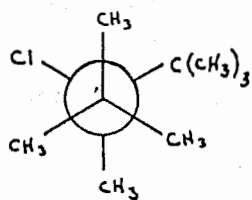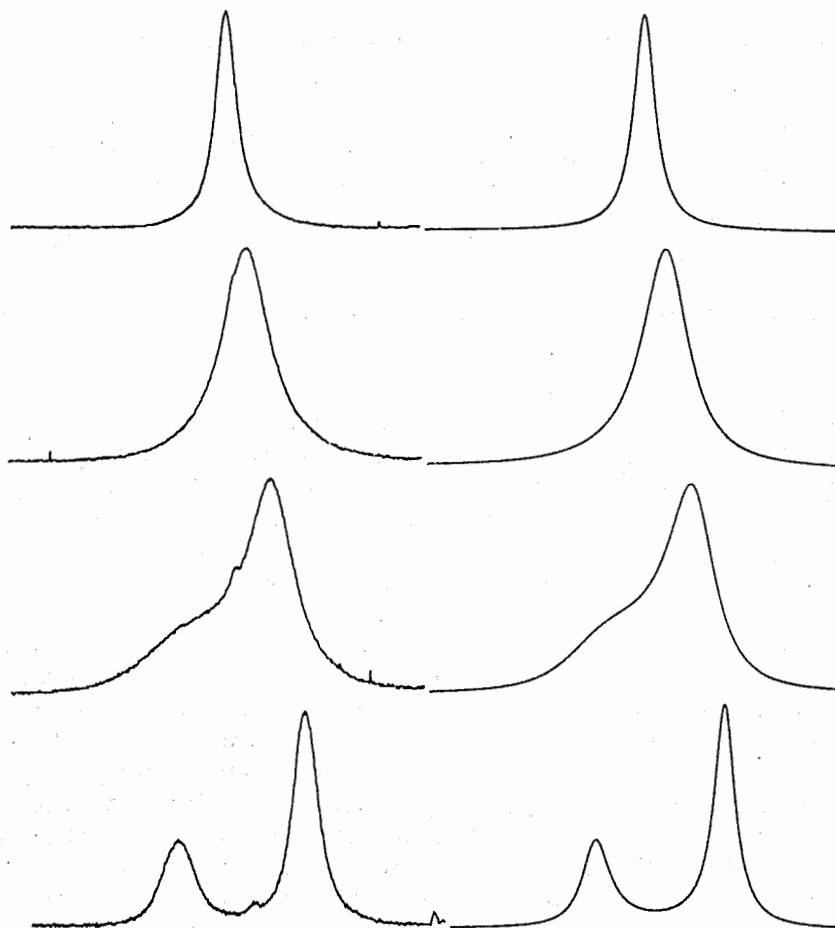
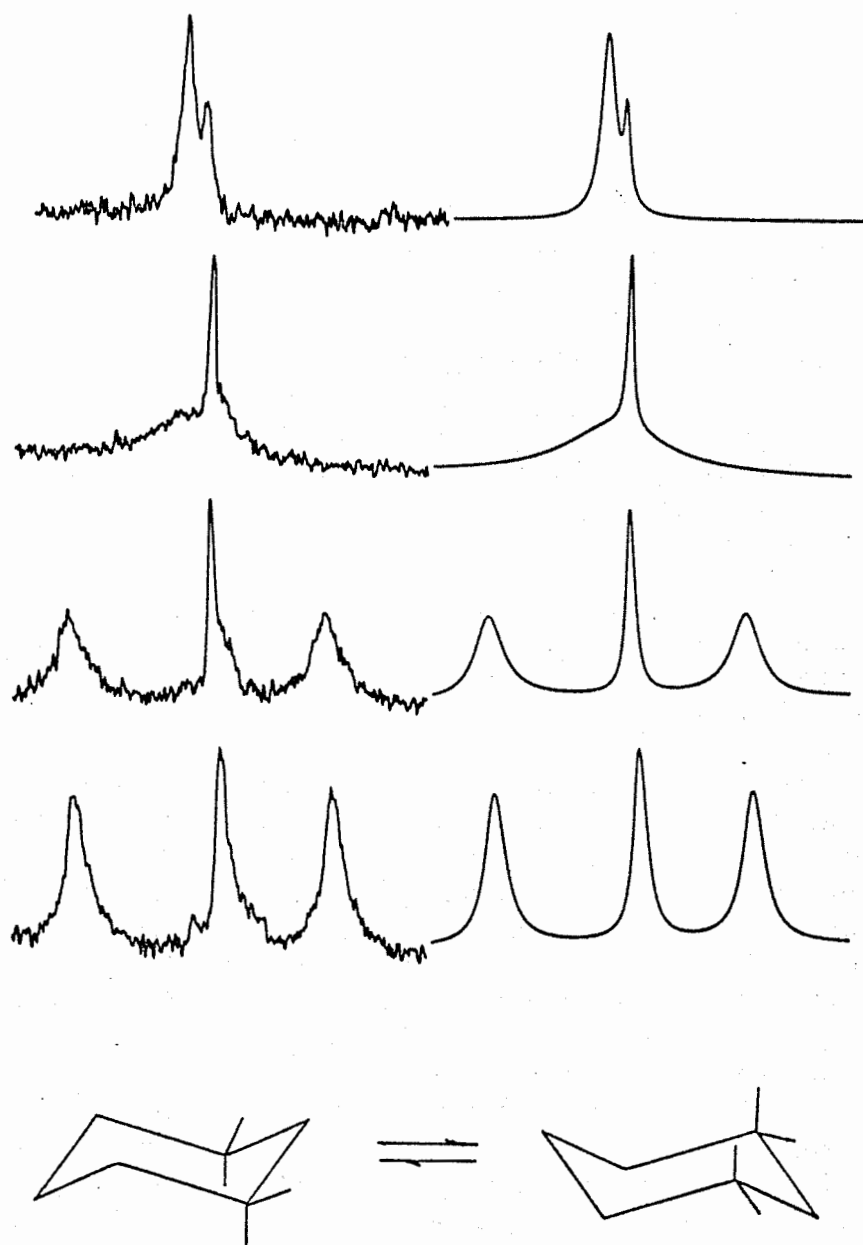(3)    G. Binsch, J. Amer. Chem. Soc., 91, 1304 (1969).



Figure 1.

Figure 2.

# STANFORD UNIVERSITY
## STANFORD, CALIFORNIA 94305

DEPARTMENT OF CHEMISTRY

20 August 1970

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

On Use of HA-100 Console with HR-60 System
Modified Pen Holder for HA-100, T-60, some A-60's

Dear Barry:

.While most of our colleagues are concerned with
the conversion of their nmr systems to higher fields
and frequencies, we have recently had occasion to re-
verse this process.

After obtaining some relaxation measurements at
100 MHz, one of our students wanted to repeat some of
the measurements at 60 MHz, only to find that our HR-60,
which has no field-frequency lock, was not stable
enough.  Since both instruments are located in the
same room, we decided to try using the HA-100 console
to control the 60 MHz RF unit, probe and field.

We were pleased to find that the extension cables
(approx. 20 ft) required to make the interconnection
did not diminish the signals below a useful level.
Thus it was not necessary to move any heavy equipment.
The conversion now requires less than five minutes and
involves the switching of a few connections from stan-
dard arrangement to an interconnecting cable which we
have tied together in a permanent harness.

For this operation, the regular cables for the
homogeneity control and slow sweep units of the HR-60

Professor Bernard L. Shapiro
20 August 1970                                             -2-


have been relocated so that the controls may be set
near the HA-100 console.  We did not attempt to
extend the homogeneity cables.  Attempts to extend
the slow sweep cables led to a poor flux stabilizer
lock.  Possibly this could have been compensated for
by readjusting the amplifier gain and magnet regulation
controls on the V-3506.  Parallel connection of the
two scopes (optional) permits monitoring the signal
while adjusting RF unit or probe at the HR-60 console.
All other adjustments are made from the HA-100 con-
sole area.

       We have had a modified pen holder made up for
use with the LeRoy lettering pens used on the HA-100,
T-60 and some A-60's which does not require removal
of the pen from the holder to cap the pen.  We believe
it is more conducive to cap the pen if no adjustment
of holder is required.  The holder is of 1/16 inch
sheet metal (see diagram).

                                Sincerely yours,
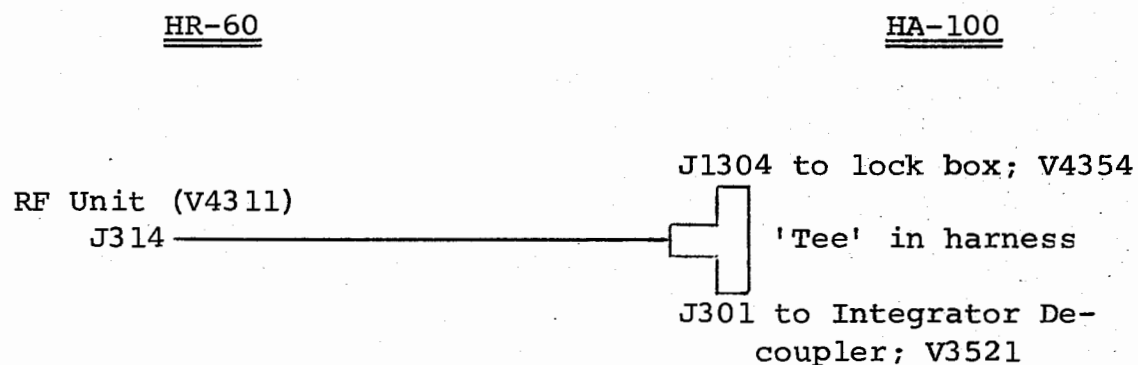
                                M. Bramwell
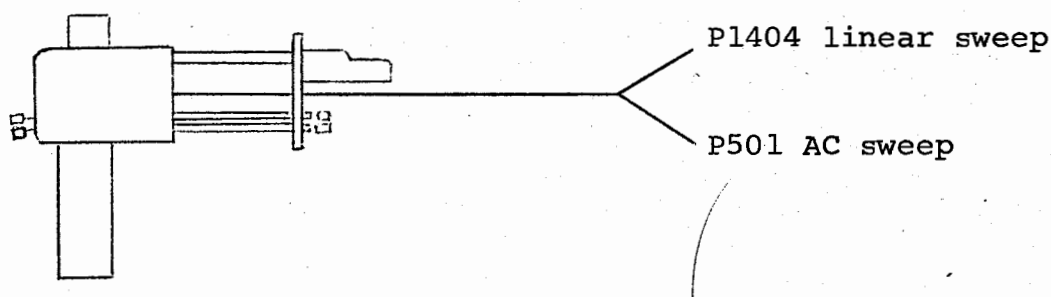
                                L. Durham

                                S. Seaver
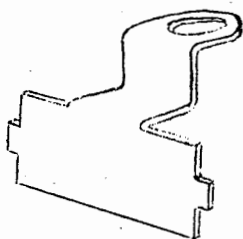

Please credit subscription
to L.J.D.

Schematic for production of an HA-60 hybrid by

crossing an HR-60 with an HA-100

HR-60                                            HA-100

J1304 to lock box; V4354

RF Unit (V4311)
  J314 ——————————————————————⊐┌     'Tee' in harness

J301 to Integrator De-
  coupler; V3521

  Probe



P1404 linear sweep

P501 AC sweep

Flux Stabilizer (V3506)

  TB1  Nos. 1
  Coils      2 ——————————— J1305          lock box, V4354

      ground ——————————— ground


  Scope                                          Scope

    vert ————————————————————————— vert

    horiz. ———————————————————————— horiz.
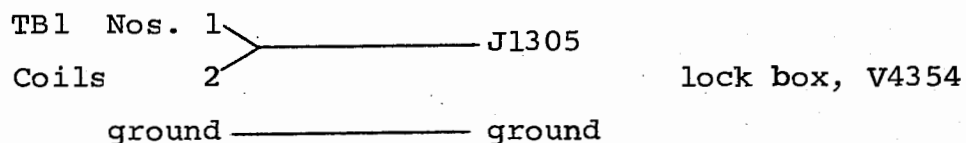
*Department of Chemistry*

# BROCK
# University

St. Catharines, Ontario

August 20, 1970

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

Dear Dr. Shapiro:

### Effects of hydrogen fluoride contamination
### on nmr spectra of $BF_3$ adducts

A number of $^{19}F$ studies of $BF_3$ adducts have shown the presence
of small amounts of a second fluorine-containing species in addition to
the simple donor-acceptor adduct.  If the Lewis base involved is suffi-
ciently weak, the second $^{19}F$ peak can arise from the $BF_3$ adduct of water
present in incompletely dried materials (1); if the adduct is unstable,
various decomposition products may appear.  However, even in stable systems
in which the Lewis base is too strong to be displaced from its adduct by
water, a second peak, usually small, may appear.  Our recent work suggests
that in at least some such cases the extra peak arises from contamination
of the system by HF, rather than from adducts of other than 1:1 stoichi-
ometry or from an associated form of the 1:1 adduct, as have on occasion
been postulated.  Some results from the $BF_3$-tetramethylurea (TMU) system
illustrate this.  We have observed similar effects in trialkylamine and
N,N-dialkylamide systems.

BF$_3$ is known to form a 1:1 adduct with TMU; thus, when TMU and
$BF_3$ in a 2:1 molar ratio are introduced into methylene chloride as solvent,
all of the $BF_3$ should be present as the 1:1 adduct.  Such a solution, when
prepared directly from commercial $BF_3$, gave the two-peak room temperature
$^{19}F$ spectrum shown in Fig. 1a.  It was possible to resolve the smaller
high-field peak into a 1:1:1:1 quartet with $J_{11_B-19_F} = 1.1$ Hz, reminiscent
of $BF_4^-$ (2).  The presence of $BF_4^-$ was confirmed by a pronounced increase
in the size of this peak, with no change in the fine structure, when n-Bu$_4$N$^+$.BF$_4^-$
was added to the solution (Fig. 1b).  Careful purification of $BF_3$, in
particular a trap-to-trap distillation from a $-112^O$ trap, gave a sample

Dr. B. L. Shapiro                    - 2 -                    August 20, 1970.

having a $^{19}$F spectrum having only one major peak; we could not, however, completely eliminate the second peak (Fig. 1c). Additions of anhydrous HF to such a solution caused the $BF_4^-$ peak to grow at the expense of the $TMU.BF_3$ peak. HF, $BF_3$, and TMU apprently react as follows, until the HF is used up:

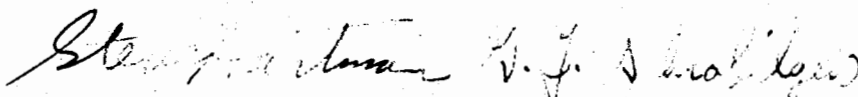$$HF + BF_3 + TMU \rightarrow TMU.H^+ + BF_4^-.$$
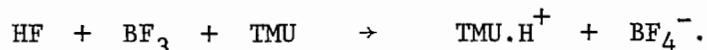
The remaining $BF_3$ forms $TMU.BF_3$. The relative $^{19}$F peak areas would thus indicate the proportion of HF in $BF_3$.

It should be noted that some samples of commercial $BF_3$, in particular those taken from nearly-empty cylinders in which the less volatile HF had become concentrated, contain up to 20% HF; normal purification procedures may not be designed to handle such large amounts of impurities. Thus it seems likely that some of the studies reported in the literature have been carried out using impure material.

All samples in which [TMU] > [$BF_3$] give two major room temperature $^1$H peaks corresponding to "free" TMU and $TMU.BF_3$. The samples which show a significant $BF_4^-$ peak in the $^{19}$F spectrum also show an abnormal low-field shift for the "free TMU" $^1$H peak. According to the above reaction, such samples should contain three TMU species, free TMU, $TMU.H^+$, and $TMU.BF_3$. Since proton exchange is generally very fast, we expect a single averaged signal for TMU and $TMU.H^+$ which should shift to low field as the relative amount of $TMU.H^+$ and $BF_4^-$ increases, as is observed. $BF_3$ exchanges much more slowly than $H^+$ among TMU molecules, so that a separate $TMU.BF_3$ peak, of fixed chemical shift, is visible up to about 90°C. A more complex case of proton transfer affecting chemical shifts of "free" base molecules has been reported in the methanol-$BF_3$ system (3).

The elimination of complications arising from HF contamination has made possible more exact studies of the surprisingly complex TMU-$BF_3$ system.

Yours sincerely,

J. S. Hartman        G. J. Schrobilgen

JSH:GJS:hk

References:

(1) R.J. Gillespie and J.S. Hartman, Can. J. Chem., 46, 2147 (1968).
(2) R.J. Gillespie, J.S. Hartman and M. Parekh, Can. J. Chem., 46, 1601 (1968).
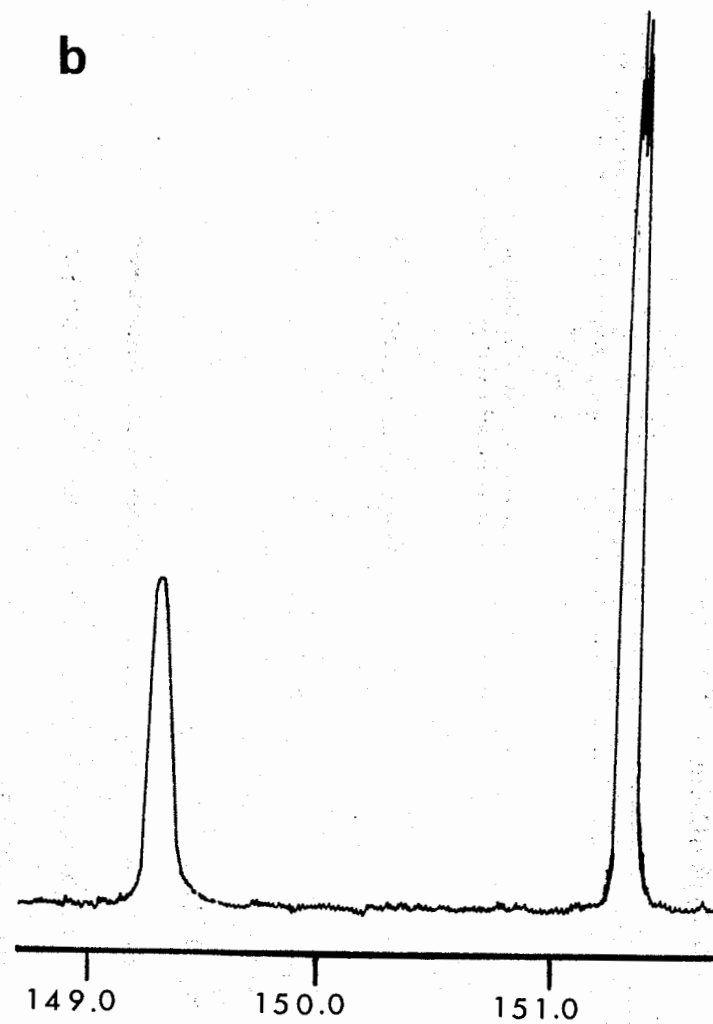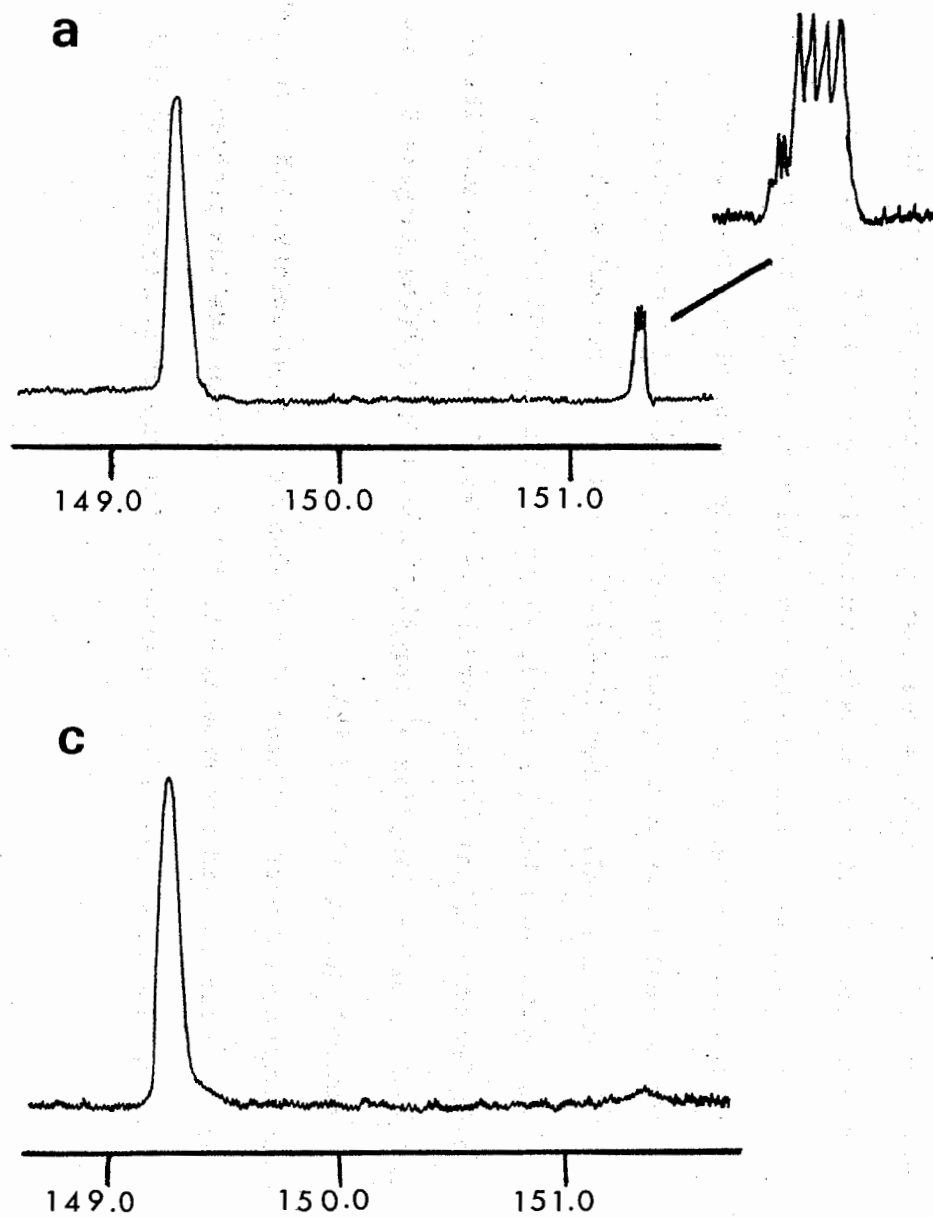(3) R.J. Gillespie and J.S. Hartman, Can. J. Chem., 45, 2243 (1967).

Fig. 1 – $^{19}F$ spectra of TMU–BF$_3$ solutions in methylene chloride. TMU is present in excess. Calibrations are in ppm from CFCl$_3$.

# UNIVERSITY OF CALIFORNIA, LOS ANGELES

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DEPARTMENT OF CHEMISTRY
LOS ANGELES, CALIFORNIA   90024

August 21, 1970

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

> Title:   The Direct Determination of the Axial Conformer
>
> of Methylcyclohexane by 63.1 MHz $^{13}$C NMR at Low
>
> Temperatures.

Dear Barry:

A great deal of work has been done on the conformational equilibria of

substituted cyclohexanes.  Perhaps the most unambiguous procedure for the

determination of the relative amounts of equatorial and axial forms is to

measure the nmr spectrum at such low temperatures (e.g. -100°) that separate

spectra are given by the two forms.[1,2]     Integration then gives the desired

result, provided that peaks do not overlap for all the nuclei under observa-

tion.  With proton nmr, this method is easy to apply to compounds such as

chlorocyclohexane or cyclohexyl acetate, where (i) the methine proton on C-1

has quite different chemical shifts for the two forms, and (ii) the equilibrium

constant (K=[equatorial form]/[axial form] is not too large (the largest K which

has been measured[1] has a value of 29).

Methylcyclohexane meets neither of the above two requirements, and further-

more partial deuteration is not expected to solve the peak overlap problem.

Thus there has been no report of the observation of the proton spectrum of the

Professor B. L. Shapiro — 2 — August 21, 1970

axial form of methylcyclohexane. We now have been able to observe the 63 MHz $^{13}$C spectrum[3] of the axial conformer of methylcyclohexane at $-100°$. (Fig. 1). The work of Dalling and Grant,[4] shows that the chemical shifts of the methyl carbon ($\alpha$) and the methylene carbons 3 and 5 should be at about 8 ppm higher field than the corresponding carbons in the equatorial form. Therefore, at 63 MHz the $\alpha$, 3 and 5 carbons should occur in a region free of bands of the equatorial form, or of its $^{13}$C satellites ($J_{C^{13}C^{13}} \simeq 35$ Hz for $sp^3$-$sp^3$ single bond). The bands in Figure 1 assigned to the axial isomer are not present at $-75°$, and are thus unlikely to be due to chemical impurities. Furthermore their chemical shifts are in close agreement with the empirical chemical shift rules of Dalling and Grant, and their relative intensities ($\simeq$ 2:1) are as expected.

The value of the equilibrium constant is about 100, corresponding to an A value for the methyl group of 1.6 kcal/mole, in good agreement with the accepted value of 1.7 kcal/mole.

Yours sincerely,

F. A. L. Anet
C. H. Bradley
G. W. Buchanan*

1) F. R. Jensen, C. H. Bushweller, and B. H. Beck, J. Amer. Chem. Soc., 91, 344 (1969).

2) F. A. L. Anet and P. M. Henrichs, Tetrahedron Letters, 741 (1969).

3) The spectrometer, which makes use of a 59 kgauss superconducting solenoid, was briefly described at the 11th Experimental NMR Conference, Pittsburgh, Pa. April 1970.

4) D. K. Dalling and D. Grant, J. Amer. Chem. Soc., 89, 6612 (1967).

*Present address:  Department of Chemistry
                    University of Windsor
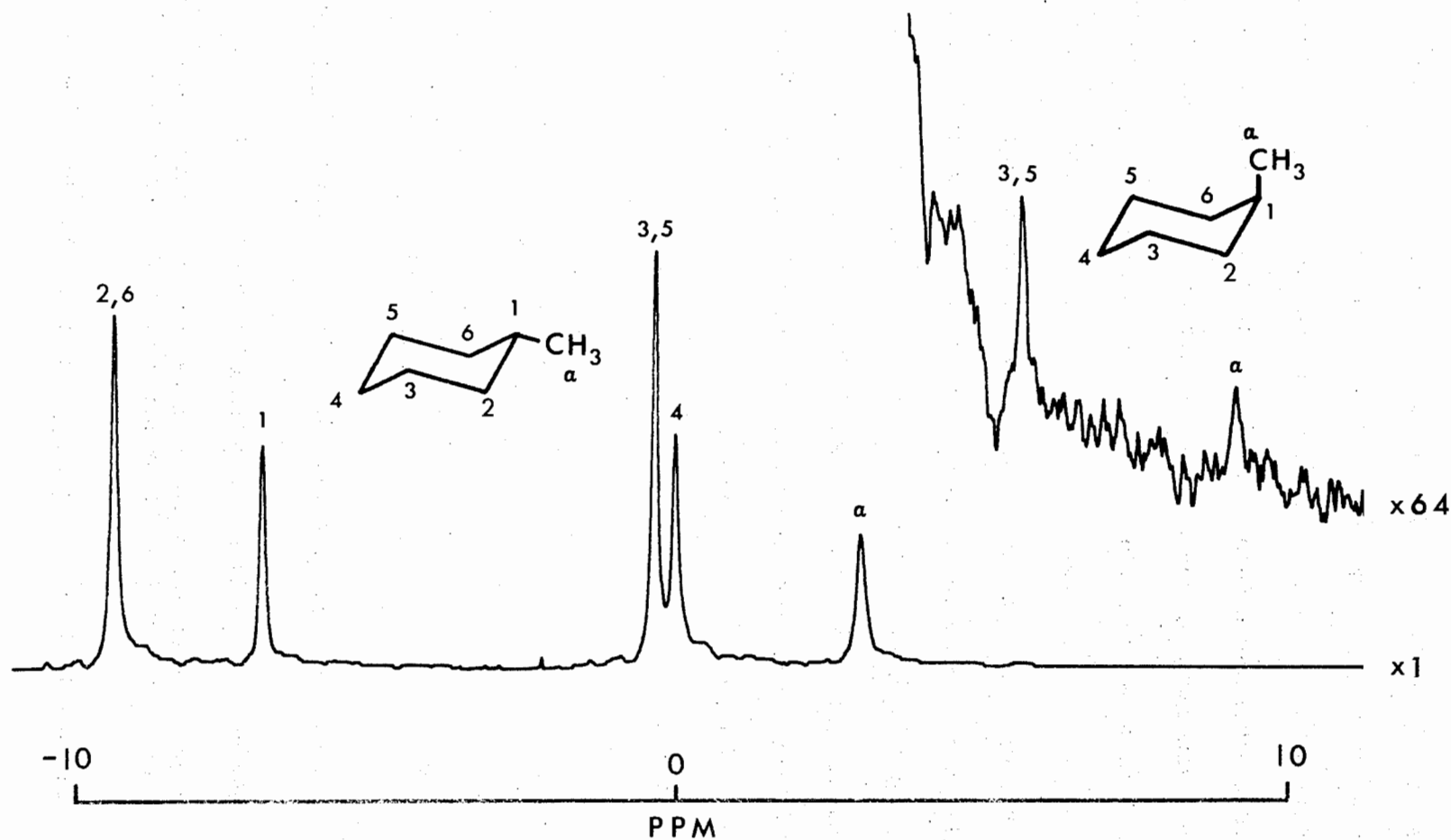                    Windsor, Ontario
                    Canada

Figure 1. 63.1 MHz ^{13}C spectrum (protons noise-decoupled at 251 MHz) of neat methylcyclohexane at −110°. Carbon 4 which is expected to have the same chemical shift in both conformers, is used as an internal reference. Zero on this scale is about 102 ppm upfield from benzene and about 27 ppm downfield from TMS. Spinning 10 mm sample tubes were used and the sweep rate was 16 Hz/sec. The spectrum represents 96 scans time-averaged on a Varian CAT.

# Imperial Chemical Industries Limited

DYESTUFFS DIVISION

P.O. Box 42, Hexagon House, Blackley, Manchester, 9

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

Your Ref:

Our Ref: PL/ARS/B5

21 August, 1970.

Dear Professor Shapiro,

Thank you for your blue letter; alas, the moving pen having writ thrice last year must still write on.

### $^{14}N$ shifts in Substituted Anilines

We have continued our study of $^{14}N$ chemical shifts obtained by the double resonance method reported previously [1,2], our attention this time being directed to meta and para substituted anilines. Measurements were made on thirteen compounds in acetone solution. The shifts are quoted in p.p.m. upfield from the nitrate nitrogen signal a 4.5M solution of ammonium nitrate in aqueous 3N-hydrochloric acid and are shown in the following table.

| Compound | | $^{14}N$ shift | Compound | $^{14}N$ shift |
|---|---|---|---|---|
| | Aniline | $321.7 \pm 0.5$ | | |
| p-NO$_2$ | " | $306.5 \pm 0.5$ | m-NO$_2$ Aniline | $317.7 \pm 0.5$ |
| p-CH$_3$CO | " | $312.7 \pm 0.5$ | m-CH$_3$CO " | $319.4 \pm 0.5$ |
| p-CH$_3$OCO | " | $312.6 \pm 0.5$ | m-CH$_3$OCO " | $319.9 \pm 2.0$ |
| p-Br | " | $320.1 \pm 1.0$ | m-CF$_3$ " | $319.3 \pm 0.5$ |
| p-Cl | | $320.5 \pm 1.0$ | | |
| p-CH$_3$ | " | $323.7 \pm 0.5$ | m-CH$_3$ " | $322.6 \pm 0.5$ |
| p-NH$_2$ | " | $330.1 \pm 1.0$ | | |

The shifts of both the meta and para substituted compounds correlate with the Hammett $\sigma$ parameters of the substituents. These results will be discussed more fully in a paper now in preparation.

We are hoping to take delivery within the next two or three months of a Ferranti Argus 500 computer and a Fourier Transform accessory for our HA-100 spectrometer and we anticipate having some results to report in our next contribution.

Yours sincerely,

P.HAMPSON, A.MATHIAS.

1. P.Hampson and A.Mathias Molec. Phys. 11, 541, 1966.
2. P.Hampson and A Mathias Nmr Newsletter 95, 1, 1966.

## NATIONAL RESEARCH COUNCIL OF CANADA
## CONSEIL NATIONAL DE RECHERCHES DU CANADA

OTTAWA 7.

31 August 1970

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

Dear Barry,    "Solvent Effects on Fluoroform Shifts"

    I was very interested in the results given by
W.B. Smith in Newsletters #143 p22 August 1970 on Solvent
Effects of fluoroform shifts and coupling for both H and
F nuclei. The statement is made that "whereas the proton
chemical shifts (except in benzene) are downfield from the
value in cyclohexane the fluorine chemical shifts move
upfield with increasing solvent polarity".

    In our work on perturber effects on the F and H
resonance in gaseous HCF$_3$ [J. Chem. Phys. $\underline{38}$ 1562 (1963)]
we obtained the same result for F in CHF$_3$ and attributed
it to the fact that the coefficient of the electric field
term is negative in the equation for the intermolecular
effect on chemical shifts viz eqn (5) in the above reference.
That is, in the equation

$$\sigma_E = -A<E_z> - B<E^2>$$

A is positive for H in CH bonds and relatively small. B is
also positive so increasing solvent polarity gives larger
downfield shifts. For F in HCF$_3$ however, A is negative and
relatively large so that although B is positive the effect of
increasing polarity is to shift the F resonance to higher
field because of the dominating effect of the term in A.

                  Yours sincerely,

                  H.J. Bernstein

HJB:sc

Gerhard Binsch
Department of Chemistry
University of Notre Dame
Notre Dame, Indiana   46556

Joseph B. Lambert
Department of Chemistry
Northwestern University
Evanston, Illinois   60201

September 1, 1970

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

Symposium on Dynamic NMR Spectroscopy

Dear Barry:

We hereby wish to announce a two-day symposium on "Dynamic NMR
Spectroscopy", to be held on March 30 and 31, 1971, jointly with the Los Angeles
ACS meeting.   This symposium will be sponsored by the Organic Division and
possibly co-sponsored by the Division of Physical Chemistry.   A decision regard-
ing the co-sponsorship will be made in September, 1970.

The backbone of the symposium will consist of a series of invited papers.
The following scientists have so far assented to contribute:

F. A. L. Anet: "Dynamic NMR Studies at 59 Kilogauss."
C. H. Bushweller: "Rate Processes in Acyclic Trialkylamines."
R. Freeman (and H. D. W. Hill): "Nuclear Spin Relaxation
   Studied by Fourier Transform Methods."
P. Jesson (and P. Meakin): "Stereochemically Nonrigid Six-
   Coordinate Hydrides."
J. Jonas: "High-Pressure NMR Relaxation Studies of Liquids."
M. Saunders: "Dynamic NMR Studies of Carbonium-Ion
   Rearrangements."

In addition, there will be room for about a dozen 15-minute presentations.
We solicit contributions from the following areas of current research:  Theoretical
and experimental aspects of exchange-broadened nmr line shapes, carbonium-ion
rearrangements by dynamic nmr, theory and applications of nuclear-spin
relaxation phenomena, dynamic aspects of multiple resonance, pseudorotation and
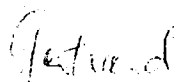
Professor Bernard L. Shapiro
Page 2
September 1, 1970

other permutational phenomena, pulse techniques in dynamic nmr, the study
of conformational interconversions, atomic inversions and valence isomerization
by dynamic nmr, nuclear-spin exchange and relaxation processes in inorganic
and organometallic compounds, and applications in biochemistry.

Those of your readers who are interested in contributing a short paper
are asked to communicate with either of us. The Standard Abstract Form for
ACS Meeting Papers is obtainable from us or from the ACS Divisional Offices.
A 200 word abstract on the official form is all that is needed in advance of the
meeting, but this abstract must be in our hands before November 25, 1970.

Sincerely yours,

Gerhard Binsch

Joseph B. Lambert

kjs

# CLEMSON UNIVERSITY

## CLEMSON, SOUTH CAROLINA 29631

**DEPARTMENT OF**
**CHEMISTRY AND GEOLOGY**
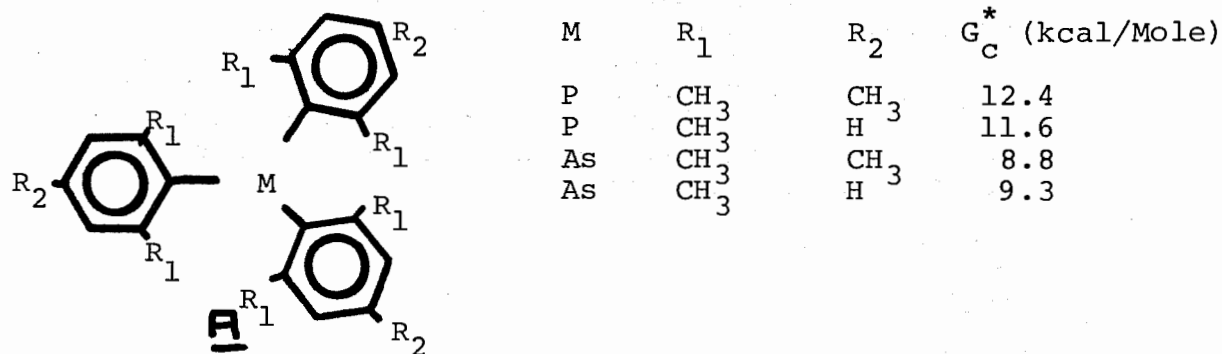
September 8, 1970

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

ROTATIONAL BARRIERS IN DIPHOSPHINES

Dear Barry:

Substantial rotational barriers about C-M bonds
in highly substituted derivatives of structure A have
been observed (1,2). A substantial barrier to rotation



| M | $R_1$ | $R_2$ | $G_c^*$ (kcal/Mole) |
|---|-------|-------|---------------------|
| P | $CH_3$ | $CH_3$ | 12.4 |
| P | $CH_3$ | H | 11.6 |
| As | $CH_3$ | $CH_3$ | 8.8 |
| As | $CH_3$ | H | 9.3 |

about the central M-M bond in compounds of type B must
be invoked to rationalize the experimental results
reported for tetrakis-(pentafluorophenyl)-diarsine (3).



**B**
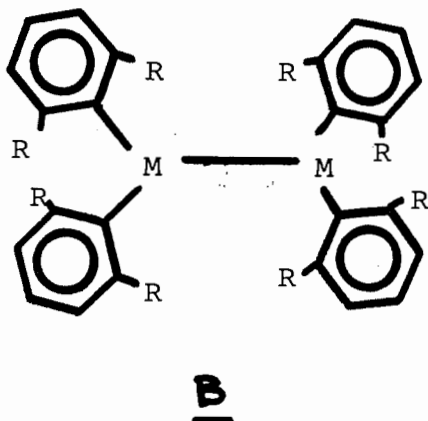
In this connection, we have studied the temperature
dependent spectra of tetrakis-(2,6-dimethylphenyl)-
diphosphine (B; R=$CH_3$, M=P). At room temperature
in toluene d$_8$ only a single methyl resonance is
observed at 145.5 Hz below internal TMS (60 MHz).
This observation is most consistent with a model
in which all molecular torsions are rapid, or, a
model in which only a single torsional M-M di-
astereomer is present (trans) and M-C rotation is
rapid. A frozen gauche diastereomer should exhibit
two methyl resonances even if C-M rotation is rapid.

At -48°, four methyl resonances are observed
at ca. 180, 157, 130, and 127 Hz, with areas 1:1:
2 (sum of areas for resonances at 130 and 127 Hz),
respectively. This observation is most succinctly
rationalized by a model in which P-P rotation is
rapid and P-C rotation is slow. The cant of the
rings can be the same on both P atoms ($C_2$ symmetry
in the eclipsed form) or opposite on the P atoms
($C_s$ symmetry in the eclipsed form). Alternatively,
slow P-C rotation in any single P-P torsional
diastereomer (preferably trans) will provide the
same result; slow P-P rotation alone does not
suffice to rationalize the experimental observation.

We are currently synthesizing systems which
will hopefully afford information on phosphorous
pyramidal inversion, P-C bond rotation, and P-P
bond rotation simultaneously.

Sincerely yours,

John Jacobus

(1)  A. Rieker and H. Kessler, Tet. Lett., 1227(1969).
(2)  Unpublished work, J. J.
(3)  M. Green and D. Kirkpatrick, Chem. Commun., 57(1967).

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