Texas
A
M &

No. 152

University
N – M – R
Newsletter

MAY, 1971

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

Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843
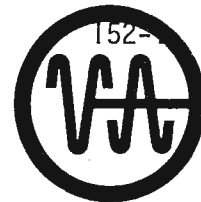
Professor B. L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station,
Texas 77843.   April 13th 1971

<u>"INEPT" or How to Make</u>
Dear Barry,   <u>Spin Echoes without Really Trying</u>
          Your computer sounded off with a blue note prematurely this
time; if you consult the Library of Congress files, TAMUNN <u>147</u>, 50 (1970),
you will see we are only four months in arrears.

          Nevertheless we would like to describe a spin echo effect that
occurs almost incidentally in a conventional Fourier transform experiment
where no refocussing 180° pulses have been introduced.   Similar observations
have been reported privately by John Waugh, Mel Klein and Wm. Wallace.

          Suppose a regular sequence of rf pulses with an arbitrary flip
angle ($\alpha = \gamma H_1 \tau$) is applied to spins in a liquid sample at a rate fast
compared with the spin-spin relaxation times.   A steady-state response
will eventually be established (1) according to the equations:

$$M_x^- = M_0(1 - E_1)(E_2 \sin\alpha \sin\theta)/D$$

$$M_y^- = M_0(1 - E_1)(E_2 \sin\alpha)(\cos\theta - E_2 \sin\alpha)/D$$

$$M_z^- = M_0(1 - E_1)(F + GE_2 \cos\alpha)/D$$

$$M_x^+ = M_x^-$$

$$M_y^+ = M_0(1 - E_1)(F \sin\alpha)/D$$

$$M_z^+ = M_0(1 - E_1)(GE_2 + F\cos\alpha)/D$$

where M_x^- is the x-component of magnetization immediately before the pulse,
and M_x^+ is the same component immediately after the pulse, and these
abbreviations have been used:

$$E_1 = \exp(-T/T_1) \qquad E_2 = \exp(-T/T_2) \qquad F = 1 - E_2\cos\theta$$

$$G = E_2 - \cos\theta \qquad D = F(1 - E_1\cos\alpha) - GE_2(E_1 - \cos\alpha).$$

A key parameter is the "excess precession angle" θ, defined by:

$$(2n\pi + \theta) = \gamma \Delta HT$$

where ΔH is the offset from resonance and T is the pulse interval.
These expressions describe the distribution of magnetization vectors in
space as a function of θ, and the geometry is much simpler than might
have been expected.   The tips of the vectors are disposed around the
circumference of ellipses (circles if $T_1 = T_2$), one ellipse (M^-) just
before the pulse, the other (M^+) just after the pulse   (obtained by
rotation of the M^- ellipse through α radians about the X axis of the
rotating reference frame). For simplicity they may be visualized in
projection on the XY plane (Fig. 1).

          Consider the case of a single resonance line with center
frequency equal to the rotational frequency of the reference frame.
Field inhomogeneity will cause a distribution of θ values for this line,
and between pulses some of the vectors (b' through j') will precess
clockwise, and others (not shown) will precess counterclockwise. The

net Y component of magnetization will thus decay (as expected), but as the vectors move toward their ending positions (a through j) around the lower ellipse they will induce an increasing (negative) Y component of magnetization which reaches its largest value immediately before the pulse. A line not centered at the frequency of the rotating frame induces a sinusoidal signal whose amplitude decays and then grows back, with the ending phase 180° shifted from the beginning phase. Thus, provided a steady-state response is established where transverse relaxation between pulses is incomplete, the regular pulse sequence has the intrinsic property of refocussing magnetization isochromats dispersed by the inhomogeneous magnetic field.

This somewhat surprising result can be thought of as a spin-echo effect by analogy with the 90°-τ- 90° echoes observed by Hahn. A regular sequence of 90° pulses would impose the third 90° pulse at the center of the Hahn echo, exciting later echoes which also coincide with 90° pulses, so that eventually a steady-state is established where there is a negative "half-echo" preceding each pulse with a positive free induction decay after each pulse.

Experimental "echoes" from a steady-state Fourier transform experiment on carbon-13 in coherently decoupled methyl iodide, averaged over 256 transients, are shown in Fig 2(a). The echoes may be destroyed by instability in the field/frequency ratio (which may explain why such effects have not been widely reported) or by deliberately introducing incoherence [Fig. 2(b)] .

The refocussing process improves the sensitivity of the Fourier transform experiment over that calculated on the assumption that the free induction signal simply decays exponentially with time constant T_2^*. Analyses of the DEFT school of Fourier transform experiments have made this assumption, and thus have shown the old-fashioned Fourier transform technique at an undeserved disadvantage (2).

It has become customary to optimize sensitivity by multiplying free induction signals with a function that enhances the early part of the signal where the signal-to-noise ratio is high. The equivalent of a "matched filter" may be achieved by weighting each point by the signal-to-noise ratio at that point. When refocussing occurs, the usual exponentially decaying function is no longer optimum for this purpose.
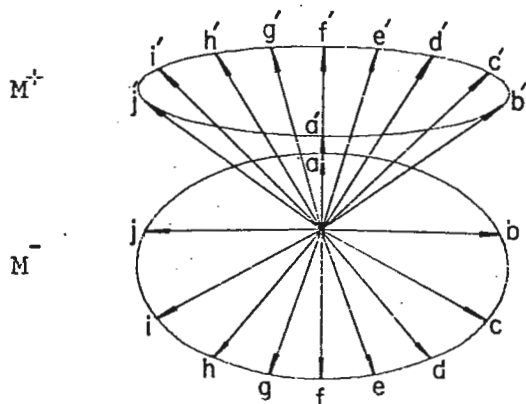
We have learnt the hard way that to send a TAMUNN letter without a title is to invite disastrous intervention by the Editor, so we have wasted a disproportionate amount of time looking for acronyms. INEPT (Incidental negative echoes in a pulse technique) contrasts nicely with DEFT, but FINESSE (Focussing of isochromats into negative echoes in a steady-state experiment) is a more positive approach.

Best wishes,

Ray

Ray Freeman   Howard Hill

Fig. 1

(1) R. R. Ernst and W. A. Anderson, Rev. Sci. Instr. <u>37</u>, 93 (1966).

(2) P. Waldstein and W. E. Wallace, Rev. Sci. Instr. (in press, 1971).
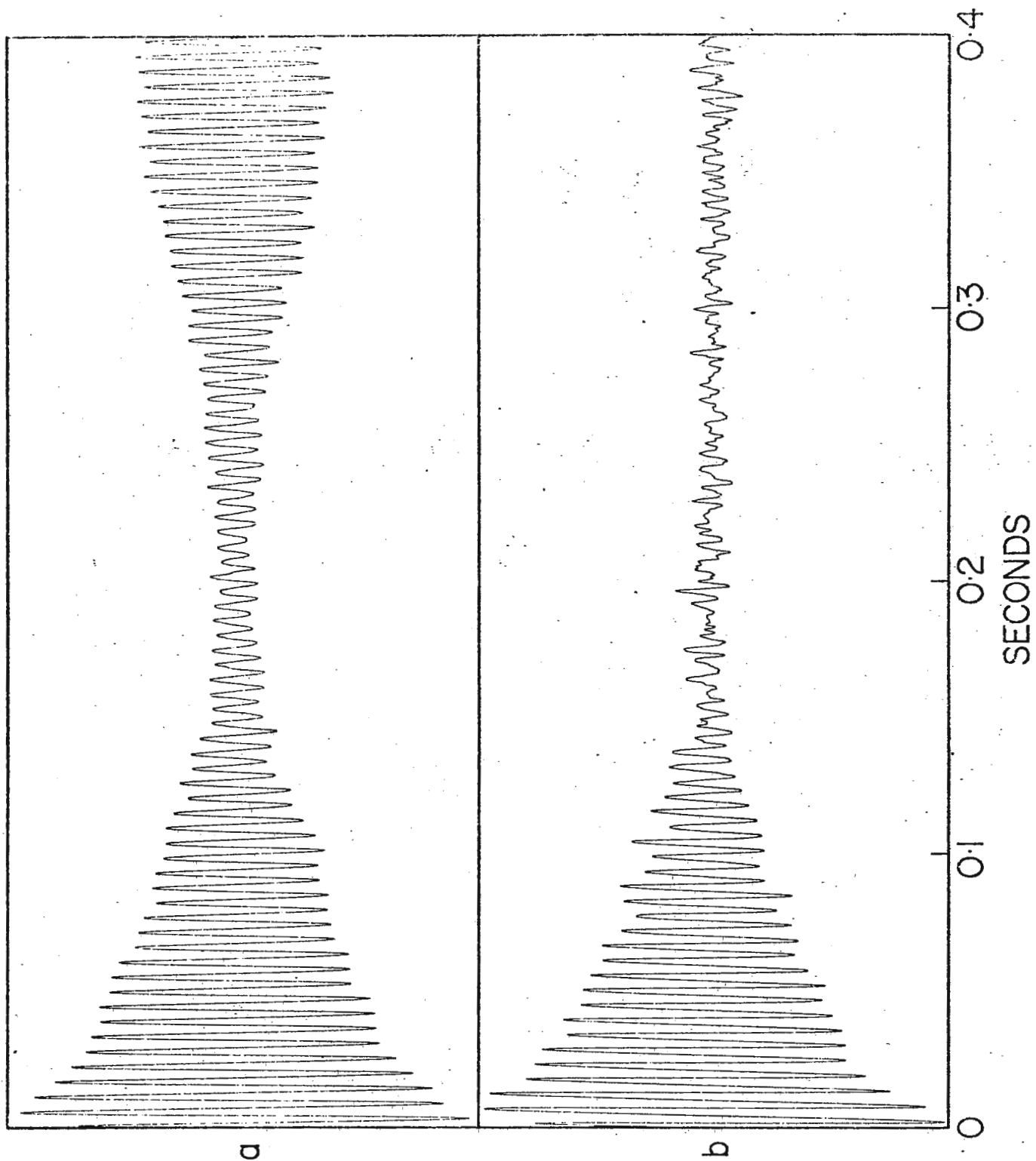
Fig. 2 (a) Refocussing effect observed with ^{13}C signal of methyl iodide.
(b) Spin echoes destroyed by deliberately introducing incoherence.

18th March, 1971.

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

Your Reference:

Our Reference: DS/cak

Dear Professor Shapiro,

Locked Deuterium Spectra from the XL-100-15

No. 147 of your News Letters has just reached England now that the postal strike
situation is back to normal. This contains a second description of how to obtain
deuterium spectra on a standard XL-100, (the first was in No. 142). Both these
methods throw away a rather useful feature of modern NMR Spectrometers by
which I mean, of course, a field frequency lock.

When the XL-100 is set for 'deuterium lock' with the field frequency control unit in
the 'adjust' position, the Spectrometer is field frequency locked to the observing
nucleus, e. g. the proton. If the recorder is now moved, one has a field sweep
Spectrometer locked through the observing nucleus. All that remains to obtain
deuterium spectra is to route the signal from the deuterium RF unit, which is doing
nothing at the present moment, into the observing audio circuitry.

The re-routing required is to disconnect the audio input on pins A and B of P801 in
the Spectrometer control module. The output from the lock receiver, which is
easiest obtained from pins 4 and 9 of J212 of the RF module, is now connected in
place of the previously disconnected audio input. This switching can be obtained
simply with a two wafer, two way switch. The switch having a 'normal' position,
where the XL observes as usual, and a 'deuterium' position. If, by chance, the
instrument is operated with the field frequency module in 'operate' and the new
switch set to 'deuterium' , all that results is the pen recorder always plots the lock
signal. The modified Spectrometer on deuterium, operates almost normally, the
only major change being that the RF power for observing comes from the lock
module attenuator and vis-versa. The phases are controlled from their normal
controls. NB. The RF phase control now affects the lock channel, not the observe
channel.

Spectra obtained by this method are calibrated in terms of 'proton ppm'. i. e. If
the Spectrometer is set on the 1,000Hz width, the resulting deuterium spectrum is
10 ppm wide, (i. e. 154 Hz). As with deuterium, shifts are looked at rather than
coupling constants, this is quite a convenient operating arrangement. The enclosed
figure shows the spectrum of approximately 45% DMSO (D_6), 45% $CDCl_3$ locked to
10% $CHCl_3$.

Cont' d ....

The disadvantages of this technique are firstly, it reverts to the use of field sweep, i.e. very fast sweeps and offsets must be avoided. (The recorder fast sweep on a 1,000Hz sweep width can be used O.K. with a reasonably good lock signal, eg. 2% TMS). Secondly, the spectra come out with field increasing to the left. This can be compensated for by putting a 180° phase shift in via the Spectrometer control module and using the chart paper up-side-down.

I must thank Dr. E. Finer of Unilever for provoking me into thinking this system up, and for allowing his XL-100-15 to be used as a test bed , and also Brian Katte of our Service Department for his help.

Further details can be obtained from here if anybody is interested.
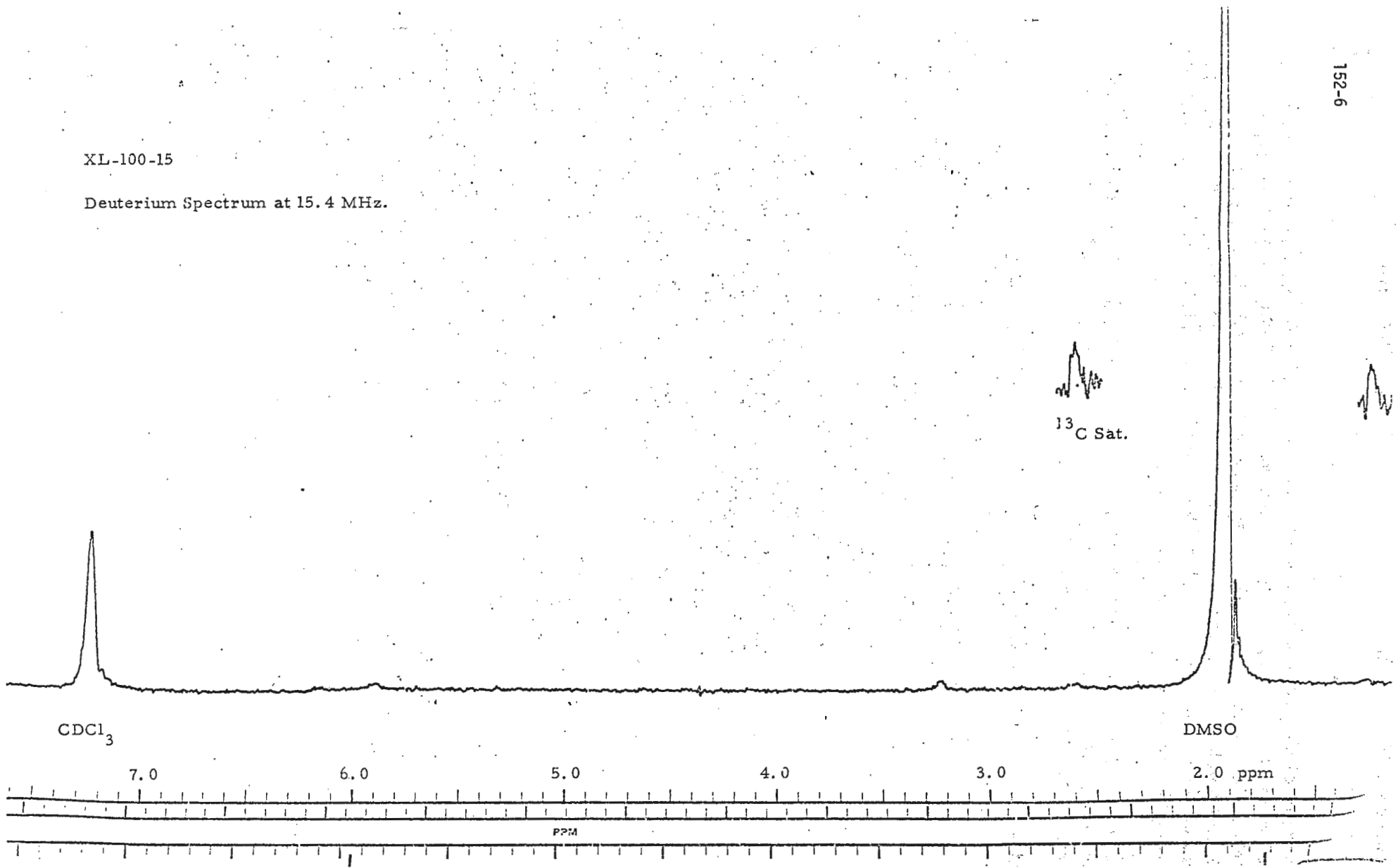
Yours sincerely,

DR. .D. SHAW

Applications Laboratory

Analytical Instrument Division.

XL-100-15

Deuterium Spectrum at 15.4 MHz.

^{13}C Sat.

CDCl$_3$

DMSO

7.0   6.0   5.0   4.0   3.0   2.0 ppm

PPM

QUEEN MARY COLLEGE

UNIVERSITY OF LONDON

DEPARTMENT OF CHEMISTRY
Professor K. W. Sykes, M A., B.Sc., D Phil.
Professor B. C. L. Weedon, Ph.D., D.Sc., F.R.I.C.
Professor D. C. Bradley, B.Sc., Ph.D., D.Sc., A.R.I.C.

MILE END ROAD
LONDON E.1
Tel. 01-980 4811

Professor Bernard L. Shapiro,   16th April, 1971
Department of Chemistry,
Texas A & M University,
College Station,
Texas 77843, U.S.A.

British ^{13}C Fourier Service

Dear Barry,

Our Bruker HFX-13 system has been installed for just over 6 months now and is operating very well. It has an 18 inch magnet; a small console; a synthesiser; noise decoupling on ^{1}H and ^{19}F frequencies; locking on ^{1}H , ^{2}H , or ^{19}F; observation of ^{1}H , ^{2}H , ^{13}C , ^{14}N , ^{15}N and ^{19}F. We also have a Fourier pulse-box, PDP8I Computer and Fabritek 1074.

We are just inaugurating the Science Research Council's national service for UK Universities under the direction of Dr. L.F. Farnell and Miss Eira Hughes. 50% of the machine time will be for users outside my group.

A report of Lanthanide induced shifts of ^{13}C resources of Borneol has just appeared (Chem. Comm. 1971, p.364) and a study by Paul Pregosin of stereochemical effects in nitrosamines should appear shortly in the same place.

Some of our nicest results are with ^{15}N Fourier (manuscript to be submitted). Alistair White has recently confirmed the dilution effect on the ^{15}N shift of N-methylformamide - ^{15}N (95% enriched) in water using the new system. These identical samples (in sealed 5mm tubes) were looked at by Duncan Gillies (and previously by Rod Chuck) using our old home-made double ^{1}H(^{15}N) resonance system in 1965 (London Univ. Thesis mentioned albeit incorrectly in Progress in NMR, No.6. p.143) which used a 9000 gauss permanent magnet.

The two sets of results are compared below. Concentrations are weight percentages.

^{15}N shifts of N-methylformamide - ^{15}N in H_2O

	Shifts are downfield in PPM				
	neat	75%	50%	25%	Errors
Gillies	0	2.83	4.63	5.42	(± 0.10)
White	0	2.61	4.48	5.69	(± 0.15)
differences	0	0.22	0.15	0.27	(± 0.25)

How gratifying!

Best regards,

Ed

EWR/PM   EDWARD W. RANDALL

Glaxo

Glaxo Research Ltd, Greenford, Middlesex

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

Prof. B.L. Shapiro,
Texas A & M University,
College Station, Texas 77843.

~~Please address reply to:~~
29th March, 1971

Dear Professor Shapiro,

Varian A60 Modifications

Varian A60 operators may be interested in modifications
that have been made to our machines. Soon after acquiring our
A60D spectrometer in November 1969, we noticed that when it was
run at the sweep-rate (1 Hz/sec), which we used routinely on our
old A60 (1962 vintage), the filter characteristics of the A60D
led to excessive damping and line-broadening, often causing
weak signals to be obscured. Better results could be obtained
by using sweep rates slower than 1 Hz/sec, but unfortunately
pressure of work precluded the routine use of long sweep times.

Inspection of the circuit diagrams, however, showed that
the capacitor network in the phase detector unit of the A60D
gave steeper attenuation of the signal than did the relatively
crude system used in the old A60 and suggested that it should
be possible to switch out some of this capacitance. Varian
after some caution accepted this suggestion and six months ago
modified our instrument so that by flicking a switch we can
change from A60D to "A60" filter characteristics. We have
found this modification most successful. For routine spectra,
the spectrometer is operated in the "A60" mode. Spectra of
chloroform obtained by the two modes using nominal filter
settings are compared in the Figure.

Varian, to whom we are indebted for the following details,
achieved the modification by inserting two sections of a multi-
pole relay in the leads between resistor R825 (200KΩ) and
positions 4 of switch S802A-R and of switch S802B-R. A third
section of the relay provides a connection from a point between
resistors R893 (3.3MΩ) and R894 (3.3MΩ) to position 5 of switch
S802B-R. The relay is energised <u>via</u> a switch from the +24 **v.**
of the recorder power supply and is arranged so that when the
relay is energised the contacts are closed and the instrument
operates in the A60D mode; when the contacts are open, capacitors
C843 to C862 are isolated giving "A60" filter characteristics.

cont/........

Comparison of 'A60' and A60D filter modes.
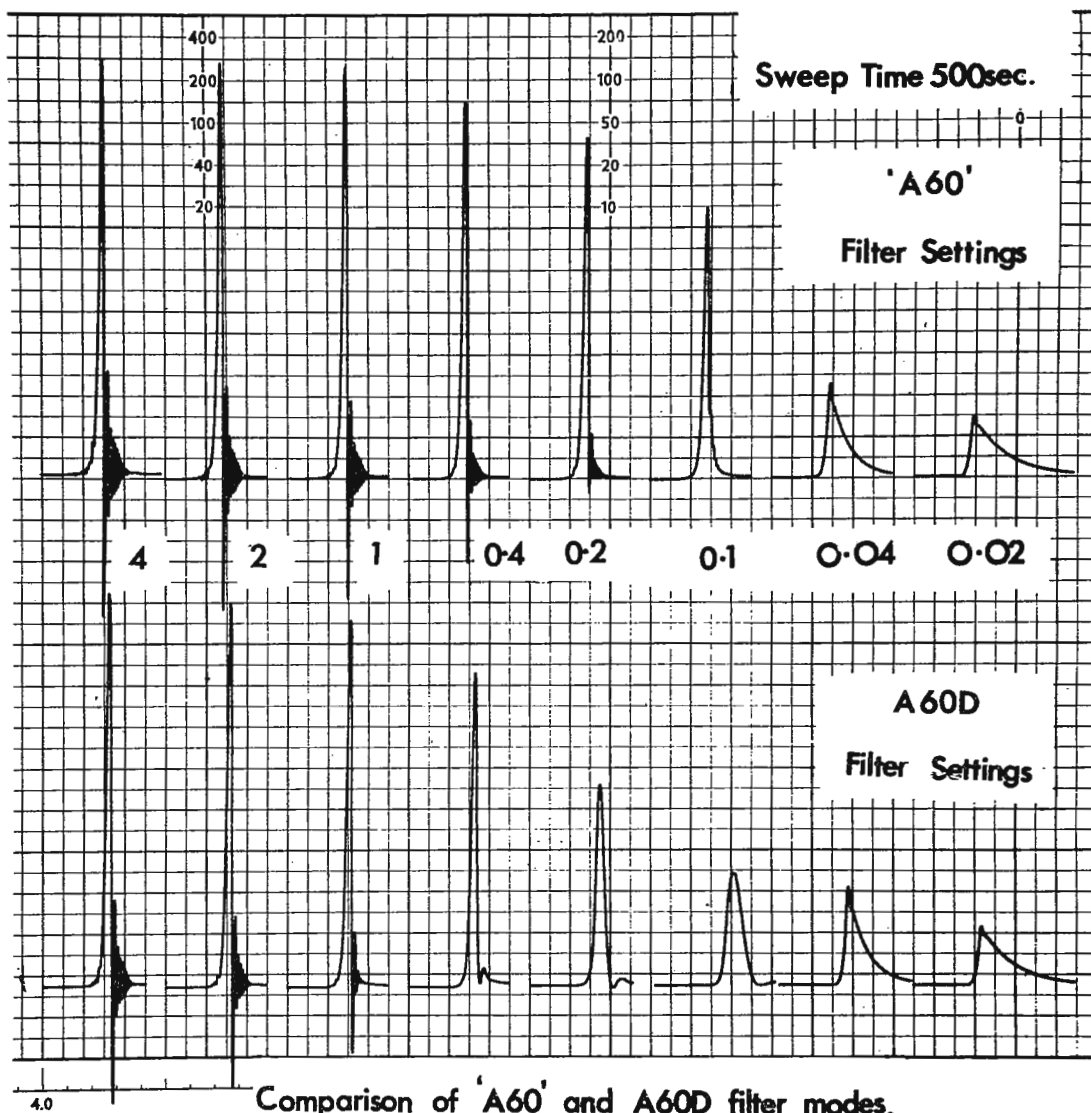
Nine months ago we arranged for Varian to rebuild the console of our old A60; this machine had given yeoman service but was beginning to suffer from noisy electronics and from recorder wear. The rebuilding operation included *inter alia* the provision of a V6031C probe and the replacement of the recorder, transmitter, sample receiver, control receiver and integrator D.C amplifier assemblies by modern units. The rebuilt machine needed some adjustment, especially to obtain suitable lock characteristics in what is admittedly a hybrid instrument, but it has since worked well and in some respects outperforms the new A60D. We are very pleased with the result.

Yours sincerely,

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

CHIMIE ORGANIQUE PHYSIQUE

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Tél. (40) 74-50-70

NANTES, le 4.3.71

Professor B.L. SHAPIRO
Chemistry Department
Texas A8 M University
College Station

TEXAS 77 843

Sign determination of the geminal and long range cumulenic coupling constants

Cher Professeur SHAPIRO,

Les constantes de couplage en série cumulénique constituant un bon test du mécanisme de couplage, elles ont suscité plusieurs études théoriques (1)(2). Cependant il existe peu de valeurs expérimentales de J et les signes n'ont pas été déterminés. Comme dans le cas du système allénique (3) une valeur fortement négative de $^2J_{H-C-H}$ est théoriquement attendue (2) pour les protons terminaux d'un triène 1,2,3. Dans le butatriène $|^5J_{H-C=C=C=C-H}|$ cis $= |^5J|$ trans = 8,95 Hz (4) ; ce couplage est supposé positif sur des bases théoriques (1) ; d'autre part des valeurs $|^6J_{H-C-C=C=C=C-H}|$ de l'ordre de 1 Hz ont été déterminées (5).

Afin de compléter et préciser ces résultats, nous avons examiné des composés triéniques du type RO CH = C = C = CH R'.

Une irradiation sélective par champ faible des transitions X relatives au système ABX_3 de $(CH_3)_3$ CO $\overset{(1)}{CH}$ = C = C = $\overset{(2)}{CH}$ $\overset{(3)}{CH_3}$ renseigne sur les signes relatifs de J_{12} J_{13} J_{23} : J_{12} et J_{13} sont de signes contraires J_{12} et J_{23} étant de même signe. Le couplage

.../...

$J_{23} = {}^{3}J_{H-C-C-H}$ étant vraisemblablement positif il en résulte que $J_{12} = {}^{5}J_{H-C=C=C=C-H}$ est positif et $J_{13} = {}^{6}J_{H-C-C=C=C=C-H}$ négatif. Le spectre du composé $C_2H_5O\ CH = C = C = C {\overset{H(2)}{\underset{H(3)}{\diagup\diagdown}}}$ est de type ABX et l'irradiation de la transition X à champ faible perturbe les doublets J_{AX} de A et J_{BX} de B situés vers les champs forts : J_{AB} est de signe opposé à celui de J_{AX} et J_{BX}. Les couplages $J_{AX} = J_{12}$ et $J_{BX} = J_{13}$ qui sont de type ${}^{5}J_{H-C=C=C=C-H}$ étant négatifs d'après les expériences précédentes le couplage entre protons géminés triéniques $J_{AB} = {}^{2}J_{H-C-H}$ est aussi négatif.

		J_{12}	J_{13}	J_{23}
$(CH_3)_3\ CO\ CH = C = C = CH\ CH_3$	A	+ 5,8	- 1,4	+ 7,6
	B	+ 5,55	- 1,45	+ 7,6
$C_2H_5O\ CH = C = C = C {\overset{H(2)}{\underset{H(3)}{\diagup\diagdown}}}$		+ 6,1	+ 5,9	- 9,55

A : isomère le plus abondant   ,   B : isomère le moins abondant

Veuillez croire, Cher Professeur SHAPIRO, à nos sentiments les meilleurs.

F. LEFEVRE   M.L. MARTIN

(1) M. KARPLUS - J. Chem. Phys. 33, 1842, 1960 - M. BARFIELD - J. Chem. Phys. 48, 4458, 1968 et 49, 2145, 1968 -

(2) J.A. POPLE et A.A. BOTHNER-BY - J. Chem. Phys. 42, 1339, 1965 -

(3) M.L. MARTIN, G.J. MARTIN et R. COUFFIGNAL - J. Chem. Phys.

(4) S.G. FRANKISS et I. MATSUBARA - J. Phys. Chem. 70, 1543, 1966 -

(5) M. BERTRAND et C. ROUVIER - C.R. Acad. Sci. 263 C, 330, 1966 -

Badische Anilin- & Soda-Fabrik AG

BASF

BASF · 6700 Ludwigshafen

Luftpost

Prof. Dr. B.L. Shapiro

Department of Chemistry
Texas A & M University.

College Station, Texas 77843

U S A

Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen WH/PV Frie/Dr	Telefon-Durchwahl (06 21) 60-	Telex 4 64-	6700 Ludwigshafen 5. April 1971

Betreff $Eu(DPM)_3$, angewandt auf Polymere

Sehr geehrter Herr Dr. Shapiro!

Von meiner Tätigkeit am Institut für Makromolekulare Chemie der Universität Freiburg sind mir die Schwierigkeiten bei der Bestimmung des konfigurativen Aufbaus, der Taktizität, von synthetischen Polymeren sehr gut vertraut. Nur bei wenigen Polymeren sind aus den Spektren direkt Aussagen möglich. Zu diesen gehören Polymethylmethacrylat (PMMA), Polypropylen und α-Methylstyrol. Bei den meisten Polymeren sind jedoch spezifisch deuterierte Verbindungen notwendig, deren Herstellung i.a. sehr aufwendig ist. Wir hatten die Hoffnung, mit Hilfe des $Eu(DPM)_3$-Komplexes als Shift-Reagenz in manchen Fällen eine Vereinfachung der Spektreninterpretation ohne Deuterierung der Substanzen zu erreichen.

Dies wollten wir zunächst am Beispiel einer Probe ataktischen Polymethylmethacrylates testen:

Im Spektrum des ataktischen PMMA (radikalisch polymerisiert) erscheinen für die $C-CH_3$-Gruppen drei Signale, die von zentralen $C-CH_3$-Gruppen in iso(i)-, hetero(h)- und syndio(s)-takti-

- 2 -

Badische Anilin- & Soda-Fabrik AG

schen Triaden herrühren. Nach der Zuordnung, die mit Hilfe
der reinen Isomeren gelingt, wird aus der Intensität der
drei Signale auf die statistische Häufigkeit der Triaden
im Polymeren rückgeschlossen.

Aus dem O-CH_3-Signal kann diese Information nicht erhal-
ten werden, da in $CHCl_3$ als Lösungsmittel die drei, den
verschiedenen Triaden zuzuordnenden Signale, zusammenfal-
len. Durch Zusatz von Eu(DPM)$_3$ fächert jedoch auch dieses
Signal in drei sich teilweise überlappende breite Linien
auf, wobei aus der Intensität der Linien - durch Vergleich
mit den Intensitäten der genau bekannten C-CH_3-Signale -
die Zuordnung getroffen werden kann (iso : δ = 4,2 ; he-
tero : δ = 4,0; syndio : δ = 3,9 ppm; Konzentration ~50 mg
PMMA + 40 mg Eu(DPM)$_3$). Der Abstand der Signale der C-CH_3-
Gruppen (i, h, s) bleibt dagegen ungefähr gleich groß; sie
zeigen jedoch weitere, im Normalspektrum nicht zu sehende
Aufspaltungen, die auf Pentadeneffekte zurückgeführt wer-
den müssen.

Wir versuchten auch, die Taktizität einer Probe Polyvinyl-
acetates zu bestimmen. Das Signal der CH_3-Gruppe fächerte
leider nicht auf. Entweder ist hier der durch die verschie-
dene sterische Umgebung bedingte Effekt nicht groß genug,
oder wir hatten eine Probe mit einheitlicher Taktizität
untersucht. Bei einer Probe mit Polyvinylacetat und Eu(DPM)$_3$
im Gewichtsverhältnis ~ 1:1 erhielten wir eine Verschiebung
des CH-O-Signals von ~ 1,7 ppm, des CH_3-Signals von ~ 0,6 ppm
und des CH_2-Signals von ~ 0,8 ppm.

Badische Anilin- & Soda-Fabrik AG

| Empfänger	Unsere Zeichen	67 Ludwigshafen am Rhein	Blatt
Prof. Shapiro	WH/PV	5. April 1971	3
Betreff	Frie/Dr		

Die Größe der gemessenen Effekte entsprach nicht ganz unseren
Erwartungen, einmal wegen der kleineren paramagnetischen Ver-
schiebungen der Signale von Polymeren (i.a. < 1 ppm) im Ver-
gleich zu denjenigen von kleinen Molekülen, zum anderen we-
gen der geringen Stereoselektivität.

Mit freundlichen Grüßen

Horst Triebolin

(Dr. H. Friebolin)

isotakt.Triade   heterotakt.Triade

syndiotakt.Triade   R = $COOCH_3$
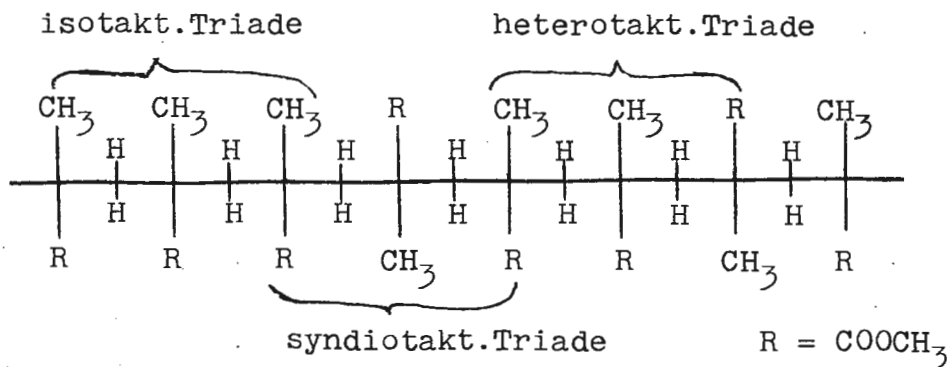
PERKIN-ELMER

THE PERKIN-ELMER CORPORATION

NORWALK, CONNECTICUT 06852

TELEPHONE: (203) 762-1000

CABLE: PECO-NORWALK

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

Re: Low Temperature Without Liquid Nitrogen Cooling

Dear Professor Shapiro:

In keeping with the concept of the Model R-12 NMR, a variable temperature accessory has been designed which does not require liquid nitrogen for low temperature spectra. Low temperatures are achieved by a Joule-Thompson gas expansion system located inside the probe. A counter flow system of gas at the sample produces a high thermal efficiency and minimizes temperature gradients in the sample region.

The probe is surrounded by a thermostatted water jacket which minimizes thermal disturbance of the magnet, thus enabling the resolution to be maintained throughout the temperature range. By choosing the gas to be expanded, the temperature range can be varied well over the useful low temperature range.

This system also allows operation of the spectrometer at low temperature for extended periods of time without concern about irregular spinning for only the lower portion of the sample tube (where the sample is placed) is being cooled. The top of the sample tube at the spinning turbine is at the ambient temperature.

Please credit this to P. Strauss' account.

Sincerely yours,

THE PERKIN-ELMER CORPORATION

JS Fleming

John S. Fleming

JSF:cr
cc: P. Strauss

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales
___

Physics Department
Perú 272
Buenos Aires
ARGENTINA

Buenos Aires, April 16th, 1971

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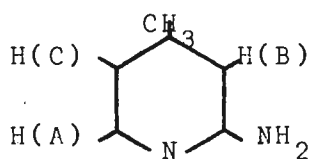College Station, Texas 77843
U.S.A.

Signs of Methyl Long-Range Coupling Constants in Pyridines.
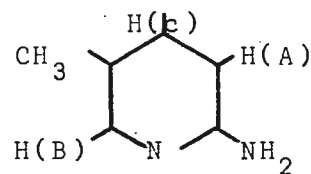
Dear Professor Shapiro:

We have recently completed a study of the long-range coupling constants of the six substituted methyl-pyridines shown in fig. I. For that, we have used the INDOR technique.
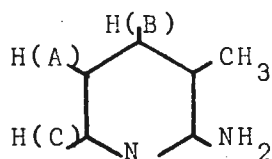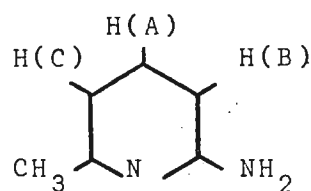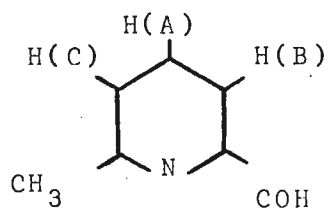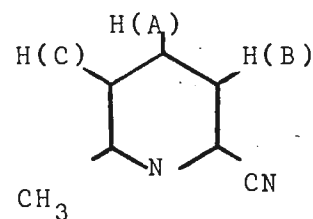

Fig.I

Universidad de Buenos Aires
Facultad de Ciencias Exactas
y Naturales

Our results are shown in Table I. There we use the following notation: $^{n}J_{AX}$ is the coupling constant between protons A and X, and n is the number of valence bonds between protons A and X. It is observed that the coupling constant is positive when this number of bonds is five, and is negative when both protons are separated by four or six valence bonds.

Table I

Substance	Long-range couplings		
I	$^{5}J_{AX} = 0.33$	$^{4}J_{BX} = -0.88$	$^{6}J_{CX} = -0,61$
II	$^{5}J_{AX} = 0.28$	$^{4}J_{BX} = -0.81$	$^{4}J_{CX} = -0.55$
III	$^{5}J_{AX} = 0.33$	$^{4}J_{BX} = -0,81$	$^{4}J_{CX} = -0.58$
IV	$^{5}J_{AX} = 0.30$	$^{6}J_{BX} = -0.57$	$^{4}J_{CX} = -0.59$
V	$^{5}J_{AX} = 0.34$	$^{6}J_{BX} = -0.64$	$^{4}J_{CX} = -0.56$
VI	$^{5}J_{AX} = 0.29$	$^{6}J_{BX} = -0.58$	$^{4}J_{CX} = -0.49$

Yours sincerely,

R. H. Contreras   J. J. Kowalewski

TELEPHONE: 660 0522.

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

The University of Sydney
Department of Organic Chemistry
SYDNEY, N.S.W. 2006

April 19, 1971

IN REPLY PLEASE QUOTE:

HOMOALLYLIC COUPLING IN FIVE MEMBERED RINGS

Dear Barry,

In collaboration with Dr. M. Barfield (Arizona) we have been looking[1] at long range coupling (J_{AB}) in system (I). Although several examples of stereo-specific coupling in (I, X=O) appear in the literature, we have encountered no case of a mono-2-substituted 2,5-dihydrofuran.

Mr. R. J. Spear has just succeeded in a complete analysis of the 100 MHz NMR spectrum of (II) in CCl_4 and obtained the results shown here which are in agreement with those calculated by Barfield[1].
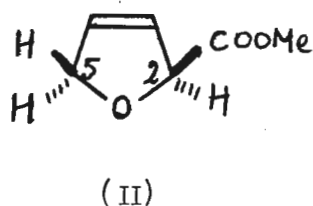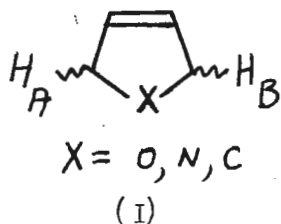
	Found[2]	Calculated[1]
$J_{2,5\alpha}$	+ 3.28	+ 2.52
$J_{2,5\beta}$	+ 6.34	+ 7.51

X = O, N, C
(I)   (II)

Mr. Spear has also prepared a series of phthalans[3] and has demonstrated, by combination of NOE and tickling experiments, that the long-range coupling constants are positive and that $J_{trans} > J_{cis}$.

Yours sincerely,

S. Sternhell

S. Sternhell

1   M. Barfield, R. J. Spear and S. Sternhell, J. Am. Chem. Soc., in press.

2   Confirmed by tickling experiments and taking $J_{vicinal}$ as positive.

3   See e.g. R. A. Smith, R. G. Parker and J. D. Roberts, Tetrahedron letters, 1763 (1970); R. R. Fraser and R. N. Renaud, Canad. J. Chem., in press. We are grateful to Prof. Fraser for very helpful correspondence.

April 20, 1971

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B. Meyer and H. Dreeskamp

Modification of a DA-60 for Kinetic Studies

Dear Barry:

Berndt Meyer of our Stuttgart-NMR-Group has just finished his PhD-Thesis on "Proton exchange in methanolic formiat buffer systems". Measurements were done on a modified VARIAN DA-60 IL-machine under conventional adiabatic slow passage conditions by observing line-shapes. We decided to use an internal standard (C_6H_6) and thus were able to drastically improve the precision of measurements (Line width were reproducible to within 0,01 Hz or better). The most important changes of the instrument were:

(i) Substitution of the "Manual oscillator" by a Schomandl ND 99 K audio frequency synthesizer and of the "sweep frequency oscillator" by a General Radio 1164 A7C Synthesizer, normally used for heteronuclear double resonance work. This instrument was swept electronically by a dc-ramp derived from the pot of the VARIAN recorder allowing to use the full 50 cm span of the recorder down to a few Hz. The GR oscillator though nominally rated for 10 kHz to 70 MHz proved to be quite reliable from 2 to 3 kHz. Before these changes our instrument was extremely sensitive to changes in room temperature (~ 1 Hz/$^\circ$C in the 50 Hz range !).

(ii) Replacement of the heater in the heater-sensor-combination by a home-made heater placed about 30 cm down-stream in the thermostating N_2 gas stream, replacement of some pots in the VARIAN 4343 unit and thermostating the N_2-gas before entering the instrument allowed to dial the temperature to better than 0,1°C.

Though using an internal standard meant extrapolating some electrochimical data about 8 kinetic terms were determined.

A manuscript describing this work should be ready for publication late this summer.

Sincerely yours

БЪЛГАРСКА
АКАДЕМИЯ НА НАУКИТЕ
ИНСТИТУТ ПО ОРГАНИЧНА ХИМИЯ

B U L G A R I A N
A C A D E M Y   O F   S C I E N C E S

INSTITUTE OF ORGANIC CHEMISTRY
Sofia 13, Bulgaria

Sofia, the ..... **April 24,** 19 **71**

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

Rotational barriers in substituted N,N-dimethylcinnamamides

Dear Professor Shapiro:

We have studied the rotational barriers about the C-N
bond in some m- and p-substituted N,N-dimethyl-trans-
cinnamamides by the iterative total line shape NMR method. The
results obtained for $\Delta G^{\neq}_{298.2}$ are presented in the table,
together with the corresponding values from a similar study on
the p-compounds carried out at the University of Amsterdam (1).
As can be seen, the discrepancies in most cases are of the
order of 0.2-0.3 kcal/mole, thus proving once more the
reliability of the method for study of relativelly small
barrier differences. The deviations between the values for
$\Delta H^{\neq}$ and $\Delta S^{\neq}$ obtained in the same studies are however
larger, often as much as 1 kcal/mole and 3-4 e.u., resp.

The $\Delta G^{\neq}_{298.2}$-values for the m- and p-N,N-dimethyl-
cinnamamides correlate satisfactorily with the σ-constants
(corr. coeff. 0.95). In comparison to the substituted
N,N-dimethylbenzamides (2), the barriers in cinnamamides are
about twice less sensitive towards the polar effect of the
substituents.

Prof. Bernard L. Shapiro

$$XC_6H_4CH=CHCON(CH_3)_2$$
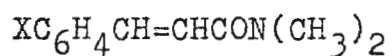
X	$\Delta G^{\ddagger}_{298.2}$ (kcal/mole)	
	Our data (0.5M $CDCl_3$, 60 MHz)	Ref.1 (0.25M $CDCl_3$, 100 MHz)
p-NO$_2$	16.80 ± 0.06	16.94 ± 0.01
m-NO$_2$	16.58 0.07	
m-Cl	16.33 0.02	
p-Cl	16.25 0.07	16.51 0.01
m-OCH$_3$	16.19 0.06	
H	16.16 0.04	16.39 0.01
p-CH$_3$	15.72 0.09	16.29 0.01
p-OCH$_3$	15.93 0.04	16.06 0.01

Yours sincerely,

S.L.Spassov   V.S.Dimitrov   M.Agova   I.Kantschowska

(1) K.Spaargaren, Thesis, Univ. of Amsterdam, 1970.

(2) L.M.Jackman, T.E.Kavanagh, and R.C.Haddon, Org.Magn. Resonance 1, 109 (1969).

ORGANISCH-CHEMISCHES INSTITUT
DER UNIVERSITÄT
Ludger Ernst, Albrecht Mannschreck

69 HEIDELBERG I. April 28, 1971
Tiergartenstraße 14
Tel. 56/2411
bei Durchwahl 56

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

Eu(DPM)$_3$-Induced Shifts in Anilines

Dear Professor Shapiro,

Beauté, Wolkowski, and Thoai[1] have shown recently that Yb(DPM)$_3$-induced ^{1}H-nmr shifts in amines are qualitatively determined by the steric accessibility of the nitrogen lone pair as well as by the basicity of the amine. We contribute further examples of steric hindrance or steric inhibition to complex formation and also one case of quantitative investigation of Eu(DPM)$_3$-induced shift[2,3] S versus basicity constant pK_b.

Methylation of aniline[4] (1) reduces the S-values of the benzene protons considerably (see formula 2). Induced shifts are negligible
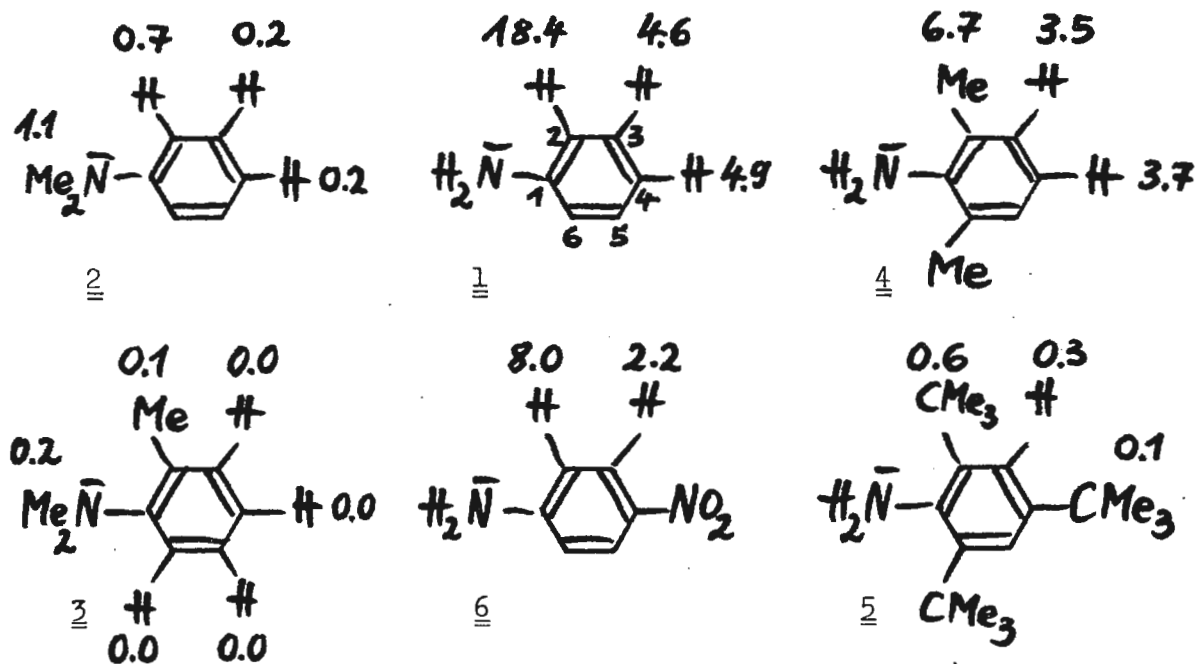
(Figures given with formulae are S-values[2].)

in N,N,2-trimethylaniline($\underline{3}$) because of steric inhibition of complexation. Therefore, our 2,6-$\underline{di}$substituted anilines[5] $H_5C_6CH_AH_B-\overline{N}(CH_3)-Ar$ do not show any shift (which might have been interesting, especially for H_A and H_B). A similar, but less pronounced decrease in S is seen by comparing the protons in the 3-position of aniline($\underline{1}$), 2,6-dimethylaniline($\underline{4}$), and 2,4,6-tri-t-butylaniline($\underline{5}$). Since anilines $\underline{1}$ through $\underline{5}$ have pK_b-values of the same order of magnitude, we attribute the above effects mainly to steric hindrance.

This factor is constant in the series 4-methoxyaniline, aniline($\underline{1}$), 4-chloroaniline, and 4-nitroaniline($\underline{6}$). The decreasing S-values for the protons in the 2- and 3-positions (cf. formulae $\underline{1}$ and $\underline{6}$) should therefore be due to the decreasing basicity in the above series. This is borne out nicely by the straight lines in our plots of S versus pK_b for the 2- and 3-positions:
$S = 44 - 2.8\ pK_b$ and $S = 11 - 0.65\ pK_b$, respectively.

Sincerely yours,

Albrecht Mannschreck

Ludger Ernst[6]   Albrecht Mannschreck

1) C.Beauté, Z.W.Wolkowski, and N.Thoai, Tetrahedron Letters <u>1971</u>, 817.
2) Our induced shifts S represent $(\delta_{Eu(DPM)_3} - \delta)$ in $CDCl_3$ at 30° for equimolar quantities of amine and tris(pivaloylmethanato)-europium(III).
3) Cf. L.Ernst, Chem.-Zeitg. <u>95</u>, 325 (1971).
4) Cf. D.F.Koster and C.C.Hinckley, TAMUNN <u>149</u>, 36 (1971).
5) A.Mannschreck and H.Muensch, Tetrahedron Letters <u>1968</u>, 3227.
6) Present address: Department of Chemistry, University of Manitoba, Winnipeg 19, Manitoba, Canada.

University of East Anglia

From The Dean
Professor N. Sheppard F.R.S.

School of Chemical Sciences
University Plain, Norwich NOR 88C
Telephone Norwich (0603) 56161
Telegraphic Address UEANOR

27th April 1971

Dear Barry,

Explosion Hazards in the Preparation of Magnesium
Perchlorate and Solutions Containing Organic Solvents

In a recent letter to the NMR Newsletter Dr. Green and I described
some results we had obtained using magnesium perchlorate/acetone/
water systems. It is well known that one has to be very careful
with perchlorates in the presence of organic molecules and we took
what seemed to us appropriate reasonable precautions. However
Dr. R.T. Iwamasa of the Dow Chemical Company has very kindly written
to me to say that it is his experience that very dangerous explosions
can result from such mixtures. He writes as follows -

"The explosive properties of perchlorates and organics are known to
most workers who deal with such systems but in many cases, I think,
not appreciated. The addition of pure organic to anhydrous
perchlorate especially aluminium or magnesium should be avoided.
The explosive power from a small quantity of materials (e.g. a few
milligrams + tenths of a c.c. of organics) is great. We had one
explosion in which the 3 sides of a glass enclosed balance were
blown out and the glass powdered (system $Mg(ClO_4)_2$-dimethylphosphite-
H_2O-acetone). Fortunately, no person was injured but such accidents
are severe enough that loss of limb or eyesight is possible unless
proper safety precautions are taken. The explosive point is illusive.
We tried duplicating conditions with various perchlorate-organic
systems. Some samples detonated whereas others did not. Some
were shock sensitive."

Anyone wishing to check on our results should bear this particular
hazard in mind. I think that we minimised the likelihood of
explosion in studying the aluminium perchlorate/acetonitrile
mixtures mentioned in that letter by using the alternative procedure
of preparing aluminium perchlorate in situ by mixing together anhydrous
solutions of silver perchlorate and aluminium chloride in that solvent.
Double decomposition led to the precipitation of the silver chloride.
Next time we try and do any experiments with magnesium perchlorate
we shall try the use of this alternative procedure.

With kind regards,

Yours sincerely,

N. Sheppard.

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

Author Index - TAMU NMR Newsletter No. 152

TAMU NMR NEWSLETTER

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