DEADLINE DATES: No. 258   3 March 1980
                   No. 259   7 April 1980

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

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

CENTRO DE INVESTIGACION DEL IPN

APARTADO POSTAL 14-740

MEXICO 14, D. F.

DEPARTAMENTO DE QUIMICA

January 4, 1980

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

Dear Professor Shapiro:

Single frecuency proton decoupling as a complementary assignment aid for methoxyl bearing carbons

The assignment of aromatic or quinonoid carbons on highly substituted rings could be difficult when similar chemical environments arise, due to the presence of equal substituents and the corresponding ipso carbons show closely spaced lines. Attempts to solve such situations have been done using coupled spectra obtained under gated decoupling, combined with deuterium exchange of label phenol protons[1]. However, in some cases the long range couplings could broaden the signals of the ipso carbons in such a way that even overlaps of two of them are present, thus making definitive assignments more difficult. This could be particularly true when methoxyl groups are present.

To overcome this inconveniences it is possible to obtain spectra under single frecuency decoupling, in which the decoupler is set at the proton methoxyl resonances. The method requires more instrument time due to the absence of NOE effects but provides satisfactory information. It is illustrate here for the dimethyl ether derived from hydroxyperezone.

The figure shows[2] a plot expansion (X2.5) of the sp^2 region of a coupled spectrum obtained under gated decoupling. The assignment of the two carbonyl signals can easily be done from their corresponding ^3J which are better seen in the further expansion (total X5) in the central insert. The lower field signal at 183.4 ppm is a quarted due to coupling with the quinonoid methyl protons and is ascribed to C-4, while the higher field carbonyl at 182.9 ppm is a doublet arrising from coupling to the isopropyl methine proton and corresponds to C-1. However the two carbons at 155.4 and 154.8 ppm, which bear the methoxyl groups, show undefined multiplicities.

The upper insert corresponds to a coupled spectrum in which only the methoxyl protons were irradiated. This shows that the signal at 155.8 ppm is a doublet and corresponds to C-3 while that at 154.4 ppm is a quarted and corresponds to C-6. The multiplicity of this two signals in the specific frecuency irradiated spectrum arise from ^3J with the methine and the methyl protons in a similar way as the long range couplings of the carbonyl carbons.

The remaining two ring carbons are also easily assigned from the coupled spectrum, since C-5 which appears at 125.3 ppm is clearly a quartet due to ^2J coupling with the methyl protons, while C-2 found at 133.0 ppm is a multiplet due to couplings with several protons from the side chain. The other two sp^2 carbons are due to the side chain double bond. The quaternary one is found at 130.4 ppm

Prof. B.L. Shapiro
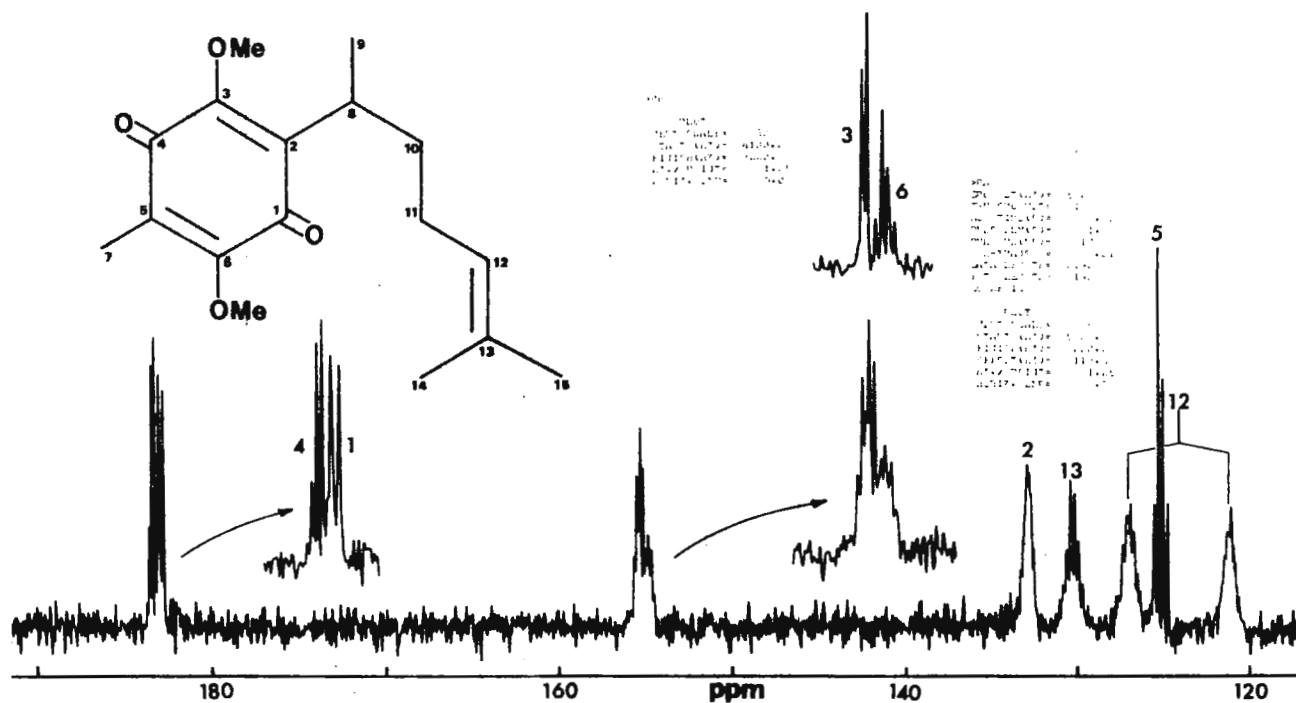
and the C-H at 124.2 ppm[3].

Pedro Joseph-Nathan
Professor of Chemistry

Sincerely yours,

D. Abramo-Bruno
Graduate Student

[1] F.W. Wehrli, J. Chem. Soc. Chem. Comm., 663 (1975).

[2] Measurements were done on XL-100A-12-FT-16K in DMSO-d_6.

[3] P. Joseph-Nathan, G. Mejía and D. Abramo-Bruno, J. Amer. Chem. Soc., 101, 1289 (1979).

BRUKER SPECTROSPIN NV

Wormer January 2, 1980

A New Noise Reduction Filter Function

Dear Professor Shapiro,

Prior to fourier transformation, the FID obtained from a pulsed NMR experiment may be manipulated in several ways, like zerofilling and digital filtering for noise suppression or resolution enhancement. Several filtering techniques have been proposed, all of which compromise between the following features of the spectrum: line width, signal to noise ratio, line shape and baseline distortion. The more sophisticated ones, like the Lorentzian-Gaussian transformation (1,2) are multiple parameter functions, bringing very good results at the cost of ease of operation.

We want to report the effect of a cosine square function upon the FID, constituting a new noise reduction filter. The function is given by $\cos^2(\frac{\pi t}{2AT})$. AT is the aquisition time, which is chosen just as long as the time domain signal can be measured, and zerofilling is applied in order to obtain sufficient digital resolution.

The filter has the following features:

-It is parameterless and thus very simple to use.

-The combination of filtering, very short aquisition time and zerofilling yields an appreciable effective noise suppression compared with the normal experiment that gives the same digital resolution.

-It affects the linewidth and the lineshape to a negligible extent.

-No baseline problems are encountered due to the zerofilling.

A more detailed description will appear shortly in J.Magn.Res.

Combination of this filter with the likewise parameterless sine bell resolution enhancement filter (3) results in a line narrowing by approximately a factor of two while keeping a satisfactory signal to noise ratio. Since this filter is zero at the

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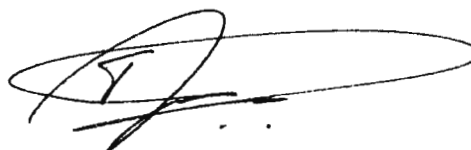
beginning of the FID it is also very effective in suppressing
broad background signals e.g. from solid materials in the probe.
This effect is illustrated in the figure, showing the proton
spectrum of benzene in a teflon cell, equipped with copper elec-
trodes and with electro dialysis membranes for experiments in
strong electric fields. The broad signal from the benzene pene-
trated into the membranes is effectively suppressed after appli-
cation of the cosine square sine bell filter.

(1) A.G. Ferrige and J.C. Lindon, J.Magn.Res.,31 (1978) 337.
(2) R.R. Ernst, in "Advances in Magnetic Resonance", vol.2
(J.S. Waugh ed., Academic Press, 1966).
(3) A. de Marco and K. Wüthrich, J.Magn.Res.,24 (1976) 201.

Sincerely yours,

Joost A.B. Lohman
Bruker Spectrospin NV
Wormer, The Netherlands.

Tj. Menno Plantenga
Free University, Chemical Laboratory
Amsterdam, The Netherlands.

10 Hz.

A.

nonfiltered

10 Hz.

B.

cosine square sine bell
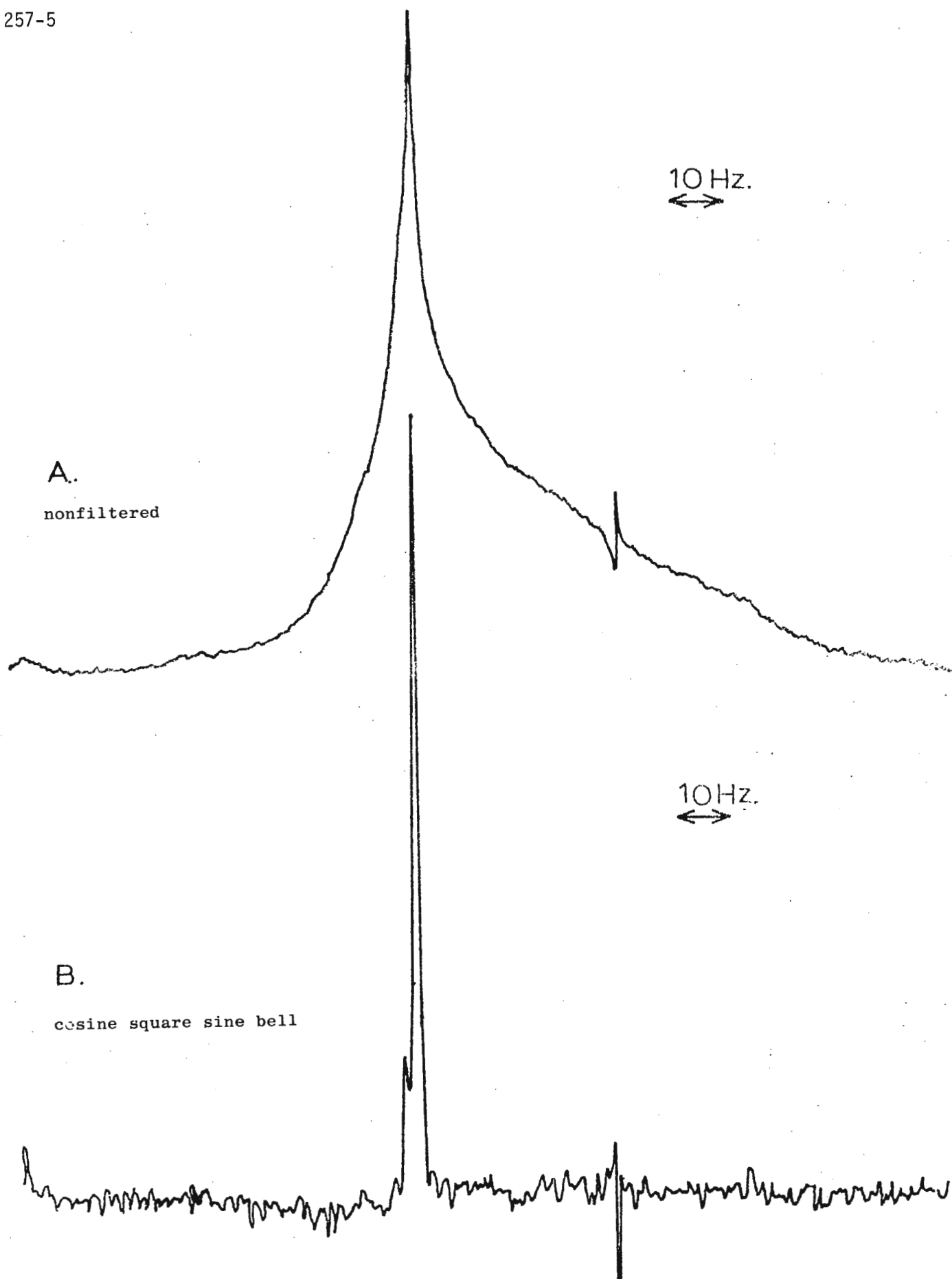
Proton NMR spectrum of Benzene in an electric field cell. Zerofilling by
a factor 2.

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90.6 MHz
^{13}C
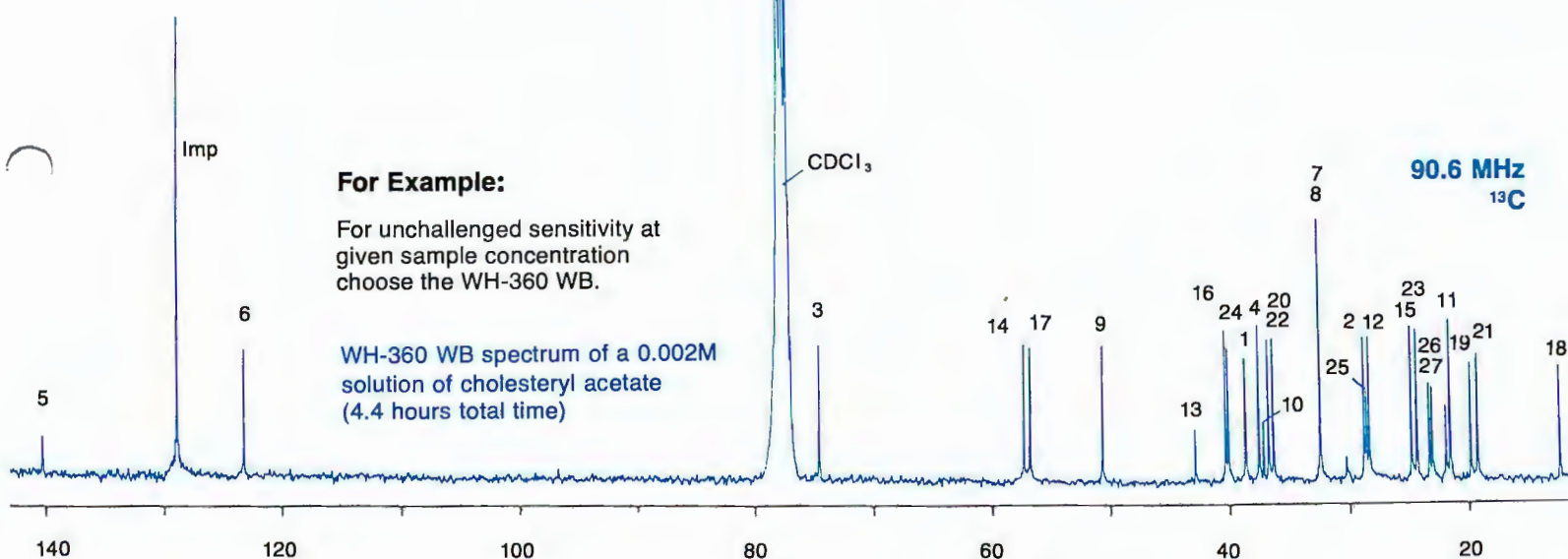
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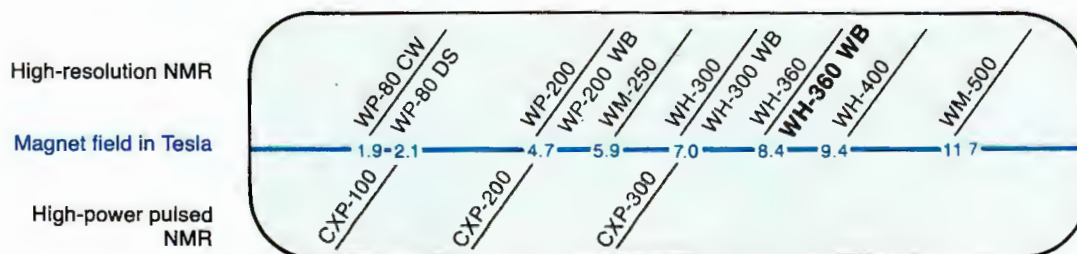
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WP-80 DS
WP-200
WP-200 WB
WM-250
WH-300
WH-300 WB
WH-360
WH-360 WB
WH-400
WM-500

Magnet field in Tesla — 1.9-2.1 — 4.7 — 5.9 — 7.0 — 8.4 — 9.4 — 11 7

High-power pulsed NMR

CXP-100
CXP-200
CXP-300

University of Illinois at Urbana-Champaign

School of Chemical Sciences
150 Roger Adams Laboratory
Urbana, IL 61801

January 2, 1980

Professor B. L. Shapiro   Printed circuit board sideplates for
Department of Chemistry   an XL-100 probe
Texas A & M University
College Station, TX 77843

Dear Dr. Shapiro:

One problem with stuffing a large (25 mm) coil in a small box (for a
34 mm gap of an XL-100-15) is Q damping by the proximity of the sideplates.
Even the thinnest aluminum sheet available significantly reduces Q, as shown
in Table I. Since the rf skin depth is a few microns for metals (copper:
20 μ @ 10 MHz), a much thinner sideplate is adequate provided it is suffi-
ciently rigid. Therefore, we constructed sideplates out of double-sided
tin-plated copper-clad printed circuit board (PCB) with a copper thickness
of 40 microns. The outside of each sideplate was left solid, the inside
contained a window in the copper somewhat larger than the coil, and the two
sides were connected for grounding as shown in Fig. 1. The measured Q for
these sideplates is also listed in Table 1.

Table I

Test Conditions	Q*
unloaded, no sideplates	276
non-aqueous sample, no sideplates	277
aqueous sample, no sideplates	41
non-aqueous sample, Al sideplates	138
non-aqueous sample, PCB sideplates	200

*measured @ 25 MHz with a vector impedance
meter.

Spectra from aqueous solutions showed little or no dependence upon
choice of sideplates, as expected from the table, while spectra from non-
aqueous solutions showed greater than 60% increase in S/N (Fig. 2) when Al
sideplates were replaced with PCB.

An additional benefit is the elimination of that part of the acoustic
response generated in the sideplates. This effect can be seen in Fig. 3,
which compares FIDs and spectra at 13.56 MHz (^{17}O) for RTV coated aluminum

sideplates and the PCB sideplates. Both tests consisted of 1 K pulses with a water sample with a delay of 50 µs before acquisition. Based on the relationship of acoustic resonance frequency to wall thickness,[1] the lowest frequency resonance is at ~37 MHz with PCB sideplates. A casual search of this region revealed no resonances, however.

Please credit this to the account of Steve Ulrich.

Sincerely,

David A. Wright

DAW/vu

[1]M. L. Buess and G. L. Peterson, Rev. Sci. Ins. 49, 1151 (1978).

Fig. 1

S/N = 105:1

/N = 65:1

PCB sideplates

Al sideplates

Fig. 2

PCB sideplates

Al sideplates

Fig. 3

BASF Aktiengesellschaft

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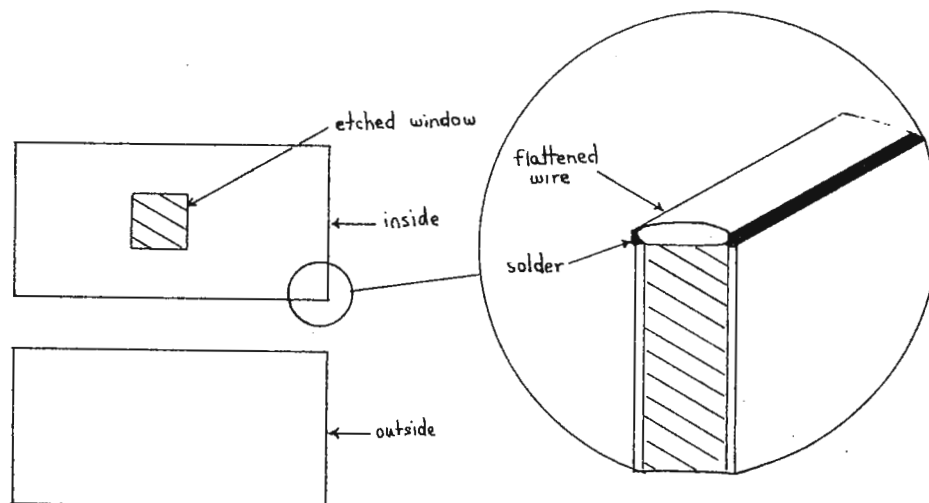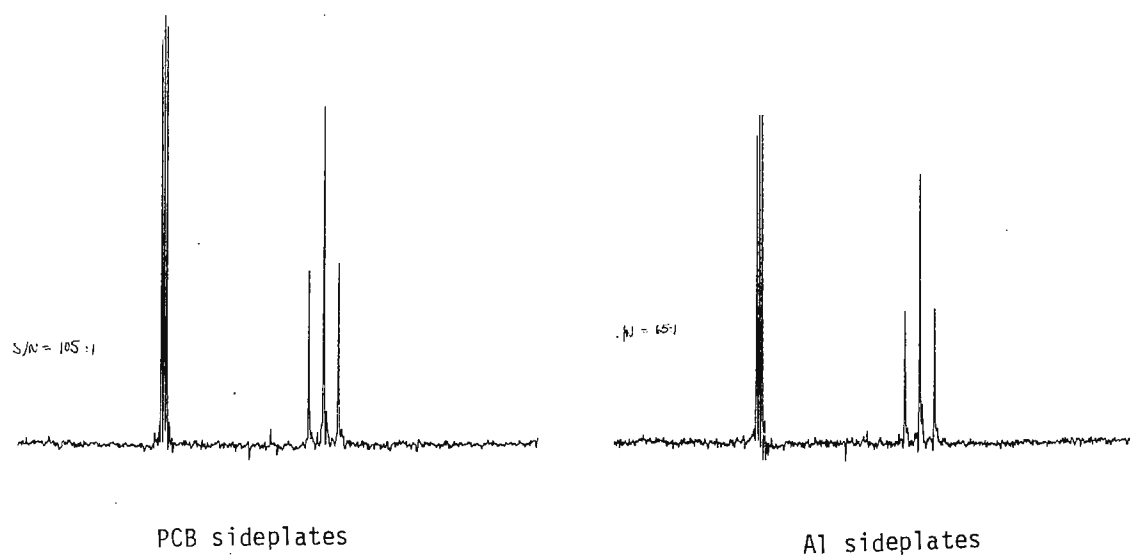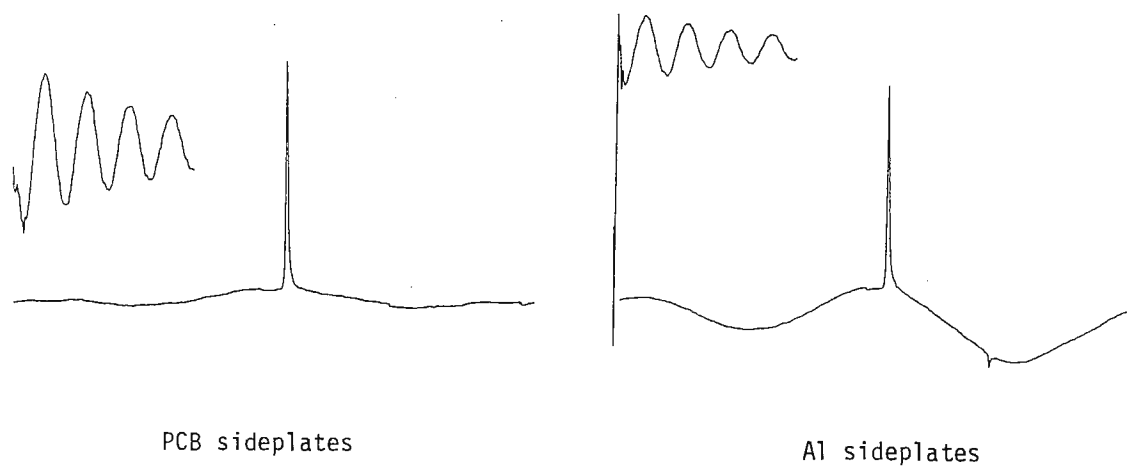
BASF · 6700 Ludwigshafen   :

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University

College Station, Texas 77843

U S A

Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen WHE-WBr/Dg	Telefon-Durchwahl (06 21) 60 8401	Telex 464·	Ludwigshafen 09.01.1980

Betreff

Diastereomers of Tocopherol

Dear Barry,

the characterization of the enantiomeric composition of synthesized
natural products is a great challenge to nmr spectroscopy. Tocopherol (1)
with 3 asymmetric centers is a good example for the small splittings to
be expected as well as the excellent resolution of modern high field
spectrometers. The partial CNMR spectra depicted in fig. 1 were run
on a Bruker WH-400. In acetone-D_6 solution at least four groups of
signals allow the quantitative determination of the four diastereomers,
two of which are marked with dots (for details cf. [1]). Due to
Gaussian filtering a line width of less than 0.005 ppm ($\triangleq$ 0.5 Hz) could
be achieved.

Dr. Werner Brügel familiar to all spectroscopists because of his pioneer
work in ir, nmr and esca spectroscopy is going to retire this summer.
His last publication [2], an updated, revised and enlarged edition of
his already classical nmr data collection, can be recommended to
everybody because of its high reliability. We wish him every success and
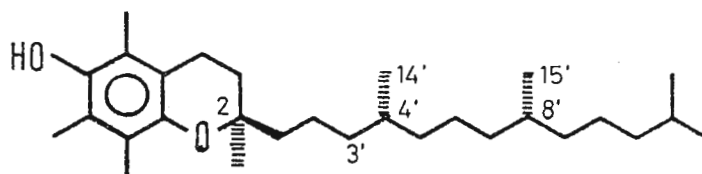
(1)

Empfänger **Prof. B. Shapiro** Unsere Zeichen **Luftpost** 257-12

College, Station, WHE-WBr/Dg 6700 Ludwigshafen Blatt

USA 09.01.1980

Betreff

an enjoyable time with his botanical (cacti) and historical studies.
Furthermore we hope to be able to continue his work at the fronteers
of practically oriented molecular spectroscopy. Please put my name on
the mailing list to ensure continuous flow of your newsletter.

Best regards,

W. Bremser

References:

[1] W. Bremser, F.G.M. Vogel, Tetrahedron Letters, submitted for
publication

[2] W. Brügel, Handbook of NMR Spectral Parameters, Heyden, London (1979)
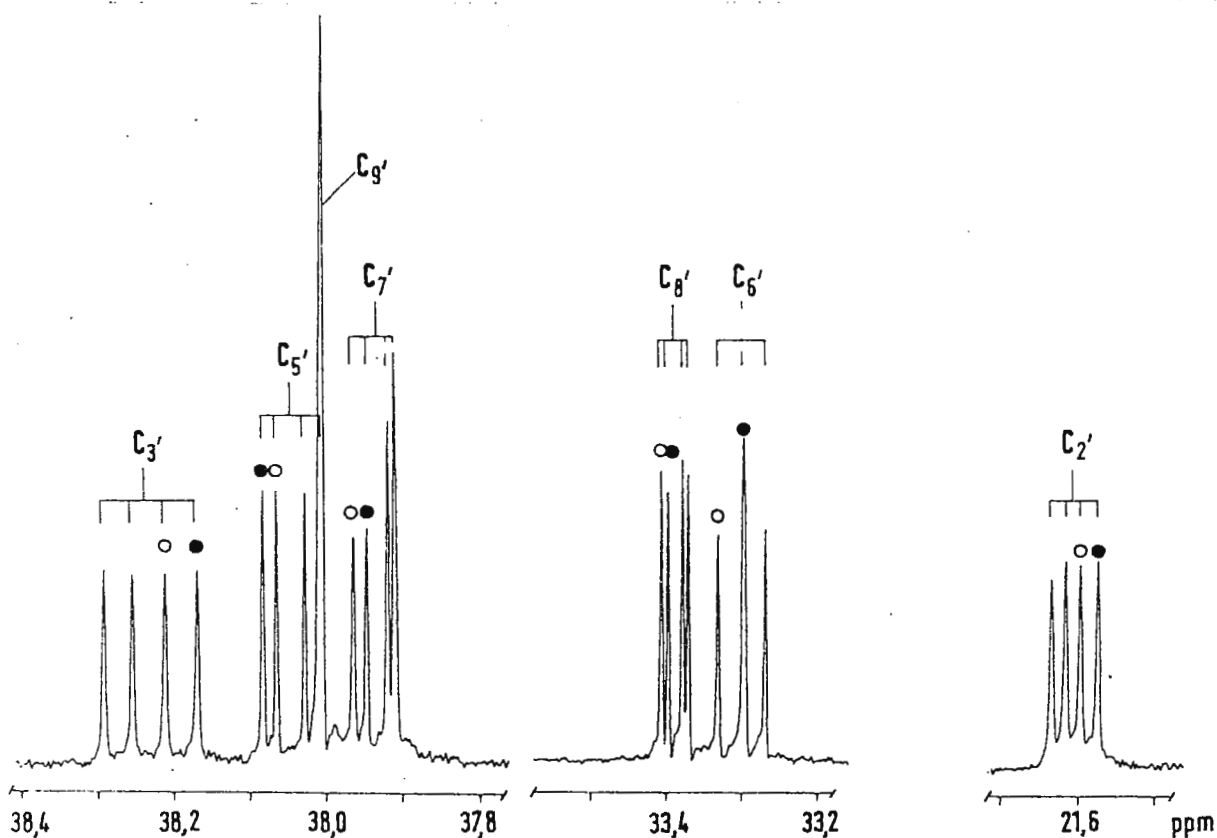
CHEMISCHES LABORATORIUM
DER UNIVERSITÄT MÜNCHEN
INSTITUT FÜR ORGANISCHE CHEMIE
   Dr. Rudolf Knorr

8000 MÜNCHEN 2, January 8, 1980
Karlstr. 23 – Tel. 59021

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

TITLE: Can Olefinic $^2J_{HH}$ Coupling Constants Serve as a Measure of
the σ-Inductive Effect ?

Dear Professor Shapiro :

   The strong influence of β-substituents on the geminal olefinic
coupling constant, $^2J(H^AH^B)$ in 1, is well known and illustrated by
some examples in entries 1-10 of the accompanying Table. Tempera-
ture and solvent effects are relatively small and can be understood
by the reaction field model; the unusually large variation in en-
tries 15-17 is noteworthy.

   The analysis by Pople and Bothner-By [1] accounts for the observed
trends and suggests that effects of the <u>olefinic</u> π-orbital system
may be of minor importance. One possibility of experimental test
would be a demonstration of ^2J being insensitive to a conformational
change as in 2; entries 18-20 show the ^2J variations to be as small
as those caused by a large series of p-substituents in styrene deri-
vatives (entry 21).

   Because of the small magnitudes of ^2J, I have checked their signs
by INDOR experiments on vinyl spectra for several known and unknown
cases in the Table (where literature references were omitted for
brevity). The total range of ^2J in entries 18-26 is rather small com-
pared to the previous examples.

Another way of testing makes use of more predictable changes in π-electron densities. The effect of strongly donating oxygen (entry 30 as compared to 26-29) is modest but in the correct direction. The nitrogen center in entries 31, 33, 35, and 37 should be less prone to ion-pair formation; the ^2J variations (entries 31-42) are even smaller. We have found that methanolysis of the lithium compounds yields meta stable sec-enamines with a small decrease of ^2J (entries 32, 34, 36, and 38). The ultimate choice of changing the total π-electron density by two formal units is documented in entries 43-47, again with only modest variation in ^2J.

These facts suggest that $^2J(H^AH^B)$ are not dominated by π-effects. The suspicion that they might be a measure of the σ-inductive effect alone finds support by INDO calculations [2]. The special situation in exocyclic methylene groups of small carbocycles could be explained along similar lines. Although hybridization was suggested to be a factor in addition [3] to electronegativity, the possibility remains to be checked that $=CH_2$ angles are also controlled by σ-donation. Furthermore, the small conformational effect is also borne out by INDO calculations [4] on coplanar and perpendicular 2-butenone (entry 25).

Resonance interactions as measured by σ_R^O substituent constants have gained improvement and reliability by IR techniques [5]; there is no correlation of ^2J with such parameters. Electronic σ-orbital effects are more difficult to assess since inductive substituent constants have often been suspected to contain contributions from polarization and hyperconjugation [6]. Not unexpectedly, the inductive σ_I or Grob's σ_I^q parameters show some correlation with ^2J but, as already noted by previous workers, with appreciable scatter. It would be of value to use ^2J as a quantitative measure of pure σ-orbital effects of the substituents X in 1. However, is there any other experimental evidence for that, except for the above mentioned [2,4] theoretical "proofs" ? (Nuclear quadrupole coupling constants do not offer a good choice since π-interactions are weak but recognizable).

If anybody has support for or objections to my speculations, I should greatly appreciate learning about it. Please credit this contribution to Gerhard Binsch's account.

Sincerely yours,
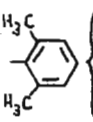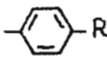
Rudolf Knorr

Rudolf Knorr

References :

1) J.A.Pople and A.A.Bothner-By, J.Chem.Phys. 42, 1339 (1965).
2) K.Yoshida, Chem.Physics 21, 317 (1977).
3) F.H.A.Rummens and L.Kaslander, Can.J.Chem. 54, 2884 (1976).
4) G.E.Maciel, J.W.McIver, N.S.Ostlund, and J.A.Pople, J.Am.Chem. Soc. 92, 4151 (1970).
5) A.R.Katritzky and R.D.Topsom, Chem.Reviews 77, 639 (1977).
6) W.Adcock and T.C.Khor, J.Org.Chem. 43, 1272 (1978).

Table. $^2J(H^A H^B)$ in Hz of $\underset{\sim}{1}$; signs omitted if not determined experimentally ($^{*)}$ = this work).

entry	-R	-X	^2J	entry	-R	-X	^2J
1	-H	$-\overset{\oplus}{N}(CH_3)_3$	-4.25	25	-H	$-CO-CH_3$	+1.2 *)
2	-H	-F	-3.2	26	-H	$-NO_2$	-1.8 *)
3	-H	$-\overset{\oplus}{P}(C_2H_5)_3$	+0.05	27	-H	-OH	1.8
4	-H	$-P(C_2H_3)_2$	+2.02	28	-H	$-OC_4H_9$	-1.8 *)
5	-H	-H	+2.4	29	-H	$-O_2CH$	-1.7
6	-H	$-C(CH_3)_3$	+1.4 *)	30	-H	-OLi	+1.56*)
7	$-CH_3$	$-Li(Et_2O)$	5.3 *)	31	$-C_2H_5$	$-NLi-C_6H_5$	2.3 *)
8	$-CH_3$	-Li(THF)	6.5 *)	32	$-C_2H_5$	$-NH-C_6H_5$	O *)
9	-H	$-Li(Et_2O)$	+7.1	33	- tBu	$-NLi-C_6H_5$	2.3 *)
10	-H	-Li(THF)	+7.6 *)	34	- tBu	$-NH-C_6H_5$	O *)
11	$-C_6H_5$	$-Li(THF,+70^O)$	7.1 *)	35	$-C_6H_5$	$-NLi-C_6H_5$	1.4 *)
12	$-C_6H_5$	$-Li(THF,+27^O)$	7.5 *)	36	$-C_6H_5$	$-NH-C_6H_5$	O *)
13	$-C_6H_5$	$-Li(THF,-40^O)$	8.0 *)	37	-H	$-NLi-cC_6H_{11}$	+1.3 *)
14	$-C_6H_5$	-Li(THF+HMPA)	8.5 *)	38	-H	$-NH-cC_6H_{11}$	O
15		-Li(pentane)	4.5 *)	39	-H		+0.8 *)
16		$-Li(THF,+27^O)$	8.4 *)				
17		$-Li(THF,-40^O)$	9.0 *)	40	-H	$-N(C_6H_5)-CO-CH_3$	O *)
18	-H	$-C_6H_5$	+1.08	41	-H	-NC	-0.5
19	-H		+2.5 *)	42	-H		-1.58*)
20	-H		+2.6 *)	43	$-CH_3$	$-\overset{\oplus}{C}(CH_3)_2$	$|\leq 1.5|$
21	-H	-R	0.6/1.3	44	-H	$-CH_2Li$	1.6
22	-H	-CN	+0.91	45	-H	$-CHLi-CH_2tBu$	1.8
23	-H	$-SO_2-C_6H_5$	-0.44*	46	-H	$-CLi(C_6H_5)_2$(THF)	+3.6 *)
24	-H	$-SO_2-C_4F_9$	-0.76*)	47	-H	$-CK(C_6H_5)_2$(NH$_3$)	3.6

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
THE CHEMICAL LABORATORIES

8 January 1980

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

Non-Linear Least Squares Analysis of Saturation Transfer NMR Data with
a Microcomputer: The General Case

Dear Professor Shapiro:

Recently we have been performing ^{31}P saturation transfer experiments on tris-
(triphenylphosphine)tetramethylene-nickel (II) at low temperatures using a
modified DANTE pulse sequence (1) on our FX-90Q spectrometer. A major problem
with the analysis of our data has been that the mole fractions of the species
which are in exchange are not always equal. Because of this, rate constants
cannot be obtained using the graphical method of Dahlquist et al (2). We have
thus resorted to analyzing our data using the general solutions to the Bloch
equations for two site exchange (3, 4).

The data are analyzed using an 8K PET 2001 microcomputer. The difference ΔM
between the areas of the exchanging peaks were fit to the following equation
using a standard least squares program (5):

$$\Delta M_\tau = \Delta M_\infty + [\Delta M_0 - \Delta M_\infty - C_2(1 - (k_{1A}-\lambda_2)/k_B)]\exp(-\lambda_1\tau)$$
$$+ C_2(1 - (k_{1A}-\lambda_2)/k_B)\exp(-\lambda_2\tau)$$

where

ΔM_∞ is the area difference at $\tau = \infty$

ΔM_0 is the area difference at $\tau = 0$

C_2 is a constant determined from the data

$k_{1A} = k_A + 1/T_{1A} = k_B P_B/P_A + 1/T_{1A}$

k_A, k_B are the rate constants $(k_A P_A = k_B P_B)$

$\lambda_1 = 1/2(1/T_{1A} + 1/T_{1B} + k_B/P_A) + [1/4(k_{1A}-k_{1B})^2 - k_B^2 P_B/P_A]^{1/2}$
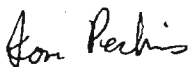
$\lambda_2 = 1/2(1/T_{1A} + 1/T_{1B} + k_B/P_A) - [1/4(k_{1A}-k_{1B})^2 - k_B^2 P_B/P_A]^{1/2}$

T_{1A}, T_{1B}, P_A, and P_B are determined before hand. ΔM_∞, ΔM_0, k_B, and C_2 are obtained from the least squares fit.
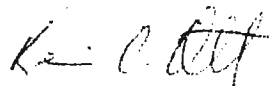
Fig. 1 is an example of the spectra obtained using the DANTE pulse sequence. Also given are the parameters resulting from the least squares fit of the data. Such an analysis not only takes into account conditions where $P_A \neq P_B$, but also allows for the reduction of data when $T_{1A} \neq T_{1B}$. This situation can arise when a small molecule is in slow exchange with a binding site on a macromolecule.

Lists of both the DANTE pulse sequence for the PG-200 pulse programmer and the least squares program in Microsoft Basic can be obtained from either of us.

Sincerely,

Tom Perkins   Kevin Ott

Please credit this contribution to Dr. J. D. Roberts' subscription.

References

1. G. A. Morris and R. Freeman, J. Magn. Reson., 29, 433 (1978).

2. F. W. Dahlquist, K. J. Longmuir, and R. B. DuVernet, J. Magn. Reson., 17, 406 (1975).

3. S. Forsen and R. A. Hoffman, J. Chem. Phys., 39, 2892 (1963).

4. J. S. Leigh, Jr., J. Magn. Reson., 4, 308 (1971).

5. W. E. Hull, Ph.D. Thesis, Harvard University (1975).

$\Delta M_\infty = 2.0 \pm 3.7$

$\Delta M_o = -161 \pm 2$

$k_B = 4.7 \pm 0.4 \ sec^{-1}$

$C_2 = 271 \pm 112$
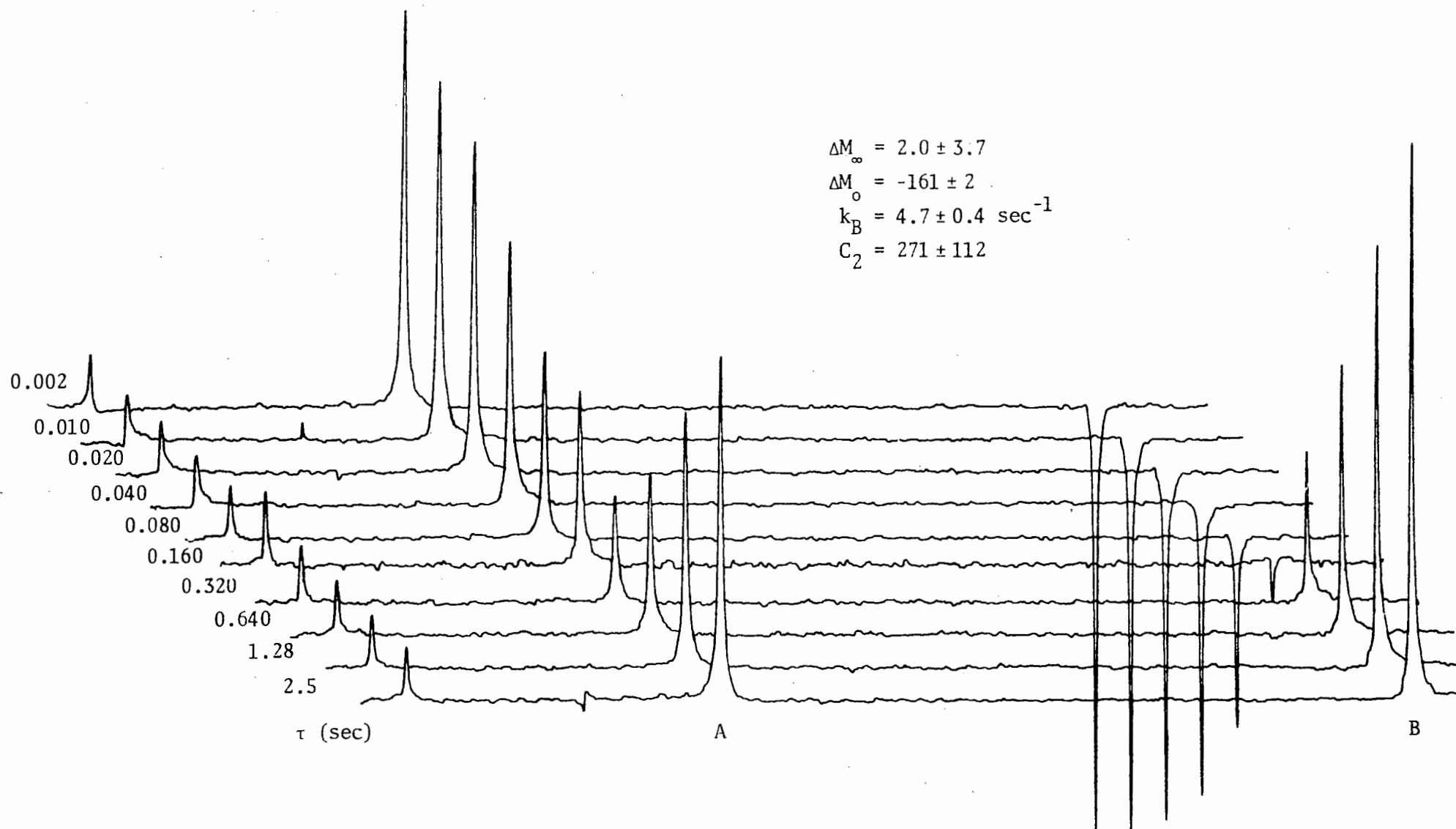
Fig. 1: ^{31}P saturation transfer spectra of triphenyl phosphine (B) and tris(triphenylphosphine)-tetramethylene-nickel(II) (A) at $-90^{\circ}C$. The DANTE pulse sequence used was $[(\pi/78\text{-}50\mu sec \ delay)_{78}\text{-}\tau\text{-}\pi\text{-}AT\text{-}PD]_n$ (peak B was positioned in the middle of the spectrum so that it was inverted selectively). $T_{1A} = 1.34 \ sec$, $T_{1B} = 1.32 \ sec$, $p_A = 0.46$, and $p_B = 0.54$.

The Wellcome Research Laboratories

The Wellcome Foundation Ltd

Langley Court
Beckenham
Kent BR3 3BS
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BMNA/80/2

11th January 1980

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

Dear Dr. Shapiro,

NOEs and ^{13}C labelling to show direction of quaternisation

A number of pharmaceutical products are based on the 1-benzyltetrahyro-isoquinoline skeleton. This type of molecule can be quaternised with various alkyl iodides to give a mixture of the cis and trans isomers and as these products may have different biological potencies this necessitates the assignment of the configurations. As an example we have used laudanosine methiodide as a model compound and its 'H NMR spectrum is shown in the figure (90 MHz, in dmso-d_6 at 80°C). Unfortunately the overlap precluded the use of any double resonance technique but we found that a 3:1 mixture of C_6D_6 and dmso-d_6 gave the left insert which shows separation of all the resonances of interest. NOE measurements by observing H_1 and irradiating at the NMe signals gave an 18% enhancement for the higher field NMe signal and a 9% rise for the lower field NMe, assigning these as trans and cis respectively to the 1-benzyl sidechain. We leave to the reader the possible interpretations of the 2:1 ratio for the NOEs. The right insert shows the spectrum of laudanosine methiodide obtained by quaternising with ^{13}CH$_3$I where the major ^{13}C coupled NMe peak is to higher field. This shows that the attack of the ^{13}CH$_3$I had proceeded from the least sterically hindered side of the ring opposite to the 1-benzyl sidechain. We hope that this contribution makes a welcome change from the subject of digitisation and dynamic range of which we threaten more later.

With best wishes.

J.C. Lindon

A.G. Ferrige

Department of Physical Chemistry

H-5,2',5',6''

H-8

H-1

CH₃O

CH₃O

CH₃N

CH₃N

CH₃N

H₂O

cis   trans

MeO

MeO

MeO

OMe

N⁺

Me

Me

I⁻

6   4   2 ppm

257-20

Rijksuniversiteit Utrecht
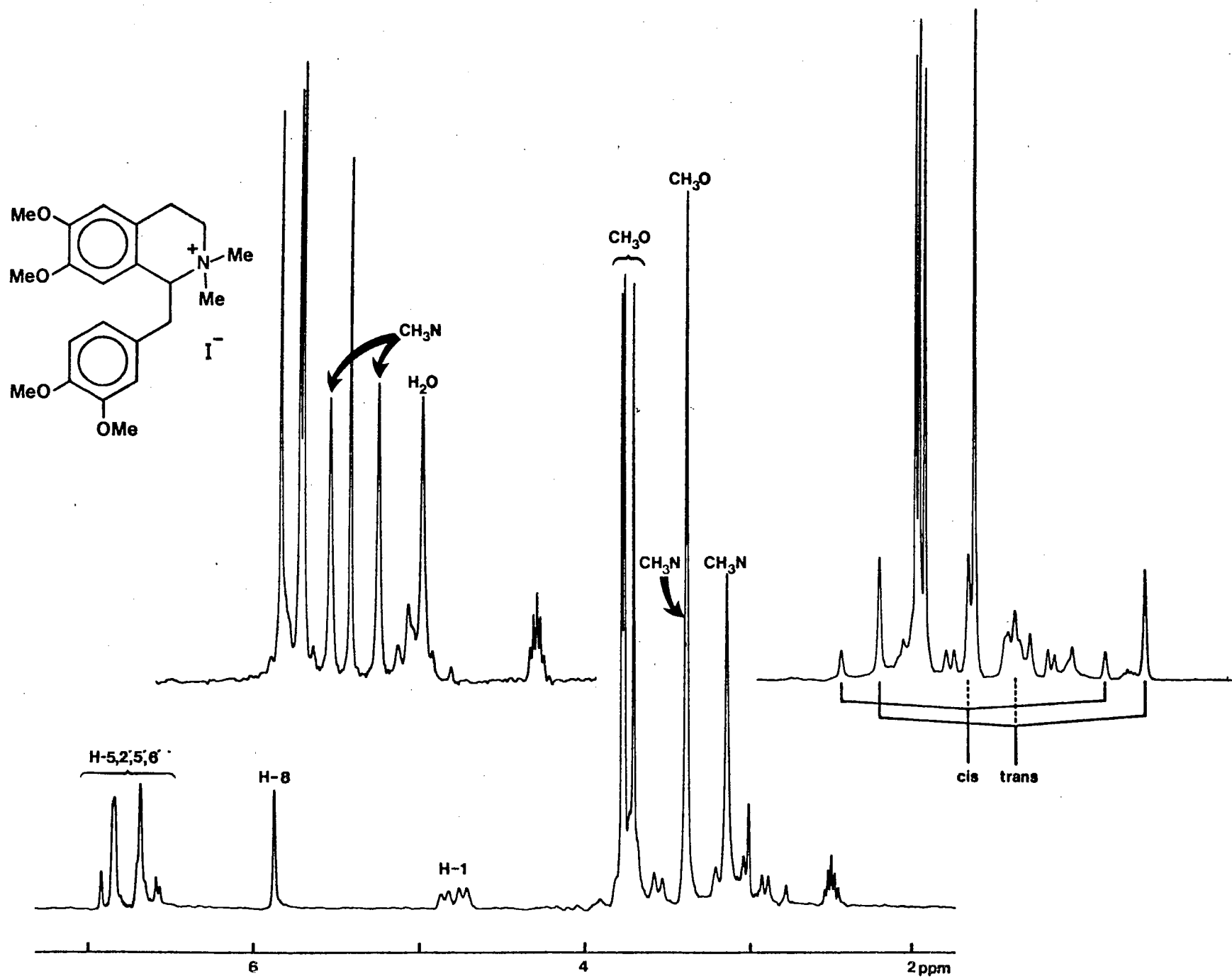
Organisch chemisch laboratorium

Croesestraat 79
3522 AD Utrecht
Telefoon 030 - 882311

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

Datum — January 8,1980

Uw kenmerk

Ons kenmerk

Onderwerp — ^{13}C-additivity rules for an estimation of the chemical shift of allene carbons.

Dear Prof. Shapiro,

Over the past decade it has been established that the ^{13}C-chemical shift incre-
ment for various substituents is a constitutive property in many cases; e.g.
for alkanes,alkenes and benzenes (Ref.1,2,3).We found that in the case of allenes
too,the substituent effects are a constitutive property (Ref 4).Our results are
given in table 1.

In describing the chemical shift of the exterior and central allene carbons,the
substituent effects in fig.1 were used.

We had to introduce some correction factors for steric crowding effects.

The calculation of the chemical shift for the exterior allene carbons is follow-
ing eq.1,

$$\delta_C = B + \sum X + \sum X_{\pi\pi} + S + nS^{\alpha} + R + R_{\pi\pi} \tag{1}$$

where B is a base value found to be 74.5 ppm (relative to TMS). X and $X_{\pi\pi}$ are
substituent contributions.S is a correction for double substitution on the carbon
of the allene which is to be calculated, and was found to be -4.6 ppm. S^{α} is a
correction for branching at an α-substituent (only C and N) and is applied twice
for each α-substituent if it is quaternary and once if the substituent is tert-
iary. R is a correction to be applied if the carbon of the allene which is to
be calculated,is part of a ring structure. $R_{\pi\pi}$ is a correction for a ring struc-
ture including the allene carbon on the other side of the allene.

The chemical shift of the central allene carbon can be calculated with eq.2,

$$\delta_C = B_{\pi} + \sum X_{\pi} + nS_{\pi}^{\alpha} + mS_{\pi} + kR_{\pi} \tag{2}$$

where B_π is a base value, found to be 214,1 ppm (relative to TMS). X_π is the substituent contribution. S_π is the correction for double substitution on an exterior allene carbon and is to be applied twice for 1,1,3,3-tetrasubstituted allenes. S_π^a is, like S^a, a correction for branching at the α-substituent (only C and N) and is to be applied twice for each α-substituent if it is quaternary and once if the α-substituent is tertiary. R_π is a ring correction.

The calculated values have a mean deviation from the observed values of 1.6 ppm for the exterior carbons and 2.3 ppm for the central carbon.

We are also able to extend table 2.5 in ref 1 in that we can provide the substituent increments of an allene for the calculation of a carbon in an alkane. These increments are : α = 14.4, β = 5.0, γ = -5.5 ppm.

Ref.1: F.Wehrli,T.Wirthlin,   Interpretation of carbon-13 NMR spectra.
Heyden-London 1978

Ref.2: G.C.Levy,G.L.Nelson,   Carbon-13 Nuclear Magnetic Resonance for organic chemists.
Wiley-Interscience New York 1972

Ref.3: J.B.Stothers,   Carbon-13 NMR spectroscopy.
Academic press 1972

Ref.4: R.H.A.M.Janssen,R.J.J.Ch.Lousberg,M.J.A.de Bie, Rec.Trav.Chem.Pays-Bas
to be published.

Fig.1
Substituent and steric contributions.
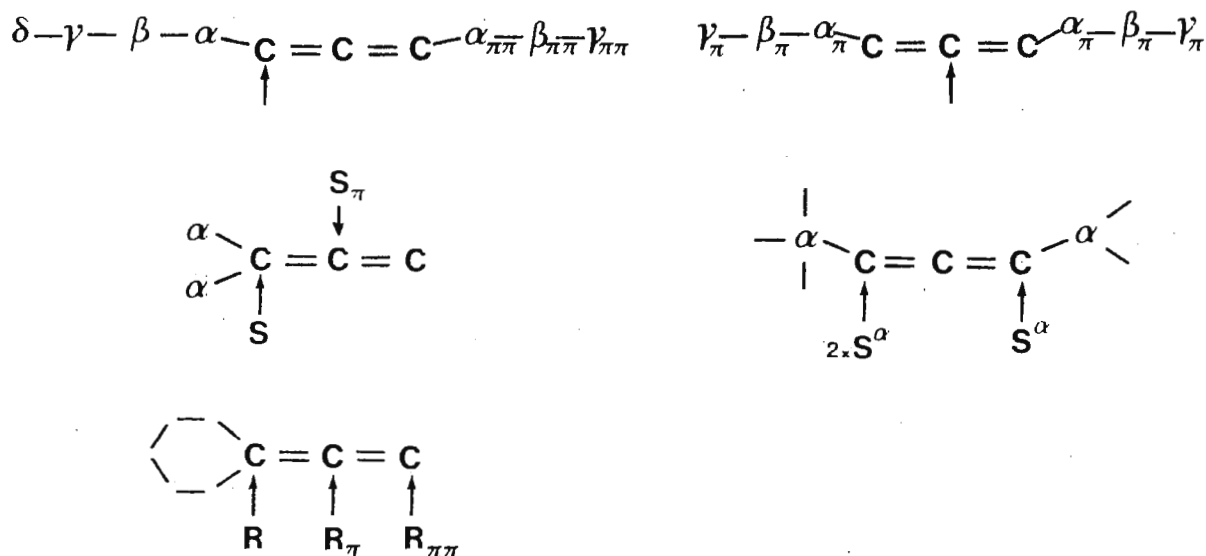
The arrows indicate the carbon to be calculated.

Table 1

Substituent increments in ppm

subst.	α	β	γ	δ	$\alpha_{\pi\pi}$	$\beta_{\pi\pi}$	$\gamma_{\pi\pi}$	α_π	β_π	γ_π
-C	11.6	7.6	-1.7	0.9	-0.2	0.3	-1.0	-4.4	-1.5	0.7
-O-	40.3	5.2	-5.3	3.3	14.9	2.2	-0.5	-12.5	-0.8	1.2
-S-	9.1	4.2			6.1	2.9		-6.8	0.2	
-Ø	19.4	3.0			2.9	-0.6		-1.3	1.1	
-N	27.6	4.3			10.6	0.4		-10.0	-0.6	
-F	55.3				19.4			-13.9		
-Cl	15.5				9.6			-7.1		
-Br	-2.9				10.7			-6.9		
-I	-39.2				3.0			-5.2		
-Si(CH$_3$)$_3$	8.9				-7.8			2.3		
-Ge(CH$_3$)$_3$	9.0				-6.8			0.0		
-Sn(CH$_3$)$_3$	4.0				-10.0			-0.1		
-Se	-3.4				4.5			-7.5		
-Li	10.1				-24.8			-18.0		
-C=C	19.8				0.6			-3.3		
-C≡C	-0.3				3.0			2.6		
-C=C=C	12.4				3.9			-3.1		
-C≡N	-6.5	-3.7			6.3	3.8		6.1	0.5	
-N≡C	11.6				11.6			-4.0		
-CO-0	13.8	-0.3			5.4	-1.3		3.6	0.7	
-CO-Ø	18.4				4.3			2.6		

B = 74.5 B_π=214.1

S =-4.6 S_π=2.1

S^α=-4.2 S^α_π=1.2
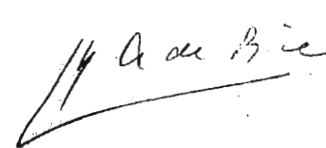
ring corrections   R $R_{\pi\pi}$ R_π

(CH$_2$)$_4$ C=C=C   -6.1   0.8   -1.7

(CH$_2$)$_5$ C=C=C   -4.7   -0.4   -1.5

note: if in the molecule there is a γ-substituent in a so called fixed γ-s-trans position to the carbon to be calculated an additional correction of 2.5 ppm is needed.

Yours Sincerely.

R.H.A.M.Janssen   M.J.A.de Bie

If you can't observe solids as readily as liquids on your superconducting FT NMR...

...you just don't have an XL-200!

50-MHz NMR Spectrum of Cured Neoprene
20 Minutes Accumulation
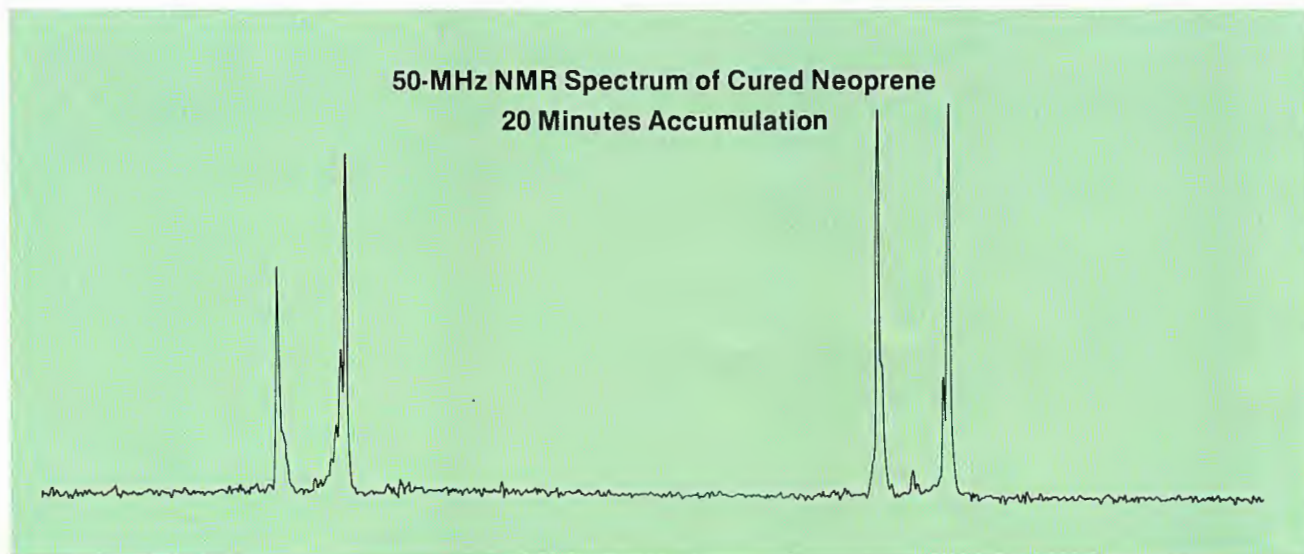
¹³C spectrum of cured neoprene with carbon black* in a Kel-F rotor using high-power gated decoupling (400 transients at 3-second intervals). The resolution has been enhanced by a Lorentzian-to-Gaussian transformation to bring out the fine structure. The width of the plot is 10 KHz.   *Sample courtesy of E. I. Du Pont de Nemours and Company

With the new ¹³C solid-state accessory for the XL-200, you can spin solid or powdered samples at the magic angle, increase sensitivity using cross-polarization, and achieve efficient line narrowing with strong dipolar decoupling. Yet operation is surprisingly simple! You can introduce and eject the rotor pneumatically without disturbing the probe or the spinning axis adjustment. You monitor the spin rate on the spectrometer's built-in tachometer, just as in liquid-sample experiments. Front panel controls let you adjust optimal cross-polarization and decoupling conditions independently and conveniently.

There are other unique aspects to the XL-200 supercon-ducting FT NMR Spectrometer, such as the data handling and spectrometer control system: a 13-bit ADC, which accommodates stronger signals on each transient; a stan-dard 32K CPU, independent of the acquisition processor and programmed in PASCAL, a high-level, structured language; a built-in interactive 5M-word disk with dual plat-ters; a large, flicker-free raster scan display.

The software, too, is exceptionally sophisticated. It per-mits multitasking (simultaneous acquisition, processing, printing, etc.) and queuing (automatic sequential execution of requested tasks) on the same or on different NMR exper-iments. You can also array parameters (up to three variables, including temperature) within a given experi-ment; generate your own convenient macro-commands;

create your own special or general-purpose pulse sequences in a simple, English-like code; even do your own computer programming in PASCAL.

Then there's the matter of the XL-200's broadband ac-cessory which, with only a single probe for liquid samples, enables you to observe a host of nuclei (including ¹³C) between 20 and 81 MHz. And there's the remarkable low-loss dewar system, which operates over three months on only 25 liters of liquid helium.

The XL-200 is in a class by itself—with a price tag and an operating economy that belie its advanced design.

varian

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
HEALTH EFFECTS RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

January 16, 1980

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

Dear Barry:

We currently have an opening for a person on an Intergovernmental Personnel Agreement (IPA) to do research on NMR of toxic materials, particularly with respect to interactions with biological substrates.

Our NMR laboratory has a Varian XL-100/Nicolet TT-100 Fourier transform nmr spectrometer, with a Nicolet multinuclear (MONA) accessory. We have 5 to 18 mm probes for 7-100 MHz. We also have access to the new 250 MHz Bruker spectrometer, also a multinuclear instrument, at the Research Triangle Institute, about a mile down the road.

This appointment would be in the Chemical Characterization Section of our Analytical Chemistry Branch. It is open only to permanent faculty members of colleges and universities and staff members of local or state government organizations. The appointment is for one or two years, with salary and fringe benefit reimbursement to the appointee's permanent institution.

We are very anxious to fill this position as soon as possible. Interested faculty members should contact me immediately by phone at 919/541-2941, or 919/541-2358 and send me a copy of their curriculum vitae and list of publications.

With best wishes.

Sincerely yours,

Nancy K. Wilson, Ph.D., Acting Chief
Chemical Characterization Section
Analytical Chemistry Branch (MD-69)

UNIVERSITY OF BRISTOL

Telephone Bristol 24161 (Ext.   )

SCHOOL OF CHEMISTRY

CANTOCK'S CLOSE

BRISTOL

BS8 1TS.

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

14th. January, 1980.

Dear Professor Shapiro,

Estimation of Mobile Fractions using N.M.R.

In December we replaced our ageing PFT 100 by a multinuclear JEOL FX 90Q and look forward to the delivery of an FX 200 in the spring. As most of our n.m.r. instruments had to be resited there was considerable disruption which is some excuse for our tardiness and by way of a change we give you a report from Terence Cosgrove and Ken Barnett in Physical Chemistry.

For several years n.m.r. has been used to estimate mobile fractions in complex solid/liquid mixtures. Inevitably this has been achieved by some type of curve fitting procedure usually a sum of an exponential and a gaussian function. However it is possible by using suitable combinations of R.F. pulses to separate signals which are strongly dipolar coupled (most solids) and those that are only weakly coupled (most liquids and some amorphous solids).

The response of a spin system to a $90_x^O - \tau - 90_y^O$ sequence is to refocus a solid echo and a liquid echo whereas the $90_x^O - \tau - 180_y^O$ sequence will only refocus a liquid echo. For the accurate determination of a solid/liquid ratio, the sequence $90_x^O - \tau - 90_y^O - 2\tau - 90_y^O - 2\tau - 180_y^O - 2\tau - 180_y^O$ is proposed. The two 90_y^O pulses and the two 180_y^O pulses are required for pulse length correction for the liquid echoes. The sequence applied to a mixture of polystyrene in water is shown in the accompanying figure. As can be seen the solid echo signal is unaffected by the 180° pulses. The relative heights of the 4th and 1st echo give the mobile fraction. This sequence can also be used to separate solid and liquid T_1's and can be incorporated in a driven equilibrium sequence. These further sequences together with a full discussion of this method applied to polymeric systems will be publised in full shortly.

Yours sincerely,

K. Barnett   T. Cosgrove   R.J. Goodfellow   M. Murray

Pulse sequence to obtain mobile fraction in a polystyrene/water mixture $\tau = 10$ µs

90°_{x}

solid echoes

90°_{y}

90°_{y}

180°_{y}

180°_{y}

Liquid echo

Baseline

257-28
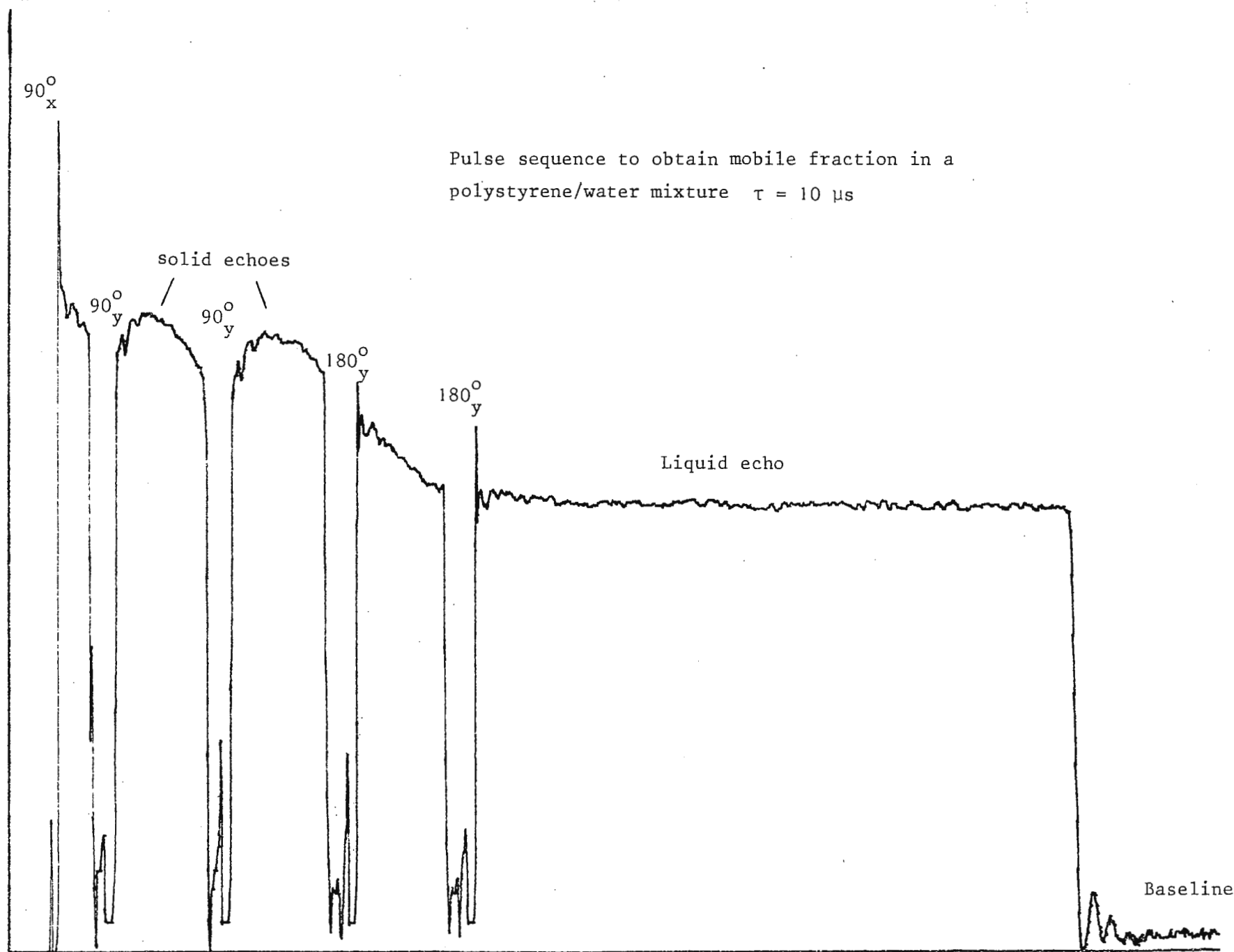
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20205

January 23, 1980

Building 2, Room B2-08

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

Title: CHARACTERIZATION OF ALTERNATING DNA CONFORMATIONS BY ^{31}P NMR
SPECTROSCOPY

Dear Barry:

In the classical Watson-Crick double-helical structure of B-DNA the sugar-
phosphate backbone was considered to be uniform. Several refined DNA
structures have been proposed, but in all cases the phosphodiester back-
bone was invariant. We now have evidence that a dinucleotide repeat unit
characterizes the phosphodiester backbone of alternating purine-pyrimidine
co-polymer DNAs in solution under various conditions.

Medium length deoxynucleotide duplexes were prepared from synthetic polymers
by continuous sonication at low temperature. The products, characterized by
gel electrophoresis, are sufficiently small for high resolution NMR studies.
We observed a doublet (splitting 22 Hz) with components of approximately
equal area in the ^{31}P NMR spectrum at 109.3 MHz for the alternating co-
polymer d(AT)·d(AT), which is consistent with our previous results on 145
bp material prepared from re-constituted nucleosomes (1). We have also
obtained a similar result for sonicated d(IC)·d(IC) (Figure). These results
(2) tend to generalize the phenomenon and indicate the existence of alternating
phosphodiester conformations in the backbone of these B-DNAs in solution.
Resolution between the singlet resonance due to melted material on heating
d(IC)·d(IC) and the residual doublet clarifies the previous work on d(AT)·
d(AT) where the signals from these components overlapped.

Sonicated d(GC)·d(GC) showed a single broad peak at low salt concentration
(0.1 M), in which the above studies were carried out. But, at high salt
concentration (4 M), two peaks with equal areas were resolved (160 Hz), with
one component shifted downfield. This is consistent with the results of
Patel et al. (3) for synthetic oligomers. However, poly(dGdC)·poly(dGdC)
is known to undergo a transition in high salt to a presumably left-handed
form (4). A novel left-handed double-helical structure for crystalline
d(CG)$_3$ has been described (5), which has a dinucleotide repeat unit and a
zig-zag phosphate backbone, and which has been termed "Z-DNA." Consequently
the doublet observed for d(GC)·d(GC) characterizes the Z-form in high salt
solution, and not the alternating B-DNA form as previously concluded (3).

From these results it can be concluded that alternating phosphodiester back-
bone conformations are present in alternating purine-pyrimidine DNAs, and
that ^{31}P NMR provides a means to observe their characteristics, transitions
and interactions in solution. These sequence-dependent conformational
effects may have important implications for DNA recognition and function.
I have written a brief review of this topic which will appear soon in Trends
in Biochemical Sciences.

Yours sincerely,

Jack S. Cohen
Developmental Pharmacology Branch
National Institute of Child
Health and Human Development

References

1. H. Shindo, R. T. Simpson and J. S. Cohen, J. Biol. Chem. 254 8125, 1979.
2. J. S. Cohen and J. B. Wooten, submitted.
3. D. J. Patel, L. L. Cannel and F. M. Pohl, Proc. Natl. Acad. Sci. U.S.A.
   76 2508, 1979.
4. F. M. Pohl and T. M. Jovin, J. Mol. Biol. 67 375, 1972.
5. H. J. Wang, G. J. Quigley, F. J. Kolpak, J. L. Crawford, J. H. van Boom,
   G. van der Mavel and A. Rich, Nature 282 680, 1979.

Figure legend:

^{31}P NMR spectrum at 109.3 MHz of sonicated poly(dIdC)·(dIdC) at 39°C
in 0.1 M NaCl solution. Trimethyl phosphate is the internal standard.
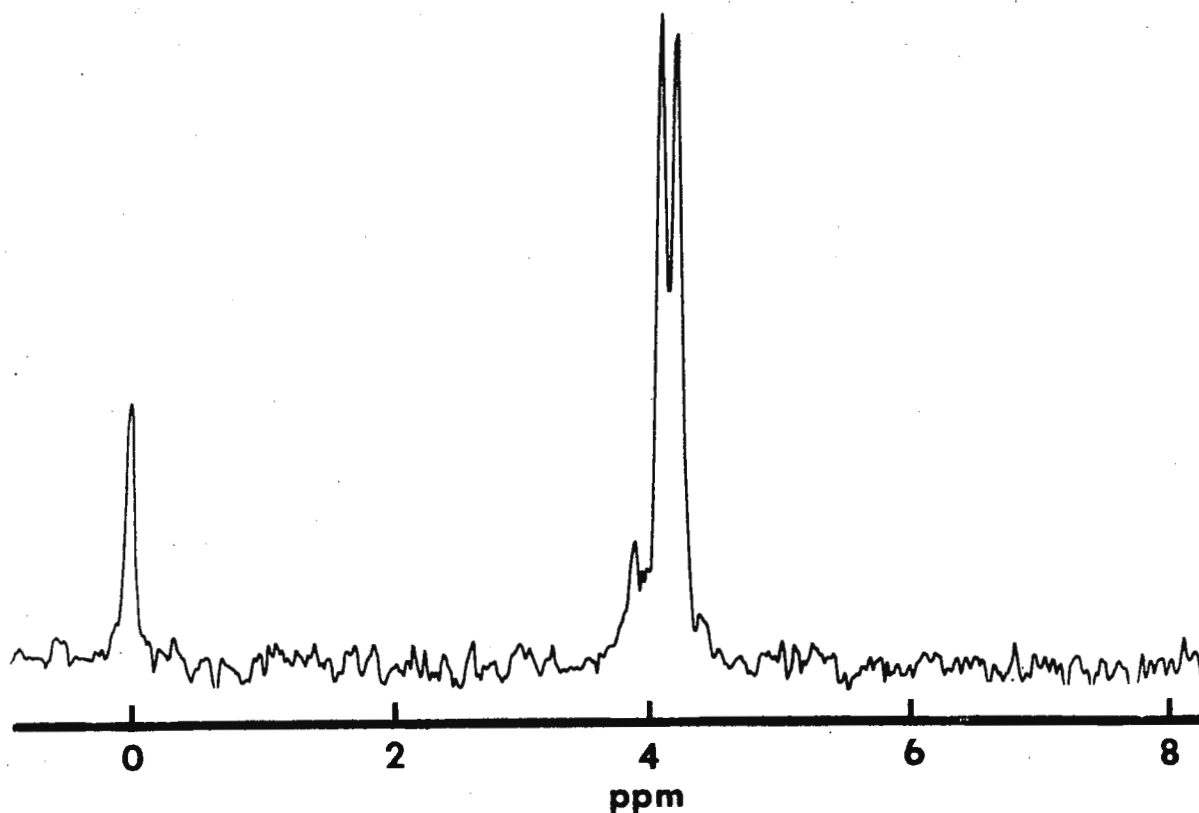
AARHUS UNIVERSITY
DEPARTMENT OF ORGANIC CHEMISTRY

H. BILDSØE

8000 AARHUS C, DENMARK January 7, 1980
HB/ATL

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

Dear Professor Shapiro,

<u>Software error in the Varian XL-100 system</u>

We have recently discovered that the timing of the pulses in the XL-100 system is in error. This was mentioned (without any details) some years ago in a paper by Armitage et al. (1), but unfortunately we found this only after having spent some time to locate and correct the error. We take this opportunity to remind other people of the error hoping that this will eliminate the need for a new re-discovery.

The error is in that part of the T1-programme ('20309-M T1 RESEARCH SPECIAL') that governs the timing of the 90° and 180° pulses. Both from direct measurements (using an oscilloscope to display the pulse-train) and from considerations of the software, we found that the pulses are longer than required by the parameter 'pw'. From the measurements we found the pulses to be approximately 4 µs too long, the software yielded 5.4 µs (the 'coarse timer-word' is one unit too large). The discrepancy can be ascribed to the finite rise-time of the pulse (ca. 1 µs).

The error is easily corrected, just change location 02613 to (02613) 140130 ,SUB,TWO

The same error is present in the FT-programme '994100-02-D'. In this case the correction is (03441) 140057 ,SUB, FOUR

The error is of no importance unless a precise value for the flip-angle is required, e.g. in the selective excitation technique by Freeman et al. (2), where many pulses are required (and the error is accumulated), or in T1-experiments. For the XL-100-15 system in our laboratory the 180° pulse-width is 200 µs and the error has given no problems until now. However, we have recently modified the system and obtained

$180°$ pulses of 40 μs. Since we calibrate the H_1-field by the pulsewidth for a $360°$ pulse, both the $180°$ and $90°$ pulses would be wrong, unless the error is taken into account. The error is sufficiently large to cause problems in the ensuing fitting procedure of the experimental data.

Sincerely,

H. Bildsøe

H. Bildsøe

P.S. Please credit this contribution to Dr. Hans Jørgen Jakobsen's account.

References

(1) I.M.Armitage, H.Huber, D.W.Live, H.Pearson, J.C. Roberts, J.Magn.Resonance, 15, 142 (1974).

(2) G.Bodenhausen, R.Freeman, G.A.Morris, J.Magn.Resonance, 23, 171 (1976).

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

Tel. (415) 493-4000

Telex 34-8476

January 16, 1980

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

Dear Barry:

SUBJECT: PULSE SEQUENCE GENERATION ON THE XL-200

I'd like to alert XL-200 owners to the availability of the Revision E software release. This new software contains several enhancements of the software capabilities of the XL-200. Although new features such as parameter set libraries, add-subtract, spin-simulation, iterative spin analysis, exponential plot graphics and automatic experiment setup have been added, the major new capability is in the Pulse Sequence Generator/PASCAL Compiler.

We have been using this for the generation of Carr-Purcell-Meiboom-Gill T_2, cross-polarization, selective excitation, quadrupole echo, spin-locking, SPI and other experiments.

The user is able to enter PASCAL text directly via the keyboard and have it displayed on the TV screen. A sophisticated editor program allows rapid and convenient text editing. PASCAL source code can be stored in a text library and pulse sequences are compiled by typing SEQGEN(NAME). The user is able to invent new parameters or delete old ones to match with his new pulse sequence, and then he can store a suitable parameter set for later use. At that time, simply recalling the parameter set and typing GO is sufficient to change to the new pulse sequence.

The pulse sequence language is comprised of high-level components with either explicit or indirect arguments. As an example, we have incorporated the interrupted decoupling experiment reported by Opella and Fry (JACS, 101, 5836 (1979) which is useful in identifying non-protonated carbons in solid magic-angle ^{13}C NMR experiments. This is given below as an example of the flexibility of the new Pulse Sequence Generator.

PSG CODE:

"XPOL. CROSS POLARIZATION WITH SPIN LOCK PHASE ALTERNATION, T_1-RHO DELAY,
AND MODULATED DECOUPLER AMPLITUDE. IF THE FLAG Q = Y THE SEQUENCE INTRO-
DUCES A DECOUPLER OFFTIME D3 FOR ELIMINATION OF PROTONATED CARBON RESON-
ANCES. IF Q = N THE SEQUENCE GIVES A DECOUPLED SPECTRUM."
PROCEDURE PULSE SEQUENCE;
    VAR P2,P3,D3: REAL;
    Q: TEXT4;
BEGIN
    GETVAL(P2,'P2   ');
    GETVAL(P3,'P3   ');
    GETVAL(D3,'D3   ');
    GETVAL(Q,'Q   ');
    "PERIOD(1)"
        STATUS(A);
        SPAREON;
        HLV(OPH,V1);
        DBL(V1,V2);
        INCR(V2);
        DELAY(D1);
        RCVROFF;
        DELAY(1E-5);
        DECPULSE(P1,V2);
    "PERIOD(2)"
        STATUS(B);
        DECPHASE(ZERO);
        MOD2(OPH,V3);
        RGPULSE(P2,V3,0.0,0.0);
    "PERIOD(3)"
        STATUS(A);
        RGPULSE(P3,V3,0.0,1E-5);
    "PERIOD(4)"
        STATUS(C);
        SPAREOFF;
        OBSPULSE;
        IF Q [1]= 'Y'
            THEN BEGIN
                    STATUS(A);
                    DELAY(D3);
                    STATUS(C);
                    DELAY(1E-5);
                END
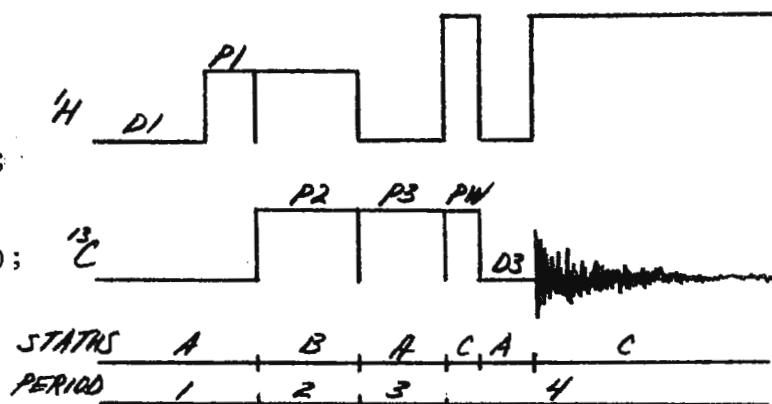   ELSE DELAY(D3+1E-5);
END;

NEW PARAMETERS:

P2 - Contact Period
P3 - T1-Rho Locking Period
D3 - Protonated Carbon Elimination
     Delay
Q - Quaternary Carbon Selection
     Flag

The sequence first obtains the parameter values for P2,P3,D3, and Q.
The section in "PERIOD(1)" serves to calculate the phase (V2), for the
proton pulse P1 from the observe phase OPH (OPH is cycled through four
phases automatically with suitable data routing.) The decoupler is kept
on during the contact period P2. P3 is provided to allow for T_1-rho exper-
iments. In "PERIOD(4)" PW is provided for the non-contact experiment (P1,P2
and P3 set to zero), otherwise its value is set to zero for the contact
experiment. The D3 delay is introduced depending on the value for Q. Note
that for either case the same time is used from the end of the P3 period to
the beginning of data acquisition, resulting in little phase change in the
resulting spectrum.

As an example of the use of the XPOL pulse sequence, the figure shows both ordinary decoupled and protonated carbon suppressed ^{13}C magic-angle spectra of sucrose. Both spectra can be automatically collected by ARRAYing Q for values of Y and N. By setting the interleave (IL) flag to Y, blocks of transients of each type can be collected, thus obtaining both sets of data at the same time. The diagnostic value of Opella and Fry's experiment is obvious in interpretating ^{13}C spectra of solids.
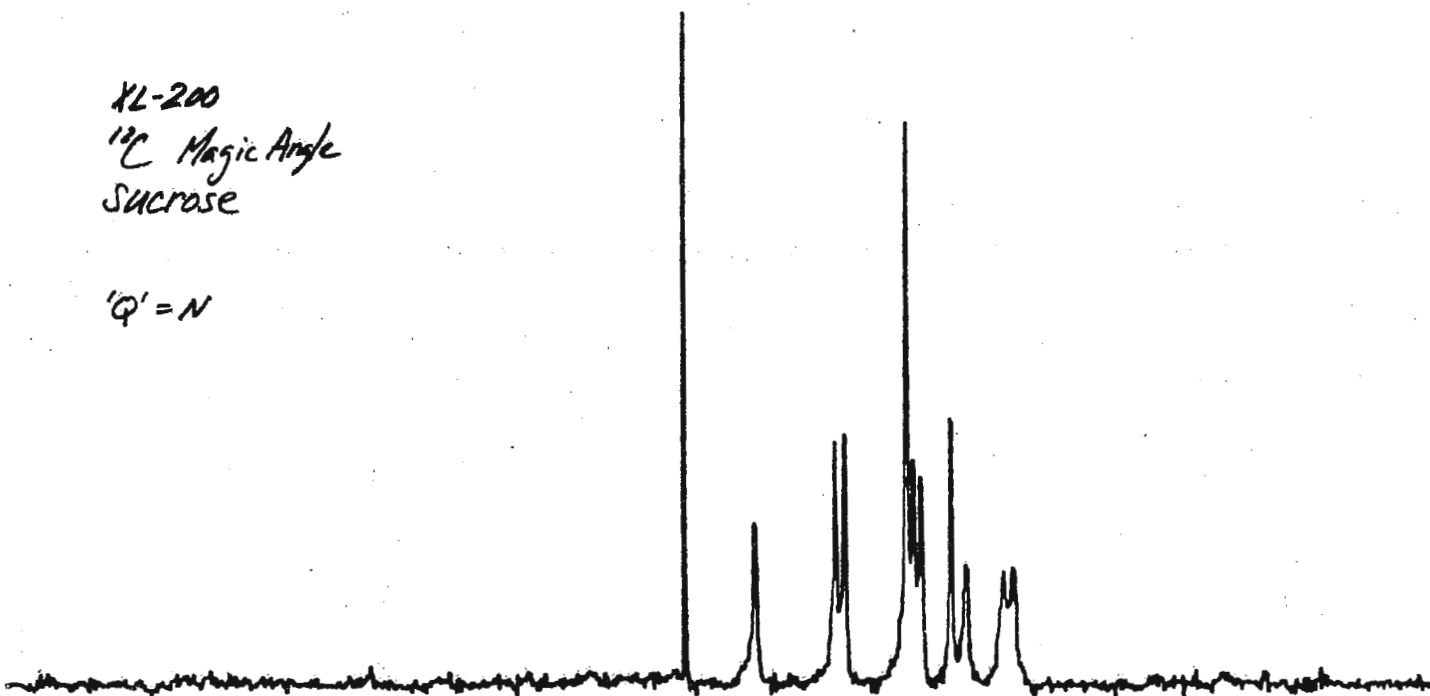
See you at ENC,

George A. Gray, Manager
NMR Applications Laboratory
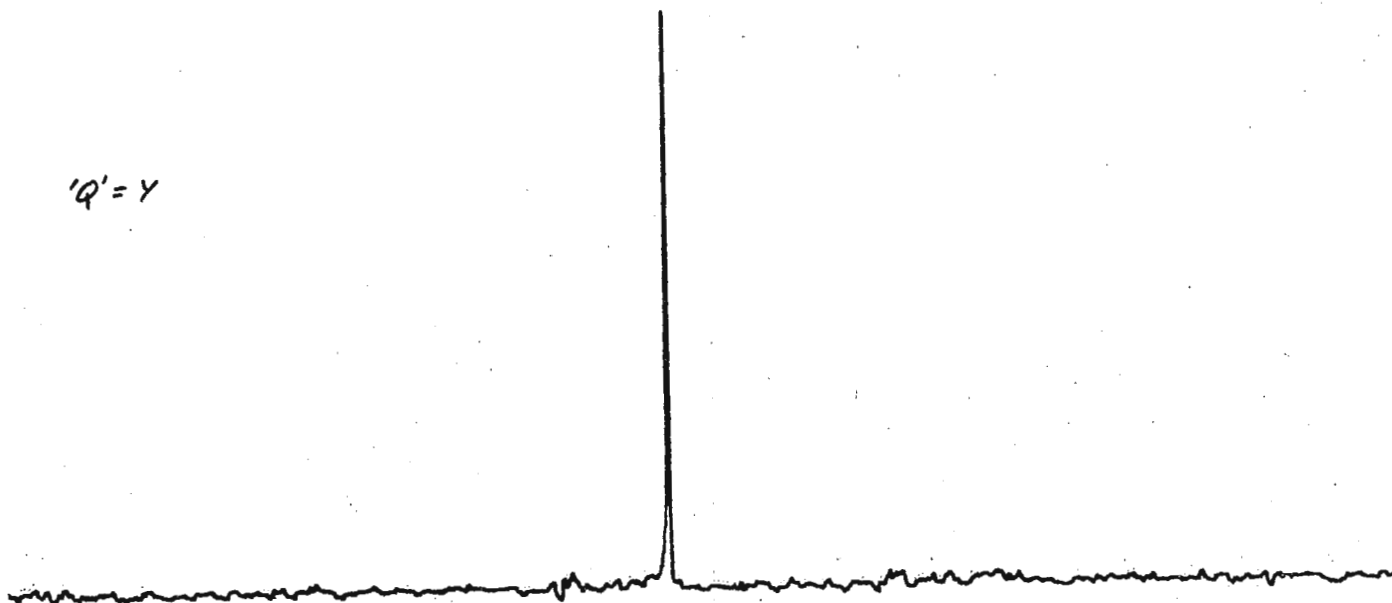Varian Instrument Division

GG/dc

XL-200
^{13}C Magic Angle
Sucrose

'Q' = N

'Q' = Y

POSITION OPEN IN NMR RESEARCH

Location: University of Florida, College of Medicine, Gainesville, Florida.

Responsibilities: Assist the senior NMR spectroscopist with:
1) Implementing an active NMR imaging (zeugmatography) research program.
2) Routine maintenance and trouble shooting of the NMR spectrometers.
3) If interested, participate in some of our other research projects such as:
   a) Computer simulation of ^1H and ^{13}C spectra of heterocycles to evaluate effects of ring closure.
   b) Parameters affecting S/N of ^{13}C NMR of microsamples.
   c) Medium effects on the ^1H NMR of polypyridyl compounds.
   d) Conformational analysis of aromatic amines as it relates to biological activity.

Instruments: A 90 MHz Bruker HX-90 Ft spectrometer with a Nicolet 1083 Computer, pulse programmer, and disk. A 300 MHz superconducting Nicolet NT-300 spectrometer with dual disk system.

Qualifications: Must be an experienced Ft NMR spectroscopist and a good instrumentalist. A Ph.D. in physics or chemistry or an M.S. in electrical engineering is desirable. Previous experience in NMR imaging would be most welcome.

Salary: Starting salary is $18,000/year or more, depending on experience and qualifications. If have previous NMR imaging experience, starting salary is $20,000/year or more. The position is a continuing one. The appointment is joint academic/government on an academic/professional level. Exact title will depend on qualifications and experience.

Starting Date: The position is available immediately, therefore, an early date is preferred. However, we are somewhat flexible on this for a promising candidate.

Send Resume and Names of Three References To: Dr. Kate Scott, NMR Spectroscopist, Box J-374, JHMHC, University of Florida, Gainesville, Florida, 32610.

UNIVERSITÉ PARIS VII

ITODYS

INSTITUT DE TOPOLOGIE ET DE DYNAMIQUE DES SYSTEMES
1, rue Guy de la Brosse - 75005 PARIS - Tél. : 336 25.25, poste 36-15

Paris, January 24th, 1980

LABORATOIRE DE CHIMIE
ORGANIQUE PHYSIQUE

J.-E. DUBOIS, *Directeur*

Dr. B. Shapiro
Texas A & M University

College Station

Texas 77843

Dear Dr. Shapiro,

^{14}N NMR Spectra of dissolved N_2 in alkanes.

Thank you for your yellow reminder which prompts us to report
some very new results concerning ^{14}N linewidth measurements.

As part of molecular reorientation studies of small molecules in
alkanes of various viscosities[1] we have undertaken ^{14}N linewidth measurements
of CH_3CN in dilute solutions, i.e. 1% V/V in several n-alkanes ranging from
C_6 to C_{16}. The measurements were performed at 14.4 MHz on our new BRUKER WP 200
supercon multinuclear NMR spectrometer. Samples were contained in 15 mm o.d.
NMR tubes. The magnetic field was locked on the deuterium signal of DMSO d_6
contained in a capillary. Given the linewidths of quadrupolar ^{14}N signal
(59 Hz $\sim$ 152 Hz), samples were not degassed. FID's were acquired using
1 K point + 15 K point zero filling for a 10 kHz spectral width with quadrature
detection. A 1.5 ms delay between pulse and acquisition was used to avoid a
spurious response from the probe. A few hour accumulation was needed to achieve
a good S/N ratio.

Each sample gave two lines, the CH_3CN line and a narrower one
(17 $\sim$ 26 Hz) at about 56 ppm downfield (cf. figure). The latter signal also
appeared for neat alkane samples, while a degassed sample gave no ^{14}N signal.
Thus we assigned this unexpected line to atmospheric N_2 naturally dissolved
in all solvents. Peak integration led to a N_2 concentration of about 7.10^{-3} Ml^{-1}
in C_6H_{14} which is consistent with N_2 solubility data.[2] Results were similar in
other solvents.

An attempt was made to record the gazeous N_2 signal with an empty NMR tube (containing the DMSO d_6 capillary). A two-day accumulation was needed, although N_2 concentration in atmosphere is about five times greater than in $n-C_6H_{14}$. The linewidth was around 20 Hz and thus cannot explain the low sensitivity which might be the result of gaseous diffusion in the probe coil.

Sincerely yours,

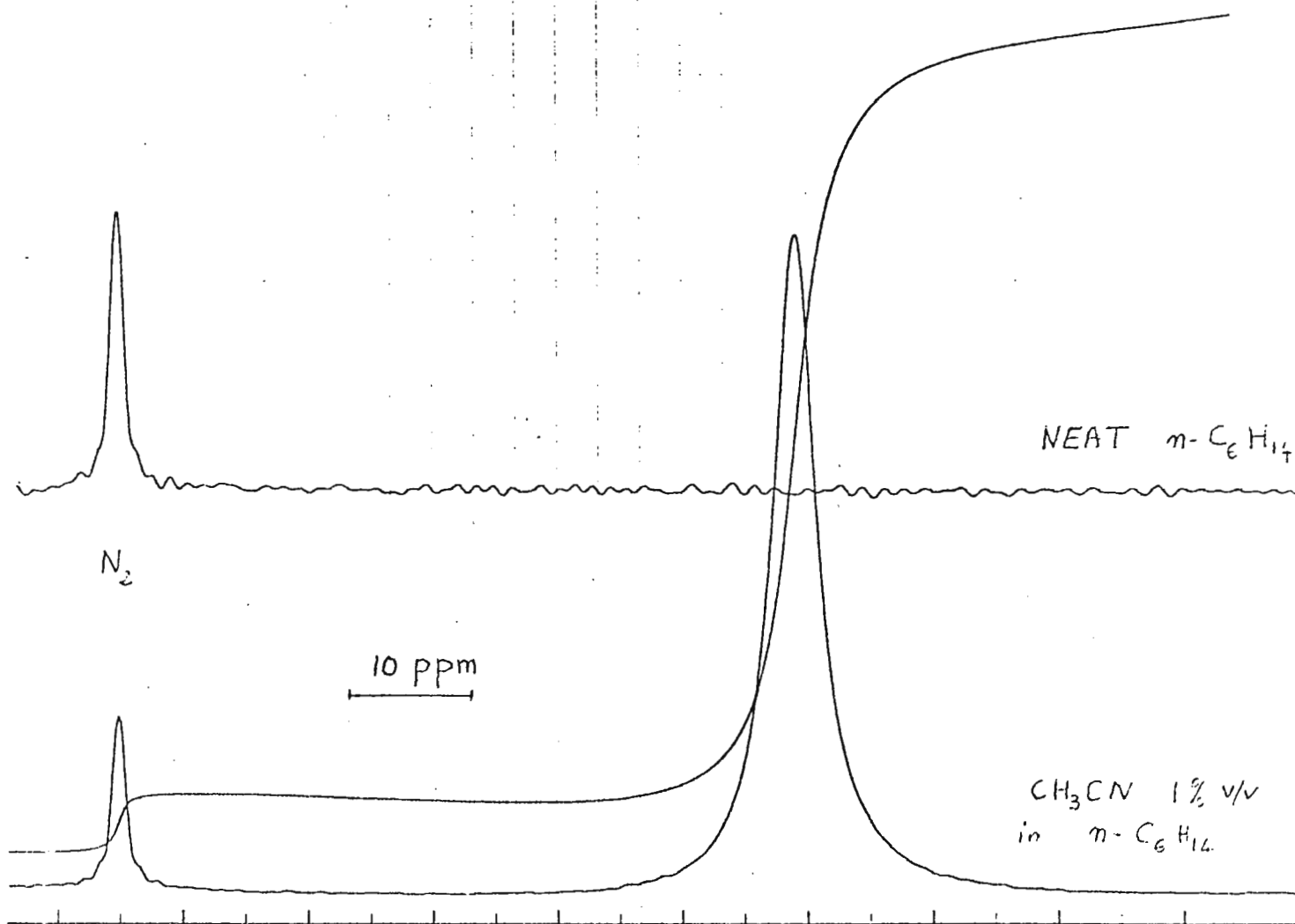B. Tiffon   B. Ancian

[1] B. Ancian, B. Tiffon and J.E. Dubois, Chem.Phys.Lett., 65, 281 (1979).

[2] Landolt-Börnstein, "Zahlenwerte und Funktionnen", II.Band, 2. Teil, Springer Verlag, Berlin (1962).

NEAT $n-C_6H_{14}$

N_2

10 PPM

CH_3CN 1% v/v in $n-C_6H_{14}$

BP RESEARCH CENTRE

SUNBURY-ON-THAMES

MIDDLESEX

ENGLAND

THE PRESENCE OF TETRASUBSTITUTED ETHYLENIC
END GROUPS IN LOW MOLECULAR
WEIGHT POLYISOBUTENES.
13C STUDY

Current knowledge of the amount and type of unsaturated end groups present in low molecular weight polyisobutenes is incomplete. In particular, the evidence for tetrasubstituted type of double bond $RR'C = CR''R'''$ is based entirely on the differences found between values obtained by protone NMR spectroscopy, infra-red spectroscopy, hydrogenation and maleic anhydride adduct formation, and those from the assumption that there is one double bond per polymer chain.

Structural studies on an end group analysis of low molecular weight polyisobutenes are being undertaken in order to further our understanding on the role of catalysts in the chain transfer and termination steps in the cationic polymerization of isobutene. As is evident from Figures 1 and 2 which show spectra of samples prepared using BF_3 and $AlCl_3$ catalysts respectively, the complexity of the carbon-13 spectra in the 145 - 110 ppm region is such that they can no longer be interpreted solely on the basis of end groups I, II and III:-

I   II   III
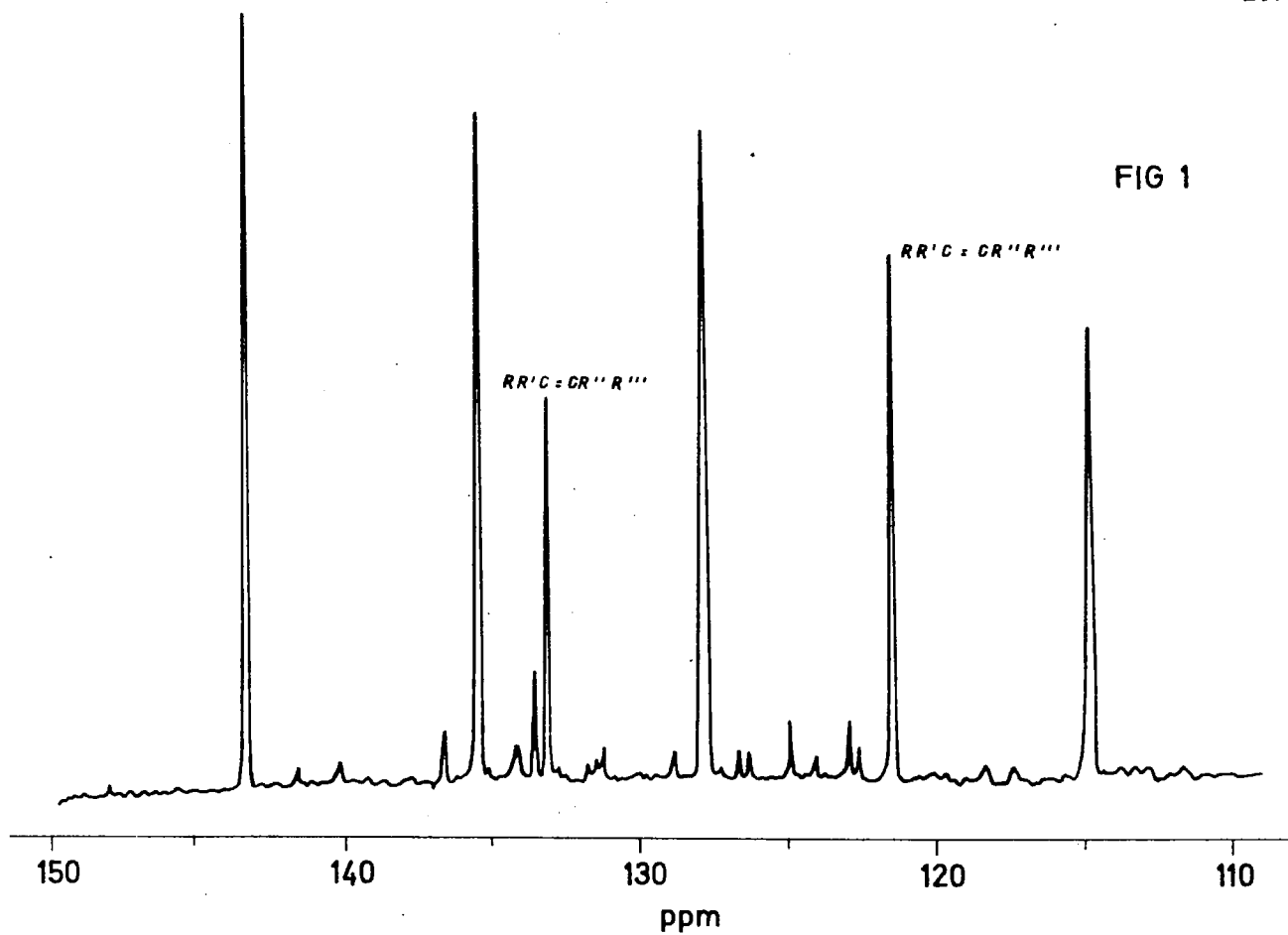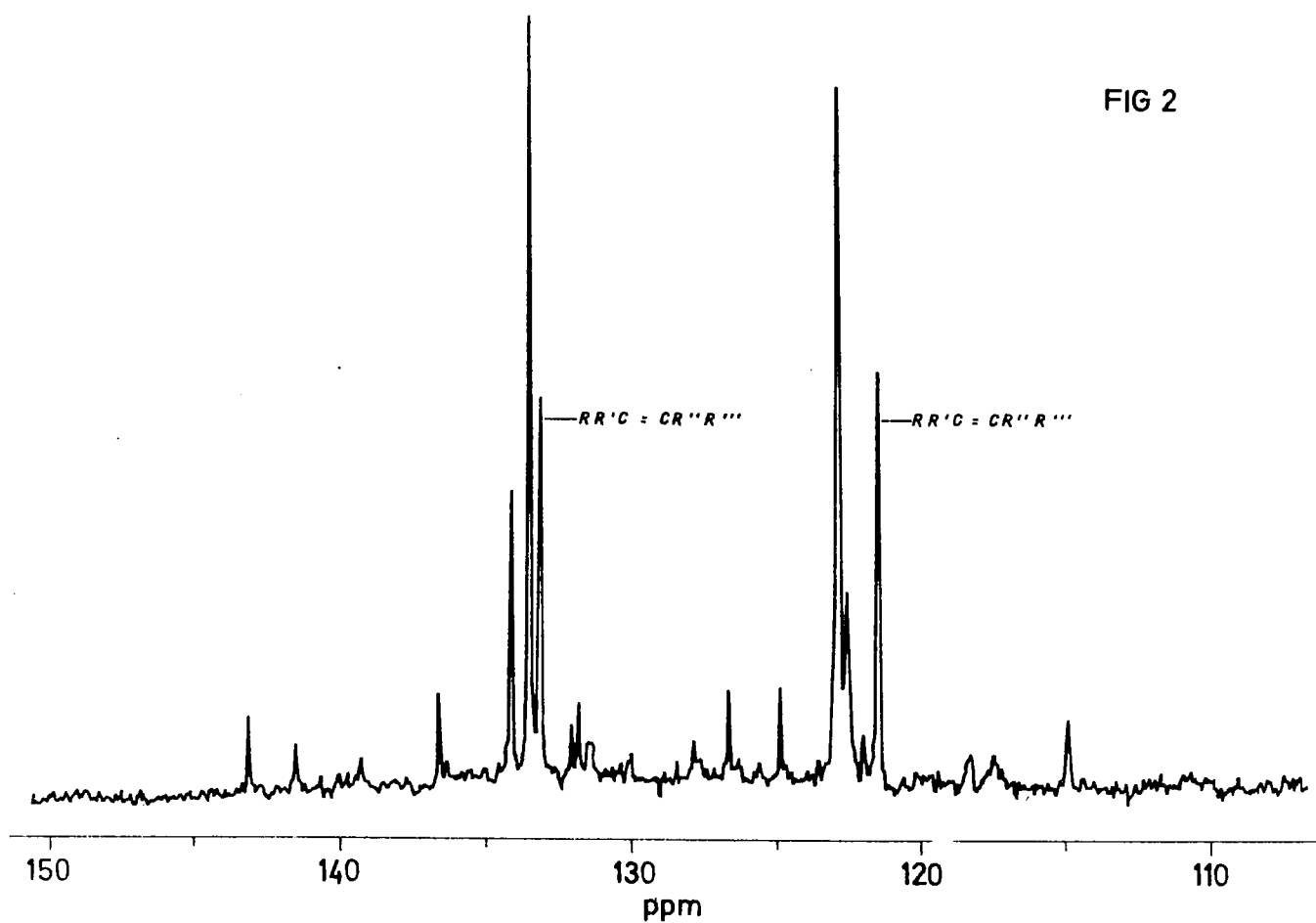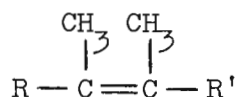
FIG 1

RR'C = CR''R'''

RR'C = CR''R'''

ppm

FIG 2

RR'C = CR''R'''

RR'C = CR''R'''

ppm
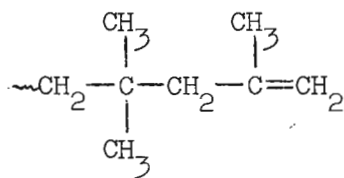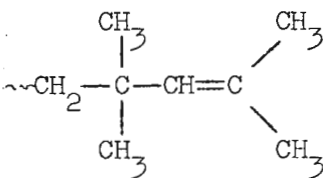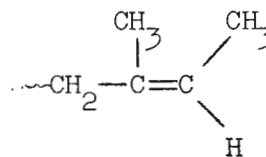
although these are some of the major components. The observation, which forms the subject of this note, is that both samples contain resonances at 133.30 and 121.53 ppm (CDCℓ_3 taken as internal reference at 70.00 ppm), which are assigned to tetrasubstituted structures (IV):-

$$R - \underset{\underset{\displaystyle R}{|}}{C} = \underset{\underset{\displaystyle R'}{|}}{C}$$

with CH$_3$ groups on each carbon.

IV

The approximate concentrations are 19 and 10 per cent for the samples whose spectra are shown in Figures 1 and 2, respectively.

H. Pyszora

H. Pyszora

UNL

The University of Nebraska–Lincoln

Department of Chemistry
Lincoln, NE 68588
402-472-3501

January 24, 1980

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

Dear Dr. Shapiro:

We would like to hear from anyone who wants to sell ^{31}P FT modules from XL-100. We would like to have FT local oscillator, FT transmitter, and the FT RF amplifier. Anyone interested in selling this is requested to contact me or call me at 402-472-6255.

Yours sincerely,

S. Rajan

SR/js

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CORPORATION** 145 East Dana Street ◦ Mountain View, California 94041 ◦ Phone: 415/969-2076

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BANGALORE NMR FACILITY

Professor C.L.Khetrapal
Dr. A.C.Kunwar
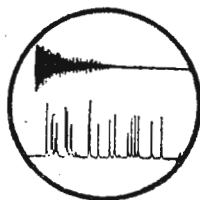
Date: January 21, 1980

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

Title: Covalent and van der Waals radii from NMR of oriented systems

Dear Prof. Shapiro,

Thank you very much for the reminder to submit a technical contribution for the TAMU-NMR Newsletter. We hope, the following contribution will be of interest to the readers of the Newsletter.

We have studied the proton NMR spectrum of phosphacymantrene oriented in nematic solvents and compared the geometrical information derived in several 5- and 6-membered heterocyclic ring systems of the type (I) and (II)

(I)

X = O, N(H), C(H), S, P, Se, Te

(II)
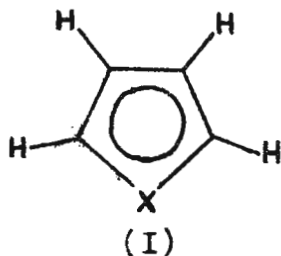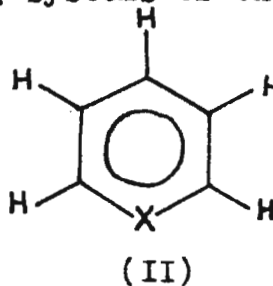
X = N, C(H), P, As

It has been observed that in these systems the ratio (R) of the distances between the two α- and the β-protons are related to the covalent or the van der Waals radii by the following relation:

$$R = A + \frac{B}{r}$$

where A = 2.16 and B = -0.44 Å for the 5-membered systems and 1.35 and -0.27 for the 6-membered heterocycles when r is the covalent radius; the constants A and B are 2.74 and -1.85 Å for the 5-membered compounds and 1.74 and -1.22 Å for the 6-membered ones when r is the van der Waals radius. The values derived are compared with those reported in the literature in the accompanying tables.

With regards,

Yours sincerely,

C.L.KHETRAPAL   A.C.KUNWAR

Tables

R-values in heterocyclic aromatic ring systems together with the values of the covalent or the van der Waals radii.

a) **From the 5-membered systems**

Hetero atom	R	Covalent radius ($\mathring{A}$) calc.	literature	van der Waals radii ($\mathring{A}$) calc.	literature
O	1.504	0.67	0.66	1.5	1.4 – 1.5
N(H)	1.551	0.72	0.70	1.56	1.5 – 1.55
C(H)	1.602	0.79	0.77	1.65	1.7
S	1.736	1.04	1.04	1.84	1.8 – 1.85
P	1.744	1.06	1.10	1.86	1.8 – 1.9
Se	1.788	1.18	1.17	1.94	1.9 – 2.0
Te	1.840	1.37	1.37	2.06	2.06 – 2.2

b) **From the 6-membered systems**

Hetero atom	R	Covalent radius ($\mathring{A}$) calc.	literature	van der Waals radii ($\mathring{A}$) calc.	literature
N	0.958	0.69	0.70	1.56	1.5 – 1.55
C(H)	1.000	0.77	0.77	1.65	1.7
P	1.092	1.05	1.10	1.88	1.8 – 1.9
As	1.126	1.21	1.21	1.99	2.0

THE UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
RIVER STATION
ROCHESTER, NEW YORK 14627

DEPARTMENT OF CHEMISTRY

January 18, 1980

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

Dear Barry:

BIOPHYSICAL POSTDOCTORAL POSITION

One of my postdoctoral fellows has just received a Damon Runyon-Walter Winchell Postdoctoral Fellowship and thus I have an immediate opening for a postdoctoral in my group. The starting date, however, is flexible. I will also have two additional postdoctoral openings which may be filled anytime during 1980. The main thrust of our research program is the spectroscopic study of drug-nucleic acid complexes using both oligonucleotides and polymers. I am particularly interested in persons with nucleic acid experience and/or a background in spectroscopy, although top-notch candidates in all areas will be considered for this biophysical postdoctoral position. We make extensive use of proton FT nmr, circular dichroism, fluorescence, and absorption spectroscopies in our studies which are designed to investigate the geometry, thermodynamics and sequence preferences that are associated with the intercalation of drugs into nucleic acids.

We will receive delivery of a Bruker 400 MHz multinuclear NMR spectrometer this month. Other readily available instrumentation includes a new (computer interfaced) Cary 219 UV/Vis spectrophotometer, a computer controlled JASCO-J40 circular dichroism instrument, a computer controlled Durrum Stopped Flow Instrument with a dual detector accessory, and a Perkin Elmer MPF44A spectrofluorimeter with a Differential Corrected Spectra Accessory.

Interested applicants should forward a cirriculum vitae, copies of their transcript(s) and arrange to have three letters of recommendation sent on their behalf.

Sincerely yours,

Tom

Thomas R. Krugh
Professor of Chemistry
716-275-4224

TRK:lcb

MANAGER

South West Ontario High Field NMR Facility; NMR Spectroscopist with experience in FT NMR Techniques.

SALARY: Negotiable but in the Assistant Professor range dependent on experience and qualifications. Position subject to final budgetary approval.

DUTIES: Include overall management of a service based on a Bruker WH-400 Multinuclear Cryospectrometer. The position will involve scheduling of time, consultation with users, supervision of an operator as well as supervision of maintenance and repair. Opportunities will exist for collaborative and other research. Successful candidate will be expected to teach a graduate or upper-level course in his/her speciality.

The High Field NMR facility is sponsered by the Guelph Waterloo Centre for Graduate Work in Chemistry, $(GWC)^2$, which plans to provide an NMR service primarily for eight South West Ontario Universities (Brock, Guelph, McMaster, Toronto, Waterloo, Western, Windsor, York). Other Universities or Industrial and Government Laboratories can also be served by special arrangement.

The position is "professional" in rank which is classified at a higher level than that of staff but not faculty. The starting salary is negotiable but at least $20,000. Probationary period is one year. Supervision of two technicians will be expected.

The facility will be equipped with a Bruker WH-400 to be delivered in March or April 1980. An application for a Bruker CXP-200 has also been submitted. Other NMR equipment in the department includes: Bruker CXP-100 and WP-60; Varian HA-100, A60, T60 and 360L.

Three $(GWC)^2$ faculty are primarily associated with research in NMR spectroscopy: L.W. Reeves (Waterloo), M. Cocivera (Guelph), C.A. Fyfe (Guelph). Opportunity for collaborative or independent research and teaching is available on both campuses (Waterloo and Guelph).

Please address inquiries to the chairman of the department of chemistry at the University of Guelph: Prof. Edward G. Janzen. Further information about $(GWC)^2$ can also be obtained from Prof. Ron Fawcett, Director of $(GWC)^2$ at the University of Guelph or Prof. Don Irish, chairman of the department of chemistry at the University of Waterloo.

HERCULES INCORPORATED

RESEARCH CENTER · WILMINGTON, DELAWARE 19899 · TELEPHONE: 302-995 3000

January 30, 1980

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

Dear Dr. Shapiro:

ESR/NMR SPECTROSCOPIST

Hercules Incorporated is seeking a Ph.D. chemist to work and provide technical leadership in a group applying NMR/ESR spectroscopy to problems of corporate interest. Work areas include: ESR of both polymeric and inorganic materials, high field (8.4 Tesla) NMR studies of polymer microstructure in solution, development of analytical NMR/ESR methods and application of multinuclear NMR techniques.

A strong background in analytical or physical organic chemistry and an interest in applied magnetic resonance spectroscopy are necessary qualifications. A minimum of three years of experience in magnetic resonance spectroscopy is essential.

Qualified applicants should send resume including salary requirements in confidence to:

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Employe Relations
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Sincerely yours,

W J Freeman/HNC

W. J. Freeman, Group Leader
Analytical Division

WJF:gtg

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- **Simultaneous acquisition, processing, and plotting for greater sample throughput.**

- **Simplified control of spectrometer operations and parameters by using easy keyboard commands.**

- **Advanced Nicolet-1180 Data System with the most comprehensive FT-NMR software package available.**

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The multiple-technique NT-Series spectrometers provide the user with the ability to easily adapt to the newest techniques and experimental configurations.

Some of these are:

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- **Automated T_1 and T_2 measurements.**

- **Chemical dynamics studies.**

- **Temperature-programmed experiments.**

- **^{31}P experiments on living organs.**

NTC **NICOLET TECHNOLOGY CORPORATION**

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Mountain View, California 94041
Telephone: 415/969-2076