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Newsletter

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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.

UNIVERSITY OF CALIFORNIA, SAN DIEGO

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Chemistry Department (M-001)
LA JOLLA, CALIFORNIA 92093
August 15, 1977

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

Dear Dr. Shapiro:

^{1}H-NMR DEMONSTRATION OF MAGNETIC NON-EQUIVALENCE IN THE TWO FATTY ACID CHAINS OF PHOSPHOLIPIDS AS MODEL MEMBRANES; POSTDOCTORAL POSITION AVAILABLE

I wish to receive the TAMUNMR Newsletter and to report that for the last several years our laboratory has been using ^{1}H- and ^{13}C-NMR techniques to examine the structure, conformation, and mobility of surfactant micelles and mixed micelles with phospholipids (1,2). The mixed micelles provide ideal surfaces for studying the interaction of proteins and phospholipids as models for their interaction in membranes, lipoproteins, and naturally occuring mixed micelles. We have found that the micellar phospholipid is in a much more fluid environment than it is in unsonicated multibilayer or sonicated vesicle structures. We have also been conducting kinetic and mechanistic studies on the interaction of enzymes such as phospholipase A_2 with phospholipid in mixed micelles (3) and have used ^{1}H-NMR at 220 MHz to examine the single histidine residue in phospholipase A_2 which is involved in its mechanism (4).

Recently, Mary Roberts in our laboratory used ^{1}H-NMR techniques to show that the α-CH_2 groups in the sn-1 and sn-2 fatty acyl chains in dipalmitoyl phosphatidylcholine are magnetically non-equivalent when the phospholipid is present in mixed micelles with the nonionic surfactant Triton X-100 (5). This difference has not been reported for sonicated vesicle or multibilayer preparations of phospholipids, whereas the mixed micelle system with its greater motional freedom and narrower linewidths provides an ideal membrane-like interface for exploring these conformational differences. We have assigned the sn-1 α-CH_2 and sn-2 α-CH_2 groups at 2.26 ppm and 2.35 ppm downfield from TSP based on the ^{1}H-NMR spectrum of 1-palmitoyl, 2-[2'H_2]palmitoyl phosphatidylcholine. The chemical shift differences between the two α-CH_2 groups persist with changes in temperature, pH, fatty acid composition of the phospholipid, and surfactant:phospholipid ratios. Phosphatidylserine gives similar results to phosphatidylcholine, but phosphatidylethanolamine gives only a single unresolved peak. The α-methylene region of phosphatidylcholine (PC) and phosphatidylethanolamine (PE) are shown in the figure on the next page:

20 Hz
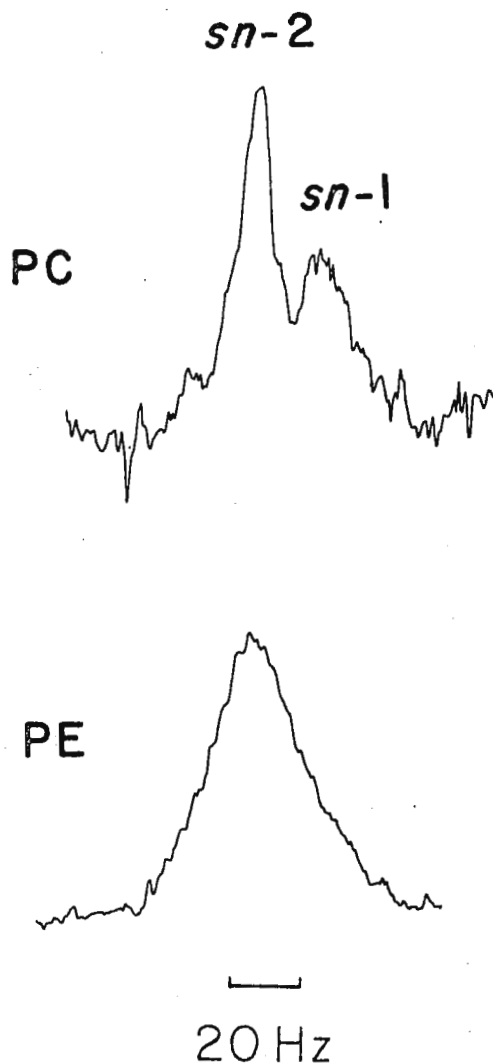
A postdoctoral position is available for further NMR work on phospholipids, surfactants, and the enzyme phospholipase A_2.

Sincerely yours,

Edward A Dennis

Edward A. Dennis
Associate Professor of Chemistry

EAD:js

1. A.A. Ribeiro and E.A. Dennis, Biochemistry 14, 3746 (1975).
2. A.A. Ribeiro and E.A. Dennis, J. Phys. Chem. 80, 1746 (1976).
3. R.A. Deems, B.R.Eaton, and E.A. Dennis, J. Biol. Chem. 250, 9013 (1975).
4. M.F. Roberts, R.A. Deems, and E.A. Dennis, J. Biol. Chem. 252, No. 16 (1977).
5. M.F. Roberts and E.A. Dennis, J. Am. Chem. Soc. 99, No. 18 (1977), in press.

EUTECO S.P.A.

CASELLA POSTALE 3843 - 20100 MILANO
TELEFONO: 02 - 64.670 - TELEX: 37111

Prof. B.L. Shapiro,   Paderno, 17-08-1977
Department of Chemistry,
Texas A & M University,
College Station, T X 7 7 8 4 3   16/SEAN/LC

Subject : LIS study on unsaturated FAME derivatives.

Dear Prof. Shapiro,
my apologies for the delay to send you our TAMU renewal con
tribution. Here we like to anticipate some NMR results got
on the epoxy derivatives of three unsaturated fatty acid me
thyl esters (FAME), namely; methyl oleate (C 18:1; 9 c), me
thyl elaidate (C 18:1 ; 9 t) and methyl linoleate (C 18 : 2 ;
9 c, 12 c).
The lanthamide, $Eu(fod)_3$, induced shifts, LIS, and the rela
tive LIS ratios of these derivatives for several $\underline{/}Eu(fod)_3\underline{/}$
$\underline{/}$ solute $\underline{/}$ ratios have been measured [1]. The data are collec
ted in the herebyattached Tables. Because of the two coordi
nation sites in the molecule, the oxirane and the carbome-
toxy group, the relative LIS ratios are not constant during
the shift reagent incremental addition.
Two conclusions are worthy to be pointed out :
 a) the relative LIS ratios for protons at C - 9,10 are al-
    ways less in the epoxy-derivative of methyl elaidate
    than in the epoxy-derivative of methyl oleate.
 b) the trend for cis-protons is just the reverse of that
    for trans-protons, namely, the LIS ratios decrease mar-
    kedly for cis-protons whereas they are almost constant
    or increase slightly for trans-protons.
This behaviour can be justified by the great coordination
capacity to the shift reagent of the cis-oxirane ring re-
spect to the trans-oxirane ring and the ester group.
These results are part of an extensive work (submitted for
publication) carried out to try to elucidate the composi-
tion and the structure of the fatty acids present in some
single cell proteins (S C P).
                                    yours sincerely,

     L. Cavalli   G. Cancellieri   L. Lanzini

1) J.P. Wineburg and D. Swern, J A O C S , 51, 528, 1975

                    EUTECO S.p.A.
                   Centro Ricerche
                     v. Reali,
              Paderno Dugnano (Milano) ITALY

Table 1 : LIS values and relative LIS ratios [a] for some absorptions of the epoxy derivative of methyl oleate (C 18 : 1; 9 c).

$$\underset{18}{CH_3}\underset{17}{CH_2}\underset{16}{CH_2}\underset{15}{CH_2}\underset{14}{CH_2}\underset{13}{CH_2}\underset{12}{CH_2}\underset{11}{CH_2}\overset{\displaystyle \underset{10}{CH}-\underset{9}{CH}}{\diagup O \diagdown}\underset{8}{CH_2}\underset{7}{CH_2}\underset{6}{CH_2}\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{CH_2}\underset{2}{CH_2}COOCH_3$$
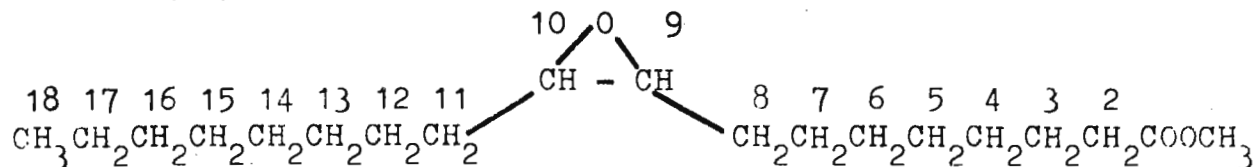
R [b]	$-CO_2CH_3$	C - 2	C - 9,10
-	3.63	2.28	2.88
0.224	4.48 (10.0)	3.25 (11.41)	5.32 (28.71)
0.481	5.62 (10.0)	4.53 (11.81)	7.97 (25.58)
0.748	6.93 (10.0)	6.00 (11.27)	10.47 (23.00)
0.994	8.20 (10.0)	7.42 (11.25)	12.50 (21.05)
1.24	9.25 (10.0)	8.57 (11.19)	14.15 (20.05)
1.54	10.27 (10.0)	9.78 (11.30)	15.73 (19.35)
1.86	11.03 (10.0)	10.67 (11.34)	16.97 (19.04)

Table 2 : LIS values and relative LIS ratios [a] for some absorptions of the epoxy derivative of methyl elaidate (C 18 : 1; 9 t)

$$\underset{18}{CH_3}\underset{17}{CH_2}\underset{16}{CH_2}\underset{15}{CH_2}\underset{14}{CH_2}\underset{13}{CH_2}\underset{12}{CH_2}\underset{11}{CH_2}\overset{\displaystyle \underset{10}{CH}-\underset{9}{CH}}{\diagdown O \diagup}\underset{8}{CH_2}\underset{7}{CH_2}\underset{6}{CH_2}\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{CH_2}\underset{2}{CH_2}COOCH_3$$
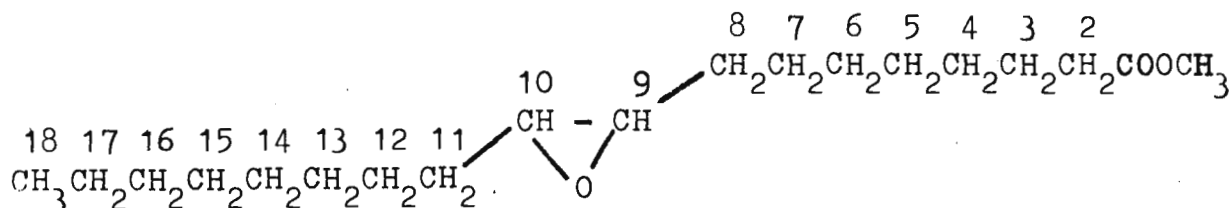
R [b]	$-CO_2CH_3$	C - 2	C - 9,10
-	3.64	2.28	2.63
0.146	4.54 (10.0)	3.28 (11.11)	4.00 (15.22)
0.326	5.65 (10.0)	4.49 (11.00)	6.31 (18.31)
0.461	6.47 (10.0)	5.39 (10.99)	7.14 (15.94)
0.728	7.91 (10.0)	7.03 (11.12)	9.71 (16.58)
0.991	9.22 (10.0)	8.48 (11.11)	12.15 (17.06)
1.333	10.50 (10.0)	9.96 (11.20)	14.71 (17.61)
1.71	11.03 (10.0)	10.57 (11.22)	15.83 (17.86)
2.03	11.54 (10.0)	11.14 (11.22)	17.00 (18.19)

a) relative LIS ratio are in parenthesis with $-CO_2\underline{CH}_3$ set at 10.0.

b) $R = \left[Eu(fod)_3\right]\Big/\left[solute\right]$

Table 3 : L I S values and relative L I S ratios [a] for some absorptions of the epoxy derivatives of methyl linoleate (C 18:2 ; 9c , 12c)

$$\underset{CH_3}{18}\underset{CH_2}{17}\underset{CH_2}{16}\underset{CH_2}{15}\underset{CH_2}{14}\ \overset{13}{CH}\!-\!\overset{12}{CH}\ \underset{CH_2}{11}\ \overset{10}{CH}\!-\!\overset{9}{CH}\ \underset{CH_2}{8}\underset{CH_2}{7}\underset{CH_2}{6}\underset{CH_2}{5}\underset{CH_2}{4}\underset{CH_2}{3}\underset{CH_2}{2}COOCH_3$$
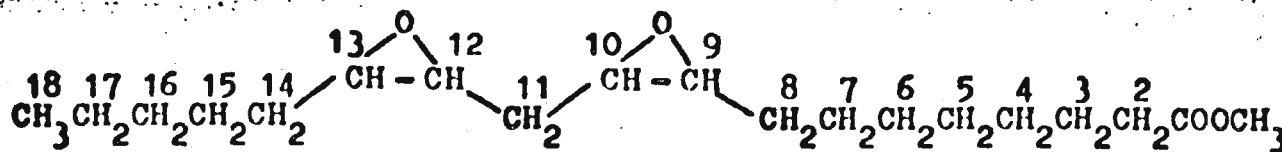
R [b]	$-CO_2CH_3$	C – 2	C – 10,12	C – 9,13	C – 11
–	3.65	2.33	3.07	3.07	1.72
0.247	4.17 (10.0)	2.85 (10.00)	– (c)	– (c)	– (c)
0.500	5.07 (10.0)	3.88 (10.92)	6.38 (23.31)	5.49 (17.04)	4.60 (20.28)
0.636	5.70 (10.0)	4.60 (11.07)	7.57 (21.95)	6.38 (16.15)	5.62 (19.02)
0.769	6.38 (10.0)	5.33 (10.99)	8.68 (20.55)	7.30 (15.49)	6.57 (17.77)
0.940	7.32 (10.0)	6.42 (11.14)	10.17 (19.35)	8.33 (14.33)	7.78 (16.51)
1.10	(d) 8.05 (10.0)	7.20 (11.07)	11.30 (18.70)	9.18 (13.89)	8.75 (15.98)
1.23	(d) 8.68 (10.0)	7.95 (11.17)	12.37 (18.49)	9.93 (13.64)	9.55 (15.57)
1.42	(d) 9.62 (10.0)	8.80 (10.84)	13.72 (17.84)	10.90 (13.12)	10.65 (14.96)
1.57	(d) 10.12 (10.0)	9.37 (10.88)	14.60 (17.82)	11.45 (12.95)	11.32 (14.84)
1.76	(d) 10.75 (10.0)	10.1 (10.94)	15.90 (18.07)	12.48 (13.25)	12.48 (15.15)
1.97	(d) 11.25 (10.0)	10.60 (10.88)	16.87 (18.16)	13.17 (13.29)	13.17 (15.07)

a) relative LIS ratios are in parenthesis with $-CO_2CH_3$ set at 10.0

b) $R = \left[Eu(fod)_3\right]\big/\left[solute\right]$

c) signals overlapped by other resonances

d) doublet

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN
Prof.Dr.H.Günther

5 KÖLN 41, Sept. 1, 1977
GREINSTRASSE 4
TELEFON: (0221) 470 1
  DURCHWAHL: 470 -4102

Prof.B.L.Shapiro
Texas A & M university
College of Science
College Station, Texas 77843
U S A

A New Technique for the Exact Determination of ^{13}C, ^{1}H Spin-Spin Coupling Constants

Dear Barry:

We have developed a new experimental technique for the exact deter-
mination of ^{13}C, ^{1}H coupling constants: all hydrogens of a compound
of interest with the exception of one single H atom are replaced by
deuterium and the ^{13}C n.m.r. spectrum is recorded with deuterium
broadband decoupling. We then observe each carbon resonance as the
X-part of an AX spin system and the magnitude of the coupling con-
stants is measured with high precision directly from the spectrum.(1).
The method is analogous to the well known isotopic substitution tech-
nique for the simplification of ^{1}H n.m.r. spectra but to our know-
ledge has never been applied to carbon n.m.r. As a by-product, in-
teresting information about H,D secondary isotope effects for carbon
chemical shifts are obtained.
Using this technique we have now measured the ^{13}C, ^{1}H coupling con-
stants for tropylium ion:
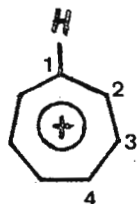
^{1}J = 166.79 Hz
^{2}J ≉ 0
^{3}J = 9.99 Hz
^{4}J = (-)0.64 Hz

A more detailed account is given in a forthcoming paper (2).

Sincerely yours,

(1) H. Günther, H. Seel and H. Schmickler, J. Magn. Res., in press
(2) H. Günther, H. Seel and M.-E. Günther, Org. Magn. Res., subm.

DR. V.F.BYSTROV

USSR Academy of Sciences

**Shemyakin Institute
of Bioorganic Chemistry**

Ul. Vavilova 32
Moscow 117312 USSR

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

September 1st, 1977

Title:Fluorine NMR of Neurotoxin II

Dear Barry,

We have incorporated fluorine labels into neurotoxin II (61 amino acid resues protein from *Naja naja oxiana* cobra venom) by selective trifluoroacetylation of the ε-amino groups of the five lysine residues and of the N-terminal α-amino group — in all six labels.

Totally hexa-N-trifluoroacetylated compound has been obtained by treatment of neurotoxin II with excess of S-ethylthiol trifluoroacetate in dimethylformamide. Its fluorine NMR spectrum (Figure, A) contains six separate singlets, evidence that each of fluorinated lysines is in a different micro-environment.

When the neurotoxin was treated with tritium labeled N-acetoxysuccinimide in aqueous solution under mild conditions one could isolate all five acetylated lysine derivatives which were then subjected to conventional tryptic degradation and the position of the radioactive label established by chromatographic separation of the tryptic digest and testing for radioactivity of the fragments. The particular derivative with one lysine residue thus selectively protected is then treated with trifluoroacetic acid thioester to obtain the penta-N-trifluoroacetylated derivative. Obviously its fluorine NMR spectrum contains only five signals, the missing signal being that of the protected lysine residue.

The fluorine spectra of thus selectively labeled compounds are shown in the Figure. The location of protected lysine residue is marked by dack circle and the position of the correspondingly missed fluorine signal is shown by vertical arrow.

An interesting feature of the two upper spectra (Figure, E and F) is the selective low field shifts of the lysine 46 and 26 signals. Obviously this must be the result of close spatial proximity between the side chains of these two residues.

All the N(ε)-lysine and N(α)-terminal trifluoroacetyl signals, exepting that of lysine 44 are pH-sensitive in the titration range of the acid groups and histidine residue. The calculated pK values (Table) correspond to the separate effects of the titration of the histidine residues(pK5.0 and 5.8[1]) and of each of the five carboxyl groups in the neurotoxin II molecule. On the latter

Figure : The ^{19}F NMR signal assignment in the 94.2 MHz spectra (Varian XL-100--15 FT) of trifluoroacetyl derivatives of neurotoxin II (0.1-0.5 mM solutions in D_2O, 0.3 M NaCl, pH* 3.5, 32°C). Totally labeled derivative (A) and with protected Lys-15(B), Lys-25( ), Lys-44(D), Lys-20(E), Lys-46(F). Chemical shifts measured relative to external CF_3COOH.
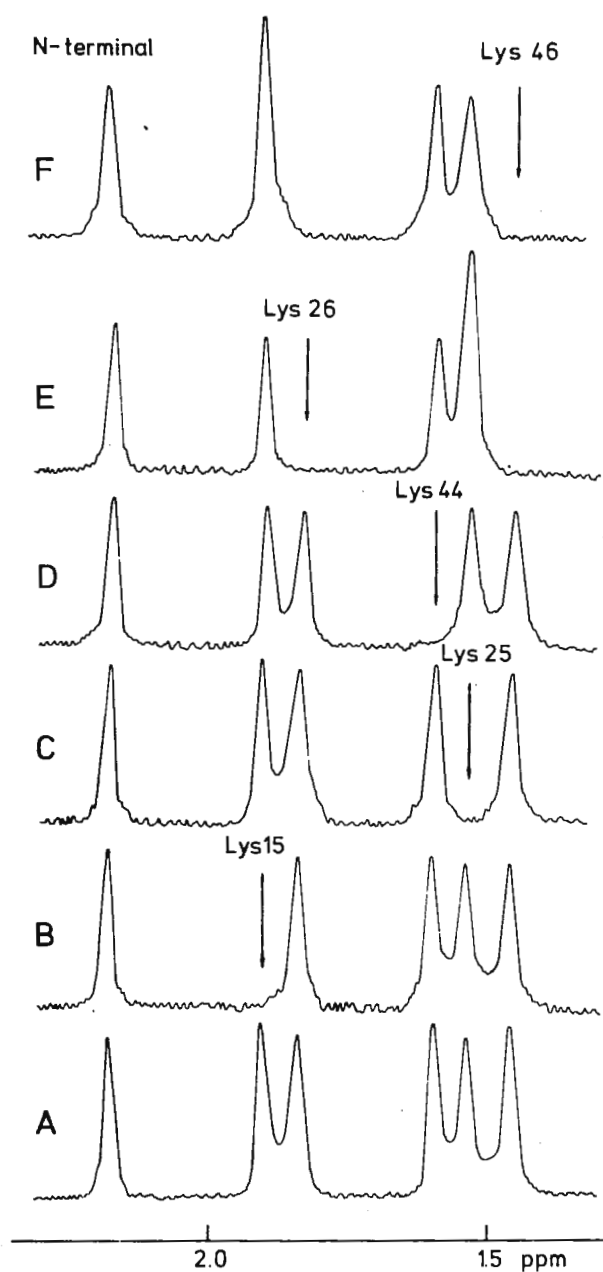
one displays abnormally low value pK 1.3 and could be assigned to the carboxyl group interacting with the tyrosine 24 phenolic hydroxyl [2]. This interaction presumably responsible for restricted rotation of the tyrosine side chain [1].

Sincerely yours,

Vladimir

Dr. Vladimir Bystrov

Table: ^{19}F NMR Chemical Shifts — pH Dependence of the Trifluoroacetylated
Neurotoxin II Derivative

Residue	"pK$_1$"	"pK$_2$"	$\Delta\delta_1$, ppm	$\Delta\delta_2$, ppm
Lys 25	5.0	1.3	-0.06	-0.28
Leu 1	5.0	3.0	-0.10	-0.16
Lys 26	5.8	3.7	-0.07	-0.10
Lys 15	4.5	3.2	0.04	-0.04
Lys 46	4.3	3.3	0.01	-0.03
Lys 44		No dependence		

REFERENCES :

1. A.S.Arseniev, T.A.Balashova, Yu.N.Utkin, V.I.Tsetlin, V.F.Bystrov, V.T.Ivanov and Yu.A.Ovchinnikov, Eur. J. Biochem. 71, 595 (1976)

2. T.Takamatsu, I.Harada, T.Shimanouchi, M.Ohta and K.Hayashi, FEBS Lett. 72, 291 (1976)

compared to the 1D case, some of them being with negative intensities. It has also been shown that it is possible to determine $|J_{AB} + 2D_{AB}|$ uniquely from the 2D-spectra of an 'oriented' AB-system - an information which cannot be derived from the corresponding single resonance spectrum.

The 2D-spin-echo spectra of 'weakly' coupled spin-systems and the cases without chemical shift such as A_2, AA'_2, AA'A", etc. are similar to their 1D spectra.

With regards,

Yours sincerely,

C.L.Khetrapal   A. Kumar

GRAMS : RAMANINST

BANGALORE NMR FACILITY

RAMAN RESEARCH INSTITUTE

HEBBAL P.O. BANGALORE 560006 INDIA

Prof. C.L. Khetrapal
Dr. A. Kumar

September 12, 1977

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

Dear Professor Shapiro,

      Title: WH-270 Spectrometer and National Workshop in
           Bangalore; 2D-NMR in 'Oriented' Systems.

     Some of the TAMU-NMR Newsletter readers might be
interested to know that a Bruker WH-270 high resolution NMR
spectrometer is currently being installed in Bangalore. It
will be an inter-institutional NMR facility, the major
participating institutions being Indian Institute of Science,
National Aeronautical Laboratory and Raman Research Institute
(all in Bangalore) and Tata Institute of Fundamental Research
(Bombay). The centre named as 'Bangalore NMR Facility' will
also be available to users from other institutions in India.

     A National Workshop on FT-NMR is being organized in
Bangalore during the week of October 10-14, 1977. The program
consists of lectures and practical demonstrations by Indian
and foreign scientists.

     On the scientific side of the contribution we report
two-dimensional (2D) NMR spectroscopic investigations of
'oriented' systems.

     The 2D-spin-echo spectra of 'oriented' 2- and 3-spin
systems have been examined with emphasis on the additional
information that can be derived from such spectra compared to
corresponding 1D cases. Since the proton NMR spectra of
'oriented' systems are more often strongly coupled, the case
of non-selective 180° pulse over all the coupled spins is
discussed. The 2D experiment considered consists of a non-
selective 180° pulse in the middle of the first and a non-
selective detection during the second period.

     It is seen that in the 2D-spin-echo spectra of the
'oriented' AB, AB_2, ABC ... systems, one gets additional lines

National Research Council   Conseil national de recherches
Canada   Canada

Division of Chemistry   Division de chimie

File Réfórence

September 7, 1977

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

Dear Barry,

Trifluoroacetate Complexes of WF_6 and MoF_6

As far as I know the fluorine resonance spectra of I and II with M = W or Mo are the first examples of magnetic resonance spectra of octaco-ordinate structures which are bicapped hexagonal pyramids, without motional averaging.
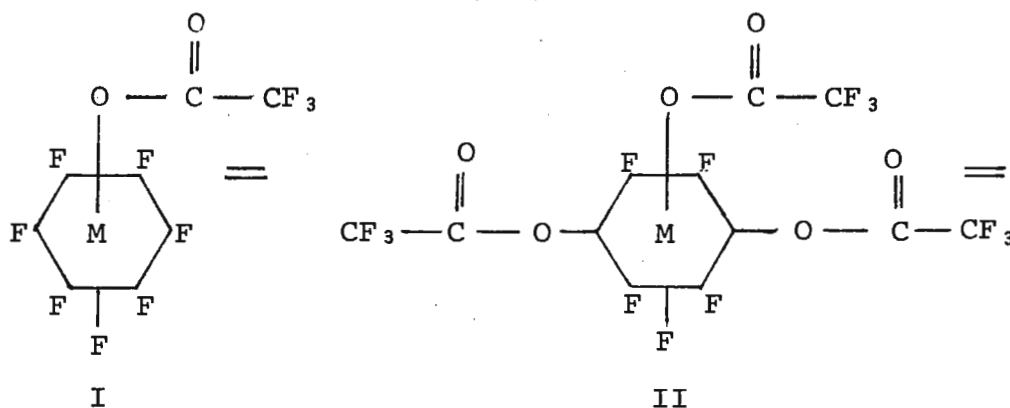
The fluorine resonance parameters are:

Structure I	W	Mo	Structure II	W	Mo
δF_6	65.6	142.8	δF_4	57.3	134.8
J_{M-F}	72	69	J_{M-F}	73	
δF_1	-145.0	-129.1	δF_1	-67.1	-60.3
J_{M-F}	48		J_{M-F}	60	
J_{F-F}	57.3	54	J_{F-F}	51	54

The fluorine resonance spectrum of I, along with some other species, where M = W is shown in the figure.

Yours sincerely,

S. Brownstein

SB/dh

Ottawa, Canada
K1A 0R9
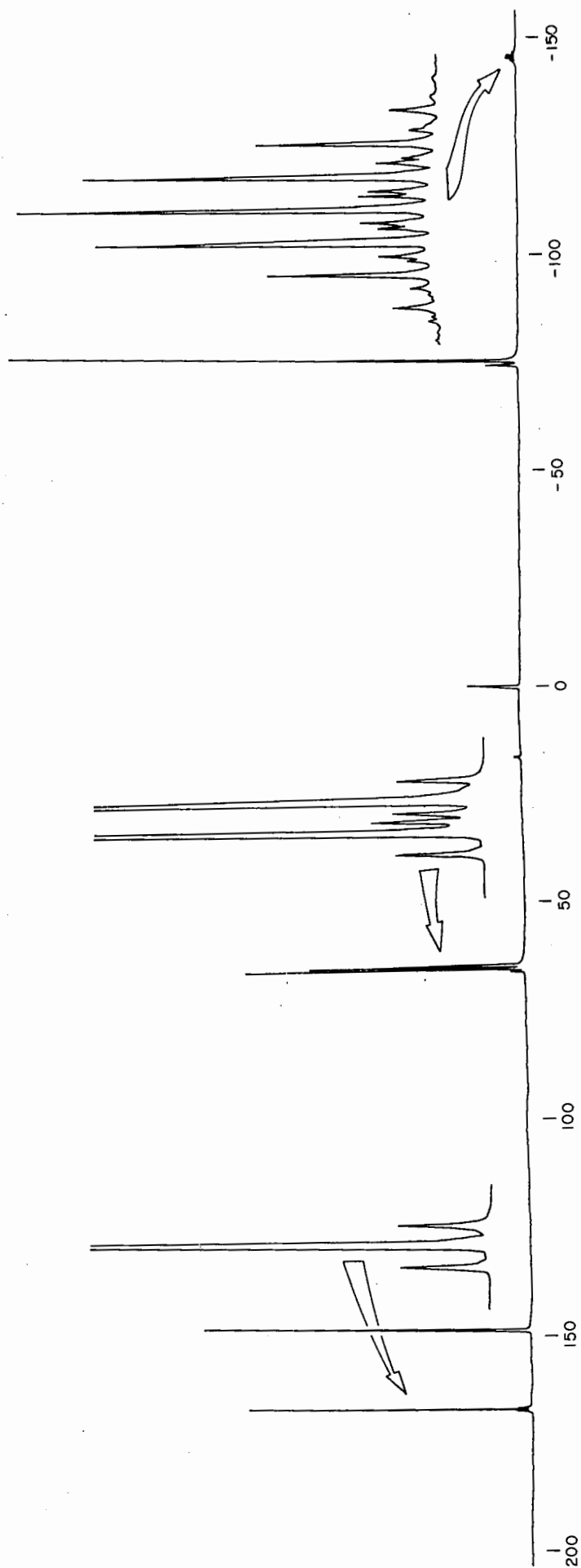
APPROACH THE SPEED AND SENSITIVITY OF PULSE FT-NMR ON YOUR CW SPECTROMETER USING A NICOLET NMR-80 DATA SYSTEM FOR RAPID SCAN CORRELATION NMR SPECTROSCOPY
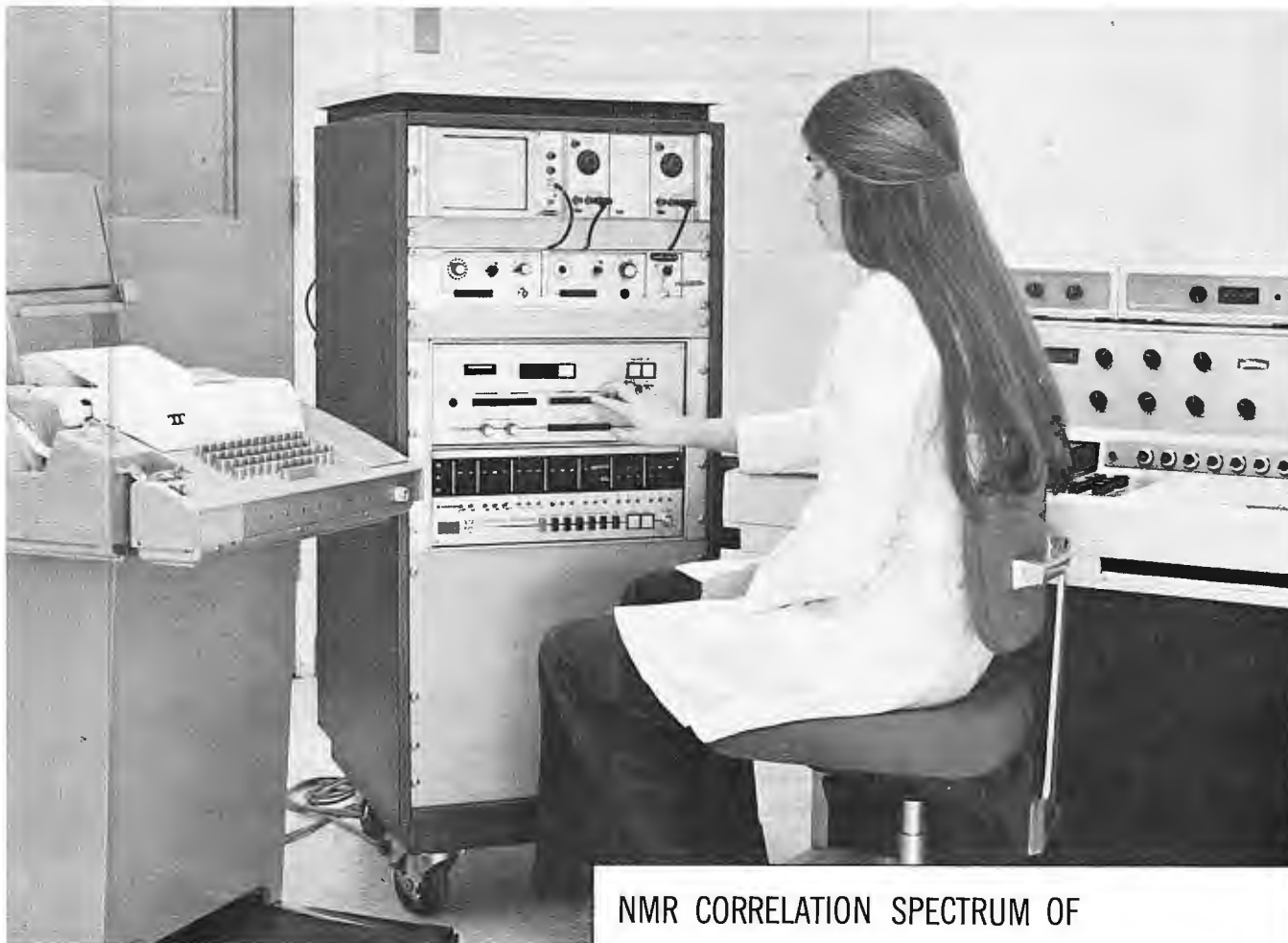
Rapid scan correlation NMR spectroscopy offers these advantages over CW techniques:

1) Greater sensitivity per unit time,
2) Greater sample throughput per unit time, and
3) The ability to follow fast reactions and produce meaningful data.

Rapid scan correlation NMR spectroscopy offers these advantages over pulsed techniques:

1) Power distribution over spectrum is exactly square and independent of sweep width.
2) Large solvent resonances can be avoided by sweeping only a small part of the total spectrum.
3) Resolution is increased because the final spectrum occupies all of data memory.

NMR CORRELATION SPECTRUM OF

50 μg ∝-ionone in spherical microcell
128 scans, 11 sec. per scan
TOTAL TIME 23 min.
Signal/Noise (Peak to Peak) of
methyl peaks = 36:1
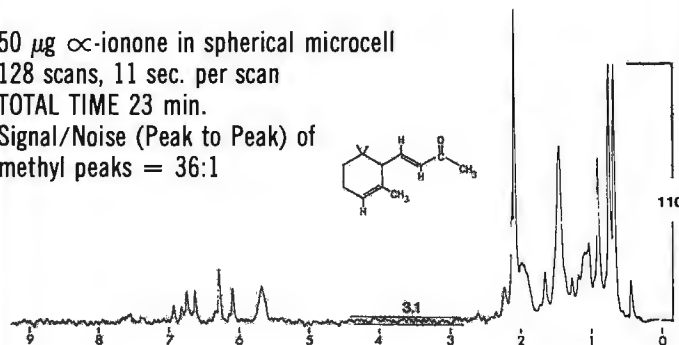
This spectrum of 50 micrograms of ∝-ionone was obtained by correlation NMR in 23 minutes. Normal CW averaging techniques would require over 4 hours.

For more information on the Nicolet NMR-80 data system for rapid scan correlation NMR spectroscopy please write or phone.

NICOLET INSTRUMENT CORPORATION

5225 Verona Road
Madison, Wisconsin 53711
Telephone: 608/271-3333

GRIFFITH UNIVERSITY

Nathan, Brisbane, Queensland, 4111. Telephone (07) 275 7111. Telegrams Unigriff Brisbane

School of Science   **Ref:** DMD.JT

7th September, 1977.

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

Dear Professor Shapiro,

Ligand-Centred ^{1}H and ^{13}C Electron-Nuclear Dipolar Relaxation in a Ni(II) Complex

Post-Doctoral Position Available

Thank you for your blue letter. I thought you might be interested in the following:

Spin-lattice (T_1) nuclear (spin I) relaxation in paramagnetic transition-metal complexes arises <u>via</u> electron-nuclear dipolar coupling. Treating the electron spin (spin S) as a point dipole located on the metal atom, Solomon in 1955 showed that T_1^{-1} is given by

$$T_1^{-1} = (2/15/\gamma_I^2 \gamma_S^2 \hbar^2 \ S(S + 1)R^{-6} \ \sum_j J_j(\omega) \tag{1}$$

where $\sum_j J_j(\omega)$ are spectral density terms. Although it is appreciated by some workers that the unpaired spin may be delocalized on to the attached ligands and whether ligand-centred or metal-centred, associated with atomic orbitals which have significant probability amplitude at distances of the same order of magnitude as the electron-nuclear separation, equation (1) has gone unchallenged since being published and forms the bases of my experimental investigation into the "geometry" of molecules in solution. In a recent MO theoretical treatment of this problem we showed that (1) needs to be modified to include the effects noted above and with certain approximations may be written

$$T_1^{-1} = (4\pi/75)\gamma_I^2 \gamma_S^2 \hbar^2 \ S(S + 1) \sum_{\nu=-2}^{+2} |\sum_i \rho_i \int F_2^\nu(\underline{r}') u_i(r_i)$$

$$\chi \ u_i^*(r_1) \ dr_1|^2 \ \sum_j J_j(\omega) \tag{2}$$

where ρ_i is the spin density associated with ith atomic orbital $u_i(r_1)$ centred at r_1 and $F_2^\nu(r')$ are the usually spatial components of the nuclear-centred (r') dipolar operator. Equation (2) can be written as the sum of three terms $T_1^{-1} = T_1^{-1}(M) + T_1^{-1}(L) + T_1^{-1}(LM)$, where $T_1^{-1}(M)$ is the metal-centred relaxation and approaches the result given by (1) for metal-nuclear separations (R) exceeding $\gtrsim 4$ Å. $T_1^{-1}(L)$ is the ligand-centred contribution and $T_1^{-1}(LM)$ arises from time correlation of ligand and metal-centred matrix elements, a consequence of the MO treatment of spin relaxation. In general $T_1^{-1}(LM) \ll T_1^{-1}(L)$ and may be neglected. In this note, we provide experimental evidence demonstrating the importance of ligand-centred effects in controlling both ^{13}C and ^1H relaxation in the Ni(II) complex bis(2-N-phenyl-4-N-phenylimino-2-pentene) Nickel(II) (1), thereby underlying the need to take such effects into account when using relaxation times as a probe into the molecular geometry in solution.
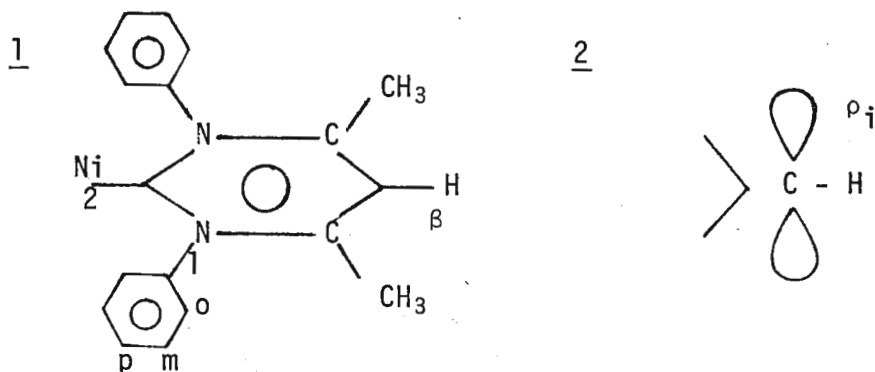
Although there are some problems in applying equation (2), most can be eliminated by considering nuclear relaxation in the molecular fragment (2).

The ^{13}C and ^1H $T_1(L)$ relaxation times are now dominated by the spin density ρ_i and for R < 4 Å $T_1^{-1}(M)$ is given by the Solomon-Bloembergen result $T_1^{-1}(L)$ may be written

$$T_1^{-1}(L) = (2/15) S(S + 1)h^2\gamma_I^2\gamma_S^2\pi_i^2\Delta \sum_j J_j(\omega) \qquad (3)$$

where $\Delta = 0.2762$ for the proton and 10.009 for the carbon, respectively. We can estimate ρ_i from the measured proton isotropic shifts (σ^H) assumed to be solely contact in origin.

In the table we list values of T_1^H, T_1^C, σ^H, and σ^C determined for 1. For complex 1, only the β- and p-positions can be readily analysed as the unknown conformation of the phenyl ring makes estimation of the metal-nuclear separations for the o- and m-positions difficult. For the β- and p-positions, SB theory predicts T_1^H/T_1^C ratios of 0.34 and 0.18, respectively, whereas the experimental values are 2.4 and 1.8, respectively. Using equation (3) we calculate 3.1 and 2.2, in far better agreement with the experimental results. Previously we showed that the SB ratio may be simply written as 0.063 R_{MH}^6/R_{MC}^6. Although in general, $R_{MH} > R_{MC}$, the difference is usually sufficiently small for T_1^H/T_1^C < 0.05. Clearly then, as well, the SB equation does not explain adequately the T_1 values of the m-C and m-H where we find experimentally a ratio of 3•1. A priori, it might be assumed, that the variation between the SB result and the experimental would arise mainly from ligand-centred relaxation of the carbon due to spin density residing in the associated p-orbital and thus

in close proximity to the carbon nucleus. Although this is partly true,
considering simply a ratio of T_1's in fact masks the importance of
ligand centred effects. For example, equation (3) predicts a ^{13}C T_1 for
the β-position, 42.4 times shorter than SB theory and a ^1H T_1 4.5 times
shorter. The corresponding factors are 27.1 and 2.1 for the p-position.
Hence, there is a significant ligand contribution to the proton relax-
ation.

TABLE

Measured σ^C, σ^H, T_1^H, and T_1^C values in the Complex 1.

Compound 1 (at 250K)

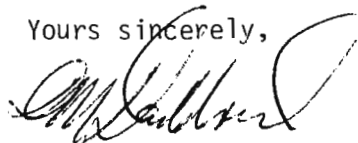| Position	α-CH₃	α	β	Cl	o	m	p
$\sigma^{C\,a}$	-797.6	+824.6	-626.2	-267.2	-576.0	+122.8	-211.5
$\sigma^{H\,a}$	-31.2	-	+135.0	-	+17.2[b]	+58.0[b]	+23.7[b]
$T_1^{H\,c}$	11.1	-	10.1	-	3.2	79.0	29.4
$T_1^{C\,c}$	2.1	5.7	4.3	37.6	5.8	25.7	16.8

[a] Isotropic shift in ppm. - = downfield, + = upfield.

[b] Shift in approximate because of difficulties of estimating the shift in
the free ligand. Here, $\sigma^i = \sigma^i_{complex} - \sigma^i_{ligand}$ (i = C or H).

[c] Spin lattice relaxation in ms measured using 180-τ-90 pulse sequence.

Lastly, I have a post-doctoral position available for one year
(renewable) beginning mid-March 1978. This arises because I become
Chairman of our School of Science at that time. I would be interested
in appointing someone with a strong background in either (or both)
experimental and theoretical (relaxation theory) magnetic resonance.
Our interests are in electron and nuclear relaxation studies of para-
magnetic molecules in solution (cf. Aust. J. Chem., 1976, 29, 1869;
Chem. Phys. Letts., 1976, 39, 65; 1976, 42, 607). We have available a
HX-90 with the Bruker multi-nuclear attachment for the experimental aspects
of the work. There is likely to be some demonstrating to our first year
students associated with the post. It is unlikely unfortunately, if any
contribution can be made to travel costs - the salary for the post is
A$12,593-$14,074 [approx. US$13,800-$15,500]. Interested people should
write to me by 14.11.77 including a full CV, c/- Prof. M. Barfield,
Department of Chemistry, University of Arizona, Tucson, Arizona, 85721
where I will be spending 3 months from 1st November 1977 to 2nd February,
1978.

Yours sincerely,

D.M. Doddrell

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
September 8, 1977

NATIONAL INSTITUTE OF
ENVIRONMENTAL HEALTH SCIENCES
P.O. BOX 12233
RESEARCH TRIANGLE PARK, N.C. 27709

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

Dear Barry:

Title: Chlorinated Polycyclodiene Pesticides and a Request

As a part of the Institute's continuing interest in pesticides, we have
obtained the ^{13}C spectra of thirty compounds related to aldrin, dieldrin,
isodrin and endrin. Included are several dechloro derivatives, photo-
products, and rearrangement products. Chemical shifts were assigned
using a variety of techniques including sford spectra and shift reagents.
In general, the chemical shifts of the pesticides closely follow the
trends expected based on the chemical shifts of the norbornane ring
system. For example, comparison of dihydroaldrin with dieldrin allows
one to establish substituent parameters for a 2,3-epoxy substituent in
the norbornane ring system as +2.5, +20.6, -2.5 and -13.6 ppm for carbons
1, 2, 5 and 7, respectively. These values compare favorably with those
established using 2,3-epoxynorbornane.[1]

Chemical shifts for the dechloro derivatives, in comparison with the
perchloroderivatives, follow the trends previously established for
perchlorohydrocarbons.[2] However, the chemical shifts do show a depen-
dence upon the stereochemistry of the chlorine removed. A preprint of
this work will be available shortly and I would be happy to send a copy
to anyone interested.

Finally, I am interested in obtaining a copy of LAOCN3 that has been
modified for liquid crystal work and would appreciate any help the
readers might offer.

Please credit this to Dr. McKinney's account.

Sincerely,

Dick

Richard H. Cox, Ph.D.
Visiting Scientist

1. A.K. Cheng and J.B. Stothers, Org. Magn. Reson., 9, 355 (1977).

2. G.E. Hawkes, R.A. Smith and J.D. Roberts, J. Org. Chem., 39, 1276
(1974).

UNIVERSITY OF DELAWARE
NEWARK, DELAWARE
19711

DEPARTMENT OF CHEMISTRY

September 9, 1977

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

^{13}C T_1's in Polyisoprene

Dear Professor Shapiro:

We have been interested in studying anisotropic motion in ordered fluids for some time. Elastomers present a good example of such systems and a body of literature has grown up around explaining the unusual characteristics of transport parameters such as T_1. Most notably perhaps is the complicated frequency dependence of T_1, which may be the result of anisotropic reorientation. It has been known for some time that high resolution ^{13}C NMR of elastomers can be obtained with a high resolution instrument such as our Bruker HFX-90 (1). Hence we set out to measure ^{13}C T_1's in bulk cis-polyisoprene under a variety of conditions. Our results are given below for ambient temperature (~300°K):

Carbon	T_1 (msec)
α	450 ± 50
β	~80 ± 25
δ	~80 ± 25
γ	~50 ± 25
ϵ	200 ± 50
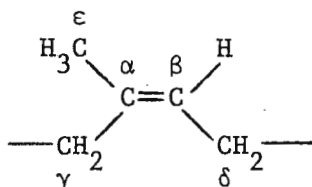
To our knowledge, the only other measurement of these ^{13}C T_1's was carried out by Schaefer a number of years ago (2). Our results are in qualitative agreement with those measurements. We observe no change of T_1 when the polymer is mechanically deformed, indicating that the reorientational modes leading to spin-lattice relaxation are unaffected by changes in chain alignment.

Please credit this contribution to Joe Noggle's account.

Yours truly,

Cecil R. Dybowski

CRD:sr

(1) M. Duch and D. Grant, Macromolecules, 3, 165 (1970).
(2) J. Schaefer, Macromolecules, 5, 427 (1972).

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C. S. YANNONI

September 29, 1977

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

<u>19th ENC   Blacksburg, Virginia   April 16-20, 1978</u>

Dear Barry;

The next annual meeting of the Experimental Nmr Conference will be held at the Donaldson Brown Center for Continuing Education on the campus of Virginia Polytechnic Institute in Blacksburg Virginia. Registration will begin late Sunday afternoon April 16th, and the program will run from Monday morning to Thursday noon. Sessions are being planned on Two-Dimensional FT, Zeugmatography, High-Resulution in the Solid State, Techniques in Biochemical Studies, Supercon Systems Developments, Less Common Nuclei, New Experimental Techniques, and perhaps a few others.

Most of the talks will be given by invited speakers, however some time is being made available for short contributed talks, as well. There will be at least two time periods set aside for poster session presentations. Anyone interested in giving a talk should contact me before Dec. 15th. Anyone interested in giving a poster presentation should contact the poster session chairman, Dr. W.W. Conover at the Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, CA 94304 before Feb. 15th.

Anyone interested in more information on the 19th ENC and who did not attend last year's ENC, should have their name put on the mailing list by contacting Dr. K.L. Williamson at the address shown on this letterhead

See you in Blacksburg.

Best Regards,

Roy

LeRoy F. Johnson
Chairman, 19th ENC

LFJ:bie

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DEPARTMENT OF CHEMISTRY
(213) 746-2780

September 8, 1977

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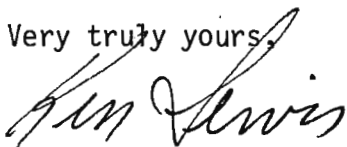College Station, Texas   77843

Dear Barry:

I would appreciate your including this letter in the next issue of TAMU
NMR Newsletter.

We are seeking an individual to fill the position of Director of Chemical
Instrumentation in our Department. Responsibilities include the supervision
of maintenance, training of users, and design and development of instrumentation
in the Department of Chemistry. While the position will not be solely dedicated
to NMR instrumentation, work with NMR spectrometers will certainly constitute
a significant portion of the responsibilities. Applicants should have suitable
experience in the maintenance of advanced electronic instrumentation and an
interest in instrument design and development. Salary will be commensurate
with experience.

Interested individuals may contact me directly (213-741-6013) for
further information or send a resume directly.

Thank you for your assistance.

Very truly yours,

Kenneth L. Servis
Associate Professor of
    Chemistry

KLS:djo

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September 12, 1977

Professor B. L. Shapiro   Title: Dispersal of ^{31}P
Department of Chemistry   Resonances with a
Texas A & M University   Derivatizing Reagent
College Station, TX 77843

Dear Barry

We were confronted recently with the problem of characterizing a
mixture of fatty acid phosphate esters. The ^{31}P spectrum of a
chloroform solution of the mixture, measured on our modified
multinuclear Bruker HFX-90 (see TAMUN, 199, p.4 (1975)) is shown
in Figure 1. The three resonances were identified by the addition
of pure compounds. Unfortunately, they are only 40 Hz apart, thus
making accurate peak integration difficult if not impossible.

The reagent bis(trimethylsilyl)trifluoroacetamide, BSTFA, commonly
used in gas chromatography as a derivatizing agent, proved to be
the solution to our problem. Addition of sufficient BSTFA to
silylate all the hydroxyl groups produced a dramatic dispersal of
the ^{31}P resonances, as is illustrated in Figure 2. Phosphoric
acid was shifted upfield by ~27 ppm, the monoester by ~18 ppm,
and the diester by ~9 ppm. It appears that the additivity rule
is -9 ppm per silylated hydroxyl group. The dispersed resonances
were integrated easily, and we were able to extract the desired
information. Perhaps this technique might prove useful to news-
letter readers for structural elucidation in other systems.

Please credit this letter to the account of C. K. Tseng.

Sincerely yours

STAUFFER CHEMICAL COMPANY

David H. Marr   William D. Vernon

DHM/WDV:sad

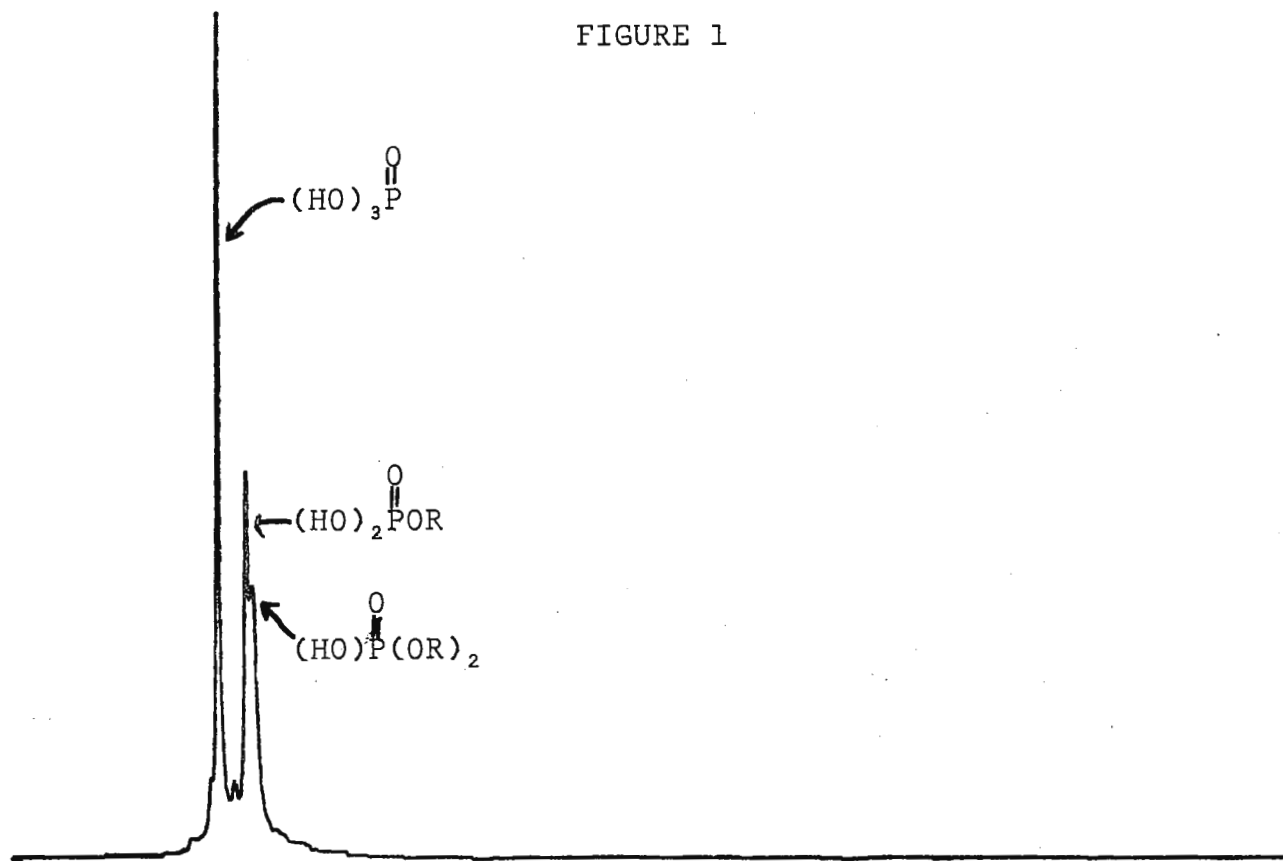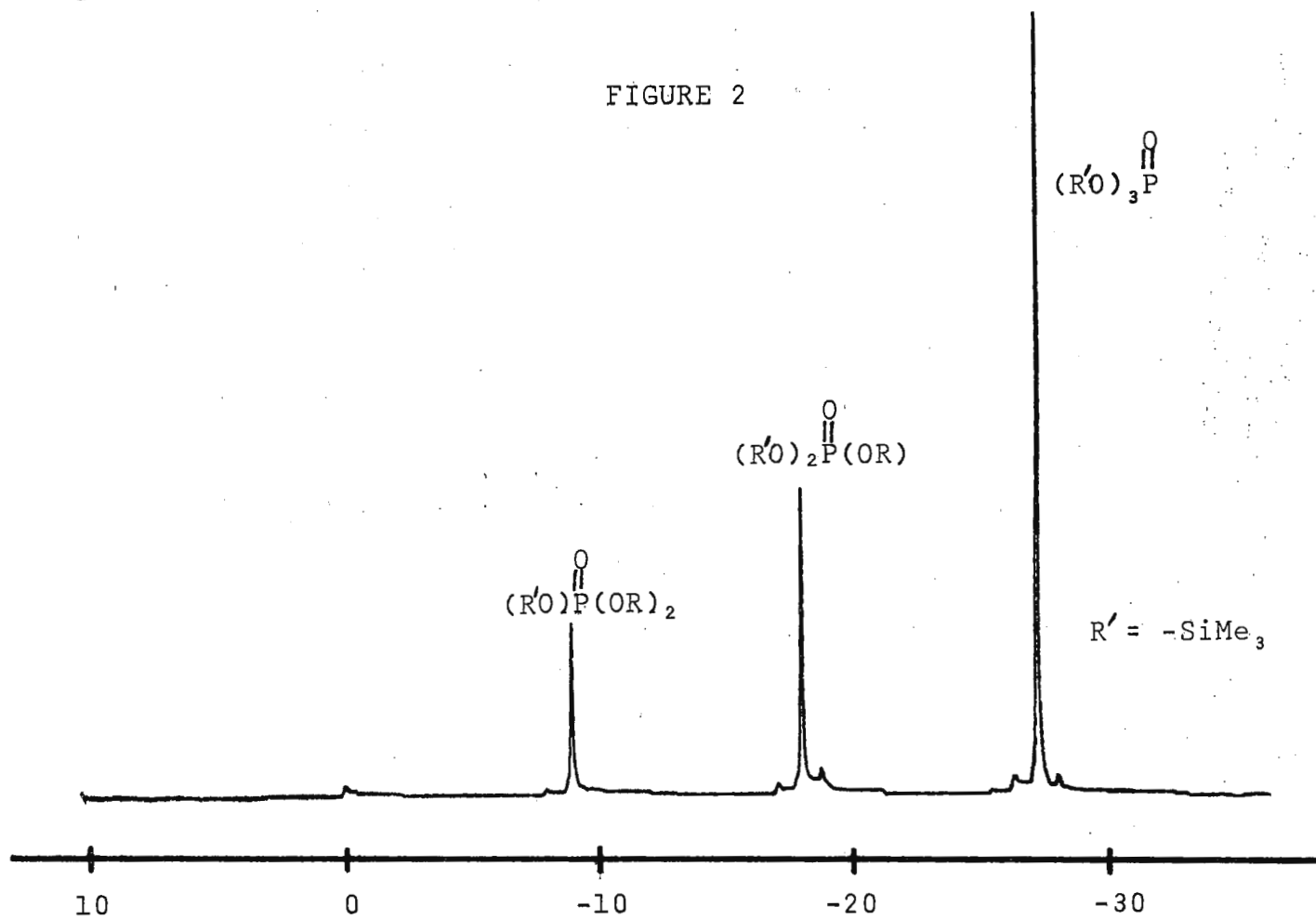FIGURE 1   229-26

FIGURE 1

FIGURE 2

DEPARTMENT OF THE NAVY
NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555

IN REPLY REFER TO:

3852/DWM:lkj
13 September 1977

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

Title: ^{15}N Shielding in Benzylamines, Benzylimines and 3-Phenyloxaziridines

Dear Barry:

This contribution, a sequel to last November's, is also the work of our prolific postdoctoral associate, Guy Jordan, now at Lederle Labs in Pearl River, New York. Earlier he had undertaken a series of ^{13}C shift measurements on alkyl benzenes to study the effects of varying para-substituents on the α-, β-, and γ-carbons of the alkyl group. Having shown that the β-carbon shift was the one which reflected the Hammett σ-value of the p-substituent, he then set out to see what would happen to ^{15}N shifts at that position in appropriate nitrogen analogs.

He synthesized a series of N-methyl benzylimines first, and observed the ^{15}N shift as a function of Hammett-σ shown in Figure 1. The effect is comparable to the positive β-shift seen in p-substituted styrenes. (The shifts are reported in ppm upfield from internal nitromethane.) The slope of 20.1 ppm is over three times the value observed for the corresponding ^{13}C shift dependence in the styrenes.

Next he ran ^{15}N shift measurements on all of the p-substituted N,N-dimethyl-benzylamines that he could find. This time the shift showed the same negative dependence on the substituent σ-value that had been seen in the ^{13}C shifts of the β-carbons in alkylbenzenes, although the slope of -1.1 ppm is only half again as large. The negative slope is again seen as evidence of an alternant inductive effect in the saturated side chain, where the positive slope found for the imines (and analogous styrenes) arises from a direct resonance interaction with the aromatic π-system.

With time nearly running out, he whipped up a series of five cis- and trans-methyl-3-phenyloxazinidines for comparison ^{15}N measurements. Figure 3 shows the Hammett-σ correlation for the trans-derivatives. The positive slope of 4.6 ppm, intermediate between the values found for amine and imine, suggests a 27% resonance interaction between the oxaziridine ring system and the aromatic ring. A comparable dependence was found for the cis-compounds, except for a large unaccountable deviation in the p-methoxy derivative. (Fig. 4)
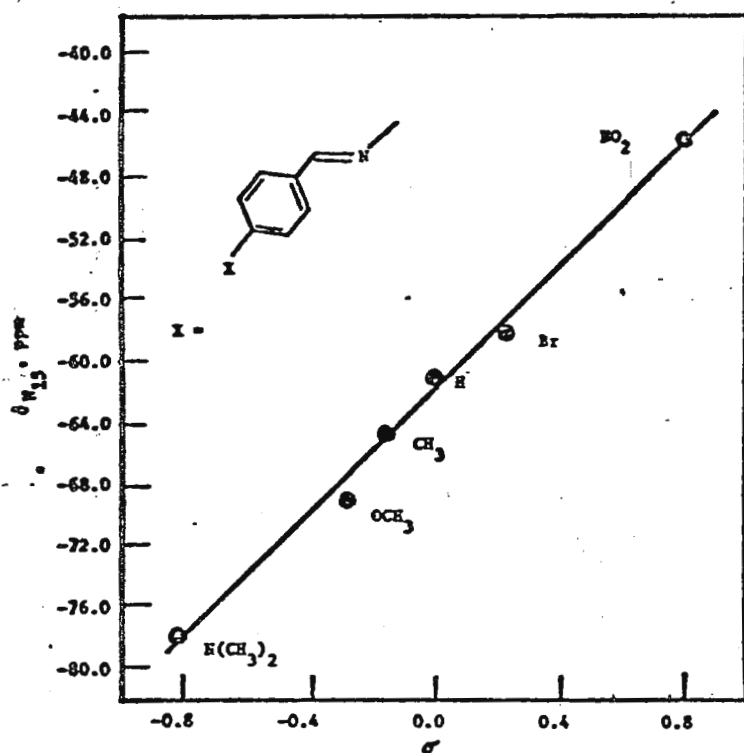
Best regards,

D. W. MOORE

Figure 1. Substituent effect on the nitrogen chemical shift of para-substituted N-methylbenzylimines.
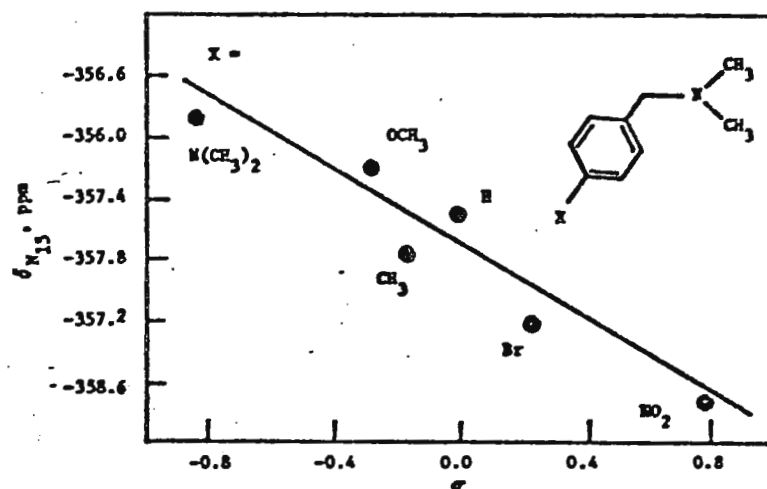

Figure 2. Substituent effect on the nitrogen chemical shift of para-substituted N,N-dimethylbenzylamines.
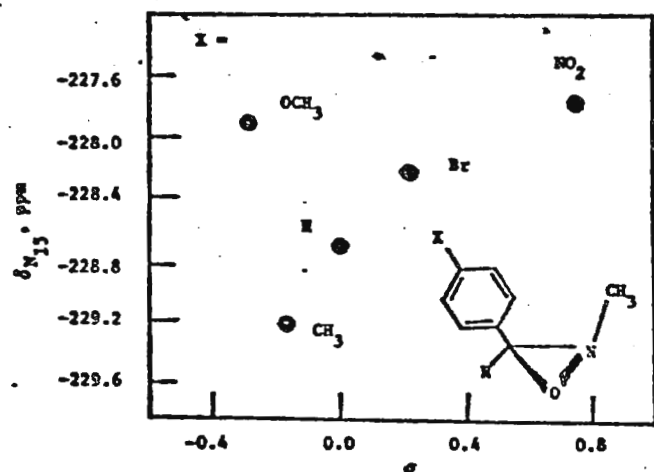

Figure 4. Substituent effect on the nitrogen chemical shift of para-substituted cis-2-methyl-3-phenyloxaziridines.
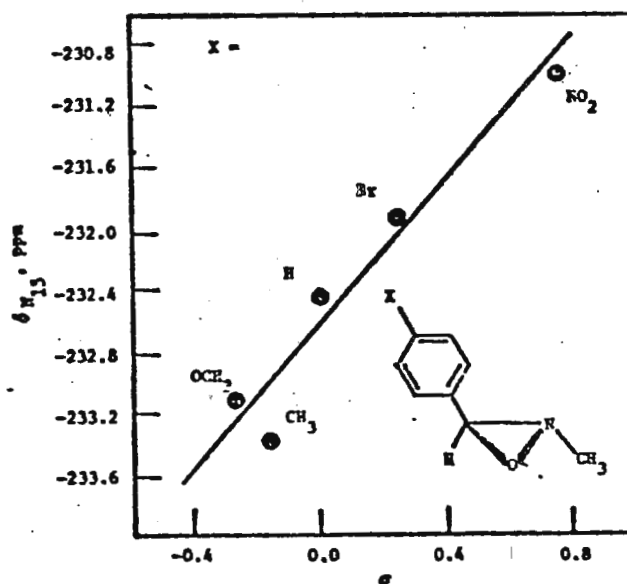

Figure 3. Substituent effect on the nitrogen chemical shift of para-substituted trans-2-methyl-3-phenyloxaziridines.

MAX-PLANCK-INSTITUT FÜR KOHLENFORSCHUNG · MÜLHEIM A. D. RUHR

Prof. Dr. E. G. Hoffmann

4330 MÜLHEIM A. D. RUHR 1. POSTFACH 0113 25

September 15, 1977

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

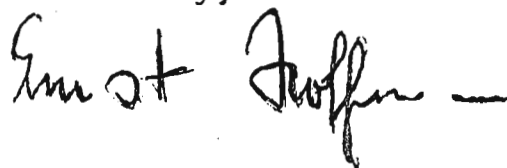Title: Fluxional Behaviour of
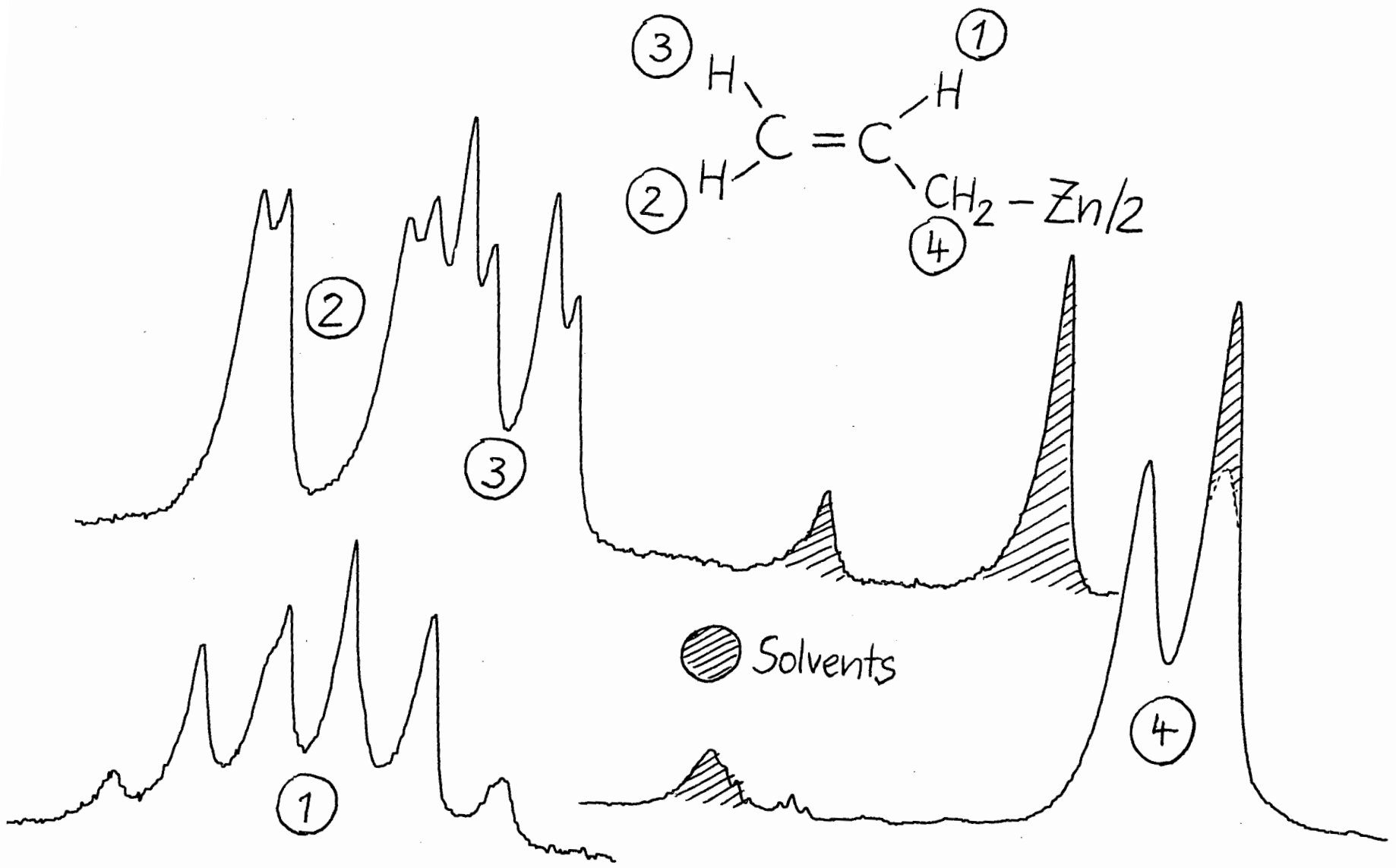   Bis(allyl)Zinc

Dear Professor Shapiro,

I hope that I am not too late with a contribution. Recently, we replaced our Varian A60 spectrometer which had done 14 years of good routine service. As new instrument we choose a Bruker's WP80 FT spectrometer equipped with ^{1}H and ^{13}C-capabilities. Stability, resolution and ease of handling are excellent. We are fortunate in the use of Bruker's variable temperature controle which is much more reliable than the Varian systems we have experienced. We calibrated the temperature controle of the 5 mm probe with a Fluke digital thermometer 2100A, the copper constantan thermocouple junction being inserted just at the height of the detection coil into a 5 mm spinning sample tube filled with diethylether. Between 303 and 148 K the reproducibility of the chosen temperature is better than 0.7°C (RMS) - including values determined with a methanol sample, see below (cooling or heating) also after the probe head had been removed and replaced several times (correlation coefficient 0.9998 with 46 values). Between -10°C and -90°C we found this calibration with thermocouple to agree fairly well with temperature measurements via methanol chemical shifts differences using van Geet's [1] empirical relation. As an example see the first reproduction of the spectrum of fluxional bis(allyl)zinc (prepared by Dr. Nehl, here) in etheral solution at -122°C the AX_4 system at room temperature having completely changed to an $AMNX_2$ one. $T_c \simeq -75^\circ$C.

With our revised version [2] of Binsch's DNMR3 we get with $\delta_1 = 6.08$; $\delta_2 = 4.33$; $\delta_3 = 4.08$; $\delta_4 = 1.12$; $J_{2,3} = 2.90$; $J_{1,3} = 9.80$; $J_{1,2} = 16.65$; $J_{1,4} = 8.95$; $J_{2,4} = -1$; $J_{3,4} = -0.4$ (ppm and Hz) $E_a = 7.3$ kcal/mole (preliminary values only).

1) A. L. van Geet, Anal. Chem. 42, 679(1970)
2) Tamun Newsletters 208, 22(1976)

Sincerely,

Ernst Hoffmann

$$\overset{\text{\textcircled{3}}}{H} \overset{}{\underset{\overset{\text{\textcircled{2}}}{H}}{C}} = \overset{}{\underset{\overset{}{CH_2 - Zn/2}}{C}} \overset{\text{\textcircled{1}}}{H}$$
$$\text{\textcircled{4}}$$

⬤ Solvents

INDIANA UNIVERSITY

Department of Chemistry

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TEL. NO. 812--- 337 5513

Dr. B. L. Shapiro   September 19, 1977
Department of Chemistry
Texas A & M University
College Station, Texas   77843

Good Old Cholesteryl Chloride. Quote or Misquote?

Dear Barry:

In TAMUNN No. 227 (August, 1977) Dr. W. B. Smith of
Texas Christian University stated:

> "Recently, we have measured the T_1s and solution
> viscosities for cholesteryl acetate in chloroform
> at various concentrations. According to simple theory
> the reciprocal of T_1 and η should be linear and so
> it is. This result contrasts with that of Allerhand,
> Doddrell and Komorski (sic), J. Chem. Phys., 55, 189
> (1971) who report a nonlinear plot of $1/T_1$ vs η for
> the carbons of cholesteryl chloride. A reinvestigation
> of the cholesteryl chloride system showed it to be
> linear also. No attempt to account for the earlier
> report will be given."

I have always been quite inactive in the area of studies
of the relationship between T_1 and viscosity, and I do not
recall making the measurements attributed to me. Not trusting
my memory, I reread my old paper in JCP on ^{13}C relaxation
behavior of large molecules. I did not find any mention of
a "plot of $1/T_1$ vs η for the carbons of cholesteryl chloride."
Viscosities were mentioned only in the following brief
paragraph (on page 8 of a 9-page paper):

> "It is traditional in the field of nuclear magnetic
> relaxation to make attempts at establishing linear
> correlations between measured $1/T_1$ values and macro-
> scopic viscosities. We have measured the viscosities
> of some of the solutions used in this work, at 27° C.
> The viscosities of 1 M cholesteryl chloride in CCl_4
> and 0.5 M sucrose in water are about 5 and 1.7 times

the viscosity of water. Thus, these solutions
have viscosities that are considered quite low in
nuclear magnetic relaxation studies. Yet most
protonated carbons in these solutions have ^{13}C
relaxation times of less than 1 sec, and even the
nonprotonated carbons have T_1 values of less than
10 sec. Moreover, there is no linear correlation
between viscosity and relaxation rates."

The last sentence of the above paragraph is ambiguous.
It refers to viscosities of various solutes (of <u>similar size</u>)
in various solvents. Only <u>one</u> measurement at <u>one</u> concentration
and <u>one</u> temperature was made on cholesteryl chloride. The
purpose of the whole paragraph (for 1971) was to point out
that ^{13}C T_1 values of most organic molecules are not prohib-
itively long, but, instead, are quite short. This is a well
known fact in 1977, but it was not generally known in 1971.
I have reason to believe that my paper in JCP, <u>55</u>, 189 (1971)
had some positive influence on the use of ^{13}C NMR and relax-
ation for studying medium-size and large molecules in solution.
I am sorry if one sentence in that paper may have resulted
in unnecessary control experiments in Dr. Smith's laboratory.
However, I would rather be accused of ambiguous phrasing
than of producing erroneous experimental results. (In short:
Not guilty as charged!)

Best regards,

Adam Allerhand
Professor of Chemistry

IBM

RESEARCH LABORATORY

International Business Machines Corporation

5600 Cottle Road
San Jose, California 95193

September 12, 1977

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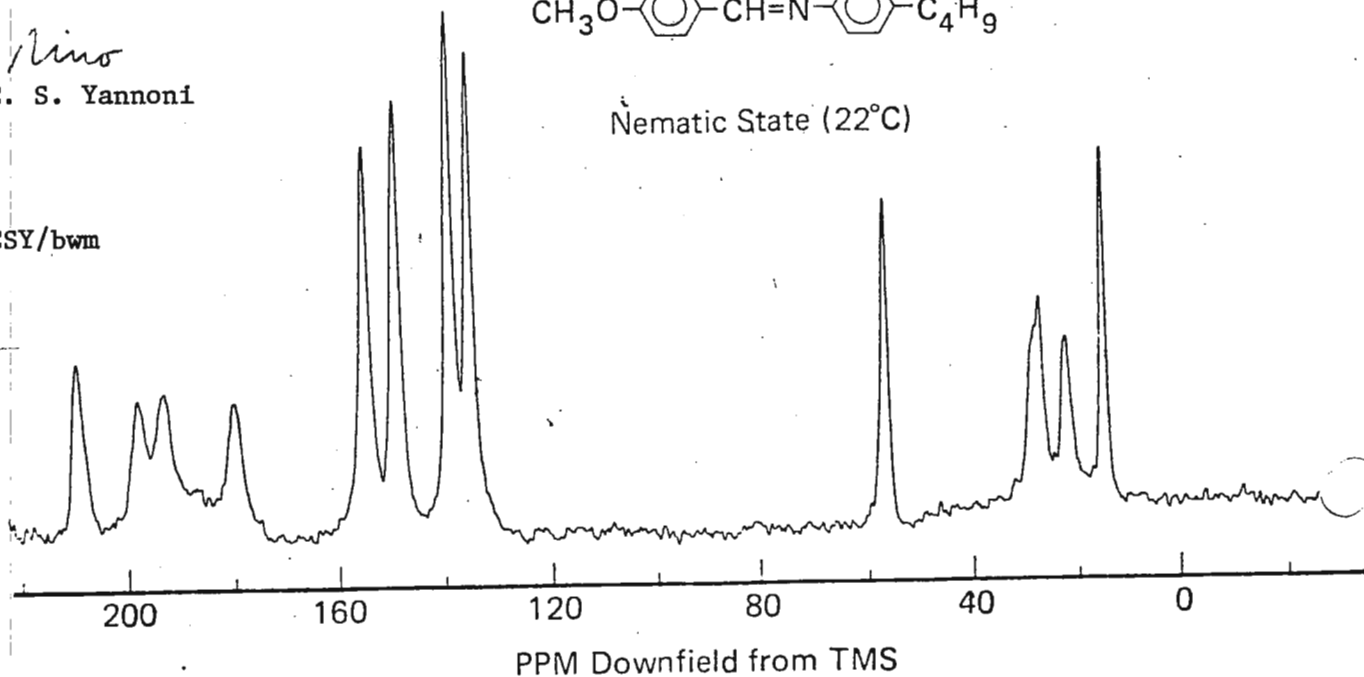College Station, Texas 77843

Egged on by a visiting iconoclast, Colin Fyfe, from Guelph, Jim Lyerla and
I reluctantly agreed some months ago to "sacrifice" Jim's CFT-20 probe to
try to get some high resolution ^{13}C spectra of non-rigid solids. We fed
the output of the decoupler into the probe via an ENI-320L. The probe
held up fine and the results were interesting -- the CFT-20 produces very
nice ^{13}C spectra for liquid crystals, both nematic and smectic, as well as
plastic crystals. We used 35 watts decoupling power, and it was a routine
matter to obtain spectra like the one of MBBA accompanying this note. We
plan to draw people's attention to this and other results in J. Mag. Res.
The use of a "liquid state" spectrometer for solids is very likely wide-
spread; we note that Jim Emsley has reported that he got proton spectra of
liquid crystals in the May issue of the newsletter using deuterium decoupling
with only minor damage to his probe.

Sincerely yours

C. S. Yannoni

CSY/bwm

$CH_3O-\bigcirc-CH=N-\bigcirc-C_4H_9$

Nematic State (22°C)

PPM Downfield from TMS
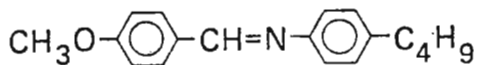
UNIVERSITY OF OULU   September 20, 1977

DEPARTMENT OF PHYSICS

LINNANMAA

SF — 90100 OULU 10

FINLAND

Professor B.L. Shapiro

Department of Chemistry

Texas A&M University

College Station, TX 77843

U.S.A.

Dear Professor Shapiro,

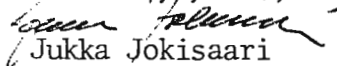### $^1\underline{J}$(Cd-C) is less anisotropic than $^1\underline{J}$(Hg-C)

Pyykkö´s relativistic theory of nuclear spin-spin coupling[1] predicts for Hg(Me)$_2$ that relativistic effects increase the relative anisotropy $\Delta K´ = (K_{\parallel} - K_{\perp})/K$ of the coupling tensor for heavy elements like Hg from the value given by Ramsey´s non-relativistic theory.
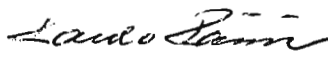
Searching for experimental support for this claim we have determined the coupling tensor $^1\underline{K}$(Cd-C) for Cd(Me)$_2$ using our JNM-FX-100 FT NMR spectrometer and a nematic Merck Phase IV solvent[2]. The experimental and calculated results for $\Delta K´$(M-C) in M(Me)$_2$,

M	Non-rel.	Rel.	Exp.	
Cd	0.285	0.30	0.36	This work
Hg	0.288	0.35	0.474 (35)	Schumann et al.[3]

show closely similar non-relativistic values for Cd and Hg. The experimental results agree with the relativistic prediction of larger $\Delta K´$ for Hg than Cd.

Sincerely yours,

Jukka Jokisaari   Kauko Räisänen   Pekka Pyykkö[§]

1. P. Pyykkö, Chem. Phys. 22 (1977) 289

2. J. Jokisaari, K. Räisänen, L. Lajunen, A. Passoja and P. Pyykkö (to be published)

3. C. Schumann, H. Dreeskamp and K. Hildenbrand, J. Magn. Res. 18 (1975) 97

[§] Department of Physical Chemistry, Åbo Akademi, 20500 Åbo (Turku), Finland

IWAN N. STRANSKI-INSTITUT
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der Technischen Universität Berlin

Berlin, den September 28, 1977
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- Prof. Dr. D. Ziessow -

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

Partial Analysis of the 270 MHz H-NMR-Spectrum of LH-RH in D_2O

Dear Dr.Shapiro,
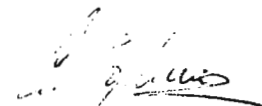
in the course of a 270 MHz H-NMR investigation of the decapeptide
LH-RH (or LRF) we have paid particular attention to the prolyl and
seryl residues. It has been derived from C-13 NMR results (1-4) that
Pro in LRF is in the trans conformation -HCα-N-CO-X, a conclusion
that up to date has not been confirmed by H NMR. Also, in aqueous
solution of LRF, the Hα Seryl peaks have yet not been detected.

We have observed the Pro and Hα-Ser peaks in LRF in neutral D_2O
solution at 270 MHz. The chemical shifts are listed in the table,
together with recently determined data for the model peptides
cis- and trans-acetylprolineamide (c,t - AcProA) (Ref.5) and
Acetyl-Ser (AcSer) (6).

We note that the resonances in Pro/LRF and in t-AcProA are shifted
highfield for Hα and Hβ1, and downfield for Hδ and Hβ2γ1γ2, relative
to the respective resonances of c-AcProA. This back-to-back pattern
has been proposed to serve as a probe for the cis/trans conformation
of the X-Pro bond (5), and based on this we conclude that X and
Cα in X-CO-N-Cα(Pro) in LRF are trans to each other. AcSer exists
completely in the trans conformation (6). From the comparison of
the chemical shifts we thus propose that X and Cα(Ser) are also
trans to each other in LRF.

We would like to thank our friend Ch.Krüger for his suggestions,
Dr.J. Sandow of the HOECHST AG for the gift of the LRF sample and
the Deutsche Forschungsgemeinschaft for financial support. Please
credit this contribution to the account of Prof.Lippert.

Yours sincerely

L. Pogliani

D. Ziessow

Compound/Solvent	pH or pD	α	δ^b	$\beta 1$	$\beta 2 \gamma 1 \gamma 2^b$	Ref.
c-AcProA/D_2O	6.9	4.528	3.528	2.406	1.959	5
t-AcProA/D_2O	6.9	4.368	3.654	2.302	2.004	5
LRF(Pro)/H_2O	2.0	-	-	2.3	2.1	1
LRF(Pro)/D_2O	6.5	4.191	3.684	2.293	2.0	our data
AcSer/D_2O	7.5	4.275				"
LRF(Ser)/H_2O	2.0	-		$3.71^{(c)}$		1
LRF(Ser)/D_2O	6.5	4.273				our data

a) The Chemical shifts are given in ppm from international DSS

b) Given are the mean value of the $\beta 2, \gamma 1, \gamma 2$ and $\delta 1, \delta 2$ peak positions, respectively.

c) for $\beta 1$ and $\beta 2$ peaks

References

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4) W.A.Thomas, "NMR and Conformation of Amino Acids,Peptites and Proteins" in Annual Reports on NMR Spectroscopy, ed. by T.Mooney, vol. 6B, pp 224 (1976), Academic Press, New York,London.

5) L.Pogliani, M.Ellenberger, J.Valat and A.M.Bellocq, Int.J.Pept. Prot.Res. 7, 345 (1975)

6) L.Pogliani, D.Ziessow and Ch.Krüger, in preparation

Carleton University
Ottawa, Canada K1S 5B6

September 21, 1977.

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

Stereochemical Effects on Direct ^{13}C-^{31}P Coupling

Below are presented some data for cyclohexyl phosphonates and hydroxyphosphonates which indicate that $^{1}J_{CP}$ can be useful for stereochemical analysis. Compounds with axial phosphorus have substantially less positive $^{1}J_{CP}$ values than their equatorial counterparts. The mechanism of the effect is presently unclear, however Gorenstein (1) has recently presented a theory relating changes in ^{1}J to bond angle distortion in the context of the Fermi contact contribution. No Calculations are yet available for pentavalent phosphorus compounds.

We plan to carry out x-ray analysis of 1 and 2 as a test of the bond angle distortion theory. Also I would be interested in hearing from others with experimental data pertaining to this problem. Please credit this to John ApSimon's subscription.
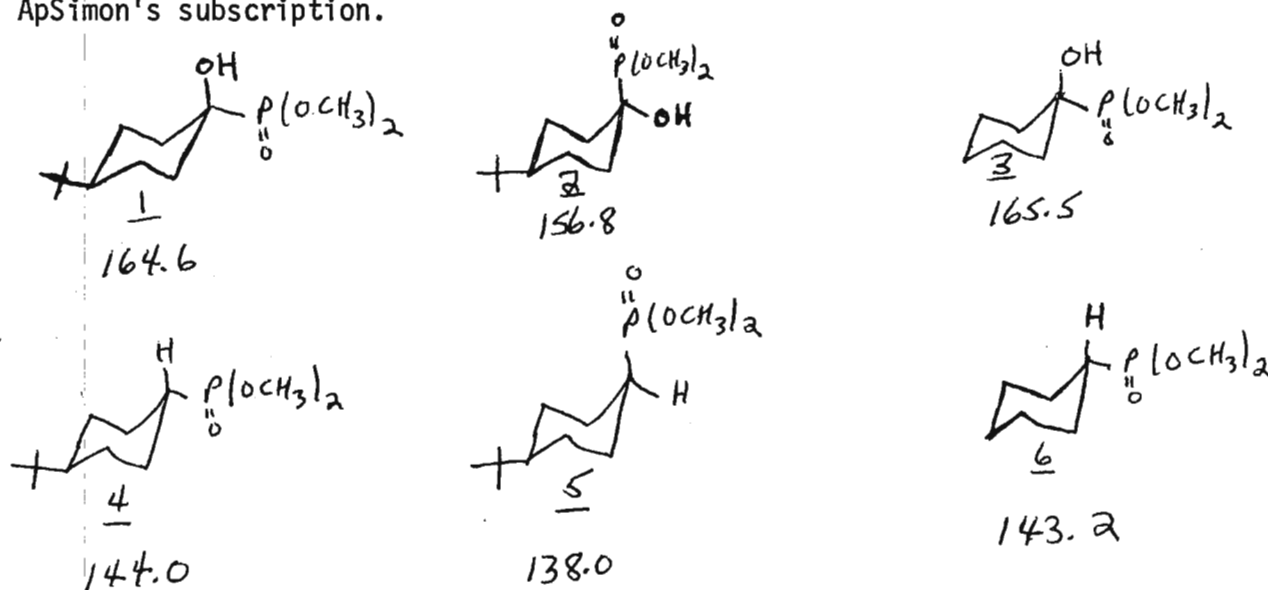
1. D.G. Gorenstein, JACS 99, 2254 (1977).

Sincerely,

G.W. Buchanan - Associate Prof.

Department of Chemistry □ Steacie Building □ (613) 231-2760

Richard W. Mattoon
1912-1977

Dr. Richard W. Mattoon passed away Sept. 24, 1977. He had
undergone a protracted period of disability arising from a
severe heart attack suffered in Oct., 1975 and subsequent
open-heart surgery in Jan., 1976. He is survived by his
wife, Jeanette, residing at 1547 N. Sheridan Rd., Lake Fo-
rest, IL 60045, sons Henry and David, and daughter Shelley.
Rememberances in his memory may be made as contributions
to Lake Forest Hospital, Lake Forest, IL 60045.

Richard was Chemical Physics Section Head at Abbott Labora-
tories prior to his retirement after 27 years of service.
One of his most proud accomplishments was bringing NMR to
Abbott and successfully applying it to chemical problems.
He was an early visionary of NMR's potential; the first
Abbott spectrum was a 40 MHz PMR recorded for him in 1957.

As a regular attendee of the Experimental NMR Conference,
Richard could recall the days when that venerable meeting
was the OCEANS conference held annually at the Mellon In-
stitute. For a number of years Richard served on the ASTM
E-13 NMR sub-committee, and attempted to bring order to this
new field with definitions and standards. Abbott's sponsor-
ship of TAMUNMR Newsletter is a direct consequence of Rich-
ard's efforts. His scientific endeavors were not limited to
NMR as he was also instrumental in bringing to Abbott X-ray
analyses, Mass Spectrometry, DTA-TGA and numerous other phy-
sical techniques.

Always active in outside professional activities, Richard was
chairman of the Chicago Section of the ACS in 1974-75. He
was also an officer of the Physics Club of Chicago and received
the Chicago Technical Councils award as Scientist of the year
in 1967. He had a personal interest in the metric system and
its use in the U.S. and served as secretary for the Metric As-
sociation for many years. He was also active in local commu-
nity affairs and for many years organized a science program for
North Chicago High School.

Truely Richard was a man of many facets and as such is mourned
by those who knew him. His passing is indeed a loss to the
scientific community.

McMASTER UNIVERSITY
Department of Chemistry

1280 Main Street West, Hamilton, Ontario, L8S 4M1
Telephone: 525-9140

September 23, 1977

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

Base-pairing in the self-complementary oligoribonucleotide CpApUpG

Dear Dr. Shapiro:

In order to probe the physical properties of helix formation in nucleic acids, we have undertaken a series of proton NMR investigations of several synthetic oligoribonucleotides. The work reported here is a variable temperature 90 MHz ^{1}H NMR examination of the self-complementary tetranucleotide CpApUpG. This is the first example of a tetrameric duplex which contains two internal AU base pairs.

Chemical shift assignments for the base and ribose C-1' protons were determined by correlating the shifts of the corresponding protons of CpA and CpApU with those of CpApUpG. The cytidine H-5 and H-6 resonances were distinguished from those of uridine by the magnitude of the coupling constant $J_{5,6}$ cytidine, $J_{5,6}$ = 7.6 Hz; uridine, $J_{5,6}$ = 8.2 Hz. Irradiation of the pyrimidine H-6 differentiates the H-5 signal from the ribose anomeric protons. These data (Table 1) were obtained at 70°C in order to minimize inter- and intra-strand effects.

Table 1: Chemical shifts[a] and coupling constants[b] for the oligoribonucleotides in D_2O[c] at 70°C.

Proton	CpA	CpApU	CpApUpG
CH-6	7.660	7.687	7.662
AH-8	8.377	8.382	8.346
AH-2	8.260	8.250	8.196
UH-6		7.744	7.692
GH-8			7.962
CH-1'	5.779	5.768	5.765
AH-1'	6.093	6.088	6.039
UH-1'		5.856	5.845
GH-1'			5.813
CH-5	5.958	5.925	5.912
UH-5		5.746	5.738

Proton	CpA	CpApU	CpApUpG
$J_{1',2'C}$	4.4	4.0	3.8
$J_{1',2'A}$	4.6	3.7	4.4
$J_{1',2'U}$		4.6	4.8
$J_{1',2'G}$			5.3

[a] Chemical shifts are in ppm relative to DSS using t-butyl alcohol-OD as an internal reference and are accurate to $\pm$ 0.005 ppm.

[b] Accurate to $\pm$ 0.2 Hz.

[c] Concentrations: CpA, 1.7×10^{-2}M; CpApU, 1.1×10^{-2}M; CpApUpG, 1.0×10^{-2}M in D_2O containing 0.01 M sodium phosphate (pD = 7.0) and 1.0 M sodium chloride.

The behaviour of the CpApUpG aromatic resonances with respect to temperature is shown in Figure 1. Above 45°C there was a linear change for these protons which is attributed to single strand intermolecular base-stacking. Below 45°C there was a general non-linear variation associated with the formation of the following base-paired duplex:

$$5'\text{-CpApUpG-}3'$$
$$3'\text{-GpUpApC-}5'$$
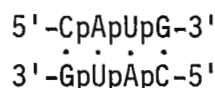
From the point of maximum slope in the curves for AH-8, AH-2, and GH-8 we have estimated the average melting temperature or T_m of the duplex to be $24 \pm 1°C$.

There was also a reduction in the value of $J_{1',2'}$ until at 20°C the anomeric protons appeared as broad singlets with $J_{1',2'}$ less than 1.0 Hz. This indicates a high percentage of the C-3' endo conformation for the ribose rings. We are currently extending this work to study duplex formation in pentaribonucleotides.

Please credit this contribution to the account of J.I.A. Thompson.

Donald W. Hughes
Department of Chemistry

Paul J. Romaniuk
Department of Biochemistry

(a)
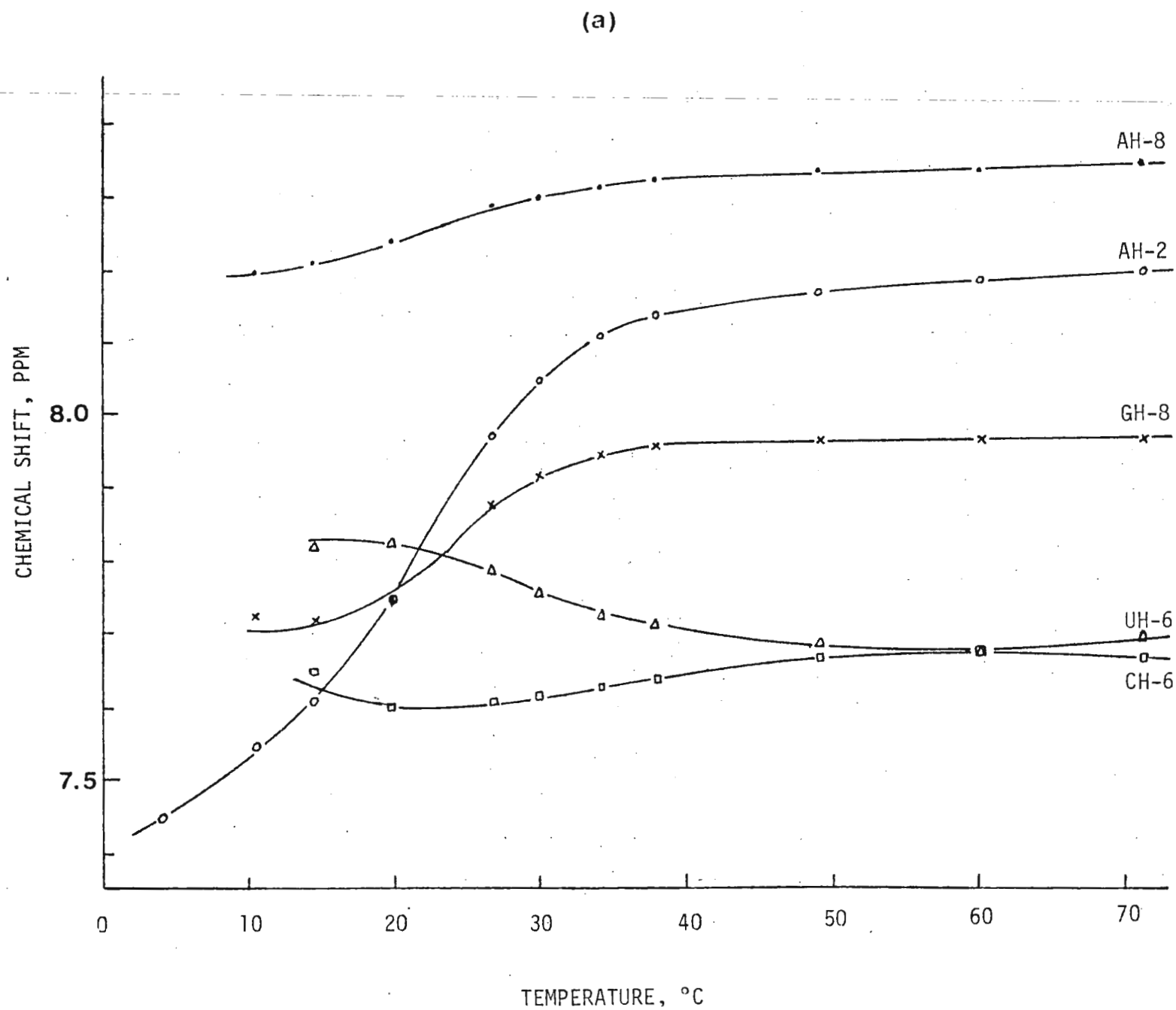
FIGURE 1: Temperature dependence of the chemical shifts of the base
protons of CpApUpG.