Illinois
Institute of
Technology
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Newsletter

No. 116
MAY, 1968

OVER

Deadline Dates: No. 117: 5 June 1968
No. 118: 2 July 1968 PLEASE NOTE!

Reminder: For the period August 10, 1967 to August 15, 1968 inclusive, all Newsletter contributions, enquiries, etc., should be addressed as follows:

Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

- CONTINUED ON THE OUTSIDE BACK COVER

INSTITUT FÜR PHYSIKALISCHE CHEMIE DER
TECHNISCHEN HOCHSCHULE STUTTGART, Germany

7 STUTTGART N
Wiederholdstraße 15
Telefon 29 97 83 93

Dr. Herbert Dreeskamp

15 March, 1968

$^4J_{HH}$ is positive in Me_4C, Me_2O, Me_2CO and Me_2SO

Dear Barry:

Recently we have been using the General Radio 1164A7C frequency synthesizer together with our Varian DA-60 for heteronuclear tickling experiments and are quite satisfied with its performance. The experimental hook-up is quite simple: We took the 5 MHz, 2 Volt of the fixed frequency output, limited this by diode clamping to 70% and coupled this directly to the grid of the first stage of the DA-60. This is as expected quite an improvement over using the NMR-Specialities decoupler, though with carefully selected and thermostated crystals a stability sufficient to determine $^4J_{HH}$ = + 0.2 Hz in TMS may be achieved (Z.Naturforschg. 22a 1458,[1967]). Some of our recent investigations concern the absolute sign of $^4J_{HH}$ in some simple Molecules. Those listed in the table all show a small but readily (if the field is good enough, that is) observable splitting of the proton spectrum of the ^{13}C-methylgroup. Each of the lines in the multiplett was disturbed in turn by tickling the corresponding ^{13}C-lines split by $^3J_{CH}$, giving $^3J_{CH}$ and the sign relative to $^4J_{HH}$. The sign of the long-range $^3J_{CH}$ was then determined in standard fashion by H-{H}, relative to $^1J_{CH}$.

	$^1J_{CH}$	$^3J_{CH}$	$^4J_{HH}$ all in [Hz]
Me_4C	+ 124,2	+ 4,4	+ 0,35
Me_2O	+ 140,2	+ 5,4	+ 0,23
Me_2CO	+ 126,6	+ 1,6	+ 0,53
Me_2SO	+ 137,6	+ 4,6	+ 0,46

Best wishes.

Sincerely yours

Herb

116-2

SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairessestraat 174 - Telefoon 71 74 51

AMSTERDAM, April 4. 1968

Uw ref.:

Onze ref.:

Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305.
U.S.A.

Dear Dr. Shapiro,

We have started an investigation on the proton magnetic resonance spectra of carbanions. Carbanions derived from aromatic dihydrocompounds can be prepared by reduction of the parent aromatic hydrocarbon and subsequent reaction with a proton donor or by reaction of the dihydrocompound with alkali metal.

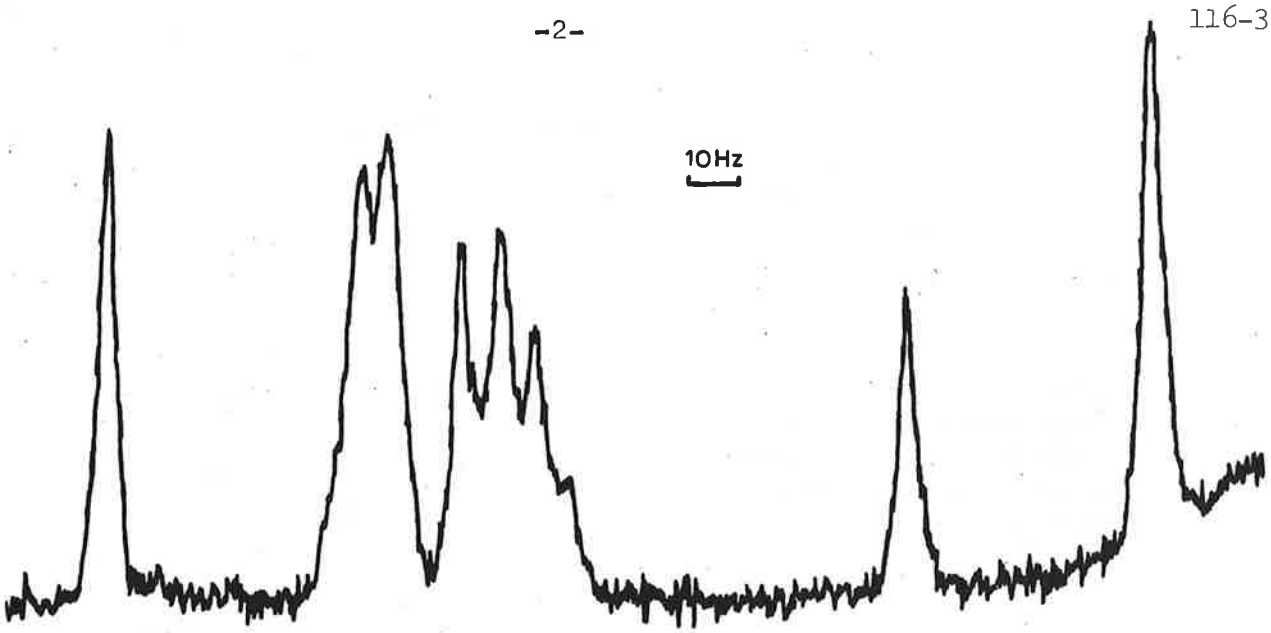
Complete reduction of a 0.1 molar solution of aromatic hydrocarbon, which is required in n.m.r. work, is rather difficult. It is preferable to use the dihydrocompound as the starting material.

On reduction with alkali metal a mononegative ion of the hydrocarbon is formed as shown by e.s.r. In many cases this radical ion is unstable in the presence of unreacted hydrocarbon. At suitable temperatures a carbanion will then be formed. As an example we give in fig. 1 the n.m.r. spectrum of the carbanion of 9,10-dihydroanthracene. The structure of this ion is analogous with the carboniumion found by protonation of the aromatic molecule*.

Other ions investigated include the carbanions fluorenyl and 4,5-methylenephenanthrenyl.

On reduction of 4,5-methylenephenanthrene an orange-red product is formed which has been identified as 9,10-dihydro - 4,5-methylene-phenanthrenyl carbanion. This was done by comparing its n.m.r. spectrum

*H.H. Perkampus and G.J. Hoijtink, J.Am.Chem.Soc, 87, 4529 (1965).



The ^{1}H resonance of the carbanion of 9.10 dihydroanthracene in liquid ammonia at 56.4 Mc sec^{-1}.
Benzene is used as internal reference (low field peak).

with that of methylsubstituted fluorenylcarbanions.

The carbanion of 4,5-methylenephenanthrene proper has been prepared by reaction with Na NH_2 in liquid ammonia.

We are now examining the chemical shifts of the proton resonance lines as a function of the excess change. Besides we investigate the reactionmechanisms of the formation of the carbanions.

With kind regards,

J. van der Kooy

C.W. Hilbers

N.H. Velthorst

C. MacLean.

CIBA RESEARCH CENTRE

GOREGAON, BOMBAY 63, INDIA

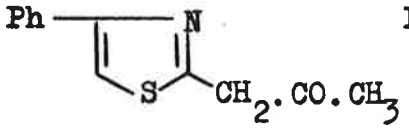
April 2, 1968

Dr. B.L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305
U.S.A.

KETO-ENOL TAUTOMERISM OF 2-THIAZOLYL ACETONES

Dear Dr. Shapiro:

We would like to report on some interesting observations we have made in the NMR spectra of (4-phenyl-2-thiazolyl) acetone and its imine. The 60 Mc spectrum of the pure ketone in CCl_4 showed two species to be present. The major component (ca. 70%) was the ketone I. The second one showed an olefinic signal at 329 cps. Of the two structures II and III possible, we prefer II because of the allylic coupling of about 0.6 cps seen for the methyl (120 cps) and the olefinic signals. The thiazole proton in the ketone was seen as a singlet at 437 cps, whereas that of the enol was a singlet at 421 cps. The



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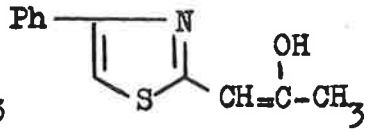
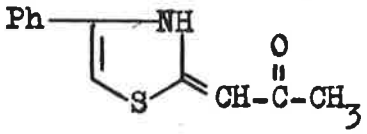


II



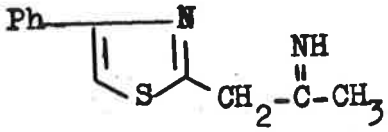
III

phenomenon of tautomerism in some heterocyclyl acetones is the subject matter of a recent publication[1]. The authors advocate a type III structure for 2-quinolyl acetone.

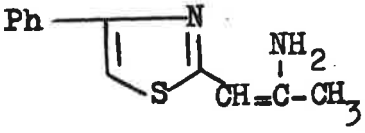
Increasing the dielectric constant of the solvent resulted in decrease of the enol content as expected.

Unlike the ketone, the corresponding imine in CCl_4 appears to exist mainly as one species ($>95\%$). The ketimine structure IV was not present to a measurable extent. Although allylic coupling was not detectable for the methyl signal at 114 cps, the olefinic signal at 308 cps had a line-width of 2.8 cps.

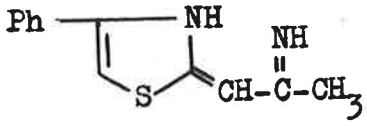
We interpret this to favour the enamine structure V over VI, although the latter is not strictly ruled out.



IV

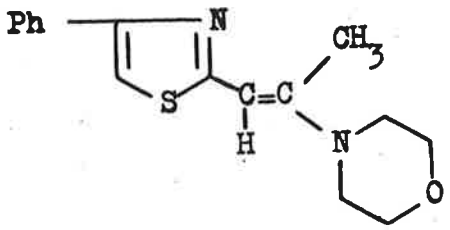


V

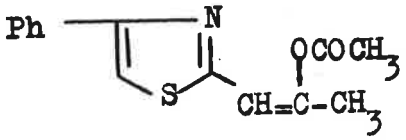


VI

The thiazole proton in this compound was present at 417 cps reminiscent of its position in the enol II. However, structure VI may also explain the upfield shift. But we prefer to ascribe it to the conjugated amine function, as such upfield shifts for the thiazole protons are seen for 4-substituted-2-aminothiazoles and for the morpholine enamine VII. On the other hand, in the enol-acetate VIII, the thiazole proton moves downfield to 443 cps.



VII



VIII

We hope to publish soon full details of our extensive studies on these compounds.

With regards,

Yours sincerely

S. Rajappa

Dr. S. Rajappa

Reference:

1. Mondelli and Merlini, Tetrahedron, 22, 3253 (1966).

UNIVERSITY OF PITTSBURGH

PITTSBURGH · PENNSYLVANIA · 15213

DEPARTMENT OF CHEMISTRY

March 28, 1968

Dr. B. L. Shapiro
Department of Chemistry
Stanford University
Palo Alto, California 94305

Dear Barry:

We have recently completed the analyses of the spectra of seventeen P-O-Et compounds; the spectra of thirteen of the esters were unexceptional and were analyzed as A_3M_2X cases. However, methylene proton non-equivalence was observed in three tetra-covalent (I-III) and one trivalent (IV) ester. The spectra of

$(CH_3CH_2O)_2P(O)Cl$ (I) $(CH_3CH_2O)_2P(O)CCl=CH_2$ (III)
$(CH_3CH_2O)_2P(S)Cl$ (II) $(CH_3CH_2O)_2PCl$ (IV)

these compounds were calculated as the sum of two A_3MN sub-spectra corresponding to the spin states α and β of the phosphorus; the experimental and calculated spectrum of the methylene region of II is representative and is shown in Figure 1.

Although the observation of geminal group non-equivalence is relatively common in non-asymmetric esters of tetra-coordinate phosphorus,[1] we are aware of only three such citations for trivalent phosphorus compounds: $C_6H_5P(O\text{-}i\text{-}C_3H_7)_2$,[1b] $(n\text{-}C_3F_7)_2PI$,[2] $C_6H_5P(i\text{-}C_3H_7)_2$.[3] Compound IV is the first trivalent compound in which methylene proton non-equivalence has been observed. The observation of this phenomenon in trivalent phosphorus compounds requires a slow inversion rate at phosphorus. The non-equivalence of the methylene protons of IV persists at temperatures up to 157 ; similar results have been obtained by Siddall and Prohaska[1b] and McFarlane[3] for methyl group non-equivalence.

Preprints of a manuscript describing these results are available.

Best regards,

M. P. Williamson C. E. Griffin

(1) (a) H. Finegold, J. Am. Chem. Soc., 82, 2641 (1960), (b) T. H. Siddall and C. A. Prohaska, ibid, 84, 3467 (1962). (2) J. F. Nixon, J. Chem. Soc., 777 (1965). (3) W. McFarlane, Chem. Commun., 229 (1968).

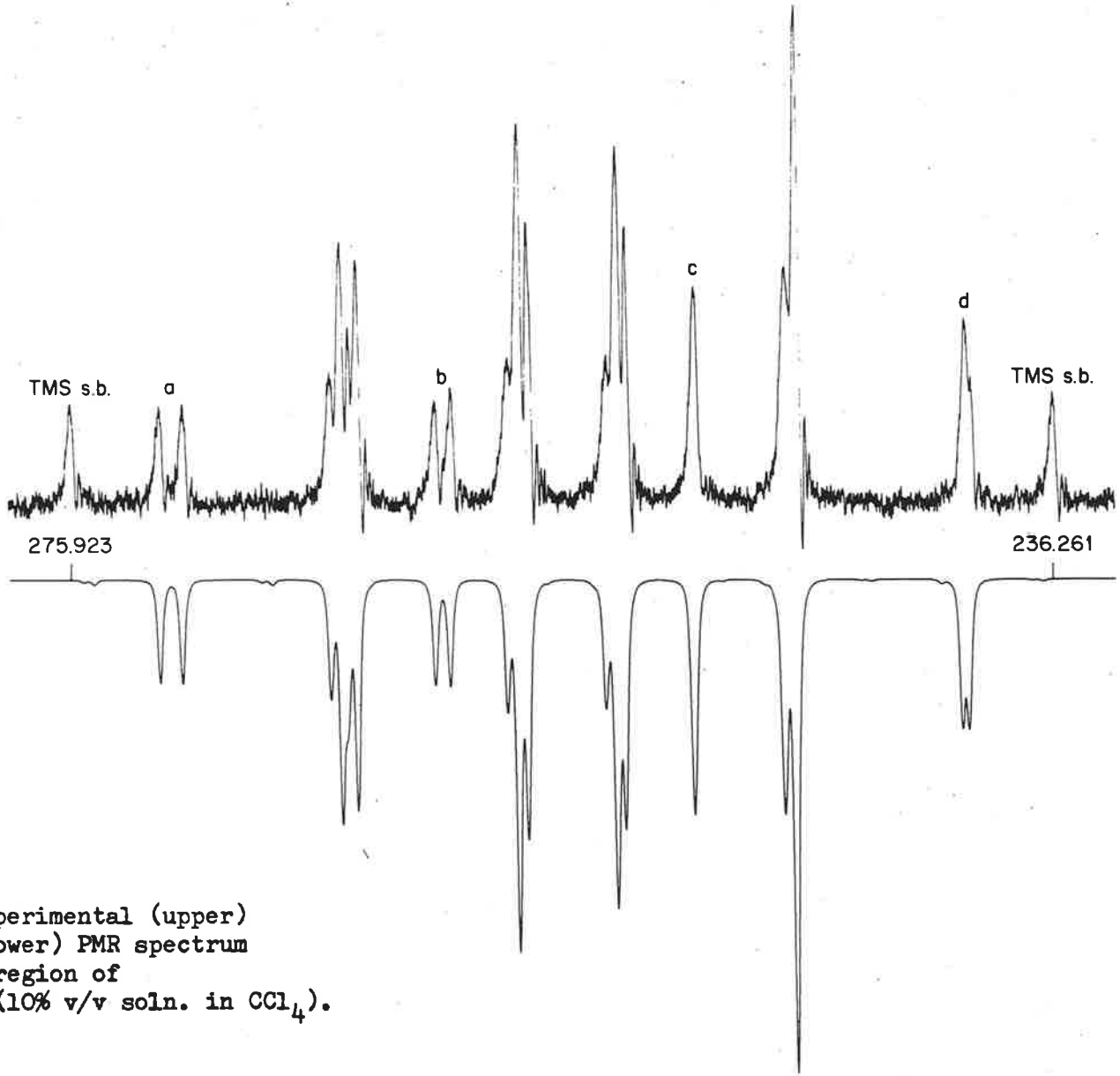


Figure 1. The experimental (upper) and calculated (lower) PMR spectrum of the methylene region of $(CH_3CH_2O)_2P(S)Cl$ (10% v/v soln. in CCl_4).

INSTITUTE OF CHEMICAL KINETICS AND
COMBUSTION ACADEMY OF SCIENCES
90,NOVOSIBIRSK
U S S R

Professor Bernard L.Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

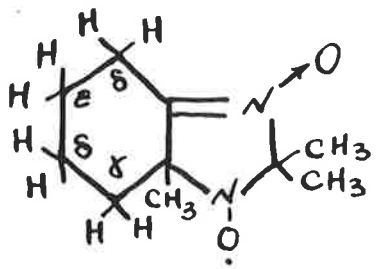
March,19, 1968

LONG-RANGE DELOCALISATION OF SPIN DENSITY ACROSS σ-BONDS IN IMINOXYL RADICAL OF 3-IMIDASOLINE--3-OXYDE

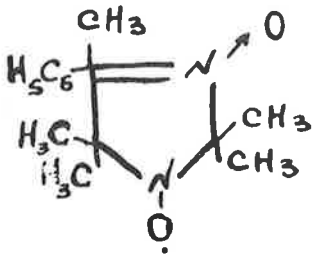
Dear Professor Shapiro!

In our last contribution on to these Newsletters (No 107, p.11) we have reported on the investigations of free radicals by NMR method in our group. We have continued the research in this field. Now we want to report some examples of the long distance spin density propagation across σ-bonds.

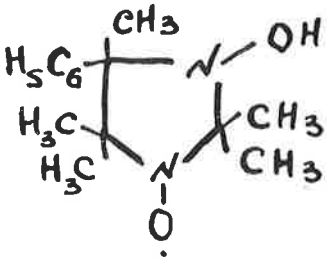
I.



II.



III.



So, coupling constants in radical I a_{ε_1}=-0,020 ± 0,007g a_{ε_2} =-0,048 ± 0,007g has been found on the remote ε-hydrogens (the coupling constants difference is connected with geometrical unequivalence of cyclohexane rings protons). The signs of coupling constants a_i on γ- and δ-hydrogens are the same as in other radicals studied earlier ($a_\gamma < 0$, $a_\delta > 0$) [1]. Therefore, the addition of each σ-bond lead to the change of the spin density sign.

We have found the propagation of spin density across σ-bonds to the aromatic ring in radical II [2]. Alternation of the coupling constant signs on the rings protons (a_{orto} = -0,016 g, a_{meta} = +0,009 g , a_{para} = -0,019 g) means that the spin density propagate in the aromatic ring across π -bonds. It is interesting to note that we haven't detected the spin density delocalisation on the aromatic protons in radical III [3]. It may be explained by the more long distance for π -system in radical III comparing with radical II.

Yours sincerely

Yu.Molin Molin

R.Sagdeev Sagdeev

Institute of Chemical Kinetics and Combustion Academy of Sciences USSR

G.Kutikova Kutikova

L.Volodarsky L.Volodarsky

Institute of Organic Chemistry Academy of Sciences USSR

Literature

1 R.Z.Sagdeev, Yu.N.Molin, Zh.Struct.Khim, 8, 4, 697-98 (1967).

R.Z.Sagdeev, Yu.N.Molin, E.G.Rozantzev, Theor.Exper.Khim., (in press).

2 L.B.Volodarsky, G.A.Kutikova, R.Z.Sagdeev, Yu.N.Molin, Tetrahedron Letters, 1968, 1065.

3 L.B.Volodarsky, G.A.Kutikova, R.Z.Sagdeev, Yu.N.Molin, Zh.Vses.Khim.Obch., (in press).

THE UNIVERSITY OF LIVERPOOL
DEPARTMENT OF INORGANIC, PHYSICAL AND INDUSTRIAL CHEMISTRY

TELEPHONE : ROYAL 6022
Extension 356

THE DONNAN LABORATORIES
LIVERPOOL, 7

Dr. B.L. Shapiro,
Chemistry Department,
Stanford University,
Stanford,
California 94305,
U.S.A.

Dear Dr. Shapiro,

^{19}F Shifts of Pentafluorophenyl Compounds of Group IV Elements

The letter by Mr. D.E. Williams (IIENMRN 113-8) has prompted us to write about some related work we have been doing. In the table are listed ^{19}F chemical shifts (ppm) we have obtained for $(C_6F_5)_4M$ compounds dissolved in carbon tetrachloride. The shifts have been referred to hexafluorobenzene hence high values indicate low shielding.

	δ_{ortho}	δ_{meta}	δ_{para}	$\delta_{para} - \delta_{meta}$
$Si(C_6F_5)_4$	35.1	2.2	15.4	13.2
$Ge(C_6F_5)_4$	34.5	2.6	14.2	11.6
$Sn(C_6F_5)_4$	40.1	4.7	16.1	11.4
$Pb(C_6F_5)_4$	40.7	5.0	15.0	10.0

As expected, the $\delta_{para} - \delta_{meta}$ parameter correlates with the electronegativity order of the elements:

$$Si > Ge \sim Sn > Pb$$

The ortho shifts apparently reflect the influence of the Group IV element only (there being negligible spatial or conjugative inter-ring interaction) because the ortho ^{19}F shifts of $(CH_3)_3SnC_6F_5$ and $(CH_3)_3PbC_6F_5$ are 40.2 and 42.0 ppm respectively. Here the shielding decreases with decrease of the electronegativity of M: since there is a good correlation with first ionisation potentials of the elements ($\delta_{ortho} \alpha I^{-1}$) we may conclude that there is a large increase in the paramagnetic contribution to the shift resulting from low values of ΔE.

Yours sincerely,

J. M. Sutcliffe

M.J. Jolley,
J.M. Sutcliffe.

April 5, 1968

Dr. Bernard Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

Subject: A-60 Magnet Cooling Problem Revisited

Dear Barry:

Our Varian Model A-60 has shut down numerous times during the past six months due to overheating of the left magnet. Standard flushing procedures would solve the problem for short periods but could not be termed as successful.

We, therefore, deduced that the left cooling coil retained enough deposits to cause a borderline situation. Two alternatives were presented: 1) ship the instrument back to Varian to have the cooling coils replaced (approximate cost - $6,000), or 2) somehow increase the flow to the cooling coil in question. We decided to at least try the latter.

The following changes were made as a result of the decision (Figure 1).

1. The rubber valve seal in the 0.6 g.p.m. flow regulator was removed.

2. The manifold accommodating the inlet and outlet connections to the magnet was modified. This included replacing the existing connections (mounted in series thus allowing more flow to the right magnet) with a "T" connection, and mounting a manually-controlled flow valve on the inlet side to the right magnet.

3. A second manually-controlled flow valve was added to the inlet side of the cold plate.

4. A thermometer was placed on the outlet side of the cold plate to monitor the outlet water temperature. This temperature indication is used as a signal to

4 cont.

increase or decrease the amount of flow to the cold plate.

The above simple modifications have apparently resolved our problem and the A-60 has operated quite satisfactorily for over two months.

Yours sincerely,

Dexter V. Dunlap

Fred

Fred F. Caserio, Jr.

STANFORD UNIVERSITY
STANFORD, CALIFORNIA

DEPARTMENT OF CHEMISTRY

17 April 1968

Fred F. Caserio, Jr., R & D
Arco Chemical Company
Anaheim, California 92803

Cooleamus

Dear Fred:

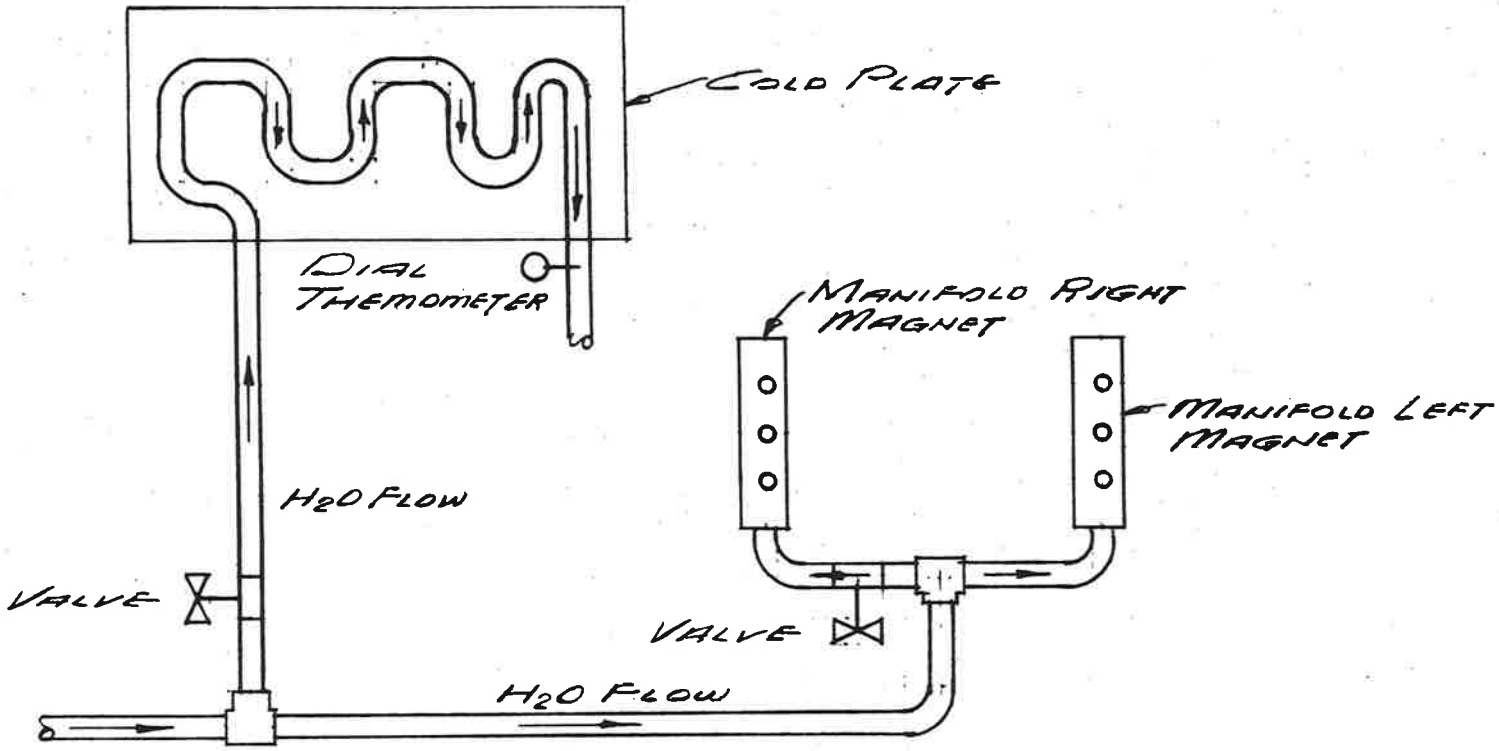
I have decided to grant your above letter the distinction of being the last contribution solely on magnet cooling coil problems which will appear in the Newsletter. I regret having to adopt this quasi-editorial stance, but I feel the time has come to lay this topic to rest. Perhaps some day we can do the same for considerations of τ, δ, $-\delta$, etc., etc., although I tend to doubt it.

With all best regards,

Sincerely,

Barry

Bernard L. Shapiro, Visiting Scholar



A-60 MODIFICATIONS

FIGURE 1

CHEMISCHE LABORATORIA
DER RIJKS-UNIVERSITEIT
Afd.: Prof. Dr. L.J. Oosterhoff
Wassenaarseweg
Leiden
Telefoon 4 83 33

LEIDEN, April 10 19 68

Dr. Bernard L. Shapiro,
Department of Chemistry,
Stanford University,
Stanford, California 94305,
USA.

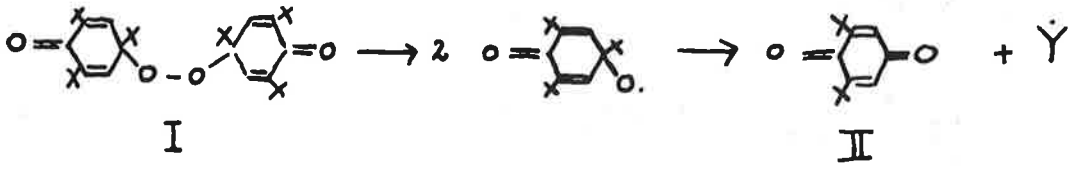
Chemically Induced Dynamic Nuclear Polarization

Dear Dr. Shapiro,

Recently Bargon and Fisher (Z.Naturf. 22a 1551, 1556 '67) and Ward and Lawler (JACS 89 5518 '67) discovered the very interesting effect, which they called CIDNP and which may occur, when reactive radicals are generated in the NMR tube at a high rate. The nuclei in the radical may be polarized by the relaxing electronspin and this polarization is transferred to the observed diamagnetic reaction products.

One of us (R. Kaptein) is studying the thermal decomposition of bis (1,3,5,-tri-tert-Butyl-2,5-cyclohexadien-4-one) peroxide (I), in which these effects are also observed due to the presence of the tert-Butyl radical.

Here the NMR spectrum is reported, recorded during the decomposition of a 0.2 M solution of I in hexachloroacetone (HCA) at 130° C. The following reactions are the most important:



I II

$\dot{Y}$ + HCA → tert-Butylchloride + PCA$^{\cdot}$ (75%)

2 $\dot{Y}$ → isobutene + isobutane (20%)

$\dot{Y}$ +PCA$^{\cdot}$ → isobutene + pentachloroacetone (PCA) (5%)

The spectrum was recorded on a Varian HA-100 spectrometer (lock signal obtained from a capillary containing H_2SO_4) 90 seconds after the sample had been inserted in the preheated probe, when the maximum emission and enhanced absorption occurred. Enhancement factor $V_{max} = \frac{I_{max} - I_0}{I_0}$. The high field part of the spectrum is presented

CHEMISCHE LABORATORIA, RIJKSUNIVERSITEIT LEIDEN
Afd. Prof. dr L. J. Oosterhoff
Wassenaarseweg, Leiden, Telefoon 48333, T. ~~3613~~ 3927

in the figure. The results are shown in the table:

δ(ppm)	V_{max}	assignment
0.84	+ 30	isobutane, high field line of methyldoublet
0.87	*	1 - tert - Butyl group of I
0.91	- 30	isobutane, low field line of methyldoublet
1.26	*	3 and 5 tert - Butyl groups of I
1.28	*	tert - Butyl groups of II
1.58	- 15	tert - Butyl-chloride
1.67	- 6/+35	isobutene methyl protons
4.60	- 7/+36	isobutene CH_2 protons
6.40	*	ring protons of II
6.60	*	ring protons of I
6.74	+ 22	possibly PCA

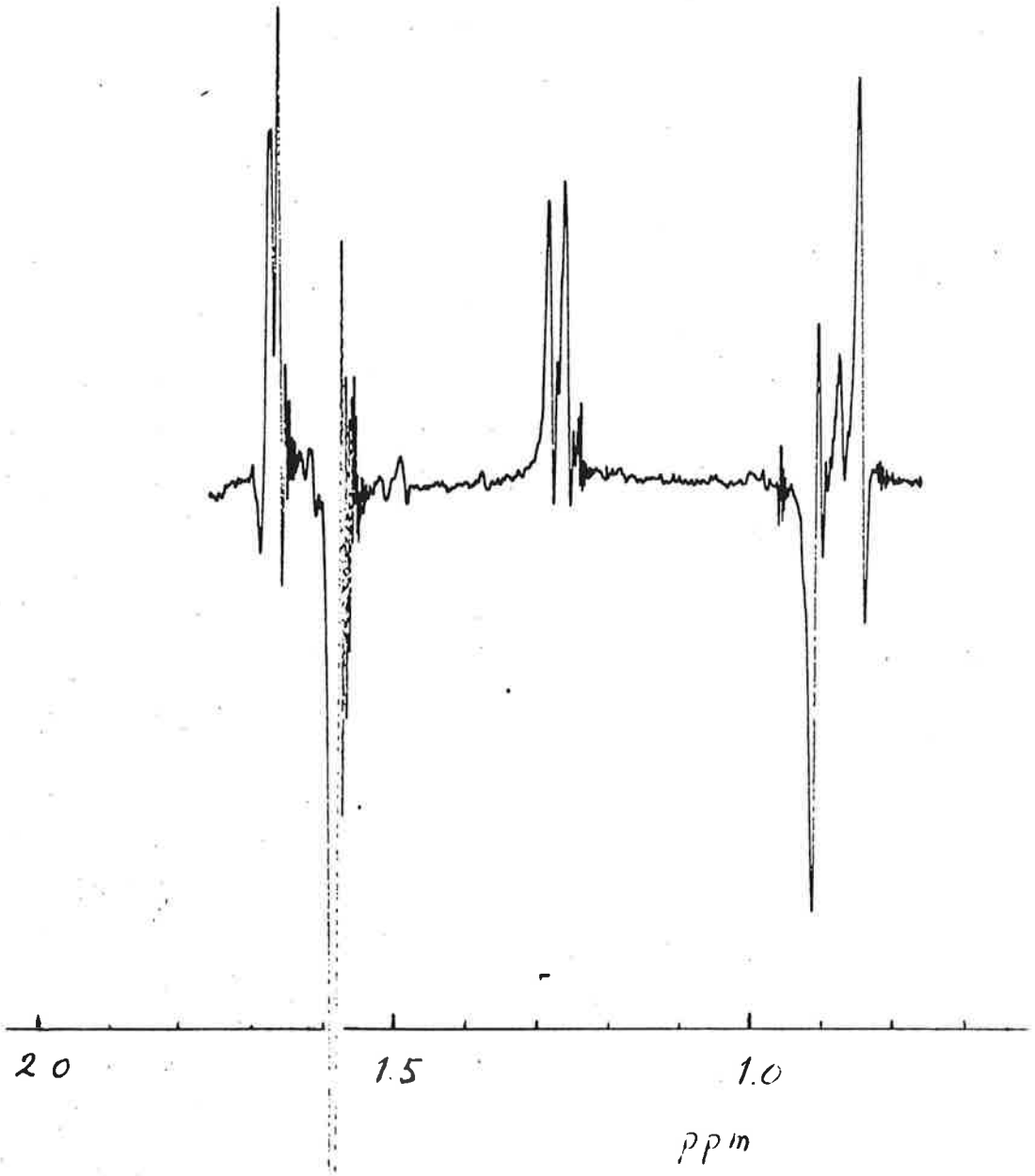
* regularly decreasing or increasing

The most remarkable features are the strong emission of the tert - Butylchloride protons (indicating a dominant dipole-dipole interaction in the radicals, that react with the solvent) and the unorthodox behaviour of multiplets arising from products of radical disproportionation: low field lines emission, high field lines absorption. This was already observed by Ward and Lawler.

We do not yet understand this and we intend to continue our investigations into these reactions to obtain an insight in the mechanism of both reactions and polarization.

Yours sincerely,

(R. Kaptein) (Th.J.Sekuur)


2.0
1.5
1.0
ppm

CABLE ADDRESS "RESEARCH"

IN YOUR REPLY PLEASE QUOTE

FILE No.

NATIONAL RESEARCH COUNCIL

CANADA

DIVISION OF APPLIED CHEMISTRY

OTTAWA 2,

April 19th, 1968

Dr. B.L. Shapiro,
Department of Chemistry,
Stanford University,
Stanford, California 94305,
U. S. A.

Dear Barry,

Recently we have begun looking at proton T_1 in two component solutions, each component being a proton containing species. The measurements have been made by the "saturation recovery" technique described at some length by Van Geet and Hume(1). The recorder charts were subsequently followed on a curve tracer whose output went to a small analogue computer. This took the logarithm of the curve and presented it as a straight line on an X-Y recorder. The slope of the line is proportional to T_1. This method of data processing has the slight advantage that the value of T_1 is obtained as some sort of eyeball average of the entire experimental record.

It was hoped that T_1 measurements, as a function of solution composition, might give some information on specific molecular interactions which do not greatly affect the chemical shift. For the system dioxane n-heptane chemical shifts (in p.p.m. from TMS) are shown in Figure 1. The product of solution viscosity and T_1, which according to the simplest theory should be a constant, is shown in Figure 2. Presumably n-heptane will not obey this theory due to the existence of pronounced intramolecular torsional motions. It is possible that dioxane shows some intermolecular aggregation in solutions of high dioxane content. We are continuing this study with other systems and hopefully will have more to say in a later newsletter.

Yours truly,

Syd

Syd Brownstein

(1) Anal. Chem. 37 983 (1965).

SB/md

Title: Proton T_1 measurements in dioxane-heptane solutions.

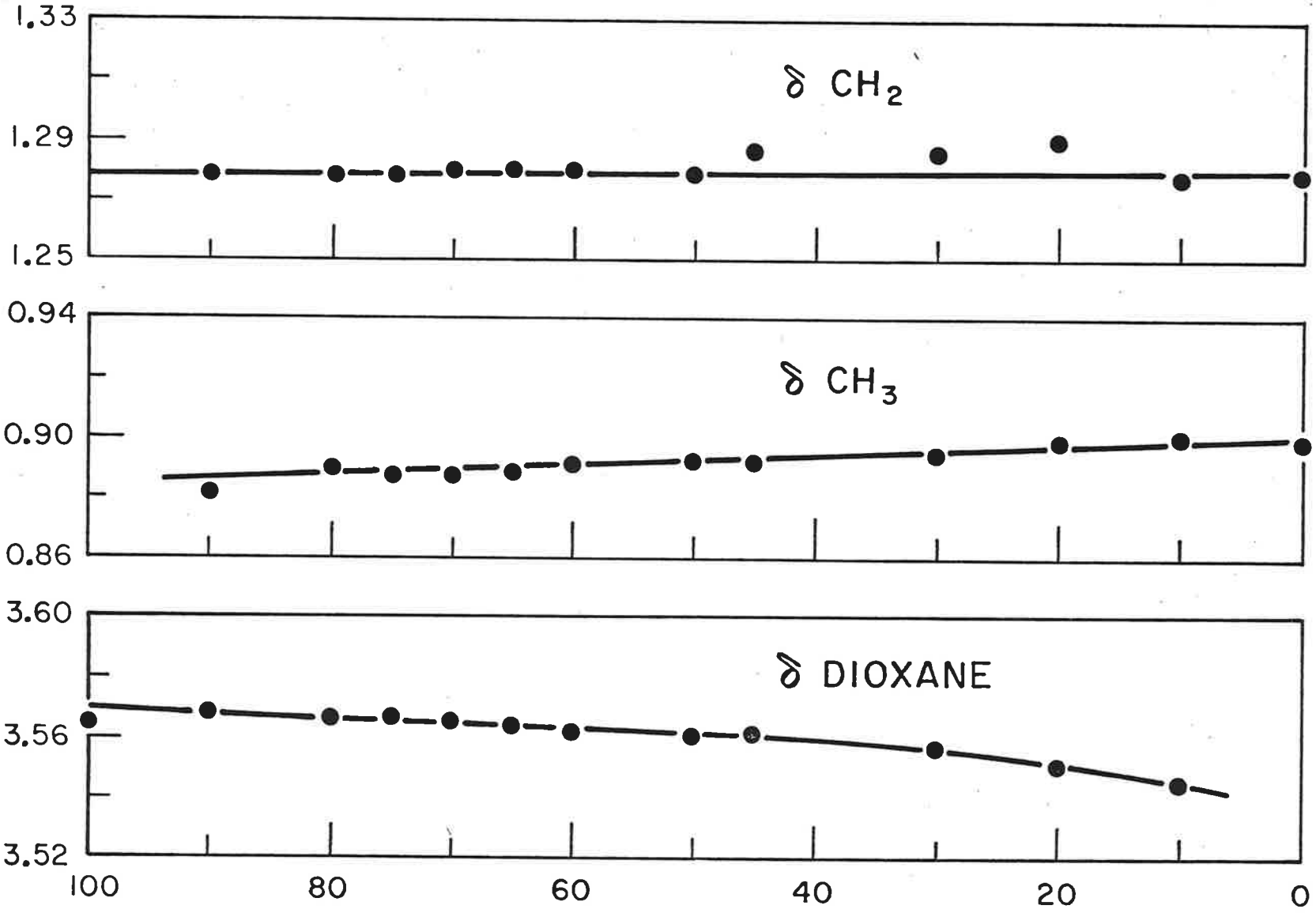

1.33
1.29
1.25
δ CH2
0.94
0.90
0.86
δ CH3
3.60
3.56
3.52
δ DIOXANE
100
80
60
40
20
0
% DIOXANE

Figure 1.

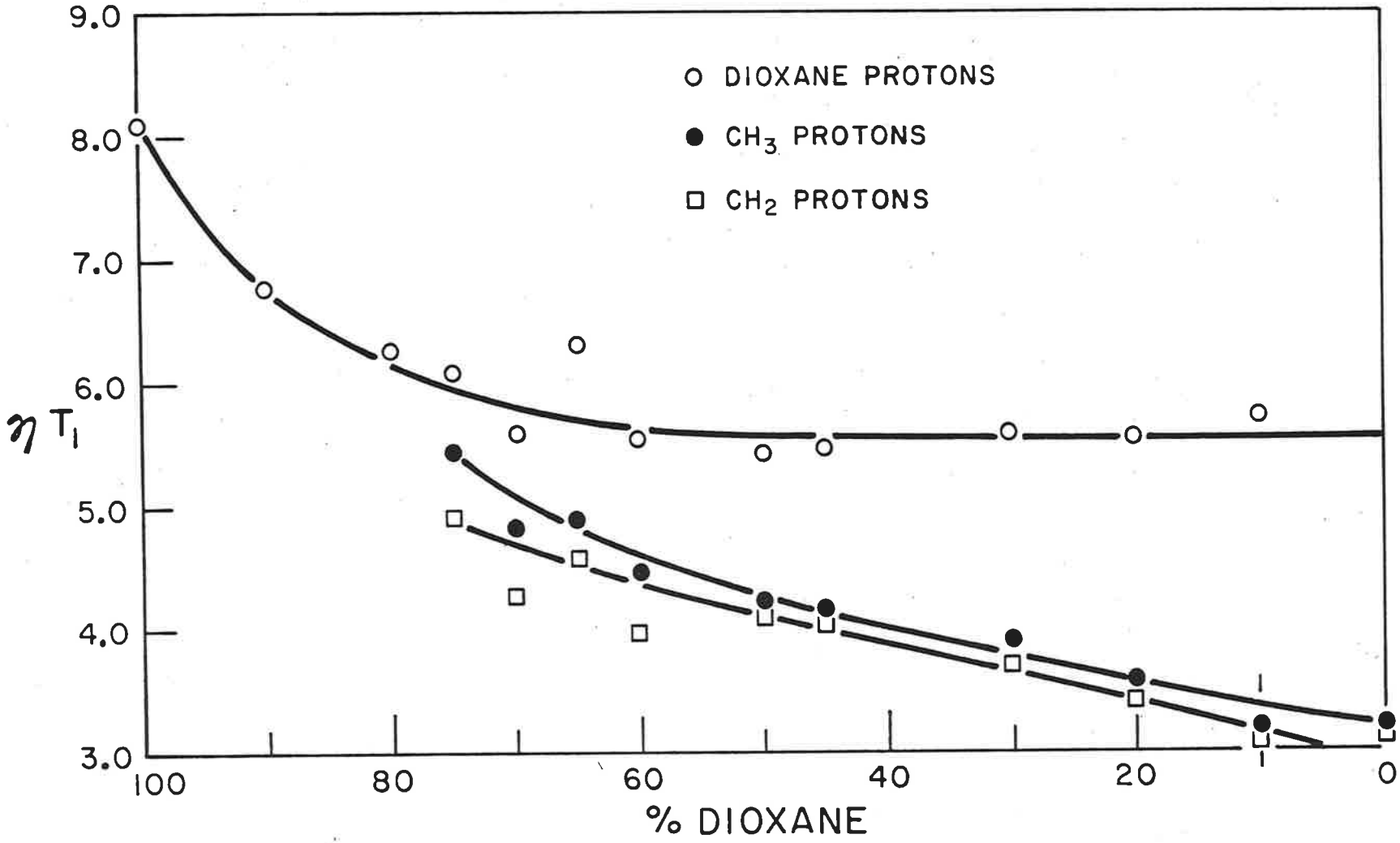

9.0
8.0
7.0
6.0
5.0
4.0
3.0
η T1
DIOXANE PROTONS
CH3 PROTONS
CH2 PROTONS
100
80
60
40
20
0
% DIOXANE

Figure 2.

DEPARTMENT OF
CHEMISTRY

THE UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA, 73069

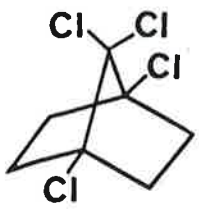
April 11, 1968

Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

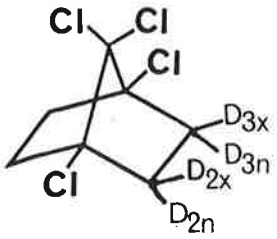
Dear Dr. Shapiro,

1,4,7,7-TETRACHLORONORBORNANE, REVISITED: OBSERVATION OF LONG-RANGE H-D COUPLING IN 1,4,7,7-TETRACHLORO-2,2,3,3-TETRADEUTERIONORBORNANE

Conversations with Professor Norman S. Bhacca prompted us to look further at the nmr spectrum of 1,4,7,7-tetrachloronorbornane (I). In a previous communication (IITNMRN, No. 108, p.2) we incorrectly referred to this as an A_2B_2 system; it is, in fact, and eight spin system, AA'A"A"'BB'B"B"'. The complexity of this system is greatly reduced (to AA'BB') upon replacement of the 2x,2n,3x, and 3n protons by deuterium. The normal 100 MHz nmr spectrum of the resulting tetrachlorotetradeuterionorbornane (II) is shown in figure 1, top.

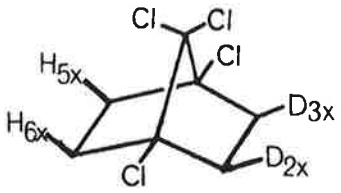


I



II

Considerable broadening of the low-field portion of the AA'BB' spectrum of II is evident. That this broadening is due to a long-range coupling involving deuterium is seen by comparison with figure 1, bottom, the deuterium-decoupled spectrum. On the basis of numerous literature examples of long-range H-H coupling in accord with the familiar "W-letter" rule, we ascribe the appearance of the normal spectrum of II to be due to the existence of a finite $J_{D_{2x}-H_{6x}} = J_{D_{3x}-H_{5x}}$, i.e.:



We have calculated the spectrum of II using the Bothner-By's LAOCOON III program. The calculated and experimental (deuterium-decoupled) spectra for II are shown in figure II. The following parameters afforded the calculated spectrum:

$$\nu_o\delta_{5n} = \nu_o\delta_{6n} = 143.14 \pm 0.03$$

$$\nu_o\delta_{5x} = \nu_o\delta_{6x} = 200.09 \pm 0.03$$

$$J_{5n,6n} = 9.97 \pm 0.04 \qquad J_{5n,6x} = 4.47 \pm 0.04$$

$$J_{5n,5x} = -12.31 \pm 0.04 \qquad J_{5x,6x} = 12.50 \pm 0.04$$

Interestingly, these calculations reveal that $J_{5n,6n} \neq J_{5x,6x}$. This same nonequivalence between endo- and exo- vicinal coupling constants has been observed in substituted norbornenes (J.C.Davis, Jr. and T.V.Van Auken, J.Am.Chem.Soc., 87, 3900 (1965)).

Similar studies of the nmr spectra of several specifically-deuterated norbornanes are currently in progress.

Please credit this contribution to APM's subscription.

Yours sincerely,

Alan P. Marchand

Alan P. Marchand
Assistant Professor

Anna Laura Segre

Anna Laura Segre
Istituto di Chimica Industriale
Politecnico
Piazza Leonardo da Vinci 32
Milan, Italy

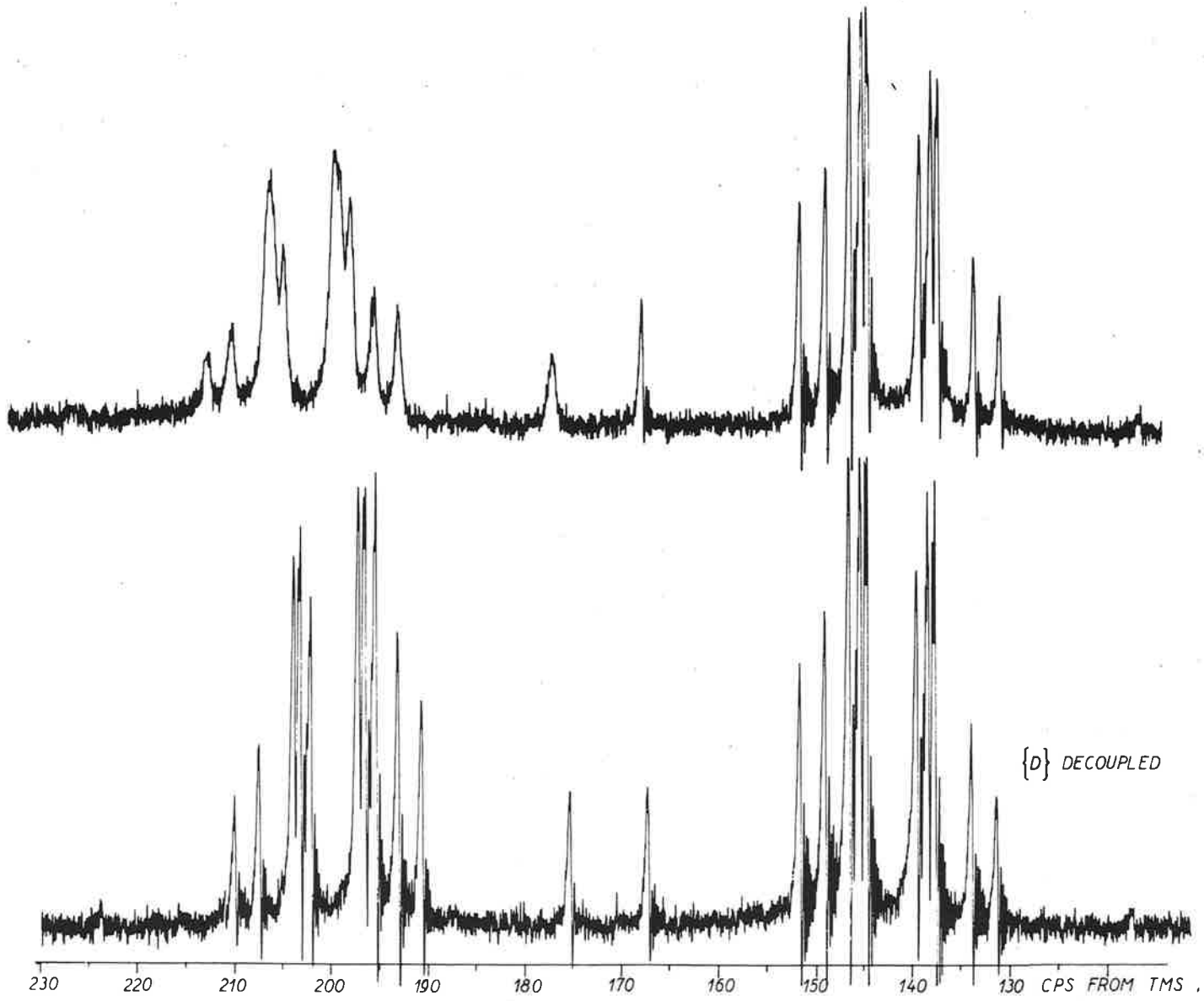
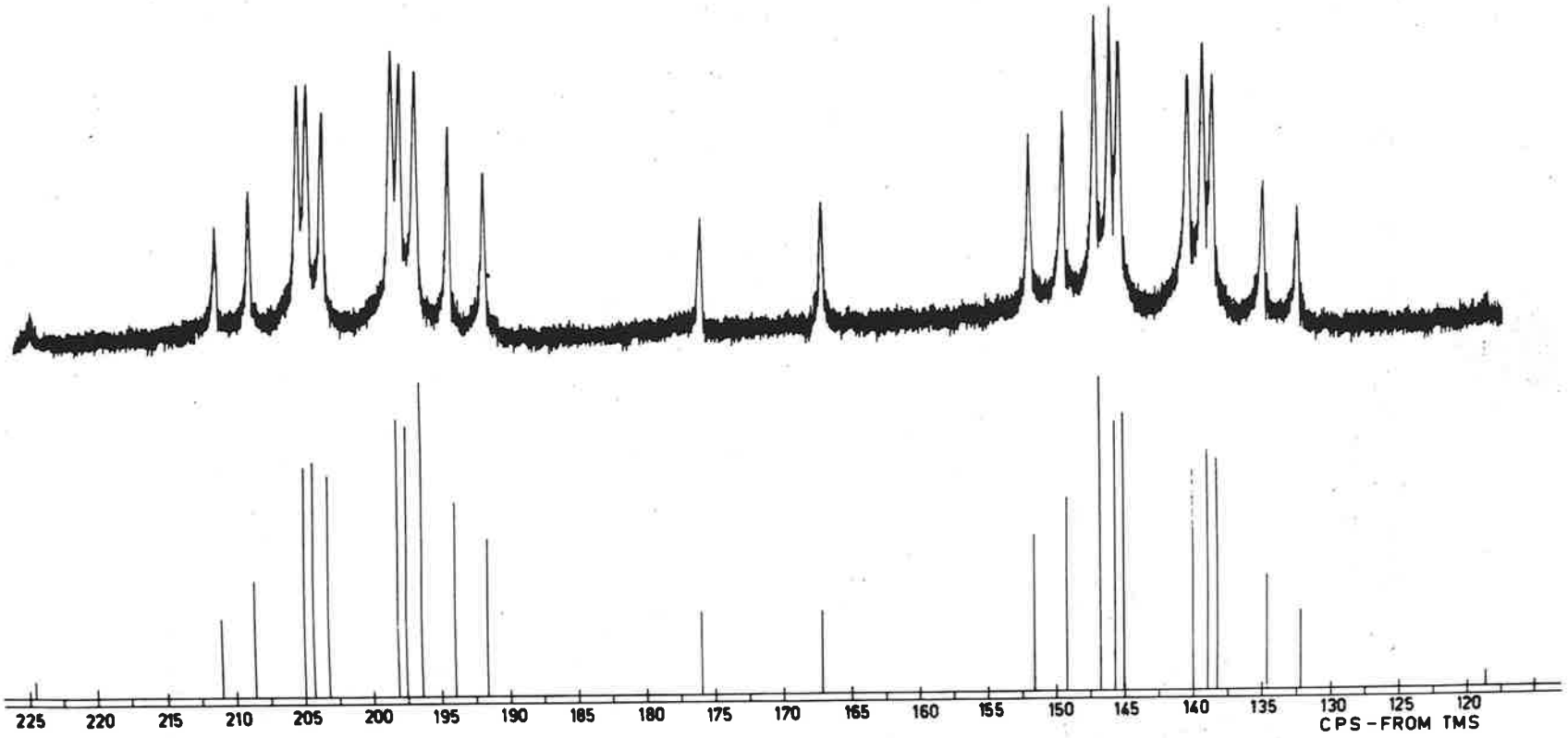

{D} DECOUPLED
230
220
210
200
190
180
170
160
150
140
130
CPS FROM TMS

FIGURE 1


225
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215
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195
190
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175
170
165
160
155
150
145
140
135
130
125
120
CPS - FROM TMS

FIGURE 2

116-24
TELEPHONE : MW 0522.

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

IN REPLY PLEASE QUOTE :

April 19,1968

Dr.B.L.Shapiro
Dept. of Chemistry
Stanford University
Stanford,California 94305,USA

GEMINAL COUPLING CONSTANTS IN Me_nX COMPOUNDS

Dear Barry,

Continuing our previous studies[1] in collaboration with Mr. M.Lacey , we have obtained J_{gem} in Me_4Sn and Me_4Pb from the appropriately deuterated compounds. The data in the table are for 5-10% solutions in carbon tetrachloride with 5% CH_2Br_2 used as lock (HA100 spectrometer).

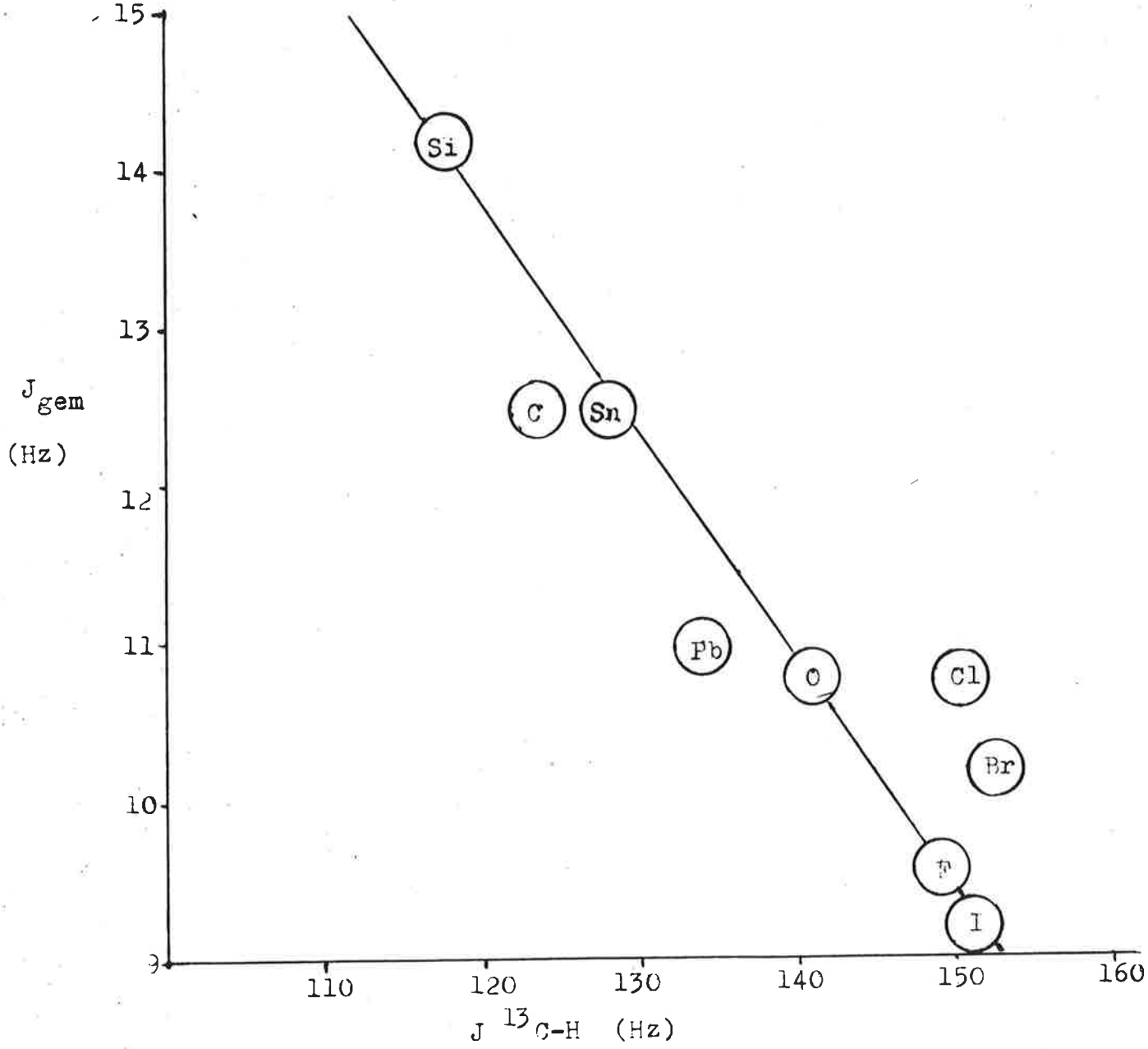
While J_{gem} in Me_nX is not expected to be simply related to electronegativity of X (E_X) , it is interesting that there is an approximately linear relation between J_{gem} and $J^{13}C\text{-}H$ in this series , which also holds reasonably well for the literature data for oxygen , fluorine and iodine and bearably for chlorine and bromine. In view of the apparently successful[2] correlation between E_X and $J^{13}C\text{-}H$ in Me_nX , it is possible that within a series confined to Me_nX (so as to avoid conformational effects) and with X bearing no pi bonds , J_{gem} may be related to E_X in a reasonably straightforward manner. Unfortunately few J_{gem} data are available and we are working on this at present.

With best regards, yours sincerely

(S. Sternhell)

[1] Macdonald,Shannon and Sternhell, Aust.J.Chem., 19 ,1527 (1966)
[2] Douglass, J.Chem.Phys., 45 , 3465 (1966)

Suostance	$\lvert J_{gem} \rvert$ (Hz)	$J^{13}C\text{-}H$ (Hz)	δ (ppm)
$Me_3C\text{-}CMe_3$	12.50±0.07	124.3±0.2	0.870
Me_4Si	14.15±0.08	117.8±0.3	0.000
Me_4Sn	12.45±0.07	127.8±0.3	0.073
Me_4Pb	11.00±0.07	134.3±0.3	0.732



116-26

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TÉL. 87-59-11

Dr Bernard L. SHAPIRO
Department of Chemistry
Stanford University

STANFORD, Calif. 94305
U.S.A.

RÉFÉRENCE A RAPPELER :
G/ COP. 1/68-

VOTRE RÉF. :

VOTRE LETTRE DU

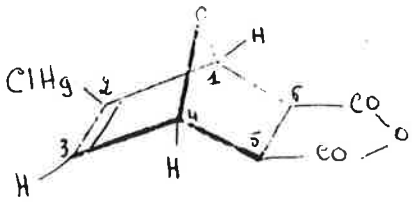
GRENOBLE LE 22 avril 1968

Cher Docteur SHAPIRO,

Je suis tout à fait désolé du délai avec lequel j'envoie cette contribution, et vous prie de bien vouloir m'en excuser.

Titre : Détermination par effet de solvant de signes relatifs de couplages ^{199}Hg-H.

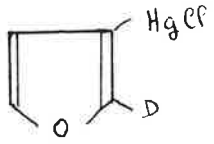
Dans le dérivé de synthèse diénique (I)



le mercure (isotope 199) est couplé aux trois protons H_1, H_3, H_4, tandis que pour H_6 le couplage n'est pas mesurable (disposition en "M" non respectée).

L'identification des protons H_1 et H_4 a été réalisée

de façon certaine en préparant un mélange de chloromercurifurannes partiellement deutérié où prédomine l'isomère :



Le spectre, schématisé sur la figure, conduit alors à l'analyse suivante :

δH_1 = 5,4 p.p.m $|J_{Hg-H_1}|$ = 10,2 c.p.s $J_{H_1H_3} \simeq 0$

δH_3 = 6,5 p.p.m $|J_{Hg-H_3}|$ = 145 c.p.s $|J_{H_1H_4}|$ = 0,8 c.p.s

δH_4 = 5,3 p.p.m $|J_{Hg-H_4}|$ = 29,6 c.p.s $|J_{H_3H_4}|$ = 1,6 c.p.s

Les signes relatifs des trois constantes de couplage ^{199}Hg avec H_1, H_3, H_4, ont été déterminés par l'utilisation d'un effet de solvant :

- dans le mélange D.M.S.O-Acétone utilisé comme solvant, les six satellites A_1B_1, A_3B_3 et A_4B_4 ont des déplacements chimiques distincts et sont tous analysables au premier ordre. En particulier le satellite B_3 est un doublet (figure de gauche, $\delta_{B_1} \neq \delta_{B_4}$) ;

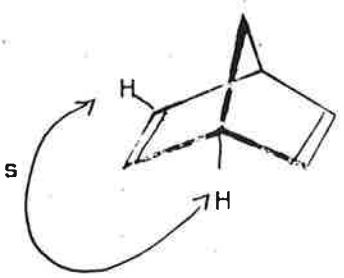
- si l'on ajoute C_6D_6 au mélange précédent, la différence entre δ_1 et δ_4 augmente, et l'on peut régler la quantité de C_6D_6 pour que B_1 et B_4 aient le même déplacement chimique. On constate alors sur B_3 des modifications explicables par des effets du second ordre : la figure de droite montre ces modifications, ainsi que le spectre théorique attendu calculé ($\delta_{B_1} = \delta_{B_4}$).

Cette expérience démontre que les trois satellites B_1, B_3 et B_4 correspondent au même état de spin du mercure, et que les trois couplages sont de même signe. Il a été

partiellement confirmé par double irradiation : l'irradiation de A_1 transforme le doublet A_3 en singulet.

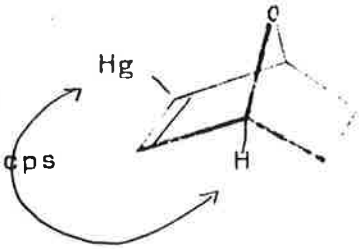
En conclusion, pour (I), dans les fragments Hg-C-C-H (J = ±10,2 c.P.s) et Hg-C≡C-H (J = ±145 c.p.s), on a trouvé un exemple où, dans le fragment Hg-C=C-C-H, le couplage est également de même signe (±29,6 c.p.s).
Ce résultat peut être rapproché des cas où les couplages allyliques H-C=C-C-H sont également positifs, comme dans l'exemple de MORTIMER :

J = +1 cps



à comparer à

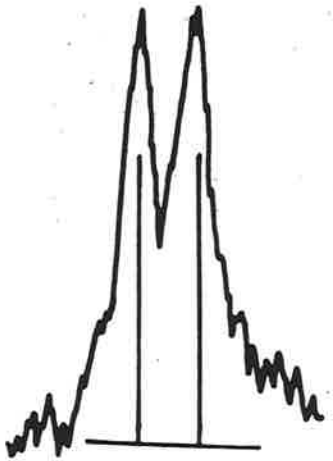
J = +29,6 cps



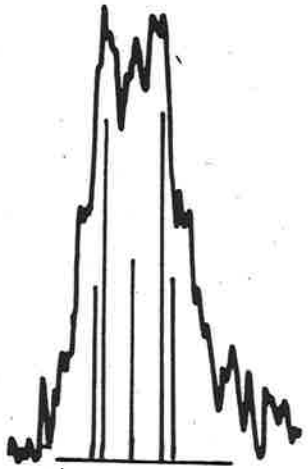
Didier GAGNAIRE

Danielle GUYOT

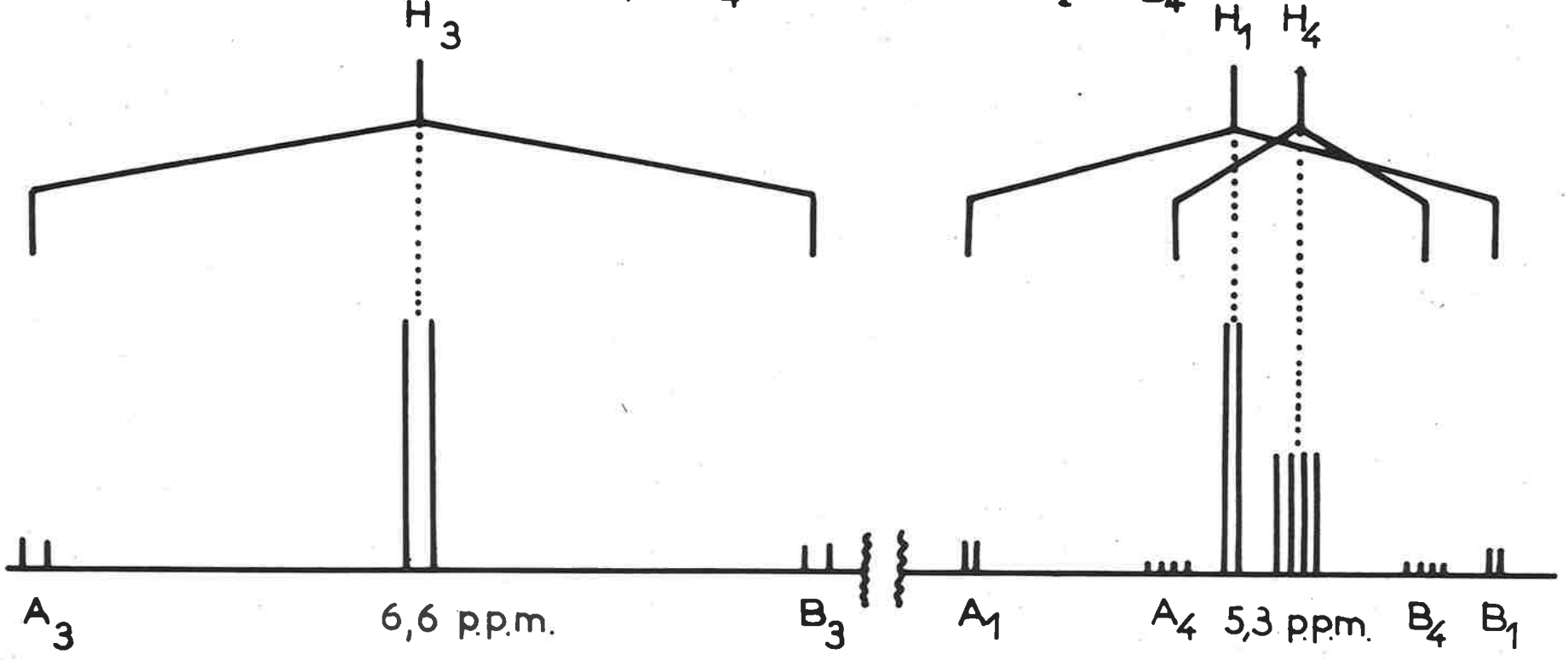
Observation
du satellite B_3



Quand $\delta_{B_1} \neq \delta_{B_4}$



Quand $\delta_{B_1} = \delta_{B_4}$



THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175
CINCINNATI, OHIO 45239

March 29, 1968

Dr. B. L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

Dear Barry:

The Tau Scale versus Delta Scale Conflict

A recent letter from Richard Mattoon to IITNMR [114, 24 (1968)] gave an account of the proposals of the American Society for Testing and Materials (ASTM) concerning NMR.

One point he raised concerned whether to use the tau (τ) or delta (δ) scales when reporting H^1 chemical shifts. He said that the NMR subcommittee (E-13·7) of the ASTM "strongly urges the τ-minority to cease using that arbitrary 10." The ASTM's proposals for referencing H^1, F^{19}, and C^{13} spectra are repeated below:

H^1 - "5·1·2 The numbers on the dimensionless (shift) scale downfield from TMS should be positive."

F^{19} - "6·1·1 The numbers on the dimensionless (shift) scale upfield from the reference should be positive."

C^{13} - "6·2·1 The numbers on the dimensionless (shift) scale upfield from the reference should be positive."

We have three comments:

(1) A survey of papers using either the τ- or δ-scales in four journals (the issues were picked at random) gave the following results:

Journal	δ-Scale	τ-Scale	Total
J.A.C.S., March, 1968	11	7	18
J. Org. Chem., March, 1968	41	20	61
Can. J. Chem., [21(Org)] 1967	5	6	11
J. Chem. Soc., [C(Org)] 1968	0	18	18
TOTALS	57	51	108

THE PROCTER & GAMBLE COMPANY

Although not statistically perfect, we do not consider that these results indicate a "τ-minority" as the ASTM would have us believe.

(2) The ASTM's proposals concerning the referencing of H^1, F^{19}, and C^{13} spectra are inconsistent (paragraphs 5·1·2, 6·1·1, 6·2·1 above).

(3) It was very obvious from the above survey several authors who used the δ-scale did not say so. Most of these did mention TMS being used as an internal reference, but that was all. It was left up to the reader to determine which scale was being used by, say, seeing whether a Me-group was given a small or a large chemical shift.

As many chemists (including ourselves) use the τ-scale, we do not feel that it is possible at the present time for the "τ-school" to change to the "δ-school" or vice versa. It is unfortunate that both scales are so well established and it seems to us that we are just going to have to live with the two side by side. This predicament is not quite as serious as that of the infrared spectroscopists, who have to take reciprocals to convert from wavenumbers to microns.

Sincerely yours,

THE PROCTER & GAMBLE COMPANY
Research and Development Department

Roger E. Reavill

Roger E. Reavill

T. J. Flautt

T. J. Flautt
Research Division

RER/lkb
cc: R. W. Mattoon
E. G. Brame

AMERICAN SOCIETY FOR TESTING AND MATERIALS

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SECRETARY: R. A. O'DELL, MC NEIL LABORATORIES, INC., CAMP HILL ROAD, FORT WASHINGTON, PA. 19034

Address reply to →

CONTROVERSY OVER TAU VERSUS DELTA SCALE IN PROTON NMR

Recently I received a copy of a letter sent to Barry Shapiro concerning the conflict of the tau scale vs. the delta scale. As chairman of ASTM E-13.7, I was most interested to read the comments made in that letter. In the first place, I would like to say that the terms, symbols, and conventions that were adopted by ASTM have taken into consideration a conflict that has existed for many years over the use of the 2 scales in proton resonance work. The decision of the ASTM committee for a number of years was to hold back on any particular recommendation until the field developed more fully. Now, of course, the field has become much more fully developed. Much of this can be credited to continued improvements in NMR instrumentation. Nevertheless, because of the reference signal from TMS occurring at high field relative to most resonances in the proton resonance spectra, the inconsistency that faces those who are working in NMR can be at least two-fold. The first of these two inconsistencies can be in the definition of direction of the scale and the second can be in the definition of the number to be assigned to the internal standard. As you pointed out in your letter, one inconsistency still shows up in the recommendations: thus for proton resonance the scale downfield from TMS should be positive whereas the scale downfield from the resonances in F^{19} and C^{13} spectra should be negative. This inconsistency can be rationalized only on the basis of the relative amount of use of the proton resonance vs. other nuclear resonances. However, the second possible inconsistency is eliminated by the adoption of these recommendations. That is the number to be assigned to primary internal (external) standards to be used in NMR. By proceeding in that fashion we would eliminate the definition of the tau scale and any other conjured up scales that might arise among any other resonances. Therefore, we wholeheartedly support the use of the delta scale in the use of proton resonance data and we hope that journal editors will adopt the recommendations of the ASTM committee for reporting NMR data in their journals.

You showed in your letter an interesting statistic in the use of the delta vs. tau scale. However, I would like to point out to you that the statistic was weighted even though you indicated that the issues were picked at random. The weighted statistic comes from the use of the Journal of the Chemical Society. Since the British Chemical Society has adopted the use of the tau scale for data to be reported in the Journal of the Chemical Society, naturally any proton data that appears in issues of that journal will be in the tau scale. Thus, if you remove the statistic of that journal from your total listing, you will find that the delta scale is used significantly more than the tau scale by the order of 57 to 33.

Thank you very much for your comments and I trust you will accept my comments in a positive way. I realize that there are some who have compiled a great amount of data using the tau scale and that it is not that difficult to translate numbers from the tau scale to the delta scale or vice versa.

Edward G. Brame, Jr.
Chairman
Sub-Committee ASTM E-13.7

EGB/dd

STANFORD UNIVERSITY
STANFORD, CALIFORNIA

DEPARTMENT OF CHEMISTRY

29 April 1968

CONCERNING PROTON CHEMICAL SHIFT SCALES

The above ever-fresh topic was one of many subjects discussed at a November 29, 1967 meeting chaired by the undersigned at the National Academy of Sciences in Washington, D.C. This meeting included twelve very diverse NMR practitioners who gathered as an ad hoc subpanel on NMR spectroscopy to advise the National Standard Reference Data System of the National Bureau of Standards through the National Research Council Office of Critical Tables.

Of the twelve NMR practitioners, nine were strongly in favor of the δ-scale for proton NMR, while only three considerably less vociferous proponents favored the τ-scale. Accordingly, the subpanel recommended that the NBS data compilation effort (see IIT NMR Newsletter No. 114, page 65 (March 1968)) adopt the (usual) δ-scale for its own use and for general promulgation.

The arguments adduced were the usual ones which I am not moved to regurgitate here. ("This is a horse which, even if it were still alive, I would not choose to ride."*) There seemed to be general feelings that this controversy has really outworn its welcome and utility, that the momentum of usage strongly favors the δ-scale, and that the lack of ambiguity was the only really important feature of any scale.

It would not surprise me if the NBS subpanel is moved to have further words on this subject as our work continues.

B L Shapiro

B. L. Shapiro, Chairman
Ad hoc Subpanel on NMR Spectroscopy
Advisory to NSRDS through NRC-OCT

* Albert J. Guérard, Jr. - Lecture in "Comparative Literature 166", Harvard University, Spring 1955 ± 1.

Dr. W. Brügel i.Fa.
Badische Anilin- & Soda-Fabrik AG · Ludwigshafen am Rhein

Luftpost

Herrn
Prof. Dr. B.L. Shapiro

Department of Chemistry
Stanford University

Stanford, California 94305
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		Dr.Brü/Fa	(0621) 60...	464...	23. 4. 1968

Betreff Corrigendum for long range coupling in lactams

Sehr geehrter Herr Professor Shapiro!

Leider hat sich in meinen letzten Brief (IITNMR-Newsletter No. 114) durch den Wegfall einer Zeile ein Widerspruch eingeschlichen. Der zweite Absatz meines Briefes muß richtig folgendermaßen lauten:

"Ein anderer Befund der genannten Autoren kann von uns ebenfalls erweitert werden. Sie fanden in ß-Lactamen keine Kopplung zwischen dem Amidproton und den Protonen in der (unmittelbar benachbarten) 4-Stellung. Dies gilt nach unseren Beobachtungen auch noch für Pyrrolidon, jedoch nicht mehr für Capro- und Capryllactam sowie für die erwähnten ungesättigten Caprolactame mit der Doppelbindung in 3-, 4- und 6-Stellung. In diesen Fällen besteht jeweils eine Kopplung mit einer Kopplungskonstante von ungefähr J = 5.5 Hz*."

Soweit mein Corrigendum. Seit ungefähr einem halben Jahr verfügt die BASF über ein HR-220. Wir haben uns inzwischen an die Eigenheiten dieses Instrumentes gewöhnt und schon viele Ergebnisse erzielt, die wir sonst nur mühevoll oder überhaupt nicht hätten gewinnen können. Ich habe auch wieder meine alten Arbeiten über die Analyse der sehr komplexen Spektren von monosubstituierten und 1.2-disubstituierten Naphthalinen aufgenommen, über die ich vor längerer Zeit (Mello-NMR, No. 59, August 1963) berichtet habe. Damals war ich bei der vollständigen Analyse gescheitert. Mit dem neuen Instrument sieht die Sache sehr viel hoffnungsvoller aus. Vermutlich werde ich in Kürze darüber weiter berichten können.

Mit den besten Grüßen

Ihr sehr ergebener

(Dr. W. Brügel)

* zwischen NH und NCH_2

057883n 25M 696 Lg.-Nr. 9030021

THE UPJOHN COMPANY

KALAMAZOO, MICHIGAN 49001
TELEPHONE (616) 345-3571

April 2, 1968

Professor B. L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

Dear Barry:

We have been calculating ABX spectra by LAOCN3 and EXAN-II to investigate some of the deceptions and pitfalls that can be encountered in this system. After studying the letter of Diehl and Chuck (IITNMR 106/31) we became interested in those cases in which the AB part had less than eight lines because

$$\nu_A - \nu_B = \frac{1}{2} (|J_{Ax}| - |J_{Bx}|).$$

Some examples were found in the Varian catalog. No 503 (Figure 1) and no 410 (Figure 2) are good examples of 5-line AB cases. The 60-mHz spectrum of no 382 (Figure 3) contains a 4-line AB part owing to the overlap of the degenerate ab singlet with one of the lines of the other ab subspectrum. R. K. Kulling has discussed a 5-line AB situation in these letters (IITNMR, 88/12) and Kim and Anderson have recorded a similar situation (IITNMR, 104/3).

Using the terminology and format of Diehl and Chuck, it appeared that the 5-line situation could be encountered in either non-eclipsed, or eclipsed cases (Figure 4-IB and -IIB, respectively) where the signs of the weak couplings are either <u>like</u> or <u>unlike</u>, respectively. With like-sign cases, the singlet could appear anywhere outside the ab of the remaining quartet and with unlike-sign cases, the singlet could appear anywhere within the ab of the remaining quartet. If J_{Bx} was zero, a degenerate 5-line case with the singlet superimposing the terminus of the ab of the remaining quartet (Figure 4-IIC) could occur.

The above examples were all like-sign cases. Since no example of an unlike-sign case was available, we have calculated one (Figure 5). Careful choice of parameters gave rise to an overlap of the degenerate singlet with one of the inside lines of the remaining ab lines yielding an ABX with a 4-line AB part and quite deceptive in general. In the X-part, the four principal lines have collapsed to two lines and the combination lines are quite intense. We tried this spectrum on a number of our chemist friends and they all agreed it was indeed deceptive.

The spectrum of 5-hydroxynaphthoquinone brought out an interesting observation on the application of LAOCN3. The three-spin system is an example of an ABC

case which is almost degenerate (Figure 6). The small shoulder in the spectrum at 438.3 is attributed to residual protons in the chloroform solvent. In analyzing the spectrum by LAOCN3 it was not detected that the tall line had a width greater than the others, hence this line was entered as a singlet. The analysis would not converge. Dr. Bothner-By pointed out that the reason for non-convergence was in the treatment of the tall line as a singlet. To assign the two center lines of an AB multiplet, the same frequency tells the iteration process that this is an A_2 subspectrum and therefore $\frac{\partial \nu}{\partial \omega} = 0$ where ν is the frequency of line B and ω is its chemical shift. To separate ν_3 and ν_4 according to $\nu_3 - \nu_4 = \Delta p \frac{\partial \nu}{\partial \omega}$ the value of Δp goes to infinity and the iteration fails. To avoid this problem, the lines were reassigned with a 0.2-Hz frequency difference and the iteration converged successfully, giving the two solutions of Figures 7 and 8. The intensity relationship of the weak lines in the spectrum leads to a choice of the parameters of Figure 7 as the true solution.

Another alternative is to leave the two tall lines out of the iteration altogether. This gave a slightly different result which may have been less accurate.

We also found a problem with LAOCN3 on the 360 computer. The DIFFER subroutine has three DO-loops and two GO TO statements all ending at statement 57. Apparently this doesn't work in a 360/30. We got to 57 from the GO TO statement without going through the DO-loops, but the computer then tried to go back through the smallest DO loop ending at 57. The calculation bombed because the values for the variables were unknown. The problem is easily corrected by separating the loops (Table I).

The LAOCN3 program was modified by Drs. B. V. Cheney and D. J. Duchamp to run on the IBM 360/30 computer. The plot program was written by Dr. Cheney and the problem in DIFFER was diagnosed by Dr. Duchamp.

Very truly yours,

George Slomp

George Slomp, Jr., Ph.D.
Physical and Analytical Chemistry

GS/elm

Enclosures

Subject: Analysis of Some ABX SPECTRA With LAOCN3.

FIGURE 1.

EXAMPLE OF A FIVE-LINE AB PART OF AN ABX SPECTRUM--LIKE SIGNS

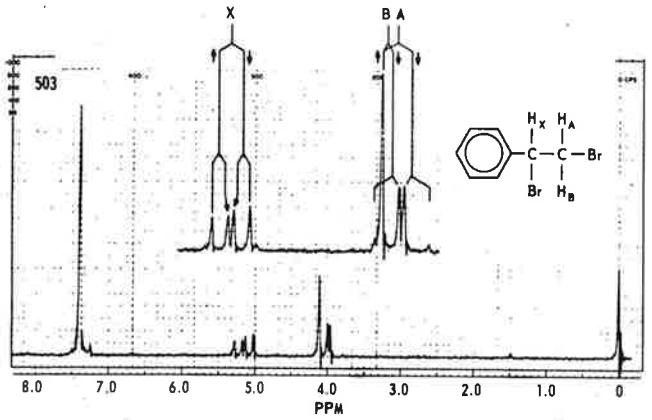
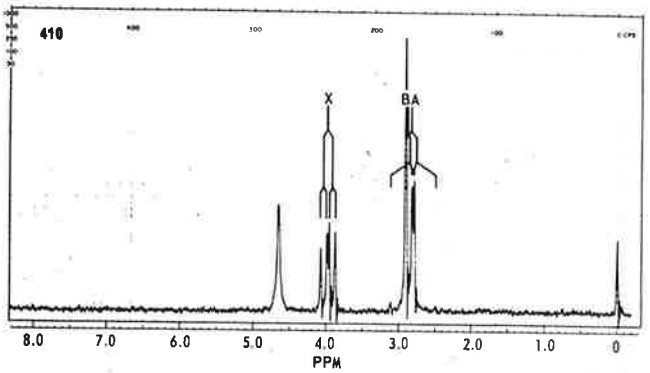


FIGURE 2.

EXAMPLE OF AN ABX SPECTRUM WITH A FIVE-LINE AB PART--LIKE SIGNS



COMPUTED SPECTRUM--ABX WITH FIVE-LINE AB--LIKE SIGNS

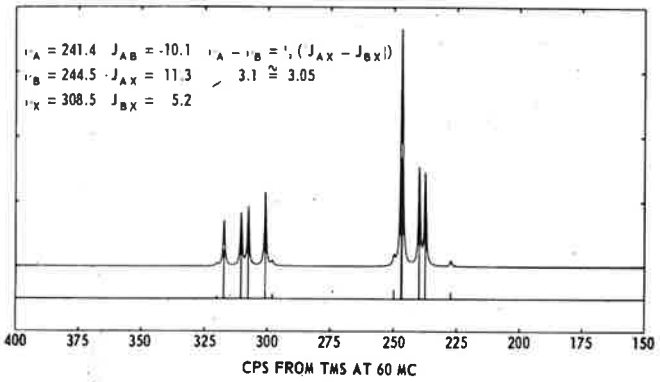


FIGURE 3.

EXAMPLES OF A SEVEN-LINE AND A FOUR-LINE AB PART OF AN ABX SPECTRUM--LIKE SIGNS

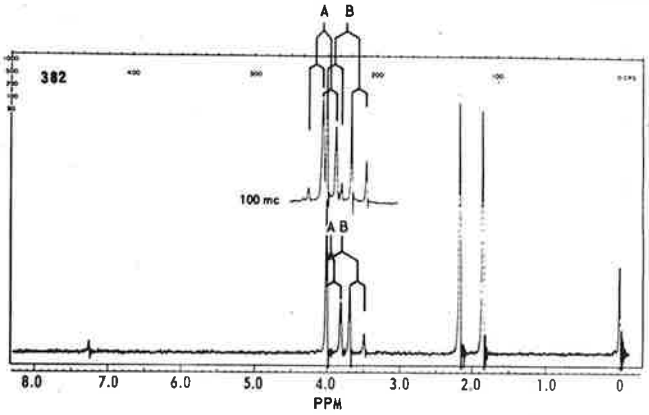


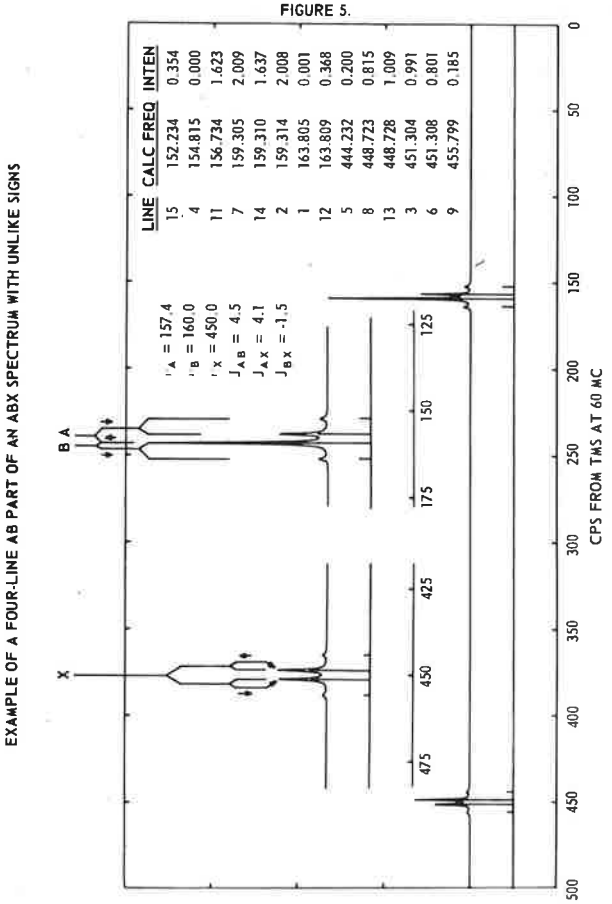
FIGURE 4.

ADDITIONAL TYPES OF AB SUBSPECTRA

AB SUBSPECTRUM	REL. SIGNS J_{AX}, J_{BX}	AB SUBSPECTRUM	REL. SIGNS J_{AX}, J_{BX}
IB. -NE. 5-LINE		III. -PARTLY ECLIPSED	
a.	LIKE	a.	LIKE
		b.	UNLIKE
IIB. -E. 5-LINE		IIC. -DEGEN. 5-LINE	
a.	UNLIKE	a.	0

FIGURE 5.

EXAMPLE OF A FOUR-LINE AB PART OF AN ABX SPECTRUM WITH UNLIKE SIGNS



CALCULATED SPECTRUM FOR 5–HYDROXYNAPHTHOQUINONE

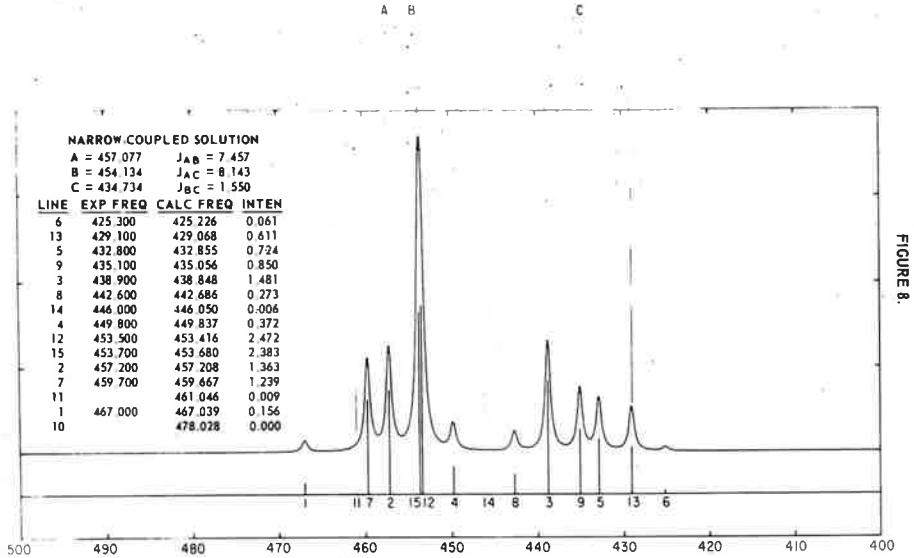


FIGURE 8.

PORTION OF THE NMR SPECTRUM OF 5–HYDROXYNAPHTHOQUINONE

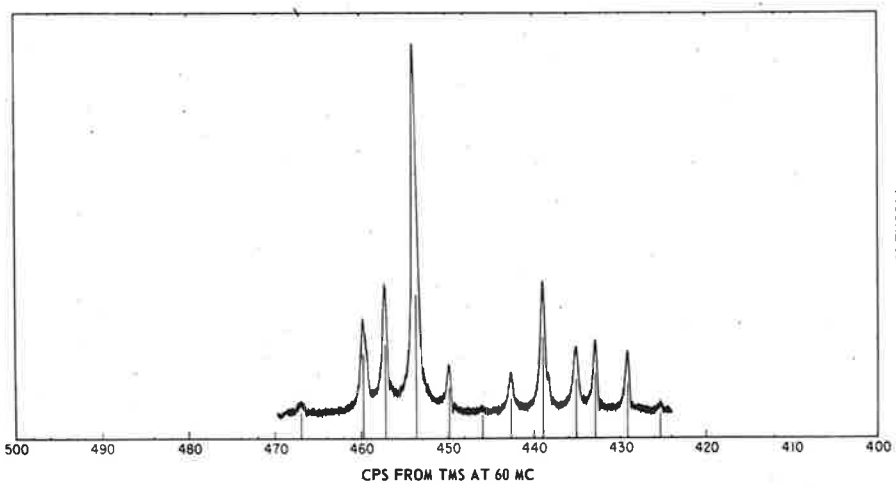


FIGURE 6.

CALCULATED SPECTRUM FOR 5–HYDROXYNAPHTHOQUINONE

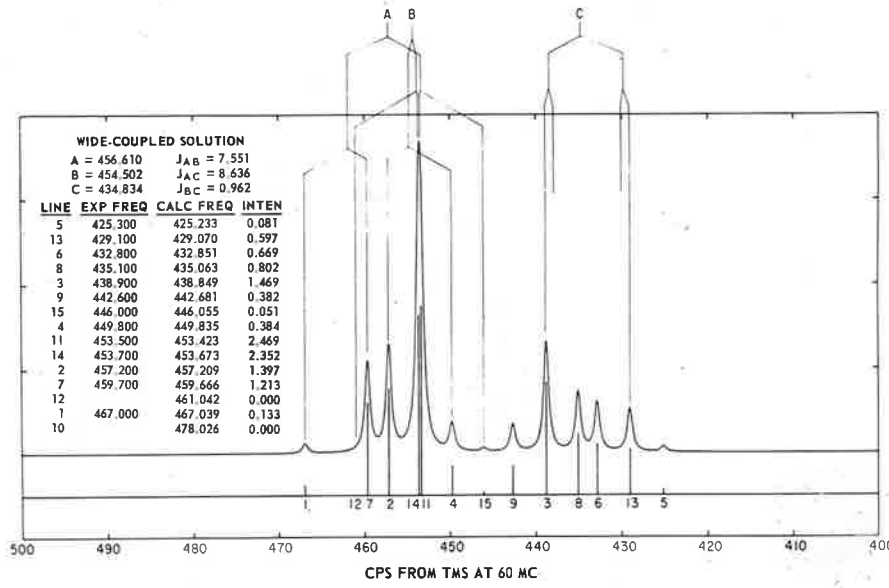


FIGURE 7.

TABLE 1. REVISED DIFFER SUBROUTINE.

```
                                DISK OPERATING SYSTEM/360 FORTRAN   360N-FO-451 22
      SUBROUTINE DIFFER(MOA,NA)
      DIMENSION IL(351),F(351),CORR(14),ISO(7),W(7),A(7,7),IA(15,6),
     1IB(15,6),FZ(128,7),NO(8),LL(8),NP(128),BI350),DI(128,14),BV(14),
     2VB(35,35),E(128),CO(128,14)
      COMMON NOS,NN,NL,NI,IL,F,CORR,ISO,W,A,IA,IB,FZ,NO,LL,NP,B,CO,D,BV,
     1VB,E
      DO 58 J=1,MOA
      JL=J+LL(NA)-1
      DO 58 NS=1,NOS
      D(JL,NS)=0.
      DO 257 NPS=1,6
      IF(IA(NS,NPS)) 9999,58,37
   37 IAS=IA(NS,NPS)
      IF(IB(NS,NPS)) 9999,39,43
   39 DO 41 K=1,MOA
      KL=K+LL(NA)-1
   41 D(JL,NS)=D(JL,NS)+VB(K,J)*VB(K,J)*FZ(KL,IAS)
      GO TO 257
   43 IBS=IB(NS,NPS)
      DO 46 K=1,MOA
      KL=K+LL(NA)-1
   46 D(JL,NS)=D(JL,NS)+VB(K,J)*VB(K,J)*FZ(KL,IAS)*FZ(KL,IBS)
      IF(ISO(IAS)-ISO(IBS)) 257,48,257
   48 MOAM=MOA-1
      IF(MOAM)257,257,54
   54 IOIF=(2**IBS-2**IAS)/2
      DO 157 JA=1,MOAM
      JAL=JA+LL(NA)-1
      JAP=JA+1
      DO 57 KA=JAP,MOA
      KAL=KA+LL(NA)-1
      IF(NP(KAL)-NP(JAL)-IOIF) 57,66,57
   66 SS=0.
      DO 68 KM=1,NN
   68 SS=SS+(FZ(KAL,KM)-FZ(JAL,KM))**2
      NTST=SS+0.1
      IF(NTST-21) 57,56,57
   56 D(JL,NS)=D(JL,NS)+VB(JA,J)*VB(KA,J)
   57 CONTINUE
  157 CONTINUE
  257 CONTINUE
   58 CONTINUE
   59 RETURN
 9999 STOP
      END
```

116-40

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
FOOD AND DRUG ADMINISTRATION
WASHINGTON, D.C. 20204

April 26, 1968

Professor Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

Dear Barry:

There is a gap to be filled in the range of precision of peak position measurements, attainable with field-frequency locked spectrometers.

On the one hand, with the usual set-up, say, an HA-100, one can determine peak positions with the DIF 1 circuit to 0.1 - 0.05 Hz, and/or perhaps by reading them off the chart directly. The latter method presupposes a certain degree of confidence in the linearity of the sweep. On the other hand, Ray Freeman and Bo Gestblom recently advanced a couple of orders of magnitude beyond 10^{-1} Hz (see IITMMRN 113,47). This required somewhat unusual instrumental conditions and a lot of patience. I should like to describe now how a precision in the centihertz region can be reached with only moderate demands on instrumentation and operator.

Coming back to DIF 1: the corresponding circuitry does not give out a clean sine wave, but a superposition of time-dependent wiggles; therefore, a counter operating in the period-averaging mode will show appreciable flutter in the last digits. The manual oscillator (MO) and sweep (SW) frequencies, when monitored separately in the same way, appear to be "steadier" than DIF 1 by at least one order of magnitude. This observation suggested the use of two separate counters for the MO and SW frequencies.

I have been using the relatively slow (and inexpensive) HP 5512A for the MO frequency, since under good ambient conditions this MO frequency drifts only very slightly; for the SW frequency, any counter capable of giving a period-average display about twice a second will do, e.g. an HP 5254L. Then, by sweeping slowly (0.01 Hz/sec), by measuring the above frequencies simultaneously, and by repeating the process at least three times, one can obtain peak positions reproducible to about 0.01 Hz.

Thus the potential of the HA-100, as far as precision measurements is concerned, has been realized in a rather simple way. This centihertz precision has made it possible to obtain more meaningful results from the iterative treatment of experimental data, than "0.05 Hz" data allowed us to do in the past. Representative r.m.s. errors were, in the case of some six-spin systems, of the order of 0.03 Hz.

Sorry for having to be reminded. Best wishes and regards.

Sincerely,

Ernest

Ernest Lustig
Division of Food Chemistry
Bureau of Science SC-410

Suggested title: One Sensible Centihertz

116-42

THE UNIVERSITY of ROCHESTER
School of Medicine and Dentistry
Rochester, New York 14620
TELEPHONE 716-473-4400

DEPARTMENT OF RADIATION BIOLOGY
AND BIOPHYSICS

April 26, 1968

Dr. Bernard L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94305

Dear Dr. Shapiro:

I am enclosing an abstract of some pmr work which we have just submitted to J. Am. Chem. Soc. I hope that it will enable me to receive the IITNMR Newsletter.

All previous interpretations of the pmr spectra of adenine 5'-nucleotides have been based on the $H_{1'}$, $H_{5'}$, H_2 and H_8 resonances because of the previous inability to obtain spectra in which the $H_{2'}$, $H_{3'}$ and $H_{4'}$ signals were separate. We have obtained spectra in D_2O in which these latter three resonances are separate and have identified them. A typical spectrum is enclosed. The $H_{2'}$ and $H_{3'}$ signals are pseudo-triplets because of the closeness of the relevant coupling constants, which are $J_{1'-2'}$ = 5.3 cps, $J_{2'-3'}$ = 4.8 cps and $J_{3'-4'}$ = 3.8 cps. The $H_{4'}$ peak is only poorly resolved because of coupling not only to $H_{3'}$ but also to $H_{5'}$, $H_{5''}$ and to P. The assignments were made by comparing 5'-AMP spectra with those of 2'-AMP and 3'-AMP. (Because I have not yet mastered the art of spin-decoupling, Laurie Colebrook has very kindly verified the $H_{2'}$ assignment for me. Irradiation of $H_{1'}$ collapsed $H_{2'}$ to a doublet. This automatically verified $H_{3'}$ and $H_{4'}$ because of the fine structure of $H_{3'}$ and poor resolution of $H_{4'}$.) Investigation of the 5'-AMP spectrum under various solution conditions and comparison with 5'-dAMP and ATP spectra has led us to relate the chemical shift of the ribose protons with the torsion angle, ϕ_{CN}, the stacking and the freedom of rotation of the phosphate group.

The relative order of the ribose protons in ATP are the same as in AMP. The coupling constants of ATP and 5'-AMP are sufficiently similar to indicate very little difference, if any, in the ribose conformation in these two nucleotides.

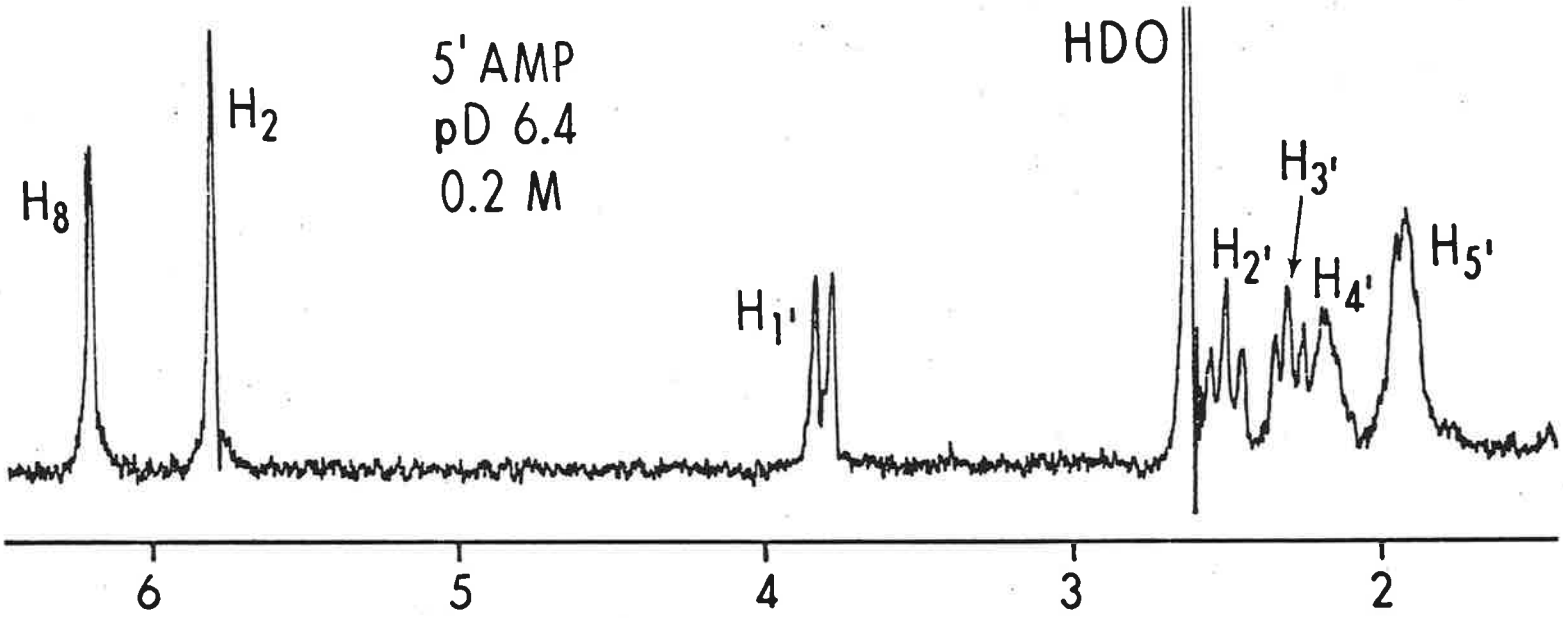
This work was done in collaboration with Dr. Raghunath P. Agarwal of Roorkee, India.

Yours sincerely,

Isaac Feldman

Isaac Feldman
Professor of Radiation Biology and
Biophysics (Physical Chemistry)

IF:jl
Enclosure



Legend to Figure 1

ppm downfield from acetone standard.

100 MHz pmr spectrum of 0.2M 5'-AMP at pD6.4 and 27°C.

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