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NOVEMBER, 1969

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                 No. 136:  5 January 1970
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All Newsletter correspondence, etc., should be addressed to:

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

UNIVERSITY OF BRADFORD

School of Chemistry
Bradford 7, England
Telephone 29567 or 33466
Telex 51309 University Brad

Vice-Chancellor and Principal
E G Edwards PhD FRIC

Please quote ref DWJ/JB

6th October, 1969.

Dr. Bernard L. Shapiro,
TAMUNMR Newsletter,
Dept. of Chemistry,
Texas A and M University,
College Station,
Texas 77843,
U.S.A.

Dear Dr. Shapiro,

"SIMPLE" ABX/ABC SPECTRA IN POLYNUCLEAR HYDROCARBONS

What we term "simple" ABX spectra, in which one AB sub-spectrum appears to be degenerate, are frequently met in the polynuclear series since the chemical shifts of the non-angular protons are usually either very close or are required by symmetry to be identical. Further, a methyl or hydroxyl substituent group in such a molecule has a similar effect on the chemical shifts of hydrogens in _meta_ as in _ortho_ positions; hence, for several 1-substituted polynuclears, $|\nu_2 - \nu_3|$ is small and approximately equal to $\frac{1}{2}(J_{24} - J_{34})$, so that the ABX/ABC spectra assume a simple form in the AB region. Among examples in the literature are (60MHz spectra) 1-methyl -, 1,8 -dimethyl- and 1-methyl -7- isopropyl phenanthrenes, 1,8 -dimethyldibenzothiophen, and 1,5 -dimethyl- and dihydroxynaphthalenes; recently, we have also found that 1,8 -dimethylnaphthalene, 3 -bromo- -1,8 -dimethylnaphthalene and 1,8 -dimethylbenzo [c] cinnoline (60 MHz), and 1,6,11 - trimethyltriphenylene (H(2) - H(4)) (100 MHz) are all of this simple ABX/ABC form. Calculation of model ABC spectra with parameters typical of 1-substituted polynuclear hydrocarbons showed that "simple" spectra may be expected for values of $\nu_A - \nu_B$ between 1 and 6Hz, and that, within these limits, the inner lines of the high-field AB sub-spectrum are unlikely to be resolved. Since, in addition, some of the outer lines are so weak that they may be lost in background noise, degenerate (usually five-line) spectra are commonly observed for each AB region.

Analysis of the "simple" three-spin systems by ABX as a preliminary to computer methods leads to a unique set of parameters provided that one of the two D values happens to coincide with $\frac{1}{2} J_{AB}$. Otherwise, two solutions are possible but use of differential solvent shifts or magnitudes of _ortho_ -coupling constants predicted from MO bond orders allowed us to distinguish between the alternatives for some of the above compounds.

The address of Dr. K.D. Bartle is now Department of Physical Chemistry, The University, Leeds, 2, England.

Yours sincerely,

K. D. Bartle.   D.W. Jones.   R.S. Matthews.

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO ·   SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY
REVELLE COLLEGE

POST OFFICE BOX 109
LA JOLLA, CALIFORNIA   92037

October 3, 1969

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

Dear Barry:

Spin-Rotation Shielding - a Useless Result?

Your little blue thing catches me with the following possibly useless calculation
of a neglected interaction.

Because of the heroic structures built upon measured chemical shift differences,
one must beware that all contributions to this shift are accounted for. The
hyperfine spin-rotation interaction $\mathcal{H}_{SR} = - I.C.J$ can contribute to the static
shielding of spin I through the trace $3C_a$ of the tensor C; the remainder of C
yields, in gases and liquids, a relaxation path for I. We have

$$< \mathcal{H}_{SR}> = - C_a<I.J> = - C_a I_z <J_z> \text{ in high field limit}$$

$$= - C_a I_z \text{Tr}\{J_z \rho_{JKM}\} \tag{1}$$

where ρ_{JKM} is the equilibrium density matrix for the molecular rotational states
and yields the normalised Boltzmann probabilities. $\langle J_z \rangle$ does not vanish in the
NMR experiment due to molecular orientation polarization from the molecular
Zeeman interaction which lifts M degeneracy:

$$\mathcal{H}_{Z,mol} = - \mathcal{G}_J \mu_N J.H = - \hbar \omega_J J_z \tag{2}$$

For a spherical top molecule in the gas phase and in the "big molecule limit"
where the summations over discrete J states can be replaced by integrals we find
that

$$<J_z> = \frac{\hbar \omega_J}{2B} \text{ (B is molecular rotational constant)} \tag{3}$$

independent of temperature but linearly dependent on H_0 through (2). For a
$\Delta m = 1$ nuclear spin transition $<\mathcal{H}_{SR}>$ thus contributes a (paramagnetic for
$\mathcal{G}_J, C_a > 0$) shielding term

$$\Delta_{SR} = C_a \frac{\hbar \omega_J}{2B} \tag{4}$$

Values of the parameters C_a and ω_J are available for several tetrahedral mole-
cules from molecular beam data of the Harvard group
[Anderson and Ramsey, Phys. Rev. <u>149</u>, 14 (1966); Yi, <u>et al.</u>, ibid <u>165</u>, 92 (1968);

Professor B. L. Shapiro
October 3, 1969
Page 2

Ozier, et al., ibid 172, 63 (1968)] and are listed in the table for two molecules often used as NMR reference compounds.

	C_a (khz)	$\omega_J/2\pi$ in H_o=25 kg (khz)	B cm^{-1}	Δ_{SR} ppm	hz at 25 kg
CH_4	+10.4	$+6.0 \times 10^3$	5.24	1.9×10^{-3}	0.20
CF_4	6.85	6.0×10^2	0.189	3.7×10^{-3}	0.38

The final shielding contributions in the gas phase are fortunately quite small, although above present resoltuion limits. C_a values for C^{13} in CH_4 or CF_4 are not available, but could well be an order of magnitude larger, since this nucleus lies at the centre of mass. Then $\Delta_{SR}(C^{13})$ might amount to 0.1 ppm.

If equipartition of rotational energy obtains for these pseudospherical molecules on passage to the liquid phase, then the Δ_{SR} values in the liquid will be equal to those in the gas. On the other hand, the liquid Δ values will be reduced if rotational quenching occurs in the condensed phase. There is some evidence [Bloom, Proc. XIV Colloque Ampére Ljubljana, p. 65 (1966)] that the rotational diffusion model may not be valid for these liquid compounds. This would imply that rotational quenching is not complete, and thus there may be measurable static contributions to the shielding in certain cases. (C^{13} solvent shifts in $C^{13}F_4$?)

Yours sincerely,

Ted

E. J. Wells

EJW:gr

P.S. I shall be returning to Simon Fraser in December after enjoying Bob Vold's hospitality here at UCSD for several months.

AKU N.V. - ARNHEM

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

U.S.A.

| Uw kenmerk	Uw brief van	Ons kenmerk	Toestel
		WH/JH	

Datum October 3, 1969.

ONDERWERP: The NMR Spectrum of Ethylene Sulphoxide

Dear Professor Shapiro :

We would like to report in this contribution to the Newsletter the NMR parameters for ethylene sulphoxide, obtained from the 60 and 100 MHz spectra with the aid of spin-tickling experiments and the computer programs NMREN and NMRIT. In this molecule, which has a plane of symmetry perpendicular to that of the ring, H(1) and H(2) are chemically equivalent, as are H(3) and H(4), the interactions between all these protons forming an AA'BB'-system:

H(1)   H(2)

H(3)   H(4)

0
|
S
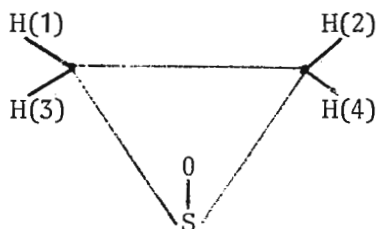
The 100 MHz spectrum of the compound dissolved in carbontetrachloride is given in Fig. 1, and consists of two sets of 10 lines, each set marked from a''' to j'''. Spin-tickling of the lines j', i' and h' leads to splitting of the groups of lines (a' and e), (b and i) and (a' g and h) respectively, as is shown in Fig. 2.

A comparison of the 60 and 100 MHz spectra, and the results of the spin-tickling experiments, enable us to assign the experimental lines to the transitions as shown in the energy level diagram given in Fig. 1.

AKU N.V.

Geadresseerde	Ons kenmerk	Datum	Bladnr.
Prof. Shapiro	WH/JH	Oct. 3, 1969.	-2-

Iterative calculations with the NMRIT computer program yield the following parameters for the 60 and 100 MHz spectra:

Table 1.

	60 MHz	100 MHz
$\delta_1 = \delta_2$ $\delta_3 = \delta_4$ } in PPM	1.869 ± 0.0005 2.252 ± 0.0005	1.869 ± 0.0003 2.251 ± 0.0003
J12 (cis)	+ 11.98 ± 0.07 Hz	+ 11.77 ± 0.08 Hz
J13 = J24 (gem)	− 6.50 ± 0.05 "	− 6.41 ± 0.05 "
J14 = J23 (trans)	+ 11.06 ± 0.05 "	+ 10.75 ± 0.05 "
J23 (cis)	+ 12.06 ± 0.07 "	+ 11.80 ± 0.08 "
average deviation from the line positions	0.07 Hz	0.06 Hz

It is interesting to note that the cis and trans coupling constants have unexpectedly high positive values, while the geminal coupling has a high negative value, relative to other three-membered rings (see Table 2).

Table 2.[1]

$CH_2 - CH_2$ x	Jgem	Jcis	Jtrans
x = CH_2	− 4.5	9.2*	5.4*
S	0 *	7.1	5.6
NH	+ 2.0*	6.3	3.8
O	+ 5.5*	4.5	3.2

* Values for methyl derivatives.

The data in this table clearly show[1] that with increasing electronegativity in the series x = CH_2, S, NH, O, the values of the observed cis and trans couplings decrease, while those of the geminal coupling increase.

(1) Nuclear Magnetic Resonance for Organic Chemists, edited by D.W.Mathieson, Academic Press, London and New York; Chapter 8: "Proton-Proton coupling and stereochemistry" by R.J. Abraham.

AKU N.V.

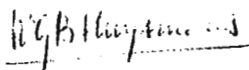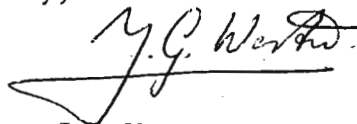| Geadresseerde	Ons kenmerk	Datum	Bladnr.
Prof. Shapiro	WH/JH	Oct. 3, 1969.	-3-

For ethylene sulphoxide, which contains the electron withdrawing S-O group, the reverse takes place: the cis and trans coupling constants increase, and Jgem decreases, to values even beyond those for cyclopropane.
We cannot offer yet an explanation of this anomaly. Further work on this matter is in progress.

Yours sincerely,

W.G.B. Huysmans   J.G. Westra
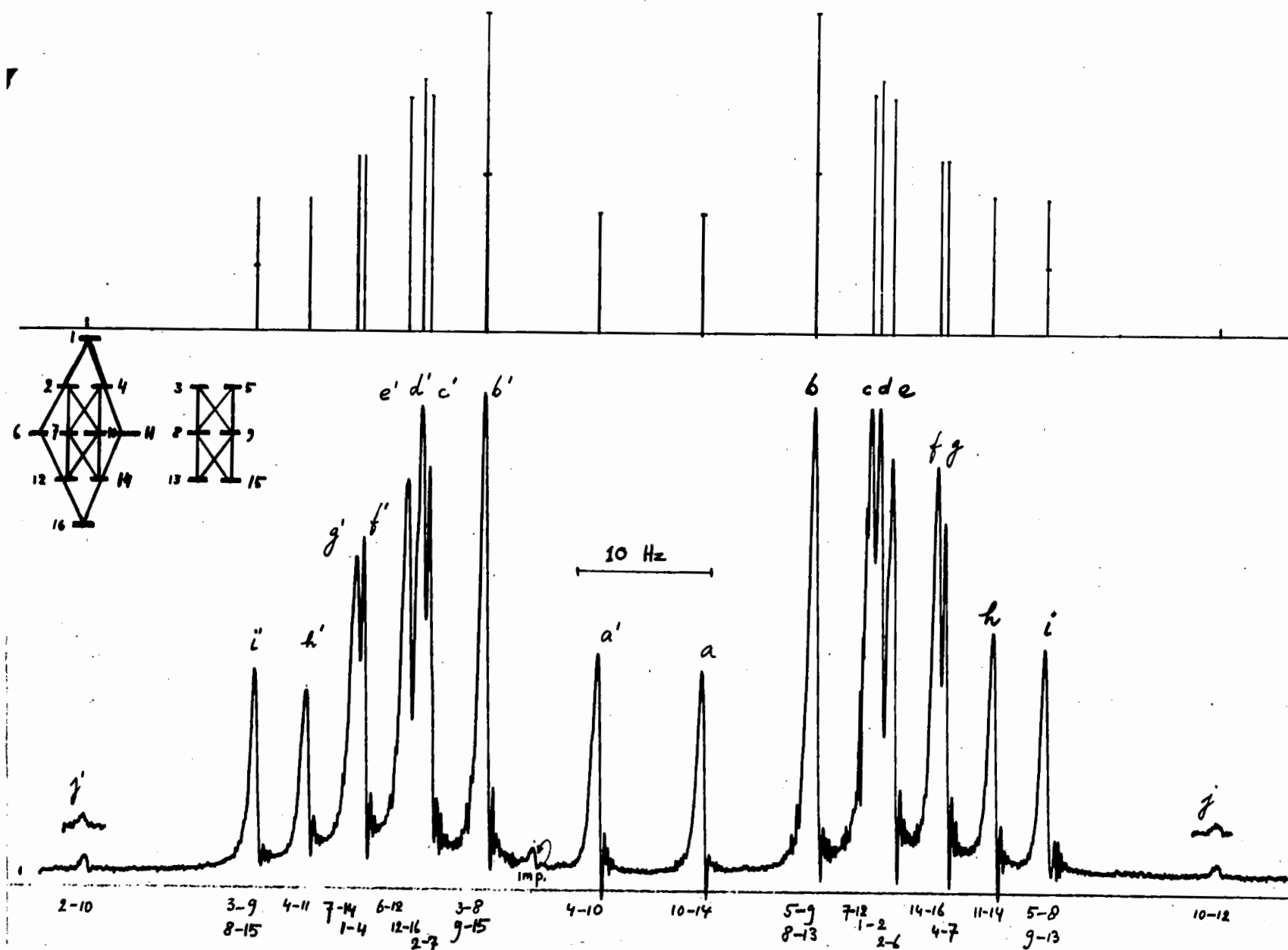
(AKU Research & Engineering Institute)

Fig. 1. The 100 MHz experimental and calculated "stick" spectrum of ethylene sulphoxide.
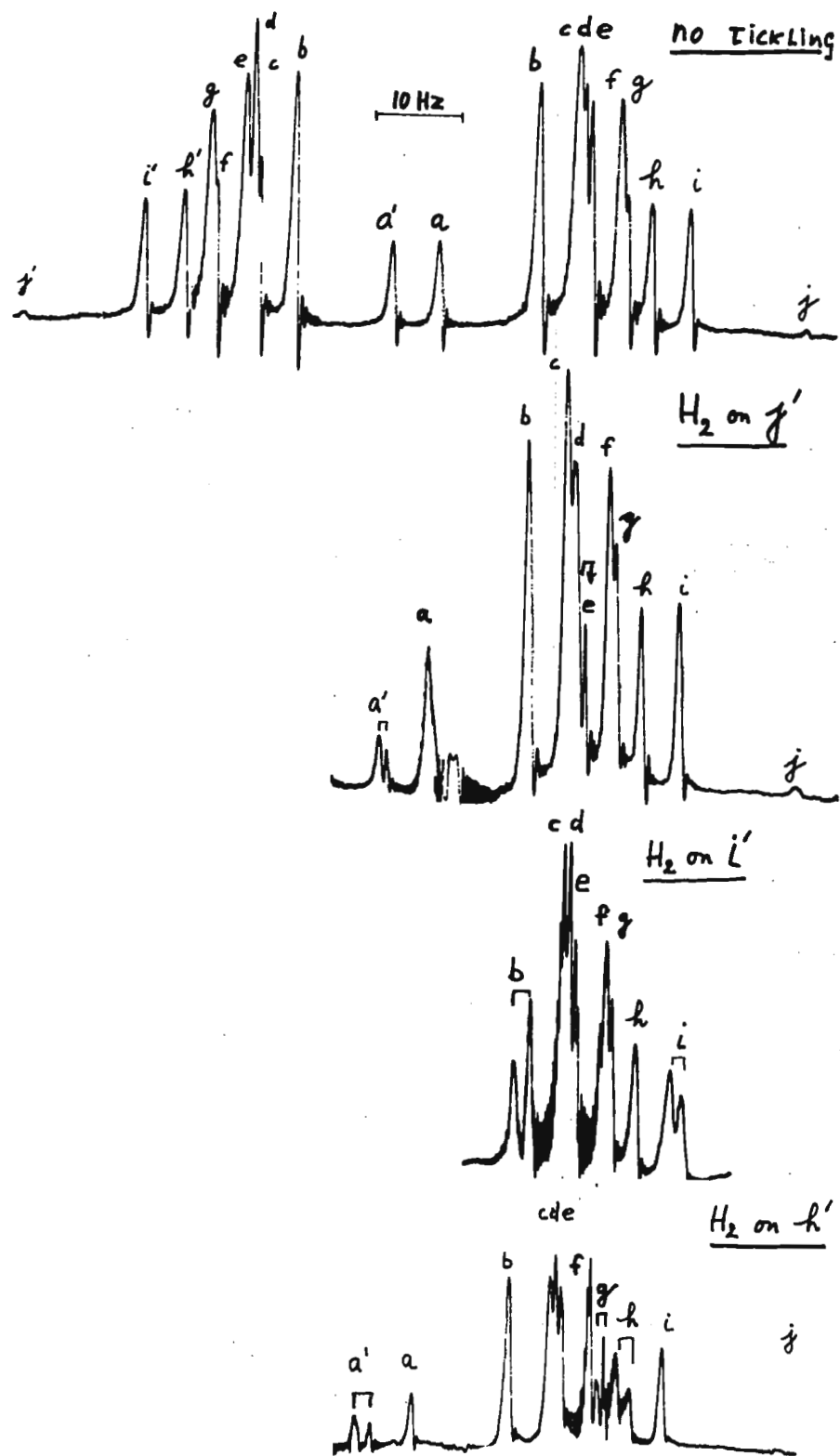
Fig. 2. Spin-tickled spectra of ethylene sulphoxide.

CALIFORNIA STATE COLLEGE   AT LOS ANGELES

5151 State College Drive, Los Angeles, California 90032
(San Bernardino and Long Beach Freeways Interchange)

Department of Chemistry

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

<u>Cation Hydration Studies</u>

Dear Barry:

Using the low temperature, direct pmr method which has been successfully applied in a variety of solvation studies, we have carried out hydration number measurements for several diamagnetic cations, including Zn^{2+}, UO_2^{2+}, and Sn^{4+}. Evidence for complex formation in the latter two systems has been found with the halides, but our studies are not complete at this point. We have completed a contact ion-pairing study of gallium halide solutions in water-acetone mixtures, using both ^1H and ^{69}Ga nmr. In all cases, the data strongly indicate that the dominant species are $Ga(H_2O)_6^{3+}$ and GaX_4^-, with negligible amounts of intermediate species. For instance, in Fig. 1, the ^{69}Ga spectra of these two species, recorded separately, are shown for the I^- case. In Fig. 2, the spectrum of a solution of Ga^{3+} and I^- in a 1:1 mole ratio is shown. Two peaks are evident, with a separation corresponding closely to that of the reference peaks. We have a manuscript describing these results in more detail if anyone is interested.

Sincerely,

Tony

A. Fratiello

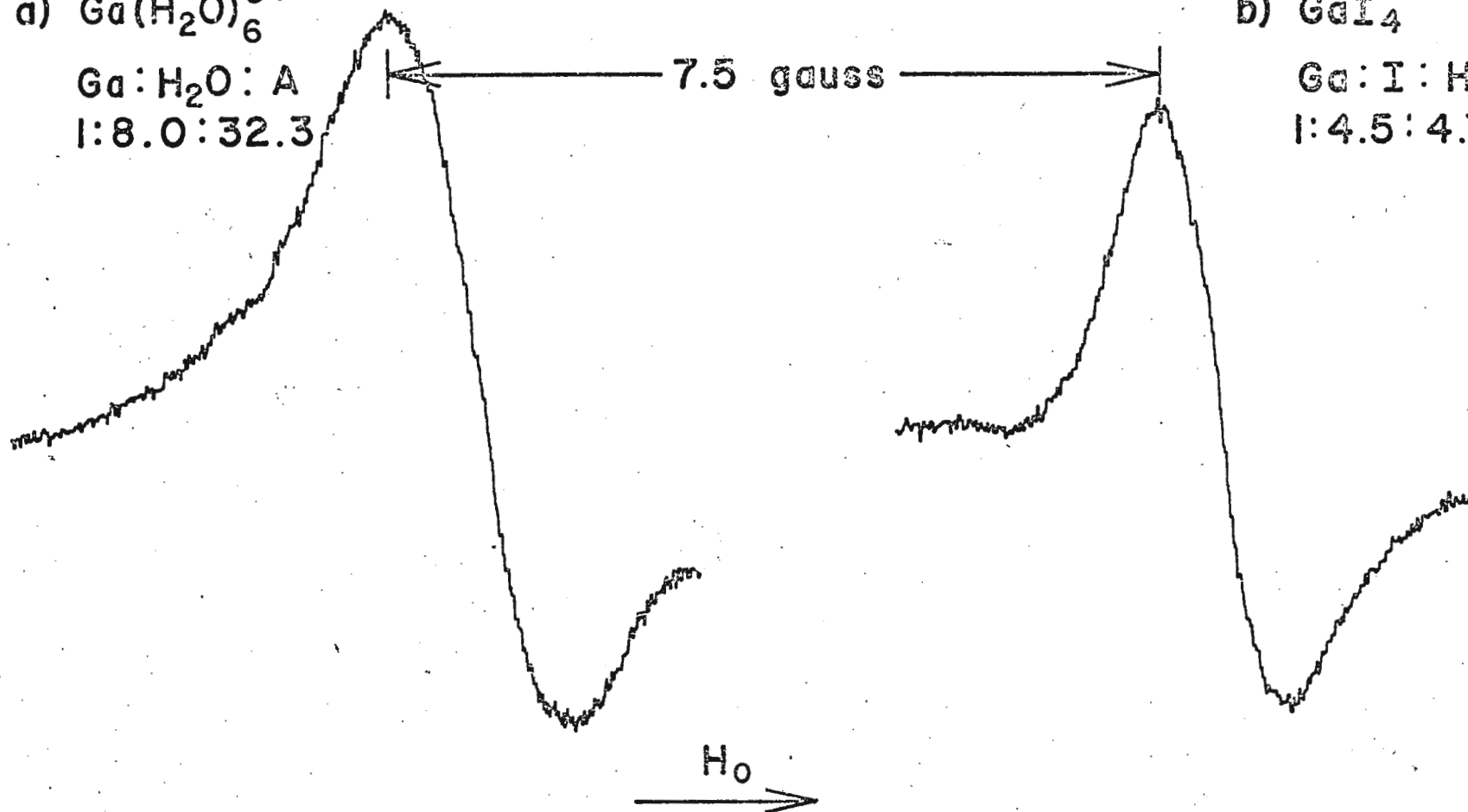*R. E. Achuster)*

R. E. Schuster

AF/RE/ml

a) $Ga(H_2O)_6^{3+}$

Ga:H_2O:A
1:8.0:32.3

7.5 gauss

b) GaI_4^-

Ga:I:H_2O:A
1:4.5:4.7:6.0

H_0

Ga : I : H₂O : A

1 : 1.02 : 13.3 : 20.1

7.4 gauss

H₀
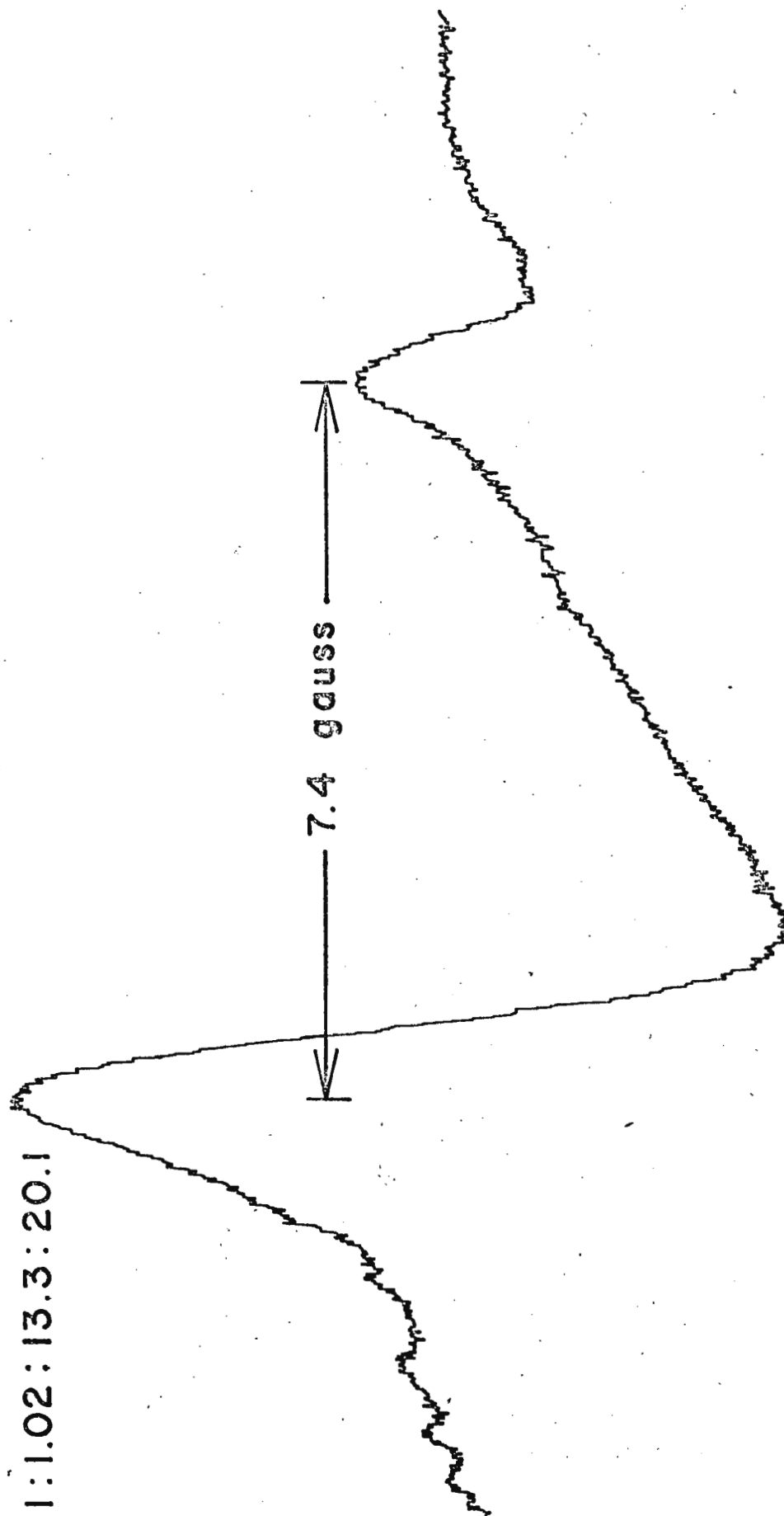
Dr. B. L. Shapiro,
Texas A and M University,
Dept. of Chemistry,
College Station
Texas 77843, USA

The University of Sydney

October 8, 1969

SYDNEY, N.S.W. 2006

IN REPLY PLEASE QUOTE:

FORMAL COUPLING CHARTS IN STRUCTURAL WORK

Dear Barry,

In investigating the structures of organic compounds by PMR
one ideally wishes to obtain all interproton coupling constants. In simple cases
this can be done by inspection and in many spectra the information is simply not
available due to overlapping of signals, as with steroids. However, not
infrequently, one comes across a compound whose PMR spectrum is complicated
but where all interproton coupling constants can be obtained.

We have found that the construction of a formal "Coupling Chart"
is very helpful on such occasions and may lead to a very rapid solution of the
structural problem. The example shown here is Carpanone, a natural product
isolated from a New Guinea plant by Dr. M. Slaytor and Mr. J. Mohandas of
our Department of Biochemistry. Mr. G. C. Brophy and myself found that the
100 MHz PMR data could be reduced from a pile of spectra a foot deep to the
neat coupling chart shown which inexorably led to the assignments, structure
and stereochemistry drawn here after proper correlation with UV, IR and MS
data. Biogenetic considerations reveal that Carpanone is a lignan but were not
used in our reasoning.

I would like to point out the heavy reliance on the stereospecificity
of several types of long-range interproton coupling constants (starred numbers)
and an instructive negligible geminal coupling (ca. 0.3 Hz for $C_{4'}$, $C_{5'}$ methylene
dioxy group).

With best regards,

Yours sincerely,

(S. Sternhell)

Assign.	δ	
H7'	7.01	
H6	6.81	
H3	6.32	
C4 & C5	5.88	ABq, J=1.5
H3'	5.68	
C4'	5.66	
C5'	5.62	
H6'	3.17	
H7	3.27	
H8'	2.21	
H8	2.52	
C9	1.13	
C9'	0.70	

0.6*   0.4   2.3*   5.0   1.0*

~0.3   7.5   1.0*

2.1   2.3*   ~1   7.5   7.0
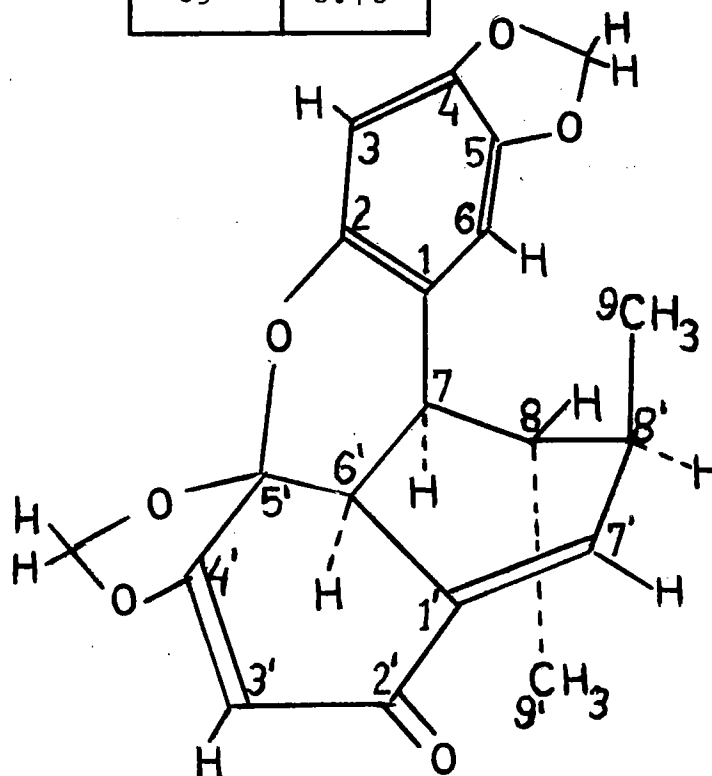
LABORATORY OF PHYSICAL CHEMISTRY

THE UNIVERSITY
BLOEMSINGEL 10, GRONINGEN
THE NETHERLANDS

Dr. B.L.Shapiro

Texas A & M University   Groningen, October 14, 1969

College of Science

College Station, Texas 77483

Dear Dr. Shapiro,

^{35}Cl NMR of mercuripapain

The titration of papain with $HgCl_2$ in the presence
of 0.3 M NaCl confirms the presence of one SH group
in the molecule. Only about 50 % of the papain preparation
is active. From the line broadening a τ_c of $3 \pm 1. 10^{-10}$ sec
is found for the papain molecule. A value of 8.10^{-9} sec
is calculated from the dimensions found by X ray analysis.
This indicates a certain looseness of structure in the
active centre.

In the presence of the substrate benzoyl-arginine
ethylester and a small excess of $HgCl_2$ no change was
found in the Cl line broadening. The tetrapeptide
ala-ala-phe-lys which inhibits strongly papain activity
also had no influence. Either the accessibility of the
-SHgCl group for Cl^- exchange is unchanged or both the
substrate and the inhibitor have too low an affinity for
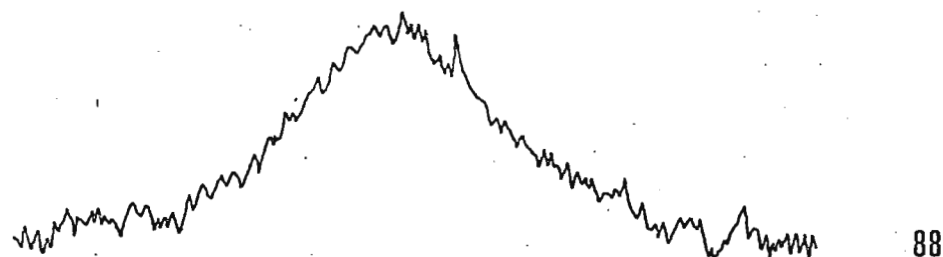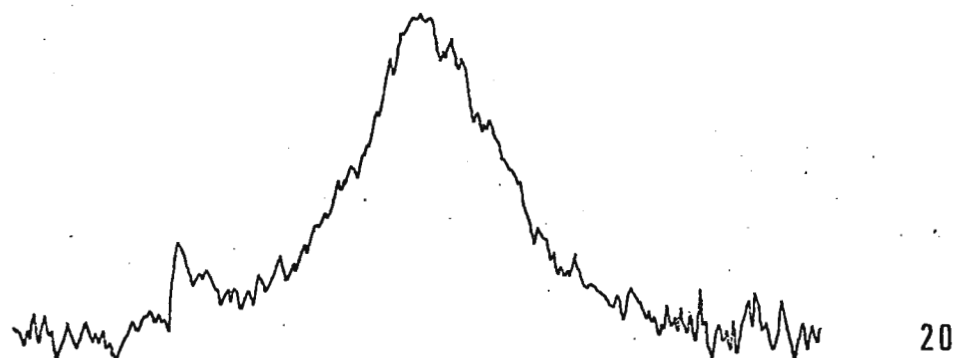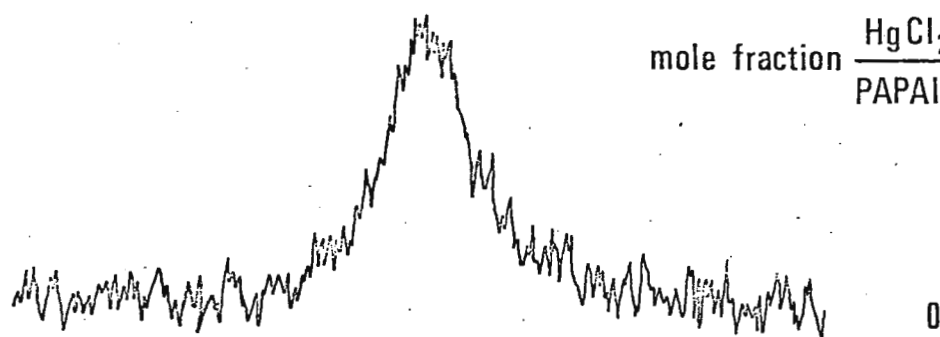mercuripapain to show any effect.

Sincerely yours,

J.C.Mensch

titration of 0.072 % PAPAIN with $HgCl_2$
in 0.3 M NaCl and 0.033 M phosphate pH 7.1

0.3 M NaCl
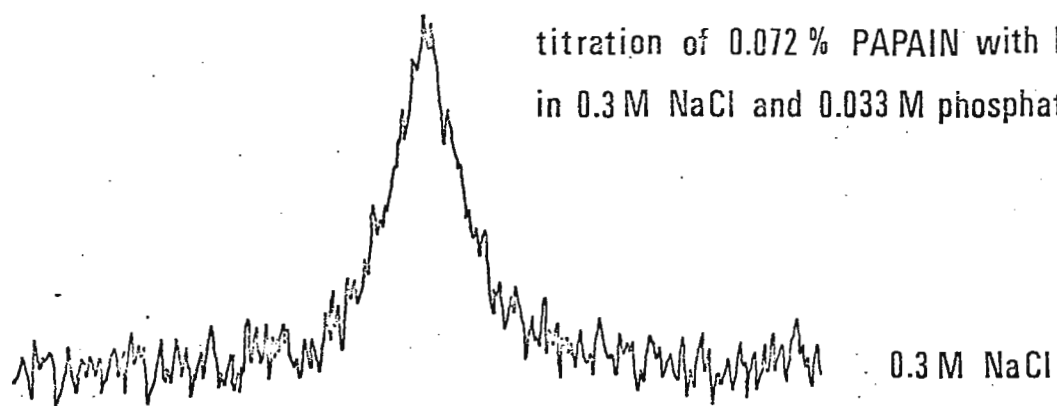
├──── 15.5 C P S.

mole fraction $\dfrac{HgCl_2}{PAPAIN}$ in % :

0

20

52

88

DIVISION OF PHYSICAL CHEMISTRY
THE ROYAL INSTITUTE OF TECHNOLOGY
100 44 STOCKHOLM 70
SWEDEN

October 15, 1969

Cable address: Technology

EF/BE

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

Wide Line Proton Magnetic Spectra of Sodium Hectorite
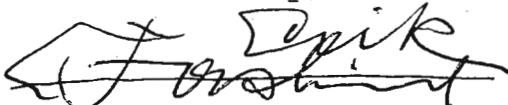
Dear Barry,

Wide line proton magnetic spectra of sodium hectorite
have revealed a temperature dependent splitting as
shown in the attached figure. Sodium montmorillonite
spectra are, however, unresolved in the same range
of temperature and water content. Since the only
known difference between the crystalline structures
of the two minerals occurs in the organization of the
central hydroxide layers, and since the sample
preparation has been identical, we conclude that the
central lattice structure may affect the adsorption
mechanism and the stabilization of the inter-
crystalline sheets of water. An obvious implication
is that the change from the dioctahedral aluminium
hydroxide layer in montmorillonite to the triocta-
hedral magnesium hydroxide layer in hectorite
influences the silica lattice dynamics and thus the
state of polarization of the hydrophilic surface
groups. Also, we have earlier shown that the
hectorite lattice is stable up to temperatures above
$300^{\circ}C$ while the montmorillonite lattice undergoes a
transition between 20 and $300^{\circ}C$.

We have so far no quantitative measure of the probable
texture effects in the powder sample. The present band
shape analyses and X-ray data, however, indicate that
the adsorbed water is accomodated in three layers,
two directly adsorbed on opposite clay faces with the
third layer sandwiched between the two. The shifted
bands are slightly broader than the central unshifted
band which agrees with the above interpretation.

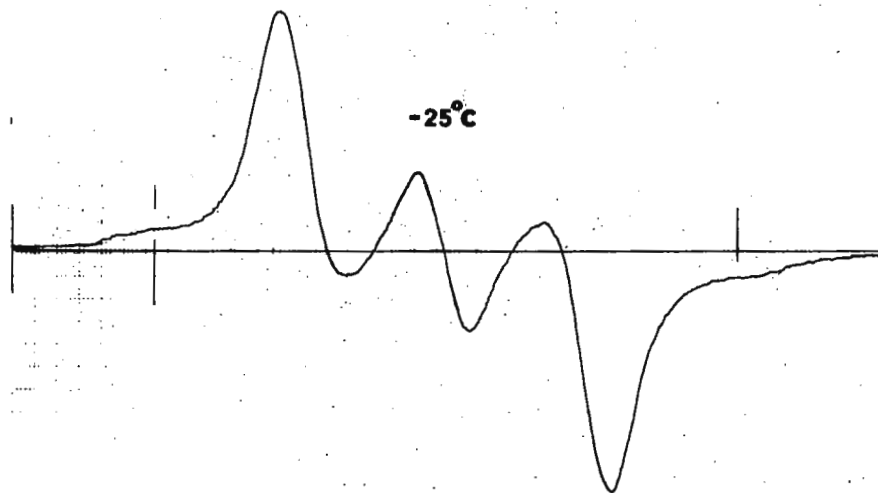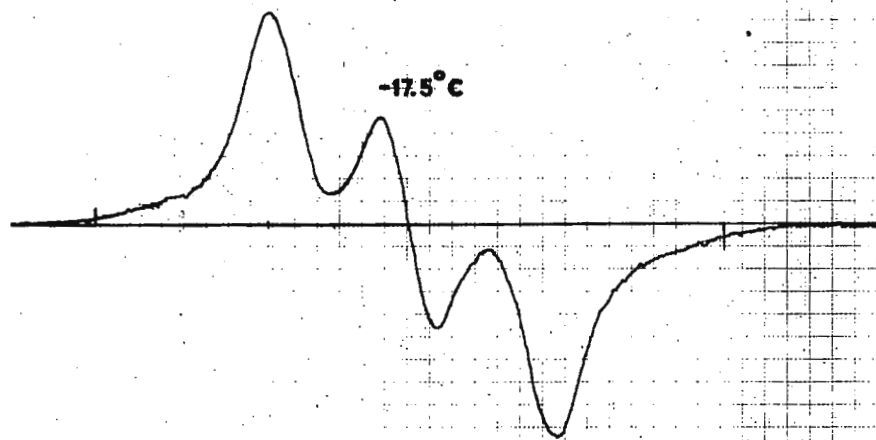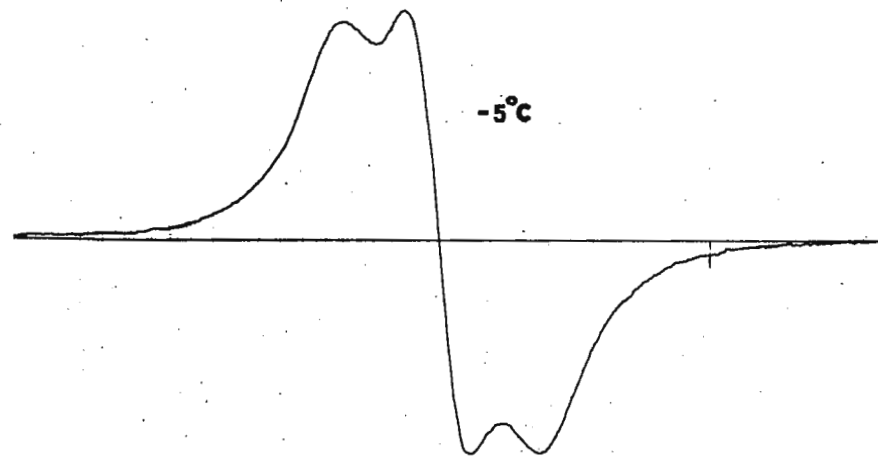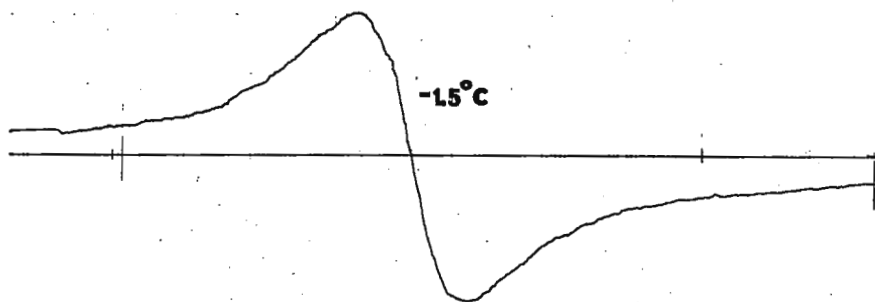A detailed band shape analysis is in progress in view
of the great interest of the specific coupling
mechanism between water and a strongly hydrophilic
substrate. In my opinion, the essential problem of
polywater is its genesis, closely tied up with
adsorption processes of the kind discussed here.

Kind regards,

Yours truly,

Erik Forslind

-1.5°C

-5°C

-17.5°C

-25°C

Na-hectorite, PMR-spectra.

LASH, MILLER CHEMICAL LABORATORIES
80 ST GEORGE ST TORONTO 5 CANADA

October 16, 1969

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

Dear Dr. Shapiro:

Interbenzylic Coupling; An Excellent Spin
Tickling Oscillator

Having viewed the NMR Newsletter from afar for some time, we
would like to be included on your mailing list. We hope that
the following report may serve as our initiation fee.

The σ-π configuration interaction mechanism successfully
predicts the signs and magnitudes of coupling constants in many
systems containing π-electrons (1,2). In connection with an
interest in long-range coupling constants, we recently deter-
mined the signs and magnitudes of the coupling between methyl
group protons in xylene derivatives (I-III) ("interbenzylic"(2)
coupling). Previous reports (magnitudes only) are scanty (3,
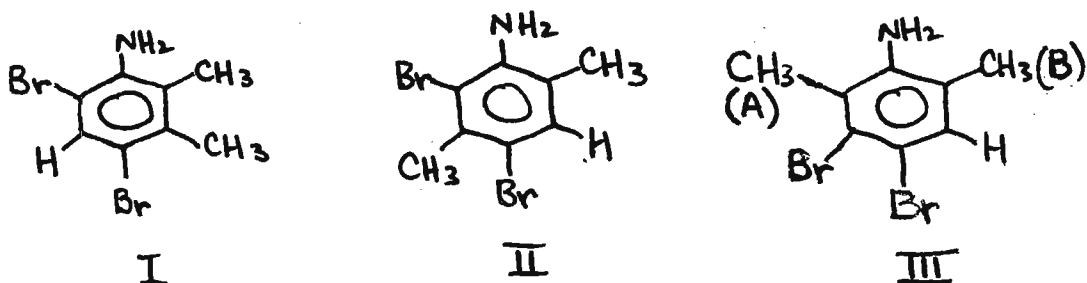
4,5). We find that, as predicted (6) orders of magnitude are
similar to the corresponding benzylic coupling constants but
the signs are inverted.

In detail, based on spin tickling experiment results and the
known signs of benzylic coupling constants (7), we find that in
I,

Dr. B. L. Shapiro   - 2 -   October 16, 1969

$$J^{ortho}_{CH_3,CH_3} = +0.40; \quad J^{meta}_{H_1CH_3} = +0.37; \quad J^{para}_{H_1CH_3} = -0.61$$

in II,

$$J^{para}_{CH_3,CH_3} = +0.62; \quad J^{meta}_{H_1CH_3} = +0.38; \quad J^{ortho}_{H_1CH_3} = -0.76$$

in III

$$J^{meta}_{CH_3,CH_3} = -0.18; \quad J^{para}_{H_1CH_3}(A) = -0.64; \quad J^{ortho}_{H_1CH_3}(B) = -0.86$$

All coupling constants are considered accurate to at least $\pm$ 0.05 Hz.

Using the recommended Hewlett Packard 200AB and 200CD oscillators, we have experienced problems associated with fine tuning and stray frequencies. It may be worth noting that we have found that the new Hewlett Packard 4204A oscillator gives a very clean output, is extremely stable and is very easy to set to $\pm$ 0.01 Hz.

We wish this contribution to be credited to Dr. Reynold's group at the University of Toronto.

Yours sincerely,

C. J. MacDonald,

W. F. Reynolds

WFR:pe

References

1. H. M. McConnell, J. Mol. Spectros. 1, 11 (1957).
2. M. Barfield and B. Chakrabarti, Chem. Rev., to be published.
3. W. Husysmans et al., Tetra. Letters, 1968, 4345.
4. H. Lund and P. Lunde, IITNMR 101, 14 (1967).
5. A. D. Cohen and K. A. McLauchlan, Mol. Phys. 9, 49 (1965).
6. M. Barfield and B. Chakrabarti, J. Am. Chem. Soc. 91, 4346 (1969)
7. G. Kotowycz and T. Schaefer, Can. J. Chem. 44, 2743 (1966).

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

October 16, 1969

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

"Music hath charms......."

Dear Barry:

I hope that this missile will be found more acceptable than the last.

As you know, we have been studying a number of derivatives which contain a variety of heternuclei. About three years ago we started building a heteronuclear decoupler for use with our Varian HA-100, and have had a reasonably successful instrument running for nearly two years. Initially we confined attention to "continuous wave" decoupling but soon became converted to the many advantages of Richard Ernst's "noise-modulated" decoupling technique.

We gained the impression that the type of "noise" used for broad-band modulation was quite critical--and indeed it is for some experiments. However, in many instances almost any type of audio-noise can be used. I think that the attached spectra demonstrate this. [A] Shows the normal ^1H spectrum of trimethylphosphite; irradiation at the ^{31}P resonance frequency readily collapsed this doublet to the anticipated singlet. However, by the time the ^{31}P field had been moved off resonance by 1KHz, it had very little effect on the ^1H resonance, as is shown in [B]. We now modulated the ^{31}P decoupling field with the output of a portable phonograph, which was playing "Midnight in Moscow" by Kenny Ball and his Jazzmen. This gave the decoupled ^1H spectrum shown in [C], thus indicating that for this particular experiment the sound track of "Midnight in Moscow" is equivalent to a noise band width of ca. 2KHz.

Admittedly the above is a trivial example, but it does prove a point and may encourage some other amateurs, such as myself, to make use of Ernst's extremely useful technique.
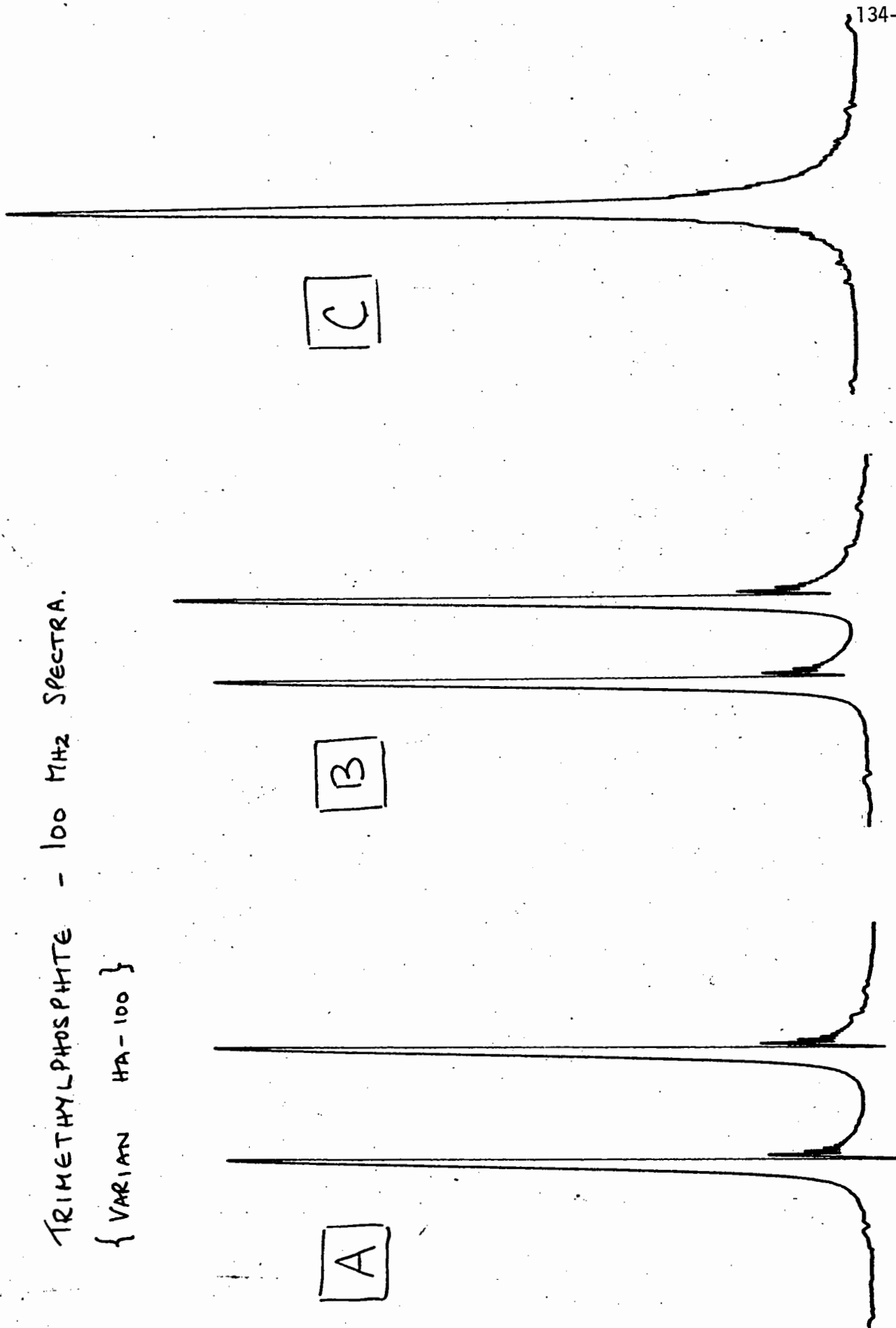
Cheers for now,

L.D. Hall
Assoc. Prof.

LD:bj

TRIMETHYLPHOSPHITE - 100 MHz SPECTRA.
{ VARIAN HA-100 }

Imperial Chemical Industries Limited

PHARMACEUTICALS DIVISION

Mereside, Alderley Park, Macclesfield, Cheshire, SK10 4TG

Telephone: ALDERLEY EDGE 2828 Telex: 669095 Cables: AVLONTEX. MACCLESFIELD

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

Your Ref:

Our Ref: GRB/EMD

15th October, 1969.

Proton Shifts in Tri-substituted Phenols

Dear Professor Shapiro,

Thank you for your colourful reminders. You will be aware of the reasons for the recent lack of a contribution from us, but obviously the "system" grinds on!

We have just taken delivery of some C^{13} accessories for our HA-100D and are obtaining our first C^{13} signals:- we hope to report on some results at a later date.

We briefly report some p.m.r. results we have obtained whilst investigating the effect of the addition of trichloroacetylisocyanate (T.C.A.1) to phenols dissolved in $CDCl_3$. Spectra were run before addition and about ten minutes after addition of T.C.A.1. In certain cases complicated spectra were obtained and were analysed using the LAOCOON 111 programme.

For a series of tri-substituted phenols where the substituents were a selection of alkyl, halogeno, alkoxy, carbonyl and nitro groups in ortho, meta or para orientation to the phenolic hydroxyl, we found:-

Proton position			Range of shift
ortho	to	OH	0.26 – 0.56 p.p.m.
meta	to	OH	0.02 – 0.26 p.p.m.
para	to	OH	0.21 – 0.42 p.p.m.

It was observed that in the same molecule there is an overlap in the values of the shifts of the ortho and para protons and thus the use of these shifts to predict the substitution pattern in phenols with unknown orientation of the substituents could be unreliable. We further noticed that when the ortho substituent was a group to which the phenolic hydroxyl could form a strong intra-molecular hydrogen bond i.e. nitro, halogeno or carboxylic ester then very slow or no reaction with T.C.A.1 occurred.

Yours sincerely,

G.R. Bedford, D. Greatbanks, B. Wright.
Biological Chemistry Department.

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19104

The School of Medicine

JOHNSON RESEARCH FOUNDATION
DEPARTMENT OF
BIOPHYSICS AND PHYSICAL BIOCHEMISTRY

October 20, 1969

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

Dear Professor Shapiro:

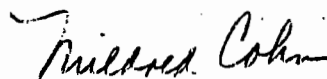Long range ^{13}C-H coupling constants in vinyl compounds

I have been working on a problem involving the stereochemistry of an enzymatic reaction and have attempted to differentiate two protons, cis and trans respectively to a carbon by their respective ^{13}C-H coupling constants. The compound in question is phosphoenolpyruvate acid labeled with 60% ^{13}C in the carboxyl group.
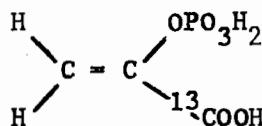
The two protons are separated by 0.18 ppm and J values are 3.4 and 9.2 cps for the low and high field peaks respectively. From other data, the evidence suggests that the low field resonance is the cis and the high field is trans to the carboxyl which would mean that $J_{trans} > J_{cis}$. I have searched the literature to see if such a relationship has been established for any similar long range coupling constants in vinyl compounds and have not succeeded in finding any published values. If any reader has relevant data on ^{13}C-H coupling constants where the stereochemistry is well established and could be cited, I would greatly appreciate hearing from him.

Please credit this to Jacques Reuben's subscription.

Sincerely yours,

Mildred Cohn

Mildred Cohn

UNIVERSITY OF CALIFORNIA

LAWRENCE RADIATION LABORATORY
BERKELEY, CALIFORNIA 94720

October 20, 1969

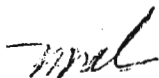Fourier Transform Spectroscopy with the HR-220.

Dear Barry:

Again apologies for the tardy contribution.

We are continuing our pursuit of the Fourier transform gadgetry and have, several months ago, performed transform spectra on our HR 220 which is somewhat less involved than first thought. The enclosed spectrum is that of CH_3-CH_2-I and was accumulated in 1 second, transformed and plotted in our PDP-8 in about 8 sec. Since the transform program in the small computer did not have facilities for correction of the various filters, one sees the phase and amplitude distortion across the spectrum. We have also achieved a first order field-frequency lock and have an automatic gradient trimmer in the works.

Our initial concern was the protection of the receiver pre-amp from the high pulse feed through without seriously affecting the signal-to-noise ratio. This was achieved by using a coaxial relay between the receiver coil and the pre-amp. The relay has an on-off ratio of greater than 100 dB and although it is slow, in the several millisecond region, the jitter in switching is less than 10 microseconds. Thus, by properly anticipating the time of the transmitter pulse, we are able to enable the receiver within 10^{-5} sec after the end of the transmitter pulse, while completely avoiding any feed through during the pulse.

Concurrently we are performing transform spectra on P^{31} in biological compounds and would like to emphasize the comments of Freeman and Hill in TAMUNN 132, 46 (1969) on the requirements for a super-field frequency lock system when doing transform experiments. We attempted again to use an external lock sample and find the phase drift of the free-decay to be so great that repetitive accumulation is not possible. Accordingly we are returning to the double tuning scheme we reported several years ago which permits us to lock and autoshim on solvent protons while pulsing the phosphorus.

Sincerely,

M.P. Klein

MK:glw

FREQUENCY (CYCLES PER SECOND)

134-25

University of East Anglia
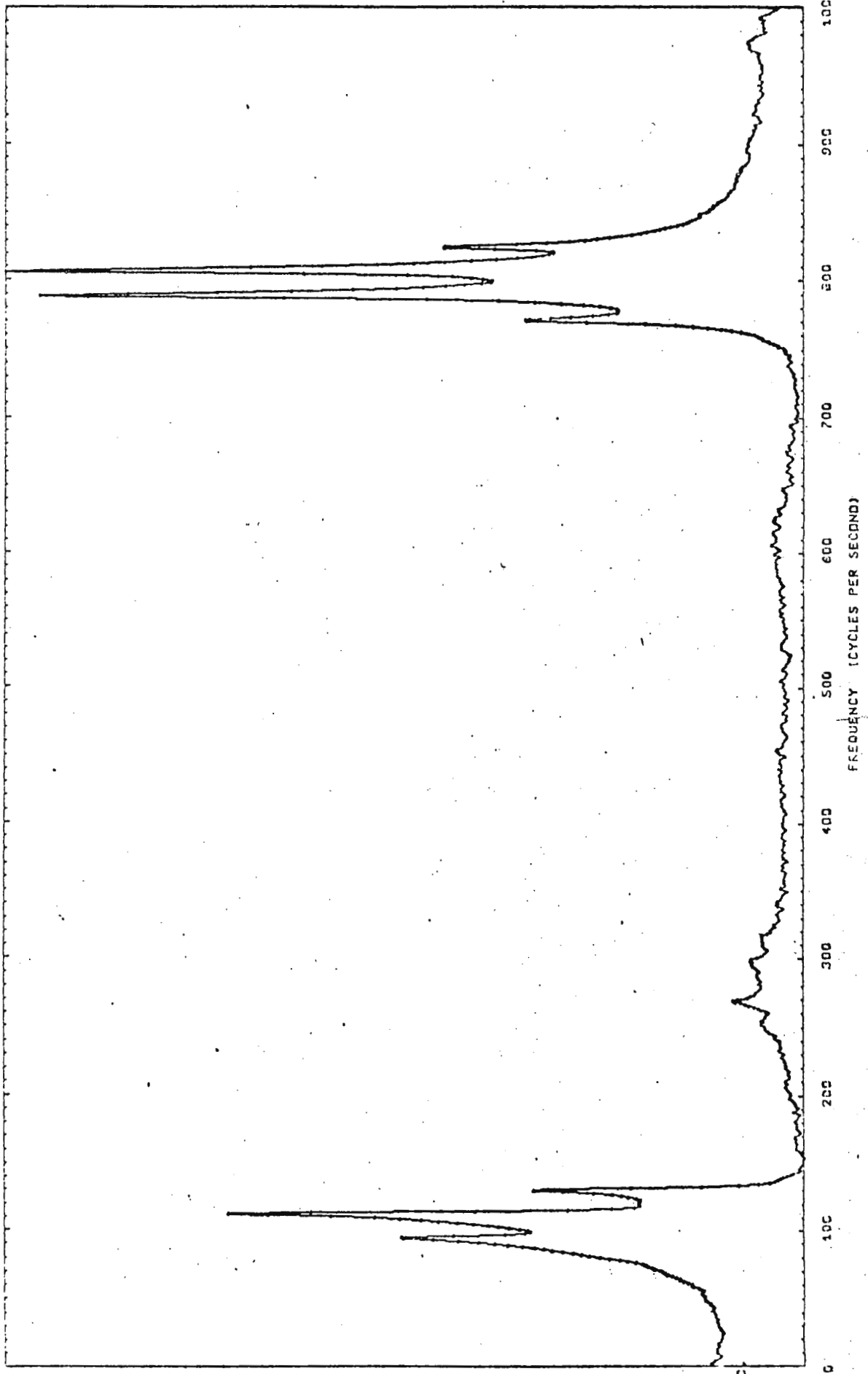
From Dr. R.K. Harris.

School of Chemical Sciences
University Plain
Norwich NOR 88C
Telephone Norwich~~xxxx~~ 56161.

20th October 1969.

Dear Barry,

SPIN-SPIN COUPLING IN LINEAR CONJUGATED POLYENES

For some considerable time we (by "we" I mean Tony Cunliffe,
Per Albriktsen, Roger Grinter and myself) have been attempting to obtain
rather precise measurements of coupling constants in methylated 1,3-buta-
dienes and 1,3,5-hexatrienes. In particular we have been interested in
long-range coupling and have carried out semi-empirical calculations of the
π-contributions to the coupling constants. We have reached a stage where
we believe we can make some useful statements about the observed effects:

1. There are probably in-plane deformations whenever there is a methyl
   group in the following situation:
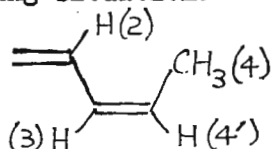
These steric effects show up in a decrease in the coupling constants
$^4J_{34}$ and $^4J_{24'}$ (i.e. the values become more negative). Other coupling
constants are also altered, and similar effects are found for the
butene-2 isomers. The relevant data are:

No steric effects:

$^4J_{34}$ (or equivalent)	-	-	-	-1.33 Hz
$^4J_{24'}$ (or equivalent)	-0.86	-0.79	-0.81	- Hz

Steric effects:

$^4J_{34}$ (or equivalent)	-1.82	-1.85	-1.87	-1.79 Hz
$^4J_{24'}$ (or equivalent)	-1.06	-1.16	-1.27	- Hz

2. The same type of steric effects are accentuated for compounds with the grouping:
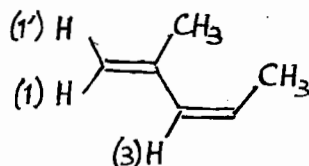
This undoubtedly causes the compound to be non-planar. For 2,4-dimethyl-2,4-pentadiene coupling constants $^4J_{13}$ and $^4J_{1'3}$ become $\pm$ 0.12 Hz and -1.20 Hz respectively ("normal" values for the s-trans conformation are $^4J_{13} \simeq {}^4J_{1'3} \simeq -0.85$ Hz). Our measurements confirm the trend of ^4J with dihedral angle established by Bothner-By and Jung (J.A.C.S., 90, 2342 (1968)), thus indicating that the electronegative substituents in their work did not affect the conclusions markedly. We suggest that the dihedral angle for 2,4-dimethyl-2,4-pentadiene is between 45° and 65° from the s-cis position.

3. No long-range coupling constants appear to have been reported for hexatrienes. We find that for allo-ocimene the value of ^6J is ca. -0.1 Hz. This agrees quite well with semi-empirical calculations of the π-contribution, based both on a modified Karplus method and on the Finite perturbation method. Similar calculations suggest that ^7J for hexatrienes should be ca. $+0.5$ Hz.

We hope that some of this work will appear in "legitimate" journals in the not-too-distant future.

Yours sincerely,

Robin Harris

R.K. Harris.

P.S. I had hoped that two contributions in one issue (see TAMUNMR 125) would entitle me to 18 months breathing space, but it seems from your reminder that this is not so!

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

RKH/MAC.

ИНСТИТУТ ХИМИИ
ПРИРОДНЫХ СОЕДИНЕНИЙ
АН СССР

INSTITUTE FOR CHEMISTRY
OF NATURAL PRODUCTS
ACADEMY OF SCIENCES OF USSR
Ul. Vavilova, 32. Moscow, USSR
« 21 » __October__ 1969 г.

Prof. Bernard L.Shapiro

Department of Chemistry

Texas A & M University

College Station, Texas 77843

U.S.A.

> **Title:** Combination Frequencies in
> Double Resonance with Irra -
> diation of a Double-Quantum
> Transition

Dear Barry:

Previously (1) the conditions for the appearance of a com -
bination frequency (2,3) in a triple resonance experiments on
single-quantum transitions in AMX system had been investigated.*
The present letter reports the results of double resonance expe-
riments in which the combination signals are observed when one
of the irradiating r.f.fields is applied to the 1-4 double-quan-
tum transition in a AB system. This transition with two single-

---

* I was very glad to know that Dr. Roger Price (private communi-
cation and in TAMU NMR Newsletters, 123-1) independently got
the same results on triple tickling experiments with an AMX
system.

-quantum transitions formes a closed system with three energy
levels. From the general theoretical prediction ($\underline{2},\underline{3}$) one may
expect, that irradiation of two of these transitions will give
rise to a combination frequency corresponding to the unirradia -
ted transition.

Fig. $\underline{a}$ shows the AB spectrum of transchloroacrylic acid
(25 Mc/sec; 10% w/v solution in 1:4 v/v $(CD_3)_2CO + CS_2$). Irra-
diation of the 1-4 double-quntum transition by the local weak
ν_2 r.f. field (Fig. $\underline{b}$) splits the components of the spectrum
into doublets (tickling of the doublequantum transition). Addi -
tional irradiation of the 3-4 transition (Fig. $\underline{c}$) or 1-2 transi-
tion (Fig. $\underline{d}$) by ν_3 r.f. field gives rise to the combination fre-
quencies ($2\nu_2 - \nu_3$) corresponding to the unirradiated 1-3 or 2-4
transitions, respectively. The method used for observation of
these frequencies has been described in ($\underline{1},\underline{2}$).

The above experiments (although not completely interpreteted
theoretically) have widened the types of energy diagram fragments
for which one can expect combination signals in multiple reso -
nance experiments. Moreover, the combination signals method al -
lows the frequencies of a weak double-quantum transitions to be
determined with a high degree of precision.

I am very grateful to Dr. S.Brownstein for the possibility
to carry out these experiments on a Varian HA-100 spectrometer
with a 25 Mc/sec RF Unit during my Postdoctorate Fellowship in
the Division of Applied Chemistry, National Research Council of
Canada (Ottawa).
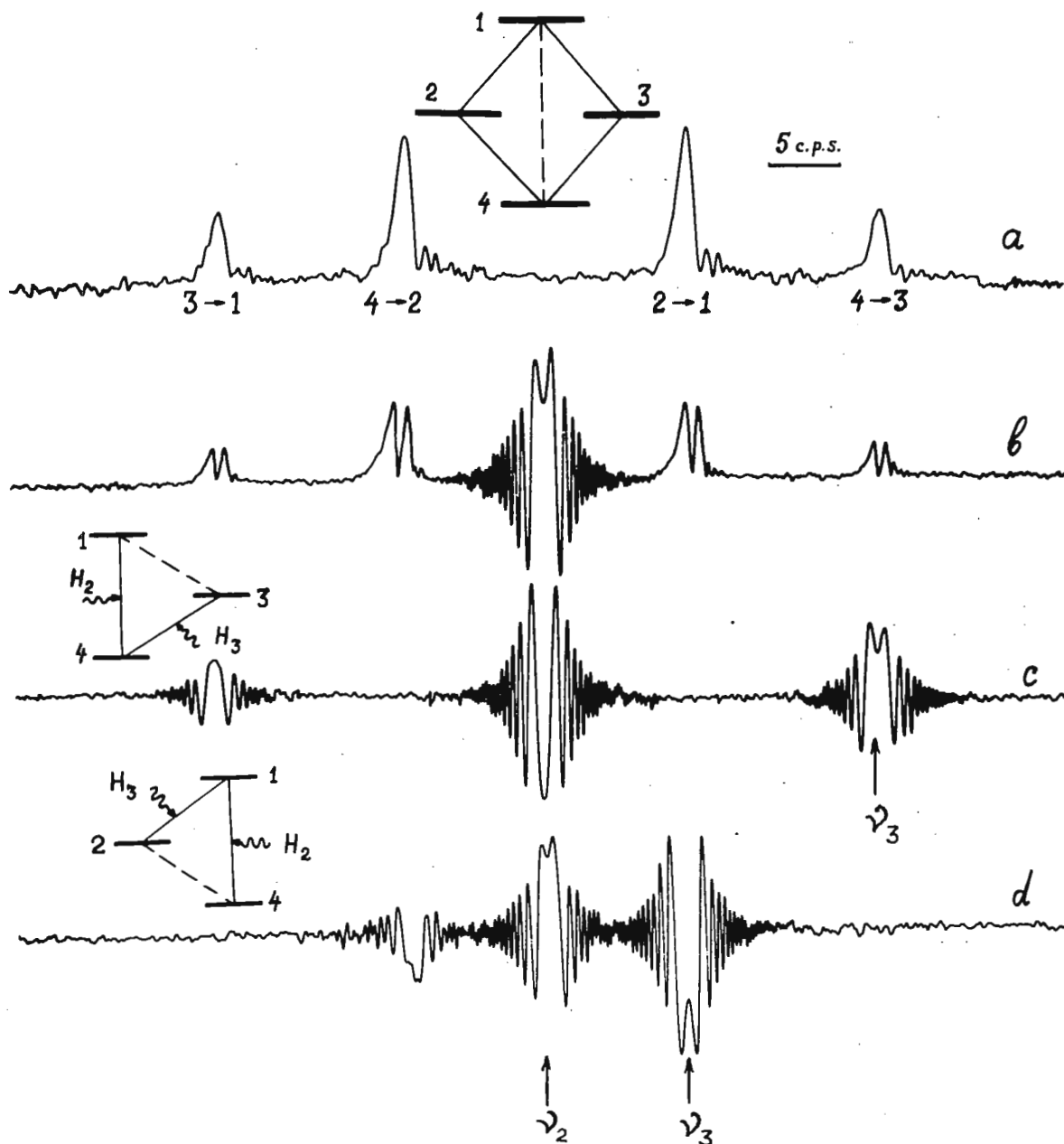
Yours sincerely

Vladimir Bystrov

Fig. (a) Normal AB spectrum; (b) Double-resonance spectrum with irradiation of the 1-4 double-resonance transition by an H_2 r.f. field; (c) Double resonance spectrum with combination frequency achieved by irradiation of the 1-4 and 3-4 transitions by H_2 and H_3 r.f. fields, respectively; (d) The same as (c) with irradiation of the 1-4 and 1-2 transitions by H_2 and H_3, respectively.

$h_2 = \gamma H_2 / 2\pi = 1.9$ cps; $h_3 = \gamma H_3 / 2\pi = 1.5$ cps.

References:

1. V. Bystrov,   IITNMR, 118-4 (1968); J. Molec. Spectry, 28, 81 (1968).

2. L.R.Anders and J.D.Baldeschwieler, J. Chem. Phys., 43, 2147 (1965).

3. V.Sinivee, Bull. Acad. Sci. Estonian SSR, Phys. Math. Sci. Ser. 16, 444 (1967); V.Sinivee and V.Salum, ibid., 17, 49 (1968); V.Sinivee, E.Kundla and V.Salum, TAMU NMR, 119-12 (1968).

MONTECATINI EDISON S.p.A.

SEDE IN MILANO - CAPITALE L. 749.000.000.000 INTERAMENTE VERSATO

DIRI
CENTRO RICERCHE DI BOLLATE

Bollate, 23.10.1969

Si prega indirizzare la risposta a:
MONTECATINI EDISON S.p.A.
DIRI Centro Ricerche di Bollate
Via S. Pietro, 50
20021 Bollate (Milano)

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

. U.S.A.

our ref.: 596-1 LC/vr

Subject: ^{19}F NMR spectrum of 1-methoxy-pentafluorocyclobutene

Dear Prof. Shapiro,

in the course of our investigation on the
"Dewar" isomers (bicyclo-[2.2.0]-exa-2,5-diene derivatives)
we have looked at the AA'BB'XP$_3$ NMR spectrum of 1-methoxy-
-pentafluorocyclobutene. The ^{19}F NMR spectrum at 94.1 Mc/s
(figure) was analysed using the iterative part of LAOCOON III
in the final part of the NMR parameter refinement. The NMR
parameters obtained are collected in the Table below:
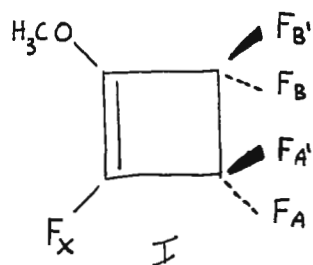
Chemical Shift (ppm frm CFCl$_3$)	Coupling Constant c/s
F_A = 119.7	$\begin{cases} J_{AB} = \pm 26.56 \\ J'_{AB} = \mp 16.85 \end{cases}$
F_B = 117.1	
F_X = 143.6	$\left\| J_{AA} - J_{BB} \right\| = 1.44$
δ_{AB} = 241.3 c/s (at 94.1 Mc/s)	$\begin{cases} J_{AX} = \pm 20.03 \\ J_{BX} = \pm 7.89 \end{cases}$
	$\left\| J_{X \cdot CH_3} \right\| = 1.40$
	$\left\| J_{B \cdot CH_3} \right\| = 0.47$

H$_3$CO, F$_{B'}$, F$_B$, F$_{A'}$, F$_A$, F$_X$, I

The different relative sign of the two F·F vicinal coupling
constants across the saturated carbon-carbon bond, J_{AB} and
J'_{AB}, comes out from the analysis and is in agreement with
recent results on some cyclobutenes and cyclobutanes. The
same sign of J_{AX} and J_{BX} was on the contrary demonstrated
by frequency sweep double resonance experiments. The numerical
values of J_{AX} (20.03) and of J_{BX} (7.89) are quite different.
The assignment of the larger value to $^3J^{FF}$ and of the smaller
one to $^4J^{FF}$ follows from the assignment of the two CF_2 groups.
This can be suggested on the basis of literature results[1,2]
in agreement with the fact that fluorines vicinal to the more
electronegative substituents are upfield.
In some other cyclobutenes[3], however, such as, for example:
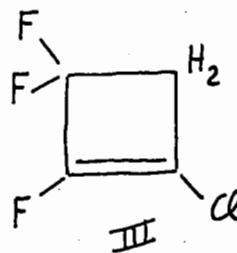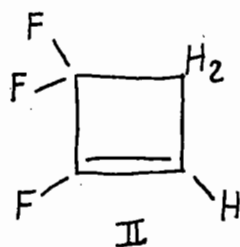
the F·F vicinal coupling constant was found unambiguously small:
$^3J^{FF} = + 3.8$ c/s in II and $^3J^{FF} = + 4.9$ c/s in III. If the assi-
gnment for our 1-methoxy-pentafluorocyclobutene which gives
value of $|^3J^{FF}| = 20.03$ c/s is correct, it comes out that this
type of coupling constant is extremely sensitive to the nature
of substituents adjacent to the interacting nuclei.

./.

MONTECATINI EDISON S.p.A.
DIPI
Centro Ricerche Bollate

Other similar compounds are under investigation because more data are clearly necessary in order to gain better insight into the different factors which influence F-F vicinal coupling constants.

L. Cavalli

1) V.W. Gash, D.J. Bauer, J. Org. Chem. **31**, 3602, 1966

2) E.F. Mooney, Annual Review of NMR Spectroscopy, V 1, pag. 260, Academic Press, 1968

3) R.A. Newmark, G.R. Apai, R.O. Michael, J. Magnetic Resonance, 1, 418, 1969

CF$_2$ (B)

CF$_2$ (A)
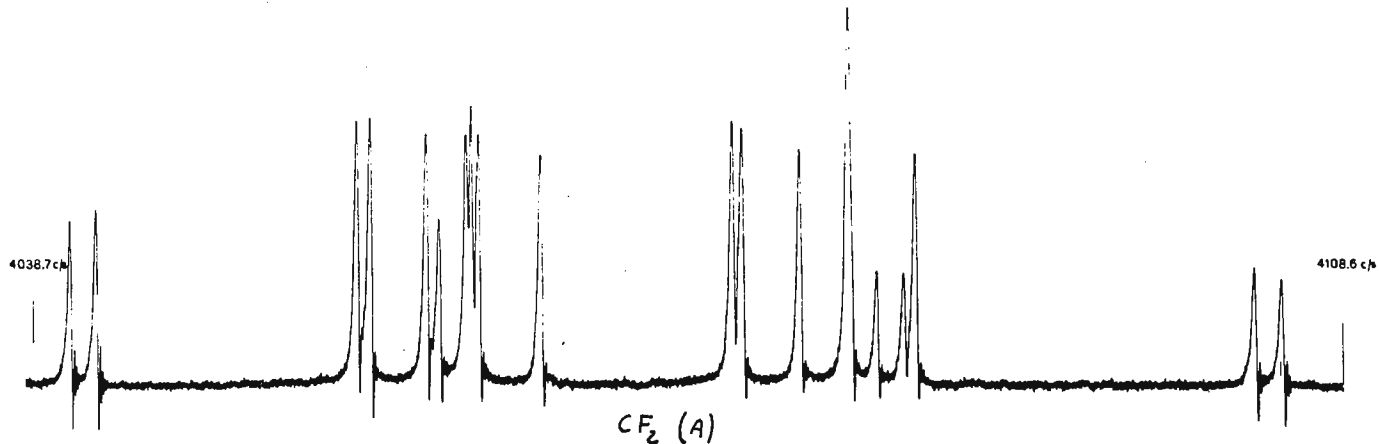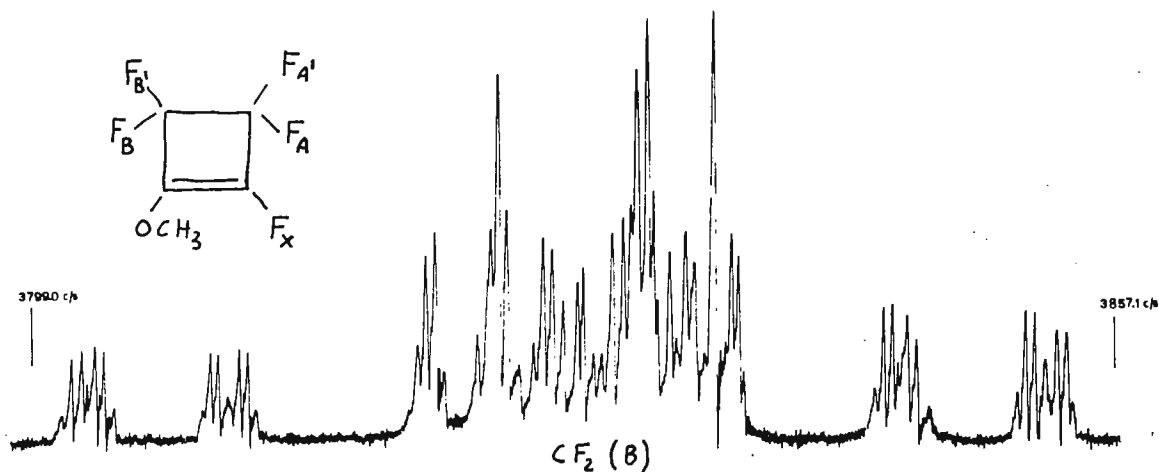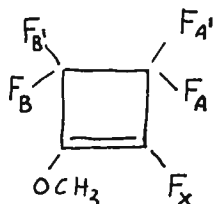
TEXAS CHRISTIAN UNIVERSITY

Fort Worth, Texas 76129

Department of Chemistry   October 21, 1969

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

AMINO ACID SPECTRA AVAILABLE

Dear Barry:

Recently Art Ihrig and I ran the eighteen common essential
amino acids under standard conditions of acid and base in
D_2O. Since there seemed to be no one place where they are
all together in the literature we had them printed up into
a small booklet (copy enclosed). We will be glad to supply
copies to all interested parties upon receipt of a request.

Yours sincerely,

Bill

W. B. Smith
Chairman
Department of Chemistry

WBS/dc
Enclosure
P. S. What happened last Saturday. I thought our team had
fallen into an infinite potential well but your well seems to
be lower yet.

Bill:

    I do not understand your postscript completely. Because of your
reference to a team and because of the time of year and where we live,
I suspect it might have something to do with minor league professional
athletics. I think that I shall write my friends in Columbus for a
clarification.

                            Barry

October 23, 1969

Degassing and Sealing Off NMR Tubes

To attach 5 mm NMR sample tubes directly to a vacuum line,
we are now using a Cajon Ultratorr union #2Y 4UT-6[1] which
we find more convenient than the device described earlier by
us[2]. It consists of one single piece, and greased joints are
omitted.

We seal off sample tubes under vacuum with a "Little Torch"[3]. It
operates on oxygen and natural gas, and yields a variety of pin-
point size flames. Neat and even seals are easily made.

The vacuum line proper is now completely greaseless, all ground-
glass joints have been replaced by O-ring connectors (including
that of the trap), and stopcocks by glass-teflon needle valves,
with an internal glass-to-O-ring seal[4]. Thus a vacuum of less than
one micron, as measured by a Pirani gauge, is obtained rather quickly.

David W. Mastbrook
NMR Group, SC-410

[1] Cajon Co., 32550 Old South Miles Rd., Solon, Ohio 44139

[2] I.T.IN.M.R.N. 80.34 (1965).

[3] Tescom Corp., Instrument Div., 2633 S. E. 4th St., Minneapolis, Minn. 55414

[4] Fusion Inc., 9681 Allen Ave., Rosemont, Ill. 60018

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
NORTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
1815 NORTH UNIVERSITY STREET
PEORIA, ILLINOIS 61604

October 24, 1969

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

Dear Barry:

Suggested Reference for Deuterium Resonance;
Digital Improvement of C-1024 Data.

In general, chemical shifts reported for a nucleus need only to be compared with shifts of the same species. The reference chosen, therefore, is largely a matter of personal preference or availability. Deuterium resonance, however, often requires comparison with proton resonance. We suggest, as a matter of convenience, that equivalent scales be employed in deuterium and proton resonance. Until per-deutero-TMS becomes generally available, the same result can be achieved by setting the $CDCl_3$ line at δ 7.26 (τ 2.74 if one prefers). On this scale similar structures will have similar chemical shifts in both deuterium and proton resonance.

We were using $CDCl_3$ as a lock signal for our HA-100 but found that olefinic deuterons were only about 20 Hz from the lock. This made any measurement poor, and quantitative measurement impossible. A better reference is benzaldehyde-d_1 which is commercially available and about $2\frac{1}{2}$ ppm lower field than chloroform. With the olefinic deuterons 60 Hz from the lock they can be easily measured.

A need existed to improve data digitally which had been accumulated by time-averaging with the C-1024. R. R. Ernst (TAMUNMRN-131-14) described an interface to a Varian 6201 but we have only an IBM 1130 available. We are now taking signals from the CAT to a Tally punch via a TMC 220C interface. We have a subroutine written in assembler to read the tape, and a FORTRAN program which corrects the baseline either linearly or on a Lorentzian curve, reads the filter constant to be applied, and performs two RC filter operations. With a judicious choice of filter constant, most of the noise is removed and the signals are only slightly broadened.

Sincerely,

Curtis A. Glass, Chemist
Cereal Properties Laboratory

David Weisleder, Chemist
Cereal Properties Laboratory

October 29, 1969

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

TITLE: Correlation of ^{13}C and ^{1}H Shifts through Off-Resonance
         Decoupling

Dear Barry:

As mentioned in my last TAMUNMR Contribution (No.123, p.42), we have
been obtaining ^{13}C spectra using our HA-100 and HA-100-15 with homo-
nuclear lock. This has worked quite well using 8 or 12 mm spinning
sample tubes with the ^{13}C lock provided by a capillary of ^{13}C
enriched (ca.50%) CH_3I, CH_2I_2, or CS_2. We have also used the signal
from certain solvents while doing proton noise decoupling. Benzene
and dioxane work particularly well in this application and we have
also used DMSO and a few others.

When using a solvent peak for lock it is possible to switch from
noise decoupling to CW decoupling, but the decoupler must be tuned to
the exact frequency for irradiation of the solvent protons. We have
found that reducing the decoupling power so that $2\pi\gamma H_2 \sim 1000$ Hz still
gives a nicely decoupled solvent peak. Then most ^{13}C signals which
arise from CH_3, CH_2 or CH groups whose proton shifts are not very near
the solvent proton shift give well-spaced multiplets which allow
appropriate assignments to be made.

More recently, we have taken to measuring the magnitude of the
residual splittings produced in the CW decoupled spectrum in an
effort to correlate ^{13}C shifts with corresponding shifts in the ^{1}H
spectrum. A nice example of this approach is seen in the spectrum
of one of the samples in the series of compounds that you and I have
been recently studying[1]. As seen in the structure drawn in the figure
one of the methyl groups lies over the plane of the napthalene rings
and its proton shift is 0.39 ppm to higher field of TMS ($\delta = -0.39$ ppm).
The other methyl groups give proton signals at $\delta = 0.84$, 1.35 and 1.66
in dioxane ($\delta = 3.52$). The lowest field signal is from the methyl
group which lies near the plane of the napthalene rings and closest
to both of them.

The partial ^{13}C spectrum seen in the figure shows peaks from the four
methyl groups and one of the quaternary carbons. The ppm scale (δ_c)
indicates shifts relative to the ^{13}C signal of dissolved TMS and uses
the same sign convention as for the δ scale in proton work. The lower
trace shows the results of noise decoupling while the upper trace was
run with CW decoupling at the frequency for the lock signal which is
from the dioxane solvent. Knowing the proton shifts of the methyl
peaks relative to dioxane it is possible to calculate the residual
splitting J_r produced by off-resonance decoupling using the expression
given by Ernst[2], $J_r = \Delta f \cdot J/2\pi\gamma H_2$. In this case Δf is the separation in
the proton spectrum between methyl peaks and the dioxane signal. J is
the ^{13}C-^1H coupling constant and for these methyl groups is simply
assumed to be 120 Hz. The strength of the decoupling field $2\pi\gamma H_2$ was
set to a value determined to be 1,120 Hz. The observed and calculated
values are shown in the following table:

δ_C	Obs.J_r	δ_H	Δf	Calc.Jr
37.0 ppm	28 Hz	0.84 ppm	268 Hz	28.7 Hz
30.8	39	-0.39	391	41.9
27.2	20	1.66	186	19.9
24.4	23	1.35	217	23.2

Agreement between observed and calculated J_r values neatly ties together
assignments for ^{13}C and ^1H signals from the same methyl group. Thus,
the highest field proton signal corresponds to the second to lowest field
^{13}C methyl peak, and so forth.

The simple expression used for calculation of J_r values requires that
$2\pi\gamma H_2$ is much greater than both Δf and J, a condition which is not really
met, especially for the larger values of Δf. Calculation of J_r using
Ernst's exact expression (47) produces values of 27.8, 39.4, 19.6, and
22.7 Hz and now the agreement is really nice.

The advantage of this technique is that it can provide with one CW
decoupled spectrum several ^{13}C assignments if corresponding assignments
are already known in the proton spectrum. We have also used this method
for assignment of methine carbons in other compounds but have not had as
good success with methylene carbons which often produce ill-resolved
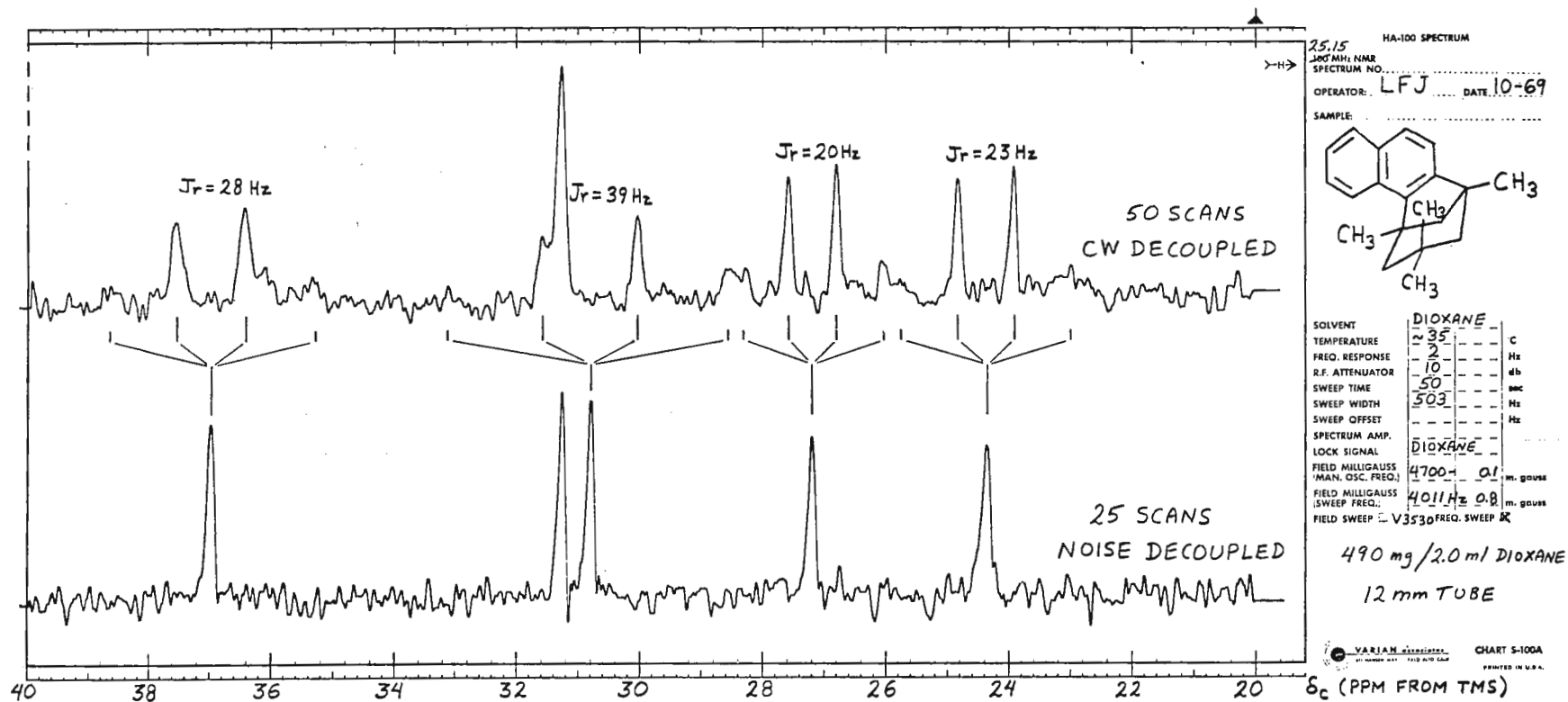triplets in the CW decoupled ^{13}C spectrum.

With best regards,

Yours sincerely,

Roy

L.F.Johnson

1. Samples prepared by M.J.Gattuso and
   G.R.Sullivan of Texas A and M.
2. R.R.Ernst, J.Chem, Phys.,45, 3854 (1966)

October 30, 1969

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

Dear Barry:

Lost and Found Department: 500MHz NMR

The attached 100 and 500MHz NMR spectra of a naphthalene derivative were
recently received in the mail by Varian's Director of NMR Operations.
Unfortunately, both the envelope and cover letter accompanying these
spectra were inadvertently misplaced, and we are unable to identify the
source of the extraordinary, high frequency spectrum.

Because your Newsletter is read by the entire NMR community, we are
appealing to you to publish these spectra and thereby assist us in
locating the spectroscopist who generated them. Surely, he will recognize
the fruits of his own labor.

We further request that the spectroscopist in question, whoever he may be,
contact the undersigned immediately and not reply directly to the Editor,
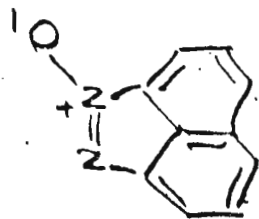TAMU N-M-R Newsletter, or to any other agency, public or private.
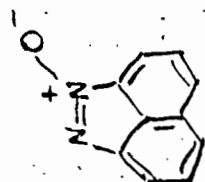
Anxiously yours,

Ray Ettinger
Product Manager, High Resolution
NMR Spectroscopy
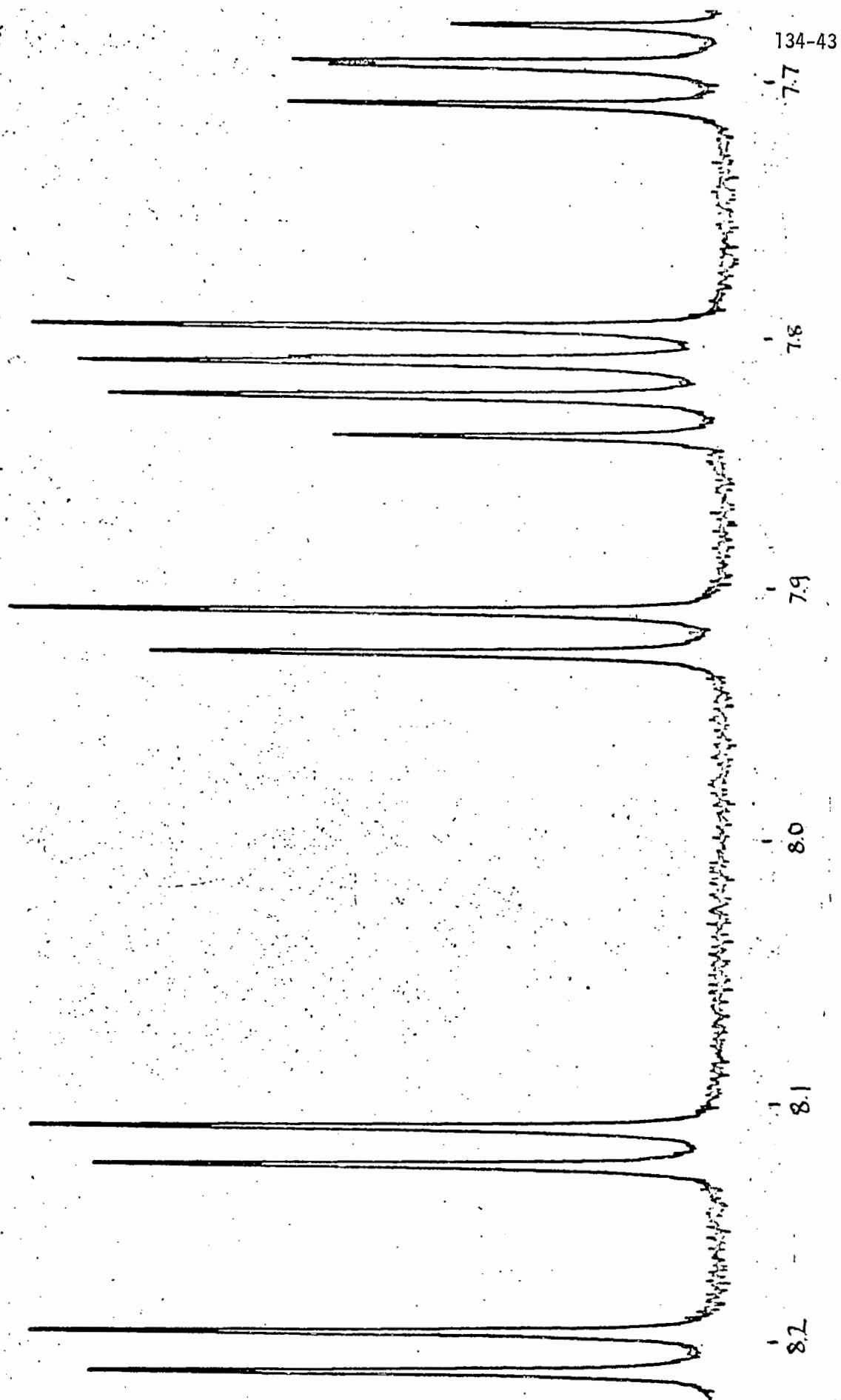Analytical Instrument Division

RE:bjs

134-42

dilute solution CDCl₃

100 MHz

8.5   8.0   7.5   ppm
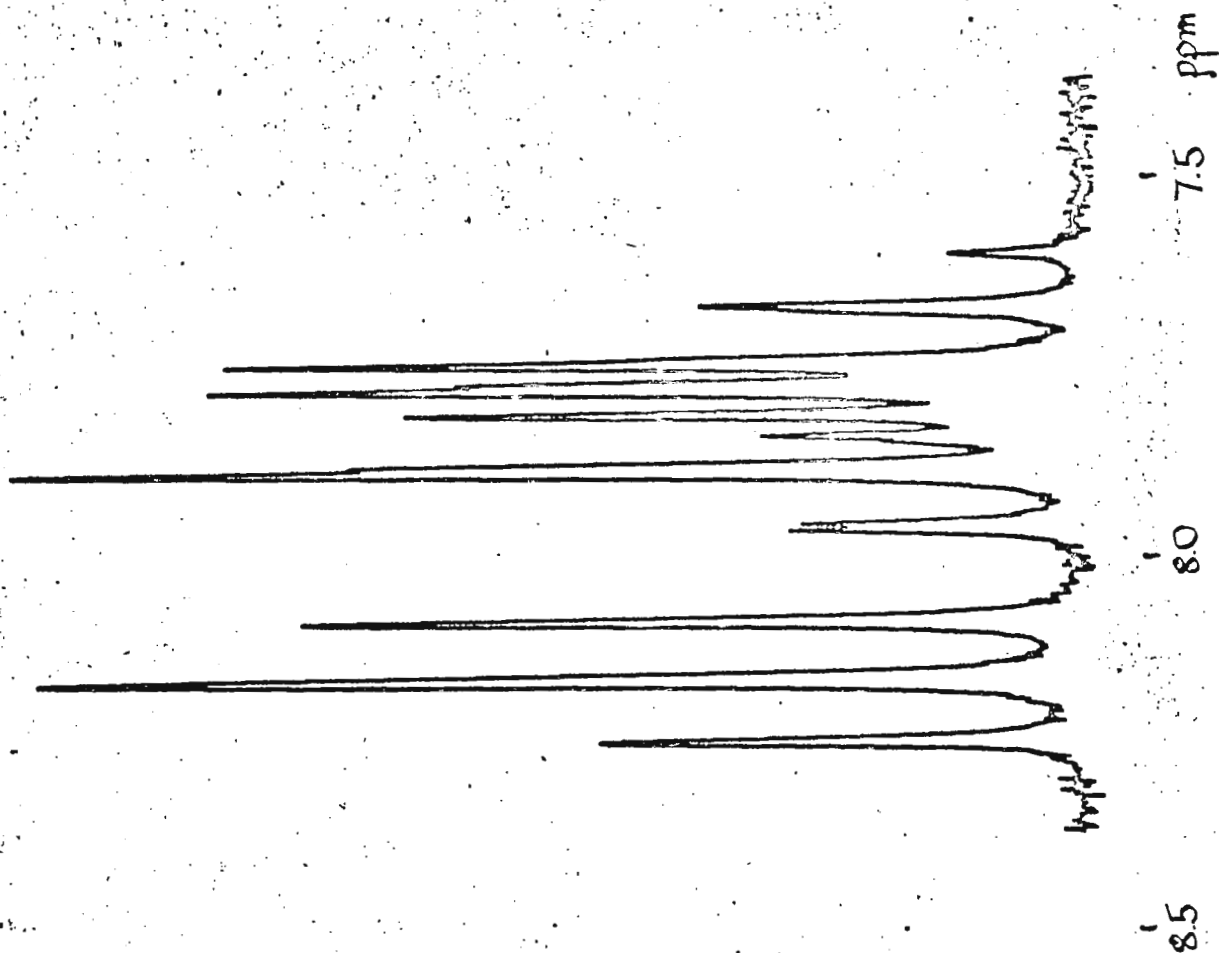
dilute solution CDCl₃

500 MHz

134-43

7.7   7.8   7.9   8.0   8.1   8.2

Dr. W. Brügel c/o

Badische Anilin- & Soda-Fabrik AG

BASF

Prof. Dr. B.L. Shapiro

Department of Chemistry
Texas A & M University

College Station, Texas 77843
U S A

Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen	Telefon-Durchwahl	Telex	6700 Ludwigshafen
		Dr.Brü/Fa	(06 21) 60-	464 -	27. Okt. 1969

Betreff **Präparationskunstgriffe beim HR-220**

Sehr geehrter Herr Dr. Shapiro!

Es tut mir leid, daß Sie mich wieder einmal an den verstriche-
nen Termin meines Beitrags zu den Newsletters erinnern mußten.
Acht oder neun Monate vergehen eben doch zu schnell, gemessen
am Fortgang mitteilungswürdiger Arbeiten.

Ich möchte Ihnen heute in Ermangelung eines besseren über ei-
nen kleinen Kunstgriff berichten, der uns eine bessere Ausnüt-
zung unseres HR-220 ermöglicht. Bei diesem Instrument kann ne-
ben der Herstellung eines optimalen Feldes (mittels der Shim-
spulen) das Auffinden der optimalen Rotation des Proberöhr-
chens zeitraubend sein. Von Röhrchen zu Röhrchen und für ein
gegebenes Röhrchen von Füllung zu Füllung wird erfahrungsge-
mäß eine andere und recht kritische Rotationsfrequenz benö-
tigt. Offensichtlich rühren die Schwierigkeiten von der unter-
schiedlichen Ausbildung des Rotationsparaboloids (vortex) der
rotierenden flüssigen Füllung des Röhrchens her. Ein Auf- und
Abtanzen der Flüssigkeit wird sich immer dann störend auswir-
ken, wenn man dabei in die Nähe des oder gar in den eigentli-
chen Meßraum kommt, der beim HR-220 ja bekanntlich viel größer
als bei den anderen Instrumententypen ist. Deshalb werden die
Röhrchen auch gewöhnlich bis zu einer Höhe von 55 - 60 mm ge-
füllt.

Meine Mitarbeiterin Fräulein Anneliese Beck hat nun den Vor-
schlag gemacht, die Ausbildung des Rotationsparaboloids durch
Einbringen eines Stöpsels unmittelbar über der Flüssigkeit
überhaupt zu unterbinden und gleichzeitig die Füllhöhe auf

- 2 -

Badische Anilin- & Soda-Fabrik AG

Empfänger	Unsere Zeichen	67 Ludwigshafen am Rhein	Blatt
Prof. Dr. B.L. Shapiro	Dr.Brü/Fa	27. Okt. 1969	2

Betreff

das unbedingt notwendige Maß zu beschränken. Dieser Vorschlag - wieder einmal ein Ei des Kolumbus - hat uns mit einem Schlag von den mit der Röhrchenrotation zusammenhängenden Schwierigkeiten befreit:

1. Die Auflösung im Spektrum ist im Gegensatz zum ursprünglichen Brauch von der Rotationsfrequenz unabhängig; die Zeit zum Aufsuchen der optimalen Rotationsfrequenz entfällt.

2. Die geringere Füllhöhe erspart uns Lösungsmittel (wenn deuteriert, meist teuer).

3. Aus demselben Grunde benötigen wir bei gleich konzentrierter Lösung nur noch die halbe Menge der zu untersuchenden Substanz.

Punkt 2 und 3 verstehen sich von selbst. Für Punkt 1 füge ich ein Beweisstück bei, in dem die Abhängigkeit eines Signals nach Höhe und Halbwertsbreite (also die Auflösung) dargestellt ist in Abhängigkeit von der Rotationsfrequenz des Meßröhrchens, einmal für die alte Präparationsmethode (Füllhöhe 55 mm, kein Stöpsel, obere Hälfte des Bildes), einmal für die neue Präparationsmethode (Füllhöhe 28 mm, Stöpsel, untere Hälfte des Bildes). Dazu wurde nach alter Präparation zunächst eine brauchbare Auflösung - (nebenbei bemerkt, nicht die beste, die mit diesem Instrument überhaupt möglich ist) - bei der Rotationsfrequenz R = 100 Hz (gemessen mittels der Rotationsseitenbänder) hergestellt. Dann wurde die Rotationsfrequenz durch Veränderung der Spinnerluft nach oben und unten ohne Änderung der Feldshims verändert und schließlich der Ausgangswert wieder eingestellt (die handschriftlichen Zahlenangaben bei den Signalen betreffen die Einstellung des Luftventils als "quasi Uhr"). Der starke Einfluß auf die Auflösung ist klar ersichtlich. Sodann wurde die halbe Füllung aus dem Röhrchen entfernt, der Stöpsel eingefügt und das Experiment wiederholt. Ich glaube, der Befund spricht für sich selbst.

Die Gestalt des Stöpsels, aus ⓇTEFLON hergestellt, ist aus dem Bild ebenfalls ersichtlich. Er hat eine zentrale Bohrung, um beim Einführen die Luft über der Füllung entweichen zu lassen, und im oberen Teil ein Innengewinde, das die Positionierung mittels eines Metallstabes gestattet. Im unteren Teil besteht er aus schmalen Lamellen, die einen festen, dicht abschließenden Sitz in einem der üblichen 5 mm-Präzisionsröhrchen gewährleisten. Ganz unten befindet sich eine kleine zentrale Bohrung, die sich mit Meßflüssigkeit füllt.

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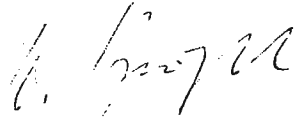| Empfänger	Unsere Zeichen	67 Ludwigshafen am Rhein	Blatt
Prof. Dr. B.L. Shapiro	Dr.Brü/Fa	27. Okt. 1969	3

Betreff

Neben den zuvor aufgeführten Vorteilen der neuen Röhrchenpräparation gibt es noch einen weiteren, der nicht unterschätzt werden soll:

4. Da die Rotationsfrequenz die Auflösung nicht mehr beeinflußt, kann sie während der Spektrenaufnahme in gewissen Grenzen verändert werden, um die beim HR-220 unvermeidlichen Rotationsseitenbänder an eine die Auswertung des Spektrums nicht störende Stelle zu verschieben.

Da wir gerade bei technischen Kunstgriffen sind, noch ein Hinweis, der uns manchmal weitergeholfen hat: Bei manchen Probenröhrchen haben wir trotz aller Sorgfalt keine brauchbare Auflösung erzielen können, obwohl die Meßsubstanz und Präparation einwandfrei waren - die Signale blieben breit. Der Verdacht auf magnetische Verunreinigungen an der Glasoberfläche drängte sich auf. Diese sind möglich, weil die Präzisionsröhrchen über einem Eisendorn gezogen werden. Kurzzeitiges Ätzen in HCl (verdünnt) hat weitergeholfen und alle derartigen Schwierigkeiten beseitigt.
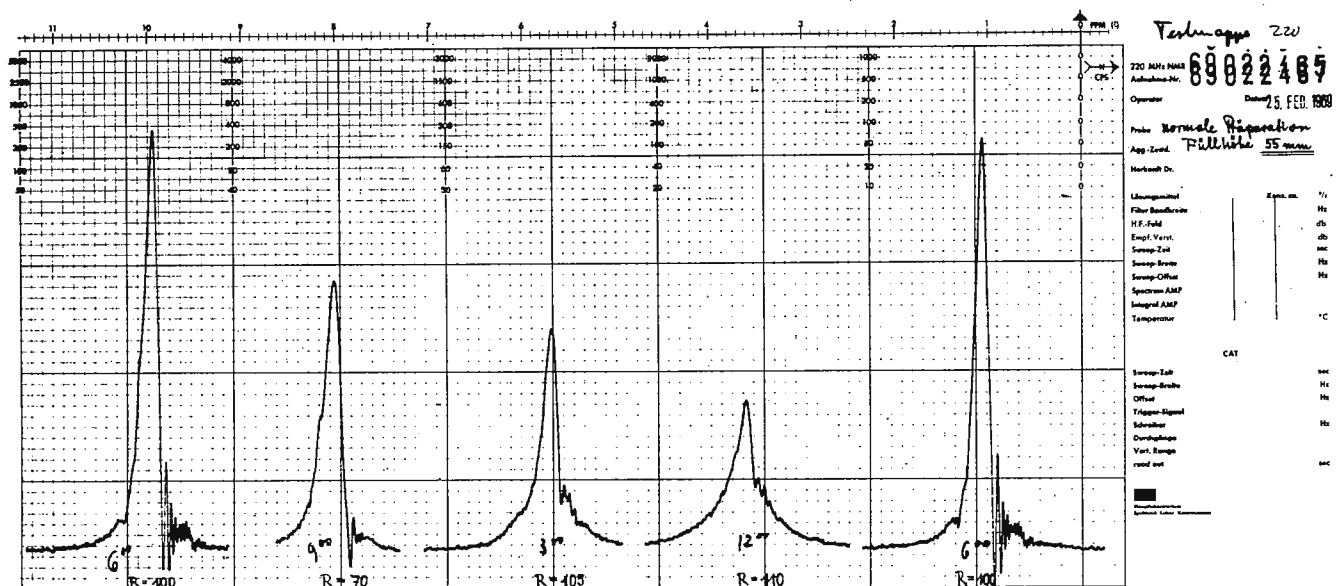
Mit freundlichen Grüßen

Ihr sehr ergebener

(Dr. W. Brügel)

Anlage
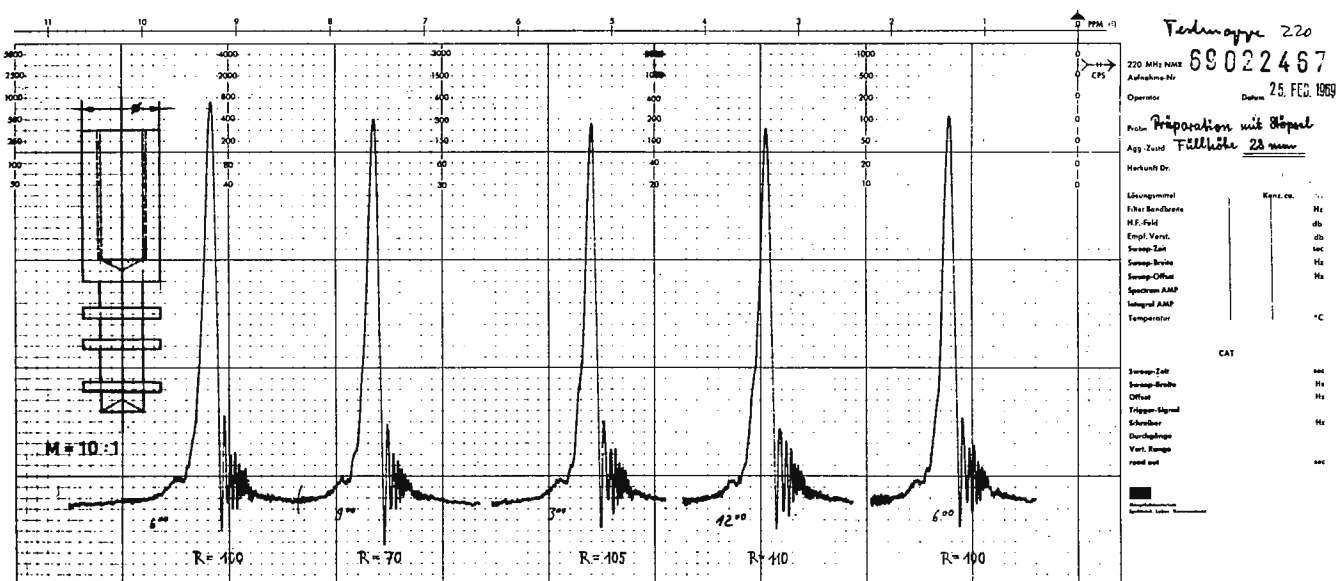
The XIth Experimental NMR Conference

The XIth Experimental NMR Conference will be held April 22-24, 1970 at Mellon Institute in Pittsburgh. Inquiries may be directed to the Chairman:

> Dr. T. J. Flautt
> Procter & Gamble - MVL
> Box 39175
> Cincinnati, Ohio 45239

> T. J. Flautt
> 4 November 1969

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