Illinois
Institute of
Technology
N – M – R
Newsletter

No. 118
JULY, 1968

Please note the following date after which all Newsletter correspondence, etc., should be addressed to my new address below:

Effective August 1* 1968:

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

*NOT August 10 as given in last month's Newsletter

           BLS
           7-2-68

COLLEGE OF NATURAL SCIENCE · DEPARTMENT OF CHEMISTRY · CHEMISTRY BUILDING

May 29, 1968

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Modification of Receiver Gain Control on V-4311

Dear Barry:

We had been having considerable difficulty with some experiments on the 100 MHz
instrument requiring high transmitter power such as triple resonance experiments
and the observation of double quantum transitions. It was suggested to us by
LeRoy Johnson of Varian Associates that we should modify the receiver gain control
to use the recorder output pot to provide an extended range of attenuation (as is
apparently now standard on the newer instruments). The modification has made it
much easier to prevent overloading the receiver and proves to be indispensable
for many experiments.

A 3P-DT switch was mounted near the receiver gain control of the V-4311 and connected
so that in the "attenuate" position the 100K recorder output pot (R358) is substituted
for the fixed 1K resistor of the receiver gain control (when it is in position 1)
to provide extended fine control of attenuation. When the switch is in the "off"
position the unit is restored to normal operation. The second and third poles of
the switch are needed because all three terminals of R358 are normally grounded
when the frequency response switch is in WL ϕ Detector or WL Diode position.
A diagram is included in case anyone with an older V-4311 unit is interested in
this low-cost modification.
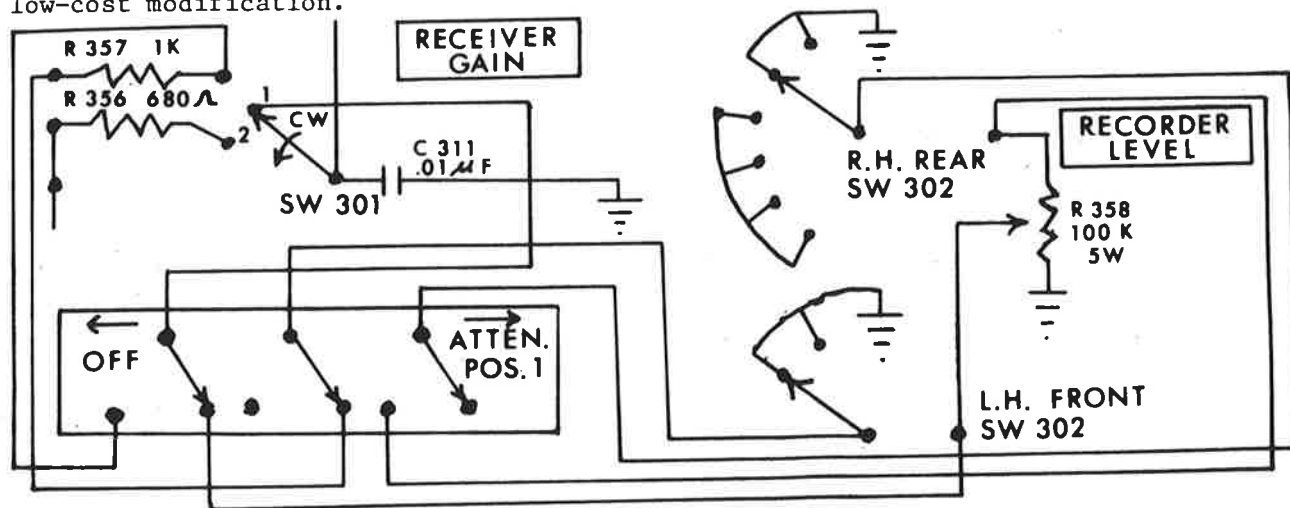
Yours sincerely,

M.H.Gross   Max T.Rogers

CALIFORNIA STATE COLLEGE   **AT LOS ANGELES**

Department of Chemistry

5151 State College Drive, Los Angeles, California   12
(San Bernardino and Long Beach Freeways Interchange)

June 3, 1968

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

Dear Barry:

In a recent publication [J. Am. Chem. Soc., 90, 1 (1968)] we demon-
strated that complexes of the boron trihalides with organic bases could
be studied directly by preparing samples with excess ligand and ob-
serving separate proton signals for bulk and complexed solvent molecules.
We have now extended these studies to complexes of BF_3 and BCl_3 with
nitrogen heterocycles, an example of which is given in the accompanying
figure. Separate signals for bulk and complexed pyridine molecules
are readily apparent, permitting accurate chemical shift and peak area
measurements. We ran a series of pyridines in this way and obtained
some interesting trends in complexing ability of the ligands. The ligands
were also studied in pairs to estimate their ability to compete with each
other for BF_3.

If anyone would like more information on these studies we would be glad
to hear from them.

Sincerely,

Tony

Anthony Fratiello

Ronald Schuster

Ronald Schuster

AF/vj

5:1, $H_2AB_3 : BF_3$

$\delta = -40°C$

$\mapsto$ 30 cm $\dashv$

$C_{2,6}$

$B_{2,6}$

$B_{3,5}$

C_4

C_3

$H_0 \longrightarrow$
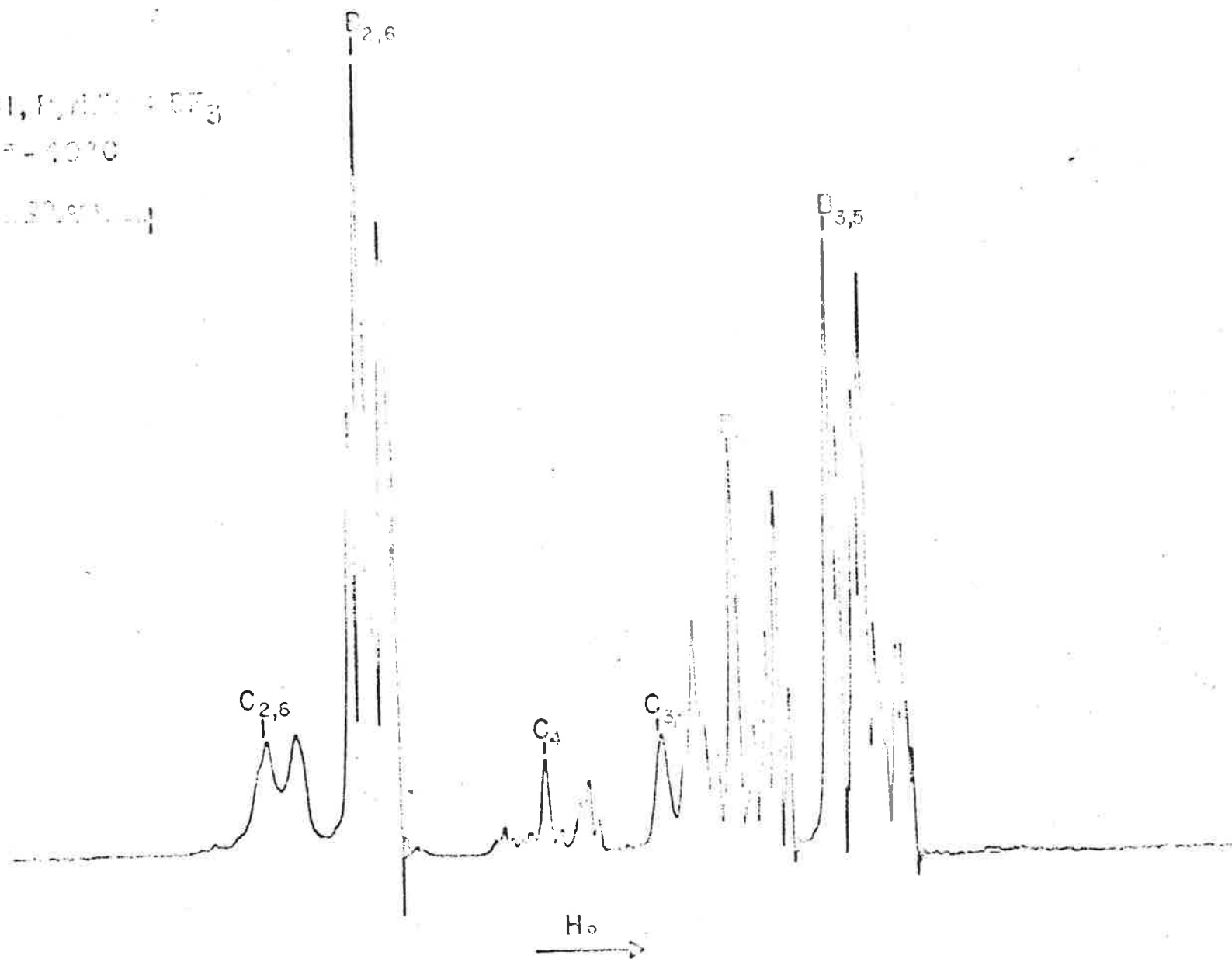
NATIONAL RESEARCH COUNCIL
CANADA

DIVISION OF APPLIED CHEMISTRY

OTTAWA 2,

11 June 1968.

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

Dear Dr. Shapiro:

Please add me to your list of subscribers of the most informative and useful "ITTNMR Newsletters". I believe the following should qualify me for a subscription.

Nuclear Triple Resonance Tickling

Recently V. Sinivee and V. Salum (1) have developed a theory for triple resonance with weak r-f fields. They calculated the line shapes and predicted a new phenomenon: the appearance under certain conditions of the signal with frequency that are combination of the basic frequencies.

The present letter reports results of some experiments carried out to test this theory and also to investigate more fully the triple resonance tickling method. The experiments were carried out on the frequency sweep NMR-H^1 spectrum of the three ring protons of 5-endo-1,2,3,4,7,7'-hexachlorobicyclo[2,2,1] hept-2-ene, which can be treated in an AMX approximation (2).

If in the AMX system the set of three energy transitions

1. V. Sinivee, Eesti NSV TA Toimetised, Füüsika*Matemaatika (Bull.Acad.Sci. Estonian SSR,Phys.Math.Sci.Ser.), 16, 444 (1967); V. Sinivee and V. Salum, ibid, 17, No. 1, 49 (1968).

2. V.F. Bystrov and A.U. Stepanyants in "Radiospektroskopicheskie i Kvantovokhimicheskie Metody v Strukturnikh Iss - ledovaniyakh" (Radiospectroscopic and Quantum Chemical Approaches to the Study of Structure), Izdat. "Nauka", Moscow, 1967, p. 147.

irradiated by fields of frequencies ν_1, ν_2 and ν_3 (of which the ν_1 is used for observing the signals) comprises a fragment of the energy diagram with just four levels then specific effects should arise (1). Fig. 1 shows the experiments on the fragment of type 22-1. Irradiation solely of the A3 transition (double resonance tickling) splits the line M3 into a doublet with narrow components ($\Lambda=0$) and the line M4 into a doublet with broadened components ($\Lambda=2$) (Fig. 1c). A similar result was obtained on irradiating of the X3 transition (Fig. 1d). Simultaneous irradiation of A3 and X3 (triple resonance tickling) with fields of the same effective intensities $h_2 = h_3$ [$h_i = \gamma H_i (I_{mn})^{\frac{1}{2}}$; I_{mn} — the intensity of the irradiated transition in the non—resonance spectrum] splits the line M3 into a triplet of equidistant spacings equal to $2h_2(=2h_3)$ and intensity ratio 1:2:1 (Fig.1e) in accord with the theory. The marked decrease in over-all intensity of line M2 is, apparently, to be ascribed to the Overhauser effect for $\Lambda=0$ transitions. Deliberate increase in field inhomogeneity up to line widths $\Delta\nu^{*}_{\frac{1}{2}} \simeq 3$ cps increases the width of the outer components of the triplet (Fig. 1f) and decreases the intensity of the central component, whose width, however, remains practically unchanged. It is note-worthy that with nonuniformly widened lines in the double resonance spectra, a well-defined splitting of the line $\Lambda=0$ into a doublet is observed even for $h_2 < \Delta\nu^{*}_{\frac{1}{2}}$. If the intensity of one of the irradiating fields is lowered the signal from the fragment of type 22-1 is transformed into a quadruplet with splittings equal $2h_2$ and $2h_3$ (Fig. 1g,h). It can be seen that with increase in the H_2/H_3 ratio the intensity of the internal components of the quartet diminishes as compared to the outer ones. On tuning out one of the irradiating fields by even 0.1 cps, the triple resonance signal becomes unsymmetric.

The appearance of a combination frequency was observed for fragments of the type 121. On triple resonance $\{X2,M4\}$

the line M2 (fragment 121-2) is split into a triplet (Fig. 2b) whose shape is determined largely by the relaxation parametars of the spin system and by the Overhauser effect (1). When the transition X4 is also irradiated with the frequency ν_4 (quadruple resonance) then if the sweep frequency ν_1 coincides with the combination frequency $\nu_2 + \nu_3 - \nu_4 = (E_4 - E_7)/h$ zero beat appears (Fig. 2c). The beat amplitude diminishes considerably on tuning out any one of the frequencies (ν_2, ν_3 and ν_4) by as little as 0.5 cps and is not observed at all if the distuning reaches a value of 5 cps (Fig. 2d,e). One may turn off the ν_1 audio frequency modulation of the constant magnetic field while leaving on the reference voltage on the phase detector of the recording channel [unit 8 of Fig. 1b in (2)]. The usual signals then obviously disappear, but the beat at the frequency $\nu_1 = \nu_2 + \nu_3 - \nu_4$ remains (Fig. 2f). Based on the theory it is to be expected that the intensity of the combination frequency signal appearing here in the presence of the weak (observing) field h_4 should be proportional to $(I_{M2} \cdot I_{X4})^{\frac{1}{2}}$. Hence, simultaneous irradiation of the transitions X2, M4 and X4 induced the combination frequency transition $E_4 - E_7$ corresponding to the unirradiated line M2.

A similar experiment was successfully carried out by irradiating the combined transition 5-4. The ABC-calculated intensity of which is only $3.3 \cdot 10^{-5}$.

The experimental results described here and those which will be discussed in a subsequent paper confirm the main conclusions of theory. It is at present difficult to discern an area where nuclear triple resonance spin-tickling will assume a particularly important place. However, despite the experimental difficulties, one may expect that the method will find application

- 4 -

in studies of relaxation mechanisms and in the construction of
energy diagrams for partially concealed spectra (especially from
observations of the combination frequencies).

Please credit this letter to obtain the ITT NMR
Letters at my permanent address:

Institute for Chemistry of Natural Products,
U.S.S.R. Academy of Sciences,
Ul. Vavilova, 32,
Moscow,
U.S.S.R.

Sincerely yours,

V. Bystrov.

/adg
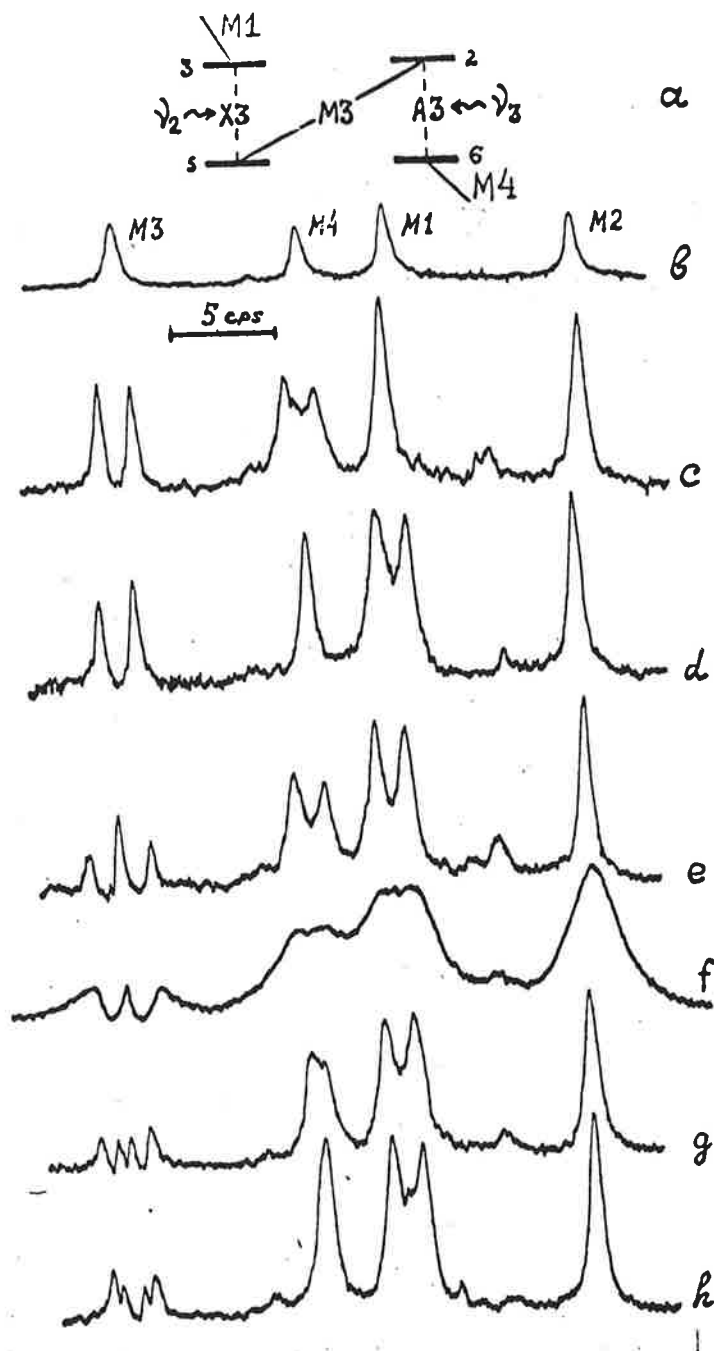
Fig. 1.
Triple resonance for the fragment 22-L.(a) the energy diagram. (b) The mono-resonance spectrum for the proton M. (c and d) Double resonance spectra for $\{A3\}$ and $\{X3\}$ respectively. (e,f) Triple resonance spectra $\{A3, X3\}$ at $2h_2 = 2h_3 = 1.5$ cps and the line width $\Delta\nu_{\frac{1}{2}} \simeq 0.5$ cps and $\Delta\nu^*_{\frac{1}{2}} \simeq 3$ cps, respectively. (g,h) Triple resonance spectra at $2h_2 = 1.5$ cps and $2h_3 = 1.0$ cps and 0.5 cps, respectively.
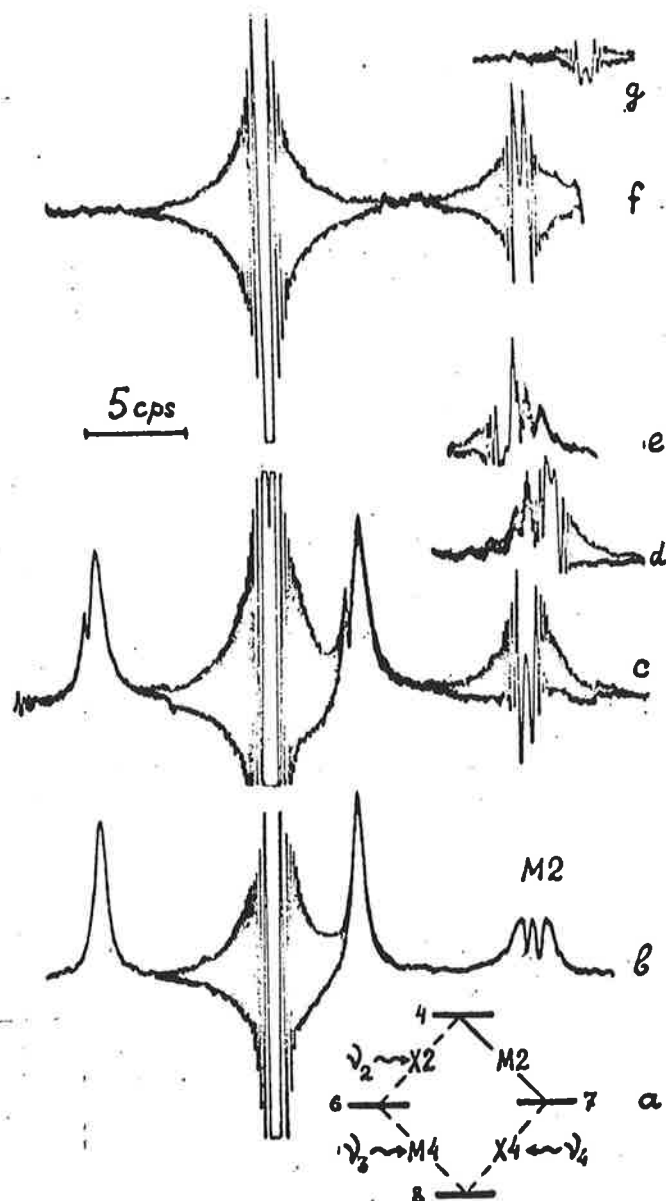
Fig. 2.
Triple resonance for the fragment 121. (a) Energy diagram.
(b) Triple resonance spectrum {M4,X2} of the type 121-2
at 2h$_2$=2h$_3$=0.7 cps. (c) Quadruple resonance spectrum
{M4,X̄2,X̄4} at 2h$_4$=0.3 cps and precisely tuned in frequencies
ν$_2$,ν$_3$ and ν$_4$.(d) Ditto, but with ν$_4$ distuned by -0.7 cps and
(e) with ν$_2$ distuned by +0.9 cps. (f) Triple resonance
spectrum {X2, M4, X4} with shut off ν$_1$ field modulation and
precise tuning in of ν$_2$ ν$_3$ and ν$_4$. (g) Ditto with ν$_2$ distuned
by 3.5 cps.

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

FOOD AND DRUG ADMINISTRATION

WASHINGTON, D.C. 20204

June 3, 1968

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

Operating Instructions for HA-100/C-1024

Dear Barry:

While using the HA-100/C-1024 team, we had a chance to revise
and update the operating instructions corresponding to the
C-1024.

We wound up writing our own set of directions which (we think)
are compact, complete, easy-to-follow and (we hope) free of
errors.

Anyone interested in these operating instructions is welcome
to a set for the asking.

Sincerely,

Ernest Lustig   Elizabeth A. Hansen
Division of Food Chemistry & Technology
Bureau of Science

UNIVERSITY OF HOUSTON
CULLEN BOULEVARD
HOUSTON, TEXAS 77004
UNITED STATES OF AMERICA

DEPARTMENT OF CHEMISTRY

12 June 1968

Dr. B. L. Shapiro
Department of Chemistry
Stanford University
Stanford, California 94395

Dear Barry:

A REITERATION OF KAISER'S CAVEAT ON DOUBLE RESONANCE

During the last eighteen months the organic chemists masquerading as
NMR spectroscopists here at the university have been attempting
sophisticated HA-100 NMR experiments. We have been especially
anxious to jump on the band wagon and do NOE experiments. We
noticed that wide variations in total signal intensity occurred
during our double resonance experiments. The situation finally
became so aggravating that we sat down and reread the IITNMR news-
letters and found that Kaiser (IITNMR-74-11 and 75-1) had anticipated
our difficulty by four years. In the simplest possible terms we
were doing the experiment incorrectly.

The significant error in our work was the over loading of the audio
phase-detectors in the lock box. A make shift remedy can be devised
by attenuating the output of the V-4311 before detection in the audio
section. A more sophisticated arrangement consists of a notched
filter that selectively removes the frequency of the double irradiation
placed between the V-4311 and the lock box. We have used both devices
and find that the signal levels during double irradiation are so much
more stable than they previously were, that we can now concern our-
selves with NOE measurements, and not electronic difficulties.

The moral of this story is 2-fold. The average organic chemist
should find out how internally locked spectrometers function before
doing fancy experiments, and the same chemist can increase his NMR
efficiency by paying attention to the newsletter.

Sincerely,

M. R. Willcott
Assistant Professor of Chemistry

MRW:la

PERKIN-ELMER

June 14, 1968

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

Title: Coupling Constants Between Carbon-13
And Protons Through Two Bonds

Dear Barry:

As you know we have been interested in Carbon-13
NMR. We have recently had an opportunity to study
carbon-hydrogen couplings through two bonds and would
like to report some preliminary observations.

Carbon-13 resonances for some simple organic
compounds were observed under slow passage conditions
at 15.085 MHz. A frequency swept Hitachi Perkin-
Elmer Model R-20 spectrometer was used with the field
locked to the proton resonance of an external sample.

The magnitude of the two-bond carbon-13 proton
coupling constants was studied in terms of substituents
and hybridization.

For the system $H-C_1-^{13}C_2$, the absolute value of
the coupling constant seems to increase with increasing
electronegativity of the substituents at C_2 and with de-
creasing electronegativity of substituents at C_1. Changes
of hybridization at C_1 also seem to have more effect on
the two-bond coupling constant than changes of C_2.

Table 1 shows chemical shift and coupling data of
functional groups in a number of organic compounds in-
cluding substituted ethanes, ethylenes, carbonyls and
nitriles. Shifts are referred to CS_2. Couplings are
estimated to within ± 0.5Hz.
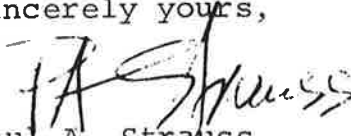
Dr. B. L. Shapiro
Page 2

June 14, 1968

As an example, the $^2J_{CH}$ coupling for ethane was reported as -4.5Hz by Lyndon-Bell some time ago. Successive chlorine substitution at the C_2 results in a significant increase in coupling constant to +5.9Hz for 1, 1, 1 - trichloroethane.

We will be doing more work in this area and will keep you informed.

Sincerely yours,

Paul A. Strauss
Product Manager
Magnetic Resonance Department

PAS:rb
Enc.

Table 1. C-13 NMR DATA OF SOME ORGANIC COMPOUNDS

No.	Compound	Functional Group	δ_{ppm}[1]	$^2J_{CH}, Hz$[2]
(A)	**Ethanes**			
1	CH_3CCl_3	CCl_3	97.5	5.9
2	CH_3CHCl_2	$CHCl_2$	124.5	5.1
3	CH_2CH_2Cl	CH_2Cl	154.5[3]	
4	CH_3CH_3		188.0[3]	-4.5[4]
5	CH_2ClCH_2Cl		142.0	< 2
6	$CH_2ClCHCl_2$	CH_2Cl	142.2	< 2
		$CHCl_2$	121.6	2.5
7	CH_2ClCH_2Br	CH_2Cl	148.7	4.3
		CH_2Br	161.2	4.3
8	CH_2BrCH_2Br		161.3	4.6
9	CH_3CH_2Br	CH_3	173.4	2.1
		CH_2Br	165.4	4.0
10	$CH_3CH_2NO_2$	CH_2NO_2	122.8	3.7
(B)	**Ethylenes**			
11	C_2Cl_4		72.3	--
12	C_2HCl_3	$CHCl$	76.2	--
		CCl_2	68.7	8.5
13	cis-$C_2H_2Cl_2$		74.4	+16.5
14	$trans$-$C_2H_2Cl_2$		72.6	< 2
15	C_2H_4			- 2.4[4]
(C)	**Carbonyl Compounds**			
16	CH_3COOH	CO	15.7	6.8
17	CH_3COCl	CO	23.2	7.3
18	$CH_2ClCOCl$	CO	24.5	5.7
19	CH_3COBr	CO	27.4	7.6
20	CH_3CH_2COOH	CO	12.4	5.9[5]
21	$CH_3(CH_2)_2COOH$	CO	13.0	[6]
22	$CH_2(COOEt)_2$	CO	27.2	[6]
23	$(CH_3)_2CO$	CO	-11.4	5.9
24	$(CH_3CO)_2O$	CO	26.4	7.4
25	CH_3CHO	CO	- 6.1	6.6

Table 1. C-13 NMR DATA OF SOME ORGANIC COMPOUNDS

(CONTINUED)

No.	Compound	Functional Group	δ ppm[1]	$^2J_{CH}$, Hz[2]
(D) Nitrile				
26	CH_3CN	CN	75.8	9.5 $\pm$0.8

[1] Referred to the external CS_2. Errors are estimated to be $\pm$ 0.3 ppm.

[2] Errors are estimated to be $\pm$ 0.5 Hz.

[3] The values observed by Spiesecke and Schneider (J. Chem. Phys., 35, 722(1961)) were converted to the values referred to CS_2 by adding +65.2 ppm.

[4] R. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc., 269, 385(1962).

[5] Estimated to be the mean of the $^3J_{CH}$ and the $^2J_{CH}$.

[6] Unresolved multiplets.

11th June 1968.

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago,
Illinois 60616,
U. S. A.

Dear Professor Shapiro

There has been considerable recent interest in the use
of high-resolution NMR in the investigation of conformation
and kinetic conformational processes of seven-membered ring
systems of both carbocyclic[1,2,3,4,5,6,7] and heterocyclic[6,8,9]
types.   For sometime now we have been particularly interested
in systems which have a 1,3-arrangement of double bonds in
the seven-membered ring, 3,6-diphenyl-2,7-dihydro-1,4,5-
thiadiazepine S,S-dioxide[10] (I) serving as a suitable hetero-
cyclic illustration.
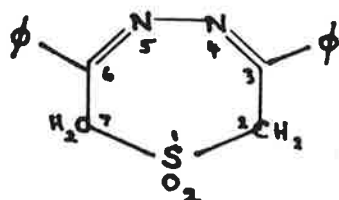
(I) $\phi \equiv$ phenyl

The 100 Mc/s proton spectrum of a dilute solution of (I)
in $CDCl_3$ measured at +34°C comprises a typical complex
aromatic absorption and, interestingly, an AA'BB' spin system
(centred at 5·60 τ) arising from the methylene protons.[11]
The fact that the methylene protons give rise to an AA'BB'

- 2 -

spectrum is particularly interesting for two reasons, the
first being that this requires ring inversion to be slow on
the NMR time scale[13] at +34°C.   As can be seen from the
scheme shown in Fig. I, ring inversion converts conformation
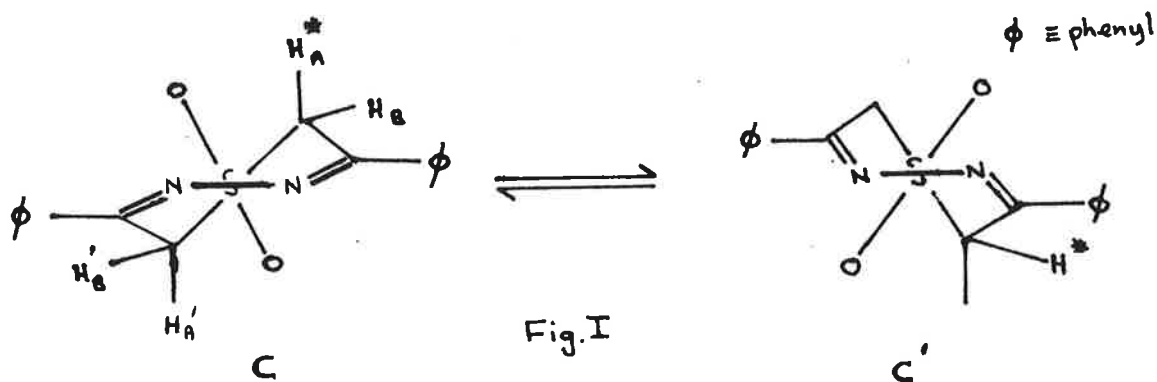C (see ref. 12) into the enantiomeric form C', and this brings
about interchange of protons between pseudo axial sites and
pseudo equatorial sites.

Fig. I

Rapid ring inversion would, therefore, be expected to lead to
collapse of the methylene resonance to a sharp single line in
the fast exchange limit.   From the observation that the
component lines of the non-averaged or "frozen" methylene
resonance show at most only slight kinetic broadening even at
+117°C (solvent 1,1,2,2-tetrachloroethane) one can, using the
slow exchange approximation[12] and an Eyring treatment of rate,
set a <u>lower limit</u> to the free energy of activation ΔG^*
for the ring inversion process at around 22 Kcal./mole at
+117°C.   This lower limit is extremely high for a simple
ring system, that is one which is neither fused nor bridged,
and indicates a resistance to conformational interconversion
which is among the highest known for simple cyclic systems.

- 3 -

The second noteworthy point is that the methylene protons give rise to an AA'BB' spectrum rather than an AB spectrum, the additional spectral complexity arising from stereospecific coupling across the sulphone, $-SO_2-$, grouping. Although numerous studies of stereospecific long range coupling corresponding to the 4 σ bond fragment H-C-C-H have been carried out,[14,15] coupling across oxygen and sulphur have been comparatively neglected,[14,16] and the present case is apparently the first observation of stereospecific coupling across the sulphone grouping. Work on this, and related molecules, will be reported in detail in a forthcoming publication.

With best wishes,

Yours sincerely,

David Dewar MacNicol

D.D. MacNicol

Douglas G. Williamson

D.G. Williamson[*]

* Present address: Chemistry Department, The University of Aberdeen, Aberdeen, Scotland.

- 4 -

References

1.   Knorr, Ganter, and Roberts, **Angew**. Chem. internat. Edit., 1967, 6, 556.

2.   Grunwald and Price, J. Amer. Chem. Soc., 1965, 87, 3139.

3.   Anet, J. Amer. Chem. Soc., 1964, 86, 458.

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5.   Buchanan and McCrae, Tetrahedron, 1967, 23, 279.

6.   Friebolin and Kabuss in "Nuclear Magnetic Resonance in Chemistry", ed. Pesce, Academic Press, 1965, p.125.

7.   Tochtermann, Schnabel, and Mannschreck, Liebigs Ann. Chem., 1968, 711, 88.

8.   Mannschreck, Rissmann, Vogtle, and Wild, Chem. Ber., 1967, 100, 335.

9.   Linscheid and Lehn, Bull. Soc. chim. France, 1967, 992.

10.   Loudon and Young, J. Chem. Soc., 1963, 5496.

11.   In fact spectra of (I) at $+34°C$ in wide variety of solvents have been measured and in all cases AA'BB' spectra (sometimes approximating to AA'XX') are observed, the chemical shift difference $| \delta_A - \delta_B |$ being highly sensitive to change of solvent, for example, ca. 0.2p.p.m. in chlorine-containing solvents such as chloroform-d or 1,1,2,2-tetrachloroethane, and 0.62p.p.m. in N,N-dimethyl-formamide.

12.   Independent ultraviolet evidence strongly supports the pseudo boat conformation shown in Fig. I.

13.   Pople, Schneider, and Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, 1959, ch. 10.

14.   Sternhell, Rev. Pure Appl. Chem., 1964, 14, 15.

15.   Bhacca and Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, 1964, p. 108.

16.   Sica, Paolillo, and Ferretti, Ricerca Scient., 1967, 2

SHELL DEVELOPMENT COMPANY

A DIVISION OF SHELL OIL COMPANY
1400-53rd STREET
EMERYVILLE, CALIFORNIA 94608

June 14, 1968

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

Dear Barry:

So much has already been written about the ABX approximation that one might think there was nothing new left to be said. Although what I have to say is not really new, I have worked out what I believe is a somewhat simpler approach to ABX analyses than has so far appeared in the literature. An outline with an example is presented here.

In setting up the spin hamiltonian for a 3-spin system we use the following set of basis functions:

i	φ_i	i	φ_i
1	$\alpha\alpha\alpha$	5	$\beta\beta\alpha$
2	$\beta\alpha\alpha$	6	$\beta\alpha\beta$
3	$\alpha\beta\alpha$	7	$\alpha\beta\beta$
4	$\alpha\alpha\beta$	8	$\beta\beta\beta$

where, as usual, $\alpha\alpha\alpha$, etc., refer to spins, 1, 2, and 3, respectively.

We also assume for labeling purposes that the chemical shifts ν_1, ν_2, and ν_3 increase downfield, i.e., that $\nu_1 < \nu_2 < \nu_3$. If we also assume, again for labeling purposes only, that $J_{AB} > J_{AX} > J_{BX} > 0$ then, in the first order limit, the numerical values of the energy levels associated with the basis functions φ_2, φ_3, and φ_4 will decrease numerically in that order; similarly for the energy levels associated with φ_5, φ_6, and φ_7. The transition frequencies in the order of increasing numerical values are then labeled by letters a, b, c, etc., as follows:

Transition Label	Origin	Frequency	Intensity
a	7-8	$1/2(\nu_A+\nu_B)-1/2J_{AB}-1/4(J_{AX}+J_{BX})-D_-$	$1-\sin 2\theta_-$
b	3-5	$1/2(\nu_A+\nu_B)-1/2J_{AB}+1/4(J_{AX}+J_{BX})-D_+$	$1-\sin 2\theta_+$
c	4-6	$1/2(\nu_A+\nu_B)+1/2J_{AB}-1/4(J_{AX}+J_{BX})-D_-$	$1+\sin 2\theta_-$

Transition Label	Origin.	Frequency	Intensity
d	1-2	$1/2(\nu_A+\nu_B)+1/2J_{AB}+1/4(J_{AX}+J_{BX})-D_+$	$1+\sin 2\Theta_+$
e	6-8	$1/2(\nu_A+\nu_B)-1/2J_{AB}-1/4(J_{AX}+J_{BX})+D_-$	$1+\sin 2\Theta_-$
f	2-5	$1/2(\nu_A+\nu_B)-1/2J_{AB}+1/4(J_{AX}+J_{BX})+D_+$	$1+\sin 2\Theta_+$
g	4-7	$1/2(\nu_A+\nu_B)+1/2J_{AB}-1/4(J_{AX}+J_{BX})+D_-$	$1-\sin 2\Theta_+$
h	1-3	$1/2(\nu_A+\nu_B)+1/2J_{AB}+1/4(J_{AX}+J_{BX})+D_+$	$1-\sin 2\Theta_-$
m	3-6	$\nu_X-(D_-+D_+)$	$\sin^2(\Theta_+-\Theta_-)$
i	5-8	$\nu_X-1/2(J_{AX}+J_{AX})$	1
j	2-6	$\nu_X-(D_--D_+)$	$\cos^2(\Theta_+-\Theta_-)$
k	3-7	$\nu_X+(D_--D_+)$	$\cos^2(\Theta_+-\Theta_-)$
l	1-4	$\nu_X+1/2(J_{AX}+J_{BX})$	1
n	2-7	$\nu_X+(D_-+D_+)$	$\sin^2(\Theta_+-\Theta_-)$

where:

$$D_{\pm}=\pm\{[(\nu_B-\nu_A)\mp 1/2(J_{AX}-J_{BX})]^2+J_{AB}^2\}^{1/2}$$

Since, in the ABX limit, a spectrum is independent of the signs of J_{AB} and $(J_{AX}+J_{BX})$, these signs will be taken positive for convenience in the ABX analysis. Of course, for subsequent iterative computer analysis, and in the absence of prior information about relative signs, both possible sign combinations ++ and -+ for J_{AB} and $(J_{AX}+J_{BX})$ must be considered. Their magnitudes found by the ABX analysis can, however, be used as starting parameters for the computer analysis.

As an example of an ABX analysis the naphthoquinone spectrum treated by George Slomp in Newsletter No. 116 will be analyzed. The experimental frequencies are tabulated in Slomp's letter.

Step 1. AB Portion of the Spectrum.

The first step is to identify the two "ab" subspectra a, c, e, g and b, d, f, h. There is only one possible way to do this as shown in the figure on p. 5 (remember the simplifying conventions we adopted above). In general, it will not be known a priori whether $(\nu_B-\nu_A)>1/2(J_{AX}-J_{BX})$ (solution I) or $(\nu_B-\nu_A)<1/2(J_{AX}-J_{BX})$ (solution II). We shall first find solution I. We have

B.L.Shapiro   -3-   6-14-68

$$J_{AB} = (c-a) = (d-b) = (g-e) = (h-f)$$
$$\qquad\quad 7.6 \qquad 7.4 \ (g\ missing)\ 7.3 \qquad\qquad Avg.=7.4$$

$$(J_{AX}+J_{BX}) = (d+f) - (c+e) = 9.7$$

$$2D_+ = (f-b) = (h-d)$$
$$\qquad\quad 9.9 \qquad 9.8 \qquad\qquad\qquad Avg.=9.9$$

$$2D_- = (e-a) = (g-c)$$
$$\qquad\quad 7.6 \quad (g\ missing) \qquad\qquad Avg.=7.6$$

$$1/2(\nu_A+\nu_B) = \frac{(c+e+d+f)}{4} = 456.0$$

Note that if both weak lines of a quartet are missing, the corresponding D equals $1/2J_{AB}$.

Step 2. X Portion of the Spectrum

The only information needed from the X portion of the spectrum is ν_X.

$$\nu_X = 1/2(j+k) = 434.0$$

Other quantities can also be calculated for arithmetic checking purposes:

$$(J_{AX}+J_{BX}) = (1-i) = 9.8 \qquad\qquad (check)$$

$$2(D_--D_+) = (k-j) = -2.3$$
$$2(D_-+D_+) = (n-m) = 17.3$$
$$\qquad\qquad 2D_+ = 9.8 \qquad\qquad\qquad (check)$$
$$\qquad\qquad 2D_- = 7.5 \qquad\qquad\qquad (check)$$

Step 3. Calculation of $(\nu_B-\nu_A)$ and $1/2(J_{AX}-J_{BX})$

$$(\nu_B-\nu_A) - 1/2(J_{AX}-J_{BX}) = [(9.8)^2-(7.4)^2]^{1/2} = 6.4$$

$$(\nu_B-\nu_A) + 1/2(J_{AX}-J_{BX}) = [(7.6)^2-(7.4)^2]^{1/2} = 1.7$$

Then

$$1/2(\nu_B-\nu_A) = 2.0$$

$$1/2(J_{AX}-J_{BX}) = 2.4$$

Step 4. Calculation of ν_A and ν_B

From Step 1

$$1/2 (\nu_B+\nu_A) = 2.0$$

From Step 3

$$\tfrac{1}{2}(\nu_B - \nu_A) = 456.0$$

Then

$$\nu_A = 454.0, \quad \nu_B = 458.0$$

Step 5.   Calculation of J_{AX} and J_{BX}

From Step 1 (and 2)

$$\tfrac{1}{2}(J_{AX} + J_{BX}) = 4.9$$

From Step 3

$$\tfrac{1}{2}(J_{AX} - J_{BX}) = -2.4$$

Then

$$J_{AX} = 2.5, \quad J_{BX} = 7.3$$

This completes solution I. To find solution II, we interchange the values found for $(\nu_B - \nu_A)$ and $\tfrac{1}{2}(J_{AX} - J_{BX})$ in Step 3, i.e., we set $(\nu_B - \nu_A) = -2.4$ and $\tfrac{1}{2}(J_{AX} - J_{BX}) = 4.0$.

The two sets of ABX parameters found in this way were then used as starting parameters for a computer analysis with NMRIT. Both solutions led to the same (and only possible) set of parameters as summarized below:

| | ABX Solutions | | Iterative Solutions | | |
	I	II	NMRIT	LAOCOON A	B
ν_1	434.0	434.0	434.8	434.7	434.8
ν_2	454.0	454.8	454.3	454.1	454.5
ν_3	458.0	457.2	456.9	457.1	456.6
J_{12}	2.5	0.9	1.3	1.6	1.0
J_{13}	7.3	8.9	8.3	8.1	8.6
J_{23}	7.4	7.4	7.5	7.5	7.6

B.L.Shapiro   -5-   6-14-68

PORTION OF THE NMR SPECTRUM OF 5-HYDROXYNAPHTHOQUINONE

FIGURE 4.

CPS FROM TMS AT 60 MC
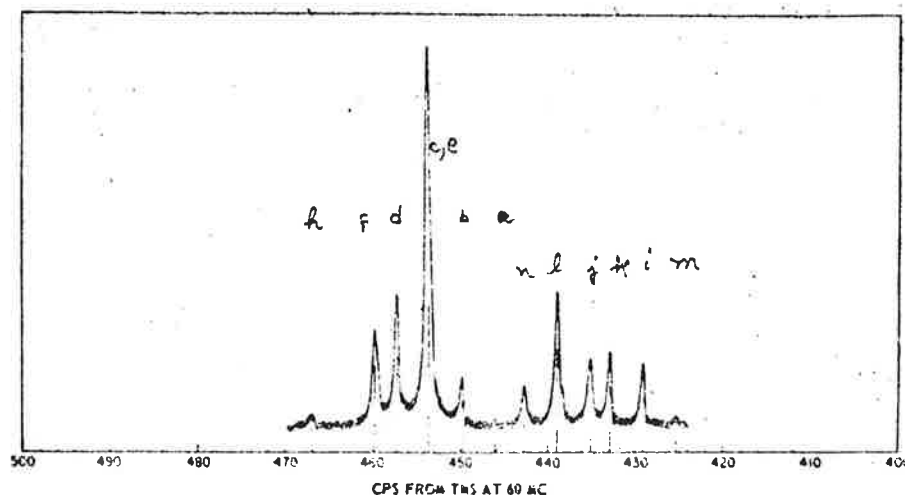
        I do not know enough about how LAOCOON operates to say why it leads to two solutions when only one is correct. I suspect that the experimental frequencies are not accurate enough for this program to give only the correct solution (as determined by the intensities of the weak lines in the spectrum). It is interesting to note that the values for the NMRIT parameters are in general between those found by LAOCOON for the corresponding ones.

        I am sorry to have been so long-winded about this problem but I thought it necessary to go into this amount of detail in order to make the procedure clear.

                            Sincerely yours

                            Charlie

                            C. A. REILLY

Short Title: A Simplified Procedure for ABX Analysis

CAR:dgm

KYOTO UNIVERSITY

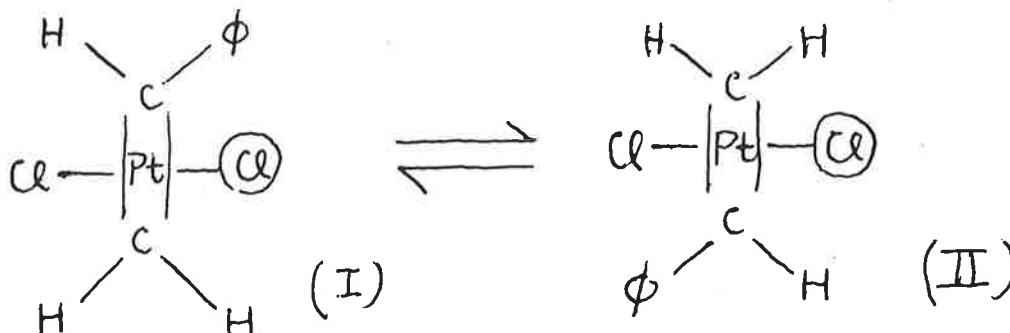### DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE

KYOTO, JAPAN

June 18, 1968

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

Dear Professor Shapiro:

Reorientation of ethylene groups in ethylene platinous and palladium chlorides

The ethylene and styrene proton resonances in ethylene and styrene platinous chlorides [$H_2C=CH_2$ $PtCl_2$]$_2$ are much broader than in Zeise's salt. The broadening can be ascribed to slow reorientation of ethylene and styrene groups in the dimer form of Zeise's salt. In the dimer the protons are not equivalent in the conformations (I) and (II), and slow rerientation may cause such broadening. The mechanism of slow exchange with free ligands has been excluded, since the phenyl proton resonances are sharp. The proton resonances in 2,3,5,6-tetramethylstyrene complexare sharp, because reorientation may be sterically hindered in this compound. In palladium complexes the proton resonances are sharp, probably because reorientation is faster on account of weaker bonding with palladium. In Zeise's salt bouding may be strong enough, and reorientation may not be occurring.

Cl : terminal Cl
(Cl) : bridge Cl

Coupling constants in diborane

The use of truncated sum approximation and the wavefunction by Palk and Lipscomb (J. Am. Chem. Soc., $\underline{88}$, 2384 (1966)) gives a large positive value (+49.7 cps) for the non-bonded bridge-bridge proton coupling constant and a negative value (-8.8 cps) for the terminal-terminal proton coupling constant in diborane. Since these theoretical results are not trustworthy, it may be of interest to determine them experimentally.

Yours sincerely,

A. Saika

A. Saika

C A S E   W E S T E R N   R E S E R V E   U N I V E R S I T Y   ·   C L E V E L A N D ,   O H I O   4 4 1 0 6

June 18, 1968

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

Dear Barry:

^{19}F shifts in m- and p-fluorophenyl substituted cations

We have recently been attempting to put the electronic effects of electron deficient centers on a more quantitative basis. A linear relation between ^{13}C shift and calculated π-electron densities was found in a number of carbonium ions [G. A. Olah and A. M. White, J. Amer. Chem. Soc., 90, 1884 (1968)]. As well as continuing these studies of ^{13}C shifts, we have been taking a look at some ^{19}F shifts in m- and p-fluorophenyl groups attached to positive carbon and nitrogen. In general the medium used to generate the ions has been a 1:1 molar FSO_3H-SbF_5 solution with 25% by volume SO_2 added, the ^{19}F spectra being recorded at $-30°$. Five per cent solutions of the fluorobenzenes were used and shifts were measured with respect to external fluorobenzene. We have not, at this time, made a study of solvent effects on the shifts although in the three cases where data in other solvents are available ($-N_2^+$, $-NH_3^+$, $-C\overset{OH}{\underset{CH_3}{\diagdown}}$) the agreement is good. The shifts

determined so far are summarized in Table I, together with substituent constants

TABLE I

Substituent	δ^F_m	δ^F_p	$\delta^F_p - \delta^F_m$	σ_I	σ_{R^o}	$\sigma_I + \sigma_{R^o}$
$-C\overset{CH_3}{\underset{CH_3}{\diagup\diagdown}}$ (+)	6.35	52.39	46.0	0.98	1.56	2.54
$-C=O$ (+)	11.03	45.13	34.1	1.64	1.16	2.80
$-C\overset{H}{\underset{OH}{\diagup\diagdown}}$ (+)	6.71	40.61	33.9	1.03	1.15	2.18
$-N\overset{OH}{\underset{O}{\diagup\diagdown}}$ (+)	8.60	39.60	31.0	1.30	1.05	2.35
$-C\overset{CH_3}{\underset{OH}{\diagup\diagdown}}$ (+)	4.63	32.43	27.8	0.74	0.94	1.68

Department of Chemistry

Professor Shapiro   - 2 -   June 18, 1968

Table I (continued)

Substituent	$\delta^F_{\underline{m}}$	$\delta^F_{\underline{p}}$	$\delta^F_{\underline{p}} - \delta^F_{\underline{m}}$	σ_I	σ_{R^o}	$\sigma_I + \sigma_{R^o}$
$\overset{+}{C}\diagup^{OH}_{\diagdown OH}$	4.90	24.92	20.0	0.77	0.67	1.44
$-\overset{+}{N}\equiv N$	10.19	32.00	11.8	1.52	0.40	1.92
$-\overset{+}{N}H_3$	5.01	3.75	-1.3	0.79	-0.04	0.75

evaluated using Tafts' equations. The trends observed, particularly in the
p-fluorine shifts, seem to be those expected from the relative extent of
interaction with the ring in phenylcarbonium ions. As for the substituent
constants, we have some ideas on testing out their usefulness in some related
systems. It remains to be seen whether these ideas work out.

Yours sincerely,

Anthony M. White   George A. Olah

GAO:df

Organisch-Chemisches Institut
der
Technischen Universität Berlin

Direktor: Prof. Dr. F. Bohlmann

Professor Dr. Bernard L. Shapiro
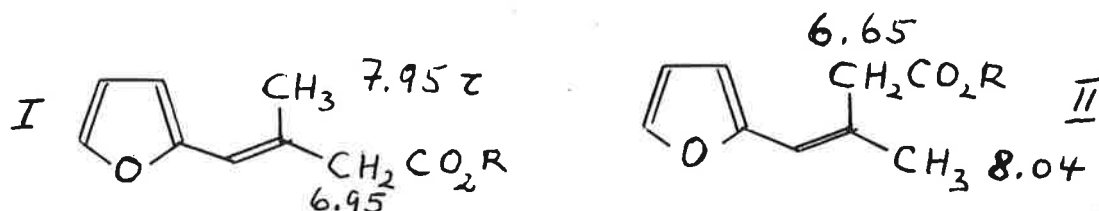Department of Chemistry
Stanford University

S t a n f o r d, California 94305
U S A

Deshielding effect of the furane ring

Dear Professor Shapiro,

We have measured the NMR-spectra of many furane compounds. Most of the spectra show no special effects. But in one case the data are somewhat surprising. We have prepared the cis-trans-isomeres I and II. The signals of the CH_2-group are very different while the difference in the position of the signals of the methylgroups are only 0.1 τ :

The only explanation for this is perhaps the none coplanarity of I.
The deshielding effect of the furane ring also can be seen in the spectra of the cis-trans-isomeres III and IV :

As the difference of the α-proton signals in III and IV is 0.6 τ perhaps also II is not really coplanar (Δ 0.3 τ).

Yours sincerely,

F. Bohlmann

MONASH UNIVERSITY
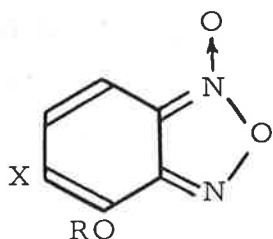
21st June, 1968

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

Dear Barry,

This brief note probably belongs under item 5 "Complete or Partial Mysteries" (IITNMR: 107-1). It concerns the asymmetry of AB quartets observed for the aromatic protons of the benzofuroxans listed below.

I: X = Cl, R = Me

II: X = Cl, R = Et

III: X = Br, R = Me

IV: X = Br, R = Et
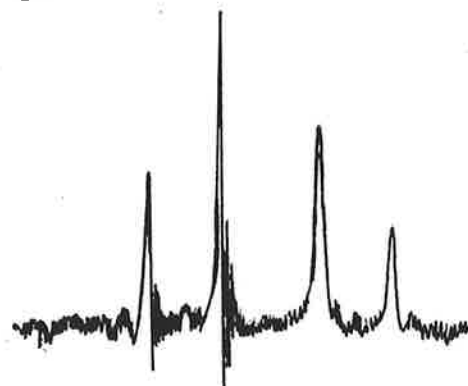
In each case the upfield half of the quartet is conspicuously broadened, as are the signals from the protons adjacent to the ether oxygen.

For example, in (I), line widths are (reading upfield): 0.72, 0.78, 1.76, 1.2 c/s cf. MeO, 2.14 c/s, internal $CHCl_3$ 0.56 c/s. However, irradiation of the methyl singlet did not affect the AB quartet. In (II), irradiation of the methylene group collapsed the methyl proton triplet but again left the quartet unaffected.

We have also observed that the asymmetry is more pronounced in $CDCl_3$ solutions than in CCl_4, and persists in MeOH. Shaking a $CDCl_3$ solution of (IV) wi sodium dithionite solution fails to affect the AB quartet. The asymmetry is more pronounced in the chloro compounds (I) and (II) than in their bromine analogues (II and (IV).

We are contemplating some experiments which might help in choosing between several explanations for this phenomenon, but it seems that the obvious ones, viz. long range coupling, selective paramagnetic broadening, are untenable.

Kind regards,

(M.L. Heffernan)   (Ian D. Rae)

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN

Dr. W. Bremser

5 KÖLN, June 24, 1968
ZÜLPICHER STRASSE 47
TELEFON: 20 24 22 39

Professor Bernard L. Shapiro
Department of Chemistry
Stanford University
Palo Alto, California 94305
U.S.A.

Dear Professor Shapiro:

One important point in using computer programs is to have not only the right mathematics, but also the adequate machines. Especially small computers cause great trouble due to their limited storage capacity. Because there have been several demands [1] in the last Mellon Letters for programs designed for the small IBM 360/30, we want to report a modified version of LAOCOON, which is in use in our laboratory since several months.

The IBM 360/30 at our local computer center can handle all our new NMR-programs, e.g. line calculations [2], fitting problems, error estimates and LAOCOON II, part one. Only the second part of LAOCOON had to be done on a computer with a greater capacity like the IBM 7090. However, if one is satisfied calculating spectra of only up to 6 spins, with variation of a maximum of 10 parameter sets and the assignment of 105 experimental frequencies, we have a special version of LAOCOON to offer.

We divided the standard program LAOCOON [3] into 27 phases, which are called into the computer separately. With this OVERLAY-technique, combined with several EQUIVALENCE-statements and a third tape, we managed to calculate 6-spin-cases with the above mentioned limitations. The INPUT is similar to the standard LAOCOON-version, exept the blank card after the first part is omitted. Comparing our results with those from the IBM 7090 (cf. OUTPUT on page 3), we did not find considerable deviations.

- 2 -

Only the convergence is usually a bit slower and we believe, that this depends on the smaller accuracy of calculations with a computer of the 360-series. Using DOUBLE PRECISION-numbers would improve the convergence, but need too much storage.

If there are still some poor institutes in the world with only a tiny computer as we have, we shall be happy to furnish them with a copy of the program. But mind you, the program is quite voluminous, because of the 27 subroutines. So we discovered a new, up-to-date meaning of LAOCOON, when we developed our version of the program: "The struggle with the paper".

Yours sincerely,

W. Bremser

(W. Bremser)

References:

[1] E. Lustig, IITNMR 107, 52 (1967)

     J.M. Read, J.H. Goldstein, IITNMR 104, 22 (1967)

[2] W. Bremser, H. Günther, IITNMR 103, 1 (1967)

[3] S. Castellano, A.A. Bothner-By, J. Chem. Phys. 41, 3863 (1964)

[4] A.A. Bothner-By, S. Castellano, LAOCN3, Mellon Institute, Pittsburg, page 41

Short title: LAOCOON 360/30

Calculation of problem 102 [4] on our IBM 360/30:

LAOCOON II PART II

  CASE 102   PYRIDINE-BEISPIEL, CASTELLANO

   NN= 5   FREQUENCY RANGE   400.000   550.000 MINIMUM INTENSITY 0.02000

   INPUT PARAMETERS


```
1              W(1)=   515.000
1              W(2)=   427.000
1              W(3)=   450.000
1              W(4)=   427.000
1              W(5)=   515.000
               A(1,2)=     5.500
               A(1,3)=     1.900
               A(1,4)=     0.900
               A(1,5)=    -0.400
               A(2,3)=     7.500
               A(2,4)=     1.600
               A(2,5)=     0.900
               A(3,4)=     7.500
               A(3,5)=     1.900
               A(4,5)=     5.500
```

      PARAMETER SETS
  1
      W(1)
      W(5)
  2
      W(2)
      W(4)
  3
      W(3)
  4
      A(1,2)
      A(4,5)
  5
      A(1,3)
      A(3,5)
  6
      A(1,4)
      A(2,5)
  7
      A(1,5)
  8
      A(2,3)
      A(3,4)
  9
      A(2,4)

- 4 -

```
                     ITERATION   0   R M S ERROR =      1.041

                     ITERATION   1   R M S ERROR =      0.056
LARGE RESIDUAL ROTATION

                     ITERATION   2   R M S ERROR =      0.056
```

BEST VALUES

```
    1          W(1)=   516.519
    1          W(2)=   427.429
    1          W(3)=   450.111
    1          W(4)=   427.429
    1          W(5)=   516.519
               A(1,2)=    4.868
               A(1,3)=    1.830
               A(1,4)=    1.000
               A(1,5)=   -0.008
               A(2,3)=    7.661
               A(2,4)=    1.392
               A(2,5)=    1.000
               A(3,4)=    7.661
               A(3,5)=    1.830
               A(4,5)=    4.868
```

VALUES OBTAINED AFTER   2 NEWTON ITERATIONS

```
    ERROR VECTORS AND PROBABLE ERRORS ARE
     0.9890    0.1103   0.0265  -0.0704  -0.0055  -0.0260   0.0272   0.0013  -0.0506
               PROBABLE ERROR=    0.013
    -0.0510    0.8090  -0.1454   0.3856   0.1574   0.1587   0.0376   0.3388   0.0833
               PROBABLE ERROR=    0.014
    -0.0377    0.2938   0.7289   0.1745   0.0208  -0.1026   0.0121  -0.5766   0.0834
               PROBABLE ERROR=    0.013
     0.1052   -0.3436  -0.1051   0.5416   0.1492   0.6822   0.0101  -0.2476   0.1315
               PROBABLE ERROR=    0.018
    -0.0042   -0.0555  -0.0391  -0.1508   0.9696  -0.1378  -0.0458  -0.0756  -0.0757
               PROBABLE ERROR=    0.017
    -0.0554    0.2215   0.1395  -0.6918   0.0086   0.6650  -0.0203  -0.0233   0.0816
               PROBABLE ERROR=    0.023
    -0.0275   -0.0317   0.0007  -0.0399   0.0370  -0.0016   0.9975  -0.0056  -0.0170
               PROBABLE ERROR=    0.015
     0.0191   -0.2612   0.6441   0.1219   0.0933   0.1129  -0.0042   0.6883  -0.0803
               PROBABLE ERROR=    0.021
     0.0502   -0.0873   0.0040  -0.0692   0.0473  -0.1555   0.0110   0.1067   0.9732
               PROBABLE ERROR=    0.025
```

PROBABLE ERRORS OF PARAMETER SETS

```
    1      0.009   CPS
    2      0.011   CPS
    3      0.012   CPS
    4      0.014   CPS
    5      0.012   CPS
    6      0.014   CPS
    7      0.010   CPS
    8      0.012   CPS
    9      0.017   CPS
```
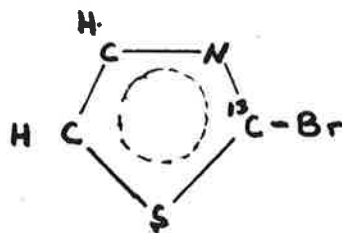
UNIVERSITY OF COPENHAGEN
DEPARTMENT OF CHEMICAL PHYSICS

H. C. ØRSTED INSTITUTET
5, UNIVERSITETSPARKEN
COPENHAGEN Ø, DENMARK

Dr. Bernard L. Shapiro
Dept.Chemistry
Stanford University
Stanford,California 94 305
U.S.A.

Dear Barry,

We should like to draw attention to a remarkable

large long-range-coupling we recently have observed

in ^{13}C - Thiazole in a 50% enriched sample. The com-

pound studied was:

2-Br$\left[2^{13}C\right]$Thiazole

As expected the normal spectrum was superposed by

two AB patterns arising from the ^{13}C-H couplings. Using

the observations of Taurins and Schneider[1] that the 2

and 4 protons give rise to broader signals as the 5 pro-

ton we can assign the AB spectra. The derived couplings

are:

$$J_{C-N-CH} = 19 \text{ Hz} \qquad J_{C-S-CH} = 9 \text{ Hz}$$

The parth of the couplings indicated in subscript should

not be taken for granted. The magnitude of these couplings

UNIVERSITY OF COPENHAGEN
DEPARTMENT OF CHEMICAL PHYSICS

H. C. ØRSTED INSTITUTET
5, UNIVERSITETSPARKEN
COPENHAGEN Ø, DENMARK

exceeds any other previously reported $\underline{2} - \underline{4}$ by a factor 3 to 8.

To our knowledge little has been done to evaluate the influence of substituents on ^{13}C-H couplings in systems having a carbon chain. Even less has been done in application of the theories on systems where the coupling proceedes via heteroatoms. To obtain further experimental data we are presently investigating a number of other ^{13}C enriched heterocyclic compounds.

Yours sincerely

Jørgen Tormod Nielsen   Kjeld   Schaumburg

1 A. Taurins, W.G. Schneider
   Canad.J.Chem $\underline{38}$ 1237 (1960)
   see also B. Bak et al. Spect, Acta $\underline{18}$ 741 (1962)
2 H. Frischleder,G.Klose,J.Ranft
   Wiss.Z.Karl Marx Univ. Leipzig $\underline{14}$ 863 (1965)
3 J.J. Karabatsos,C.E. Orzech Jr.
   J.Am.Chem.Soc. $\underline{87}$ 560 (1965)
4 H. Dreeskampf et al. Z.Phys. Chem. N.F. $\underline{34}$ 261 (1962)

UNIVERSITY OF CALIFORNIA, RIVERSIDE

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DEPARTMENT OF CHEMISTRY   RIVERSIDE, CALIFORNIA 92502

June 26, 1968

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

Self-Association of Amides and Thioamides

Dear Barry:

In connection with our studies of hindered rotation in amides, thioamides and related systems[1-3] we have examined the concentration dependence, at ambient temperature, of the n.m.r. spectral properties of the N,N-dimethyl derivatives (1) of formamide, thioformamide, acetamide and thioacetamide in carbon tetrachloride.[4] Analyses of the concentra-

$$X \diagdown \diagup CH_3 (A)$$
$$ C\!-\!N$$
$$R \diagup \diagdown CH_3 (B)$$

$$\underset{\sim}{1}$$
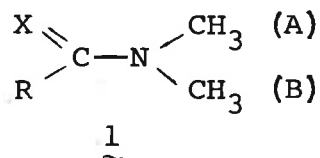
tion dependence of the non-exchanging chemical shift $\nu_A-\nu_B$ (see 1) indicate that these compounds may be involved in a monomer-dimer self-association equilibrium. Values of $\nu_A-\nu_B$ for the monomer ($\delta\nu_M$) and the dimer ($\delta\nu_D$) have been calculated as well as the equilibrium constants. These data are given below.

Professor Bernard L. Shapiro
June 26, 1968
Page Two

Compound	K $(1.m^{-1})$	$\delta\nu_M$ (cps)	$\delta\nu_D$ (cps)
DMTA	0.64	-7.1	-1.8
DMTF	1.22	+4.3	+8.9
DMA	0.37	+7.3	+13.8
DMF	0.60	+6.3	+11.6

The negative values of $\nu_A-\nu_B$ for DMTA reflect the unusual shielding inversion of the $\overset{\cdot}{N}(CH_3)_2$ resonance lines in this compound[5] compared to the other compounds and the data seem to indicate that this shielding inversion is not the result of self-association as was suggested for dimethylthiocarbamoyl chloride.[2]

These data further indicate that care must be exercised in the use of values of $\nu_A-\nu_B$ in anisotropy calculations for C=O and C=S groups in these compounds if results applicable to the monomers are desired.

Sincerely yours,

Bob

Robert C. Neuman, Jr.
Associate Professor of Chemistry

RCN/nl

1.) R. C. Neuman, Jr. and V. Jonas, J. Am. Chem. Soc., 90, 1970 (1968).

2.) R. C. Neuman, Jr., D. N. Roark and V. Jonas, ibid, 89, 3412 (1967).

3.) R. C. Neuman, Jr. and L. B. Young, J. Phys. Chem., 69, 2570 (1965).

4.) R. C. Neuman, Jr., W. Snider and V. Jonas, ibid, In Press.

5.) R. C. Neuman, Jr. and L. B. Young, ibid, 69, 1777 (1965).

OKLAHOMA STATE UNIVERSITY · STILLWATER

Department of Chemistry
FRontier 2-6211, Ext. 7215-7218

June 17, 1968

74074

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

<u>P</u>hosphorus-<u>C</u>ontaining <u>O</u>ximes <u>C</u>oupling <u>C</u>onstants for J_{PCCH} <u>In</u>

P—C=N—CH <u>S</u>ystems
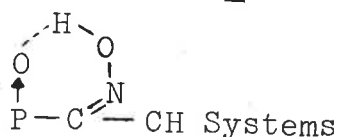
Dear Dr. Shapiro:

We have recently found a simple synthetic approach to phosphorus-containing oximes I. As our contribution, we should like to report that coupling between P and H occurs through the α-carbon atom
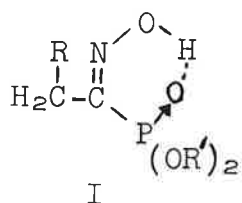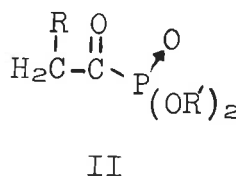
I	II	III
J_{PCCH} = ~11 cps	J_{PCCH} = ~5 cps	J_{PCCH} = ~11 cps
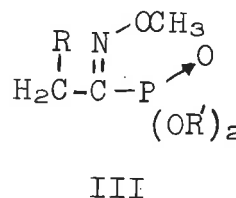
as observed in CCl_4. The influence of H-bonding may not be very significant regarding the drastic changes in J values for I and II. This is based on the fact that III gives a J value nearly identical to that for I. We are continuing our study of these interesting families of compounds in an effort to evaluate the influence of multiply bonded systems on PCC-H coupling.

Sincerely yours,

K. D. Berlin
Professor

KDB/caf

UNIVERSITY OF COLORADO

BOULDER, COLORADO 80302

June 26, 1968

DEPARTMENT OF CHEMISTRY

Title: Positive and negative vicinal $^3J_{FF}$ in cyclobutenes;
Guanosine-Cytidine hydrogen bonding.

Dear Prof. Shapiro,

We have just completed the analysis of the fluorine spectrum of
1-Chloro-2-ethoxytetrafluoro cyclobutene. The AA'BB' spectrum is sketched
below. Since the BB' peaks are broadened by coupling to the methylene pro-
tons of the ethoxy group, only the AA' peaks were used in the iterative
analysis for the coupling constants. "Spin tickling" proved that peaks
1, 2, 9, 10, 1', 2', 9', and 10' comprise the transitions between the "B"
energy levels, from which we unambiguously determine that $L = J_{AB} - J_{AB'} =$
41.8 Hz and $M = J_{AA'} - J_{BB'} = 9.2$ Hz (see E. Lustig et. al., J. Am. Chem.
Soc. 89, 3953 (1967) for details of the use of spin tickling experiments
in the analysis of AA'BB' systems). It was possible to "tickle" 3' + 4',
5', 6', 7', and 8' and observe the effects on the transitions 3-8, but
we didn't attempt to build the "A" energy level diagram using these limited
results. However, a few trial and error runs on NMRIT gave $N = J_{AB} + J_{AB'} =$
8.5 and $K = J_{AA'} + J_{BB'} = 388$. Hz, and the tickling experiments
confirm this choice of signs for N and K. (The spectra are independent
of the signs of L and M.) The main interest in the result is that we
obtain two moderately large vicinal coupling constants of opposite sign,
+25.2 Hz and - 16.7 Hz (relative to + 198.8 and + 189.6 Hz for the geminal
couplings).

Similar results were obtained on 1,4-dichloro-3,3,4-trifluoro-
cyclobutene in which J(gem) = + 188 Hz and the vicinal couplings are + 26
and - 12 Hz. Preliminary experiments on 1,2-dichloro-2,3,3-trifluoro-
cyclobutane also give opposite signs for the vicinal couplings ($\pm$ 9 and $\mp$ 2).

Other work in the laboratory concerns hydrogen bonding in the
nucleosides and amino acids. We recently completed a paper (to be published
in September in J. Am. Chem. Soc.) on the hydrogen bonding between guanosine
and cytidine in DMSO in which we obtained the equilibrium constant and
enthalpy for guanosine-cytidine hydrogen bonded dimers in this solvent.

Sincerely yours,

Richard A. Newmark

Richard A. Newmark
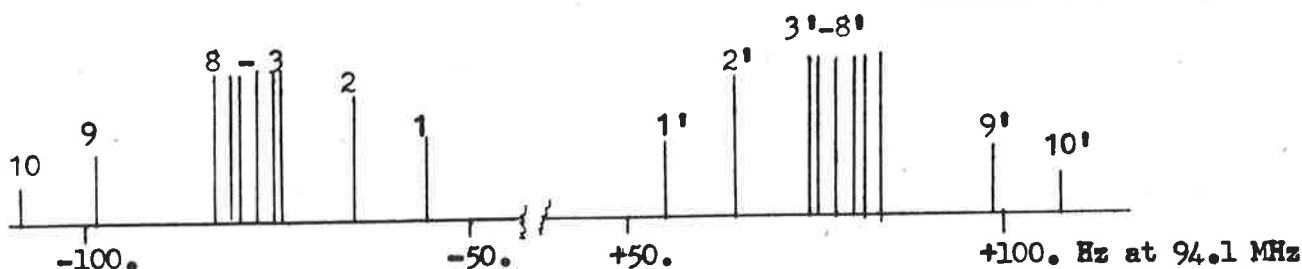
Carnegie-Mellon University

Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213
[412] 621-1100

June 27, 1968

(Suggested Title)

SOLVENT AND pH DEPENDENCE OF ^{13}C - H COUPLING CONSTANTS

IN FORMIC ACID

Dear Barry:

We have recently been studying the variation of ^{13}C - H coupling constants in formic acid and other organic acids with solvent and pH[1]. In an effort to understand the behavior given in the table, we have attempted a correlation with changes in chemical shifts (proton and carbon-13) and various IR frequencies reflecting hydrogen bonding with the solvent.

Although this mass of data is not yet digested (or excreted), it does appear that the ^{13}C - H coupling reflects changes in hydrogen bond strength (by way of correlation with IR frequencies, particularly the OH stretching frequency).

We are also putting together a qualitative theoretical picture, but any comments from the readers of IITNMR would be welcome. It might be noted that Gary Maciel has done a CNDO calculation of $J(^{13}$C - H) in the formate ion[2] and that the calculated change from unionized formic acid, while much larger than that observed, is in the right direction. Further, there does not appear to be a correlation of $J(^{13}$C - H) with the dielectric constant of the solvents.

Sincerely,

E. Bastian, R. J. Kurland

RJK:nm

---

[1] J. M. Read, Jr. and J. H. Goldstein, J. Am. Chem. Soc. <u>87</u>, 3440 (1965), have observed changes in $J(^{13}$C - H) with pH changes for purine.

[2] G. Maciel, private communication.

TABLE OF $J(^{13}C - H)$, ^{13}C CHEMICAL SHIFT AND OH STRETCHING FREQUENCY
IN VARIOUS SOLVENTS FOR FORMIC ACID AND FORMATE ION

Solvent	$J(^{13}C - H)^{a}$ (Hz)	$\nu(^{13}C)^{b}$ (Hz)	$\nu_{s}(OH)^{c}$ (cm^{-1})
Acetonitrile	220.4	446	3140 $\pm$ 20
Dioxane	219.5	457	3000 $\pm$ 20
Ethyl Acetate	219.6	449	3100 $\pm$ 20
Water, Acidic^{d}	218.8	407	--
Acetone	218.3	459	2940 $\pm$ 10
THF	216.9	462	2920 $\pm$ 30
DMSO	215.2	447	2740 $\pm$ 10
DMF	215.1	453	2800 $\pm$ 20
Pyridine	210.5	438	2700 $\pm$ 50
Water, Basic^{e}	194.9	324	--
Formic Acid (Neat)	222.6	404	3000 $\pm$ 50

[a] For a ca. 5 M concentration of formic acid; for 0.5 M concentrations of formic acid, the change in $J(^{13}C - H)$ was within the precision of the measurements, $\pm$ 0.3 Hz.

[b] Measured upfield from CS_2 (neat) as an external reference at 15.085 MHz; susceptibility corrections have been made.

[c] OH stretching frequency.

[d] 5 Molar.

[e] pH such that greater than 99% of acid present as formate ion; $J(^{13}C - H)$ approximately independent of ionic strength in basic and acidic solutions.

ARCO Chemical Company

Division of AtlanticRichfieldCompany
500 South Ridgeway Avenue
Glenolden. Pennsylvania 19036
Telephone 215 586 4700

Research Division
Research & Development—Philadelphia

June 25, 1968

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

Dear Barry:

Some recent results on some rather complicated
biological polymers may be of interest. The extension of the
NMR results and techniques concerning synthetic polymers appears
reasonable at first, but has received only limited attention.
This lack of attention particularly with respect to proteins
is undoubtedly due to the difficulties encountered in not
only obtaining the spectra, but also the interpretation which
is even more difficult.

We have conducted a rather detailed study of the amino
acids which is of course a prerequisite for the interpretation
of protein spectra. In most cases even the simplest amino
acids do not yield high resolution spectra, but this is expected
and interpretable in terms of the various equilibrations,
conformations and reactions. In Figures 1 and 2 are shown
the 60 MHz spectra for the common amino acids in solution in
CF_3COOH as obtained at 30°C.
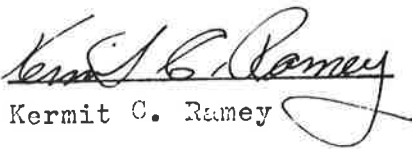
In Figure 3 is shown the 60 MHz spectrum of pork insulin
in solution in CF_3COOH. Included are the tentative assignments
for some of the amino acids. Similar results were obtained at
100 MHz and they are consistent with those observed at 220 MHz(1).
While the primary structure could be obtained directly from the
spectra the results would be questionable and current chemical
techniques are available.

Of course the secondary and tertiary structures are
of more interest. However, the application of current NMR

techniques within this area is at best questionable. Currently we are studying small fragments of the polymer chain and even these are somewhat difficult to interpret.

(1) B. Bak, C. Dambmann, F.Nicolaisen, E.J.Petersen and
    N. Bhacca, J. Mol. Spect. <u>26</u>, 78 (1968).

Sincerely yours,

Kermit C. Ramey

KCR:LH
Encl.

<u>Short Title</u>:   NMR Study of Insulin.
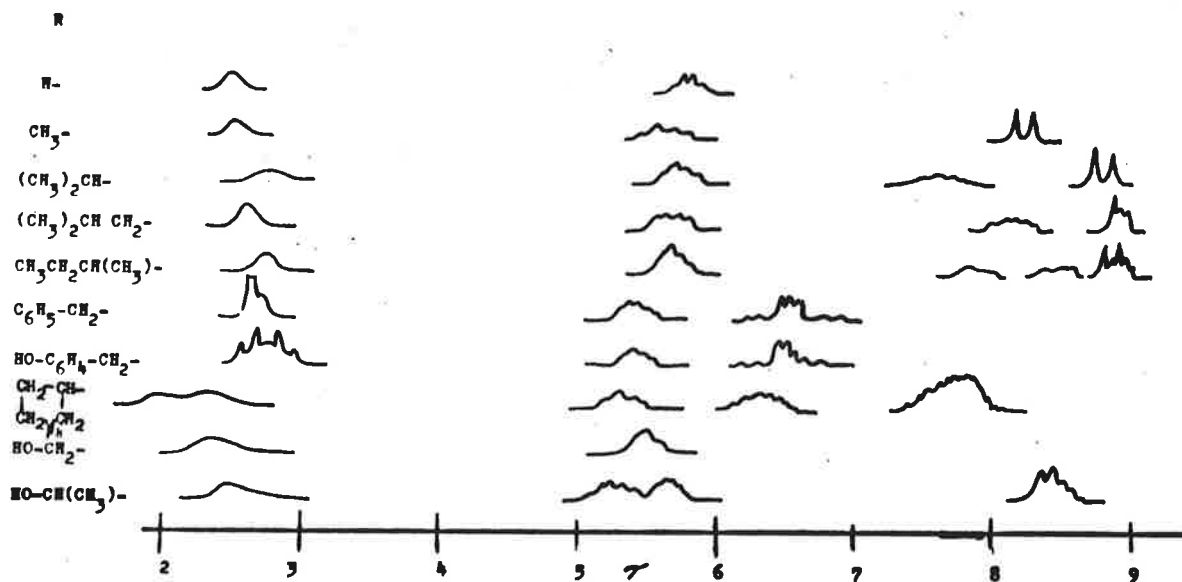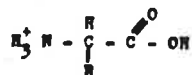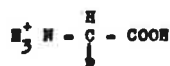
FIGURE 1. NMR Spectra of Some Common Amino Acids
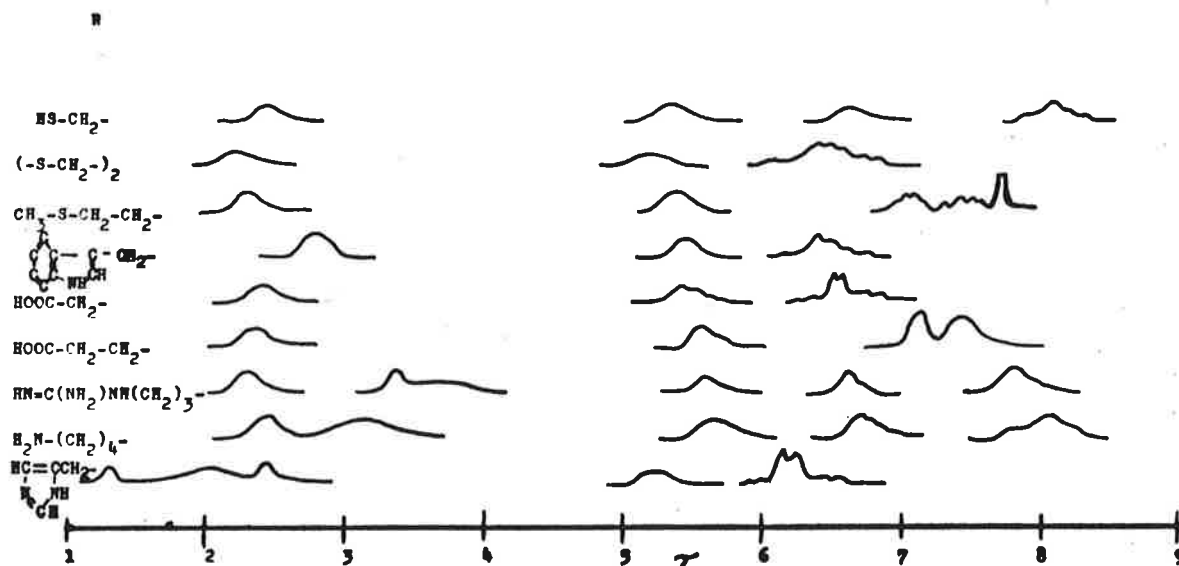
FIGURE 2. NMR Spectra of Some Common Amino Acids

Pork Insulin
60 MHz
30°
CF₃COOH

FIGURE 3.

Glaxo Research Limited
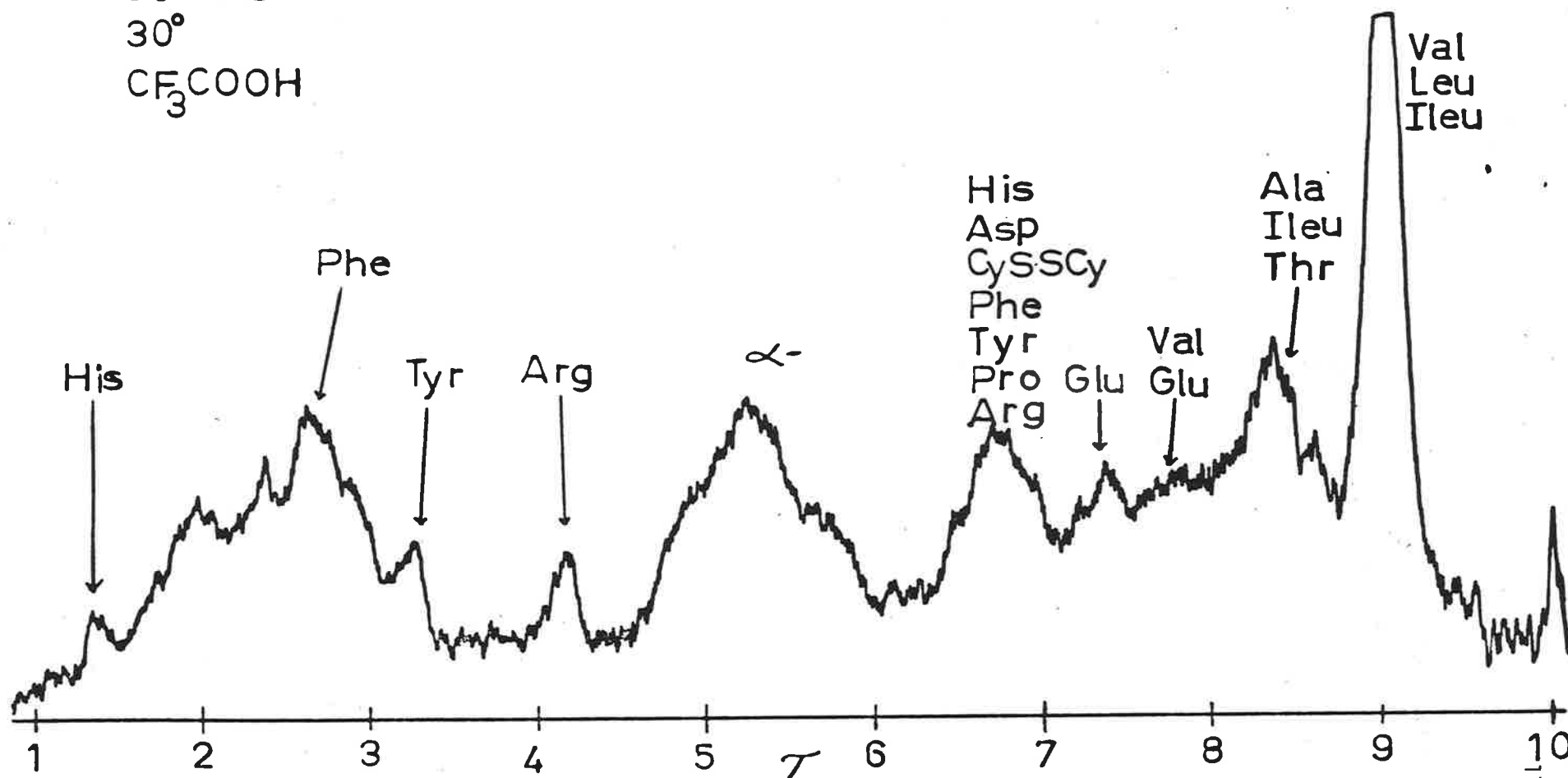
Greenford · Middlesex

TELEPHONE: BYRON 3434   TELEGRAMS: Glaxotha, London, Telex   CODE: New Standard, Bentleys

16th May, 1968.

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

Dear Dr. Shapiro,

Pen Conversion for A-60 Spectrometer

We find our HA-100 spectrometer, which has been in routine use for four months, a fascinating machine and hope to report in our next letter some work done with it.

After experience with the Leroy reservoir pen supplied with the HA-100 (but using Parker black Quink instead of the gummy, heavy ink supplied), we successfully modified the recorder of our old A-60 spectrometer to take these pens. This conversion may interest owners of older A-60 spectrometers.
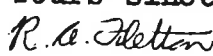
A piece of ¼" thick Perspex sheet was drilled and filed to accept as a push fit a small sintered magnet (7/8" x 9/16" x 3/16") obtained from a cheap magnetic door catch. The magnet and Perspex surround were cemented to a second piece of Perspex (1/8" thick) and then filed to give a block, the same size as the A-60 pen reservoir (3/8" x 1½" x ¾") with the magnet inset by 1/16".

Two pen brackets were cut from thin sheet steel (not stainless!), as shown in Fig. 1, and grooves filed in the Perspex block, so that each bracket could locate in contact with the magnet in the same way as in the aluminium blocks of the HA-100 and A-60A recorders.

The extra weight of the new pen assembly necessitated a counter-balance. A strip of thin stainless steel (2½" x 3/8") was drilled and tapped near one end to take a 6BA screw and the other end of the strip drilled to take the small Phillips' screw that secures the A-60 pen clip. The steel strip fitted under the clip and under the main block of the Y-axis pen-trolley of the recorder carriage, projecting about ¾" to the right of the carriage. A set in the strip, shown in Fig. 2, cleared the tensioning spring of the Y-axis drive. Slots to fit the A-60 pen-holder were filed in the top and bottom of the Perspex block. After fitting the block to the pen-holder and mounting a filled pen, sufficient mass was assembled on the 6BA screw at the end of the counter-balance arm to enable the pen-raising and -lowering device to function.

In the U.K., suitable pens (Rotring 0.4 mm) are obtainable from Messrs. Hartley Reece & Co., Berk House, 8 Baker Street, London, W.1.

Yours sincerely,

J.E. Page   R.A. Fletton   G.F.H. Green
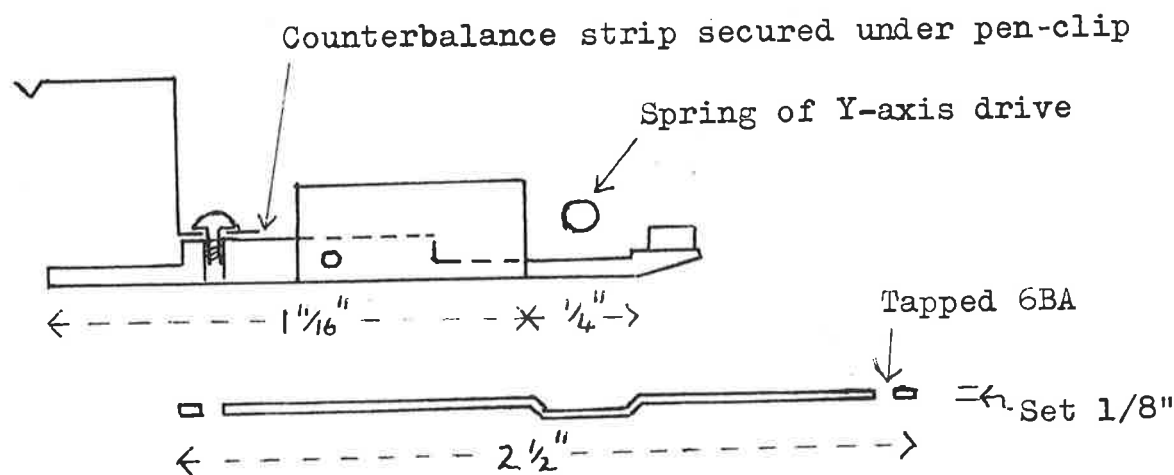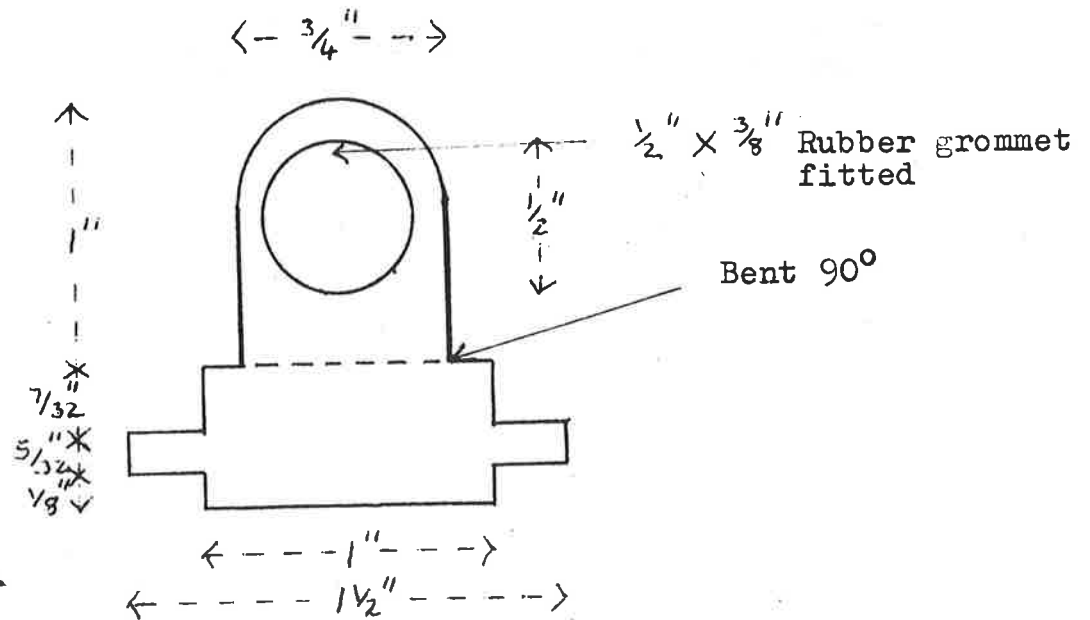
$\longleftarrow \frac{3}{4}'' \dashrightarrow$

$\frac{1}{2}'' \times \frac{3}{8}''$ Rubber grommet
fitted

$\frac{1}{2}''$

Bent 90°

$1''$

$\frac{7}{32}''$

$\frac{5}{32}''$

$\frac{1}{8}''$

$\longleftarrow - - - 1'' - - \longrightarrow$

$\longleftarrow - - - - 1\frac{1}{2}'' - - - - \longrightarrow$

FIG. 1
PEN BRACKET

Counterbalance strip secured under pen-clip

Spring of Y-axis drive

$\longleftarrow - - - - 1''\!\!/_{16}'' - - - * \frac{1}{4}'' \rightarrow$

Tapped 6BA

Set 1/8"

$\longleftarrow - - - - - 2\frac{1}{2}'' - - - - - \longrightarrow$

FIG. 2
END-ON VIEW OF Y-AXIS TROLLEY AND COUNTERBLANCE

AMERICAN OIL COMPANY

June 3, 1968

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

Dear Dr. Shapiro:

RE: "MULTI-CLOISTERED" NMR CELLS

During the past 10 years, our laboratory has used "multi-cloistered" n.m.r. cells with progressive frequency. These cells enable us to trace composite n.m.r. spectra of two or more samples. Relative chemical shifts are recorded conjointly on the same graph. This has been useful in the analyses of stereo-isomers, especially those that exhibit very small chemical shift differences. The technique is valuable when costly separations cannot be physically mixed. The multi-cloistered cells are applied in other studies also, e.g., solute, or solvent, effects.

The cells are easily constructed. We shall describe two types: I) the "quadra-cloistered" and II) the "hepta-cloistered" cell.
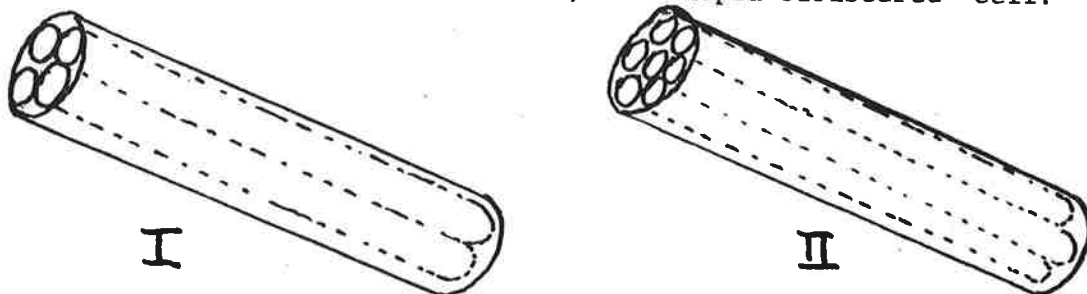
These were particularly selected because they can be made from standard stock items. The quadra-cloister is made up of an outer standard 5 mm. n.m.r. tube and four inner (selected for a snug fit) Kimax #34505 melting point capillary tubes with one end sealed. The hepta-cloister is made up of a 5 mm. tube and seven (selected) Fisher-Scientific (5-962) coagulation capillary tubes sealed at one end. One can assemble many other combinations of outer and inner tubes.

With the quadra-cloistered cell, we find that we can ignore effective external magnetic field effects, susceptibility corrections, intermolecular association effects, shapes of sample, and achieve suitable relative chemical shifts. As a result, very rapid analyses can be made, especially on a large number of samples.

Dr. Bernard L. Shapiro   - 2 -   June 3, 1968
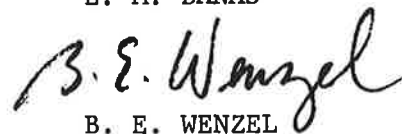
     Figure 1 shows an application of the technique (we wish to thank D. Slupski for these recordings). The composite spectrum, 1A, of three isomers of methyltetralin is compared with their individual spectra, 1B, C and D (all spectra are referenced externally). On occasion, we have observed shift differences of 1 part in 10^8. Homogeneous fields and spinning are essential.
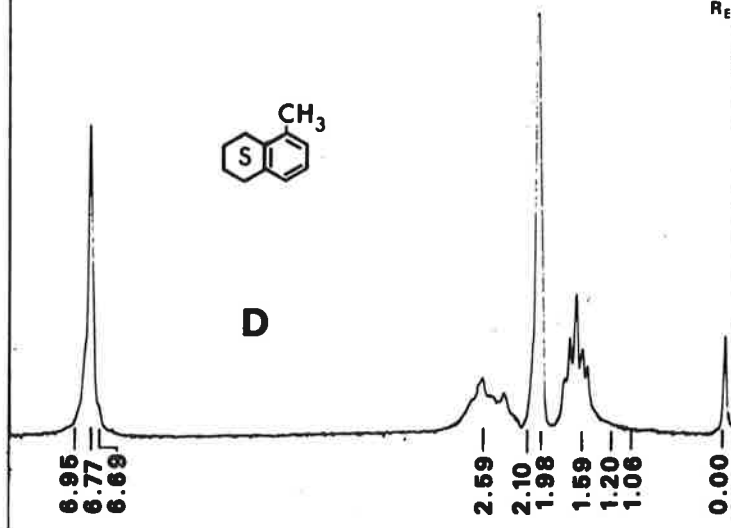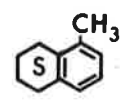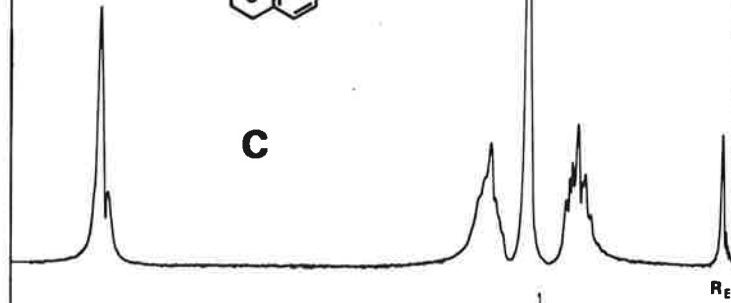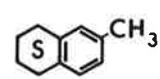
Sincerely,

E. M. BANAS

B. E. WENZEL

EMB:BEW/crh
Attachment

ISOMERS B., C., & D. BELOW
AND TMS$_{O=O}$ (R$_E$)IN OUR 5mm
"QUADRA-CLOISTERED"
NMR CELL
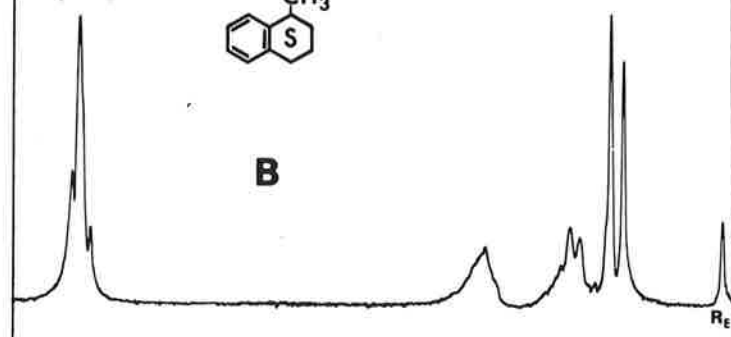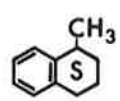
Iwan N. Stranski-Institut

II. Institut für Physikalische Chemie
der Technischen Universität Berlin

1 Berlin (West) 12,   June 24, 1968
Postanschrift: Hardenbergstr. 34
Tel.: (0311) 31 07 81, App. 3571
Institutseingang im Ernst-Reuter-Haus

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

Re.: Transient Nutations in Heteronuclear Magnetic Double Resonance.
Our letter of May 27, 1968, addressed to Chicago

Dear Dr. Shapiro,

Being closely engaged with NMR research at least since June 1967 when a Spectrospin High resolution NMR apparatus KIS-HFX$_1$X$_2$X$_3$ has been established in our laboratory, we should appreciate to be kept on your mailing list in future.

As our first contribution to these Newsletters we may give some comments concerning the utilisation of transient nutations (1) in H–{C-13} double resonance (2). Similar to the INDOR experiment in this method the C-13 satellite signal of a proton line is monitored by the observing field H$_1$ while sweeping the irradiation field H$_2$ in the range of the C-13 resonances. Contrary to the former, H$_1$ is purposely set high enough (0.04-0.15 mG) to saturate the observed transition. If the radiofrequency ω_2 is swept through a connected line in such a way to fulfill the adiabatic rapid passage condition (3) the characteristic Torrey oscillations (1) are observed. This effect can be explained by means of population inversion and describes at least qualitatively the different phase of the regressive connected transition in the observed H–{H} and H–{C-13} spectra in terms of the different magnetogyric ratio of the H and C-13 nucleus. As illustrations the AX spectra of CHCl$_2$CHO (+ 40 vol.% TMS) and ^{13}CHCl$_2$COOH (+ 10 vol.% TMS, nat. abundance) are shown in fig. 1 respectively in fig. 2. In the homonuclear case ω_2 is swept in the region of the aldehyde proton resonances (0.015 Hz/s) while saturating the low frequency doublet line of the CHCl$_2$ proton. In the corresponding heteronuclear case (fig. 2) the high frequency doublet line (J_{AX}=181.5 Hz) of the ^{13}CHCl$_2$ proton is saturated and ω_2 swept in the region of the ^{13}CHCl$_2$ resonances ($\approx$2Hz/s). The regressive connected transition is indicated by the negative sense of the oscillations (3) respectively by the small signal (2).

Iwan N. Stranski-Institut
II. Institut für Physikalische Chemie
der Technischen Universität Berlin

1 Berlin (West) 12,
Postanschrift: Hardenbergstr. 34
Tel.: (0311) 31 07 81, App. 3571
Institutseingang Im Ernst-Reuter-Haus

For the purpose of C-13 line position measurements ω_2 is swept over the line in both the directions, the larger the ratio of the nutation frequency $\Omega = \gamma H_1$ ($T_1 \approx T_2$, exact resonance for the saturated line) to the sweep rate, the better is the precision. The magnitude of H_1 is limited because of the unwanted splittings of the C-13 lines (and vice versa H_2); in fact, the above ratio depends on the sweep rate which in turn is determined by the relaxation times in order to fulfill the adiabatic rapid passage conditions. For $T_1 \approx 20$ s ($CHCl_2C\underline{H}O$) we obtained an error of ± 0.2 Hz (ratio ≈ 1 sec).

We use this method for studying the concentration dependence of C-13 chemical shifts due to intermolecular interactions. In these cases we modulated the irradiation frequency ω_2 with the corresponding coupling constant which is known from the proton spectrum. By this the populations of the regressive and progressive connected transition are inverted simultanously leading to a slight improvement of the sensitivity. Fig. 3 shows a typical spectrum of this kind, the central signal of which corresponds to the left one in fig. 2.
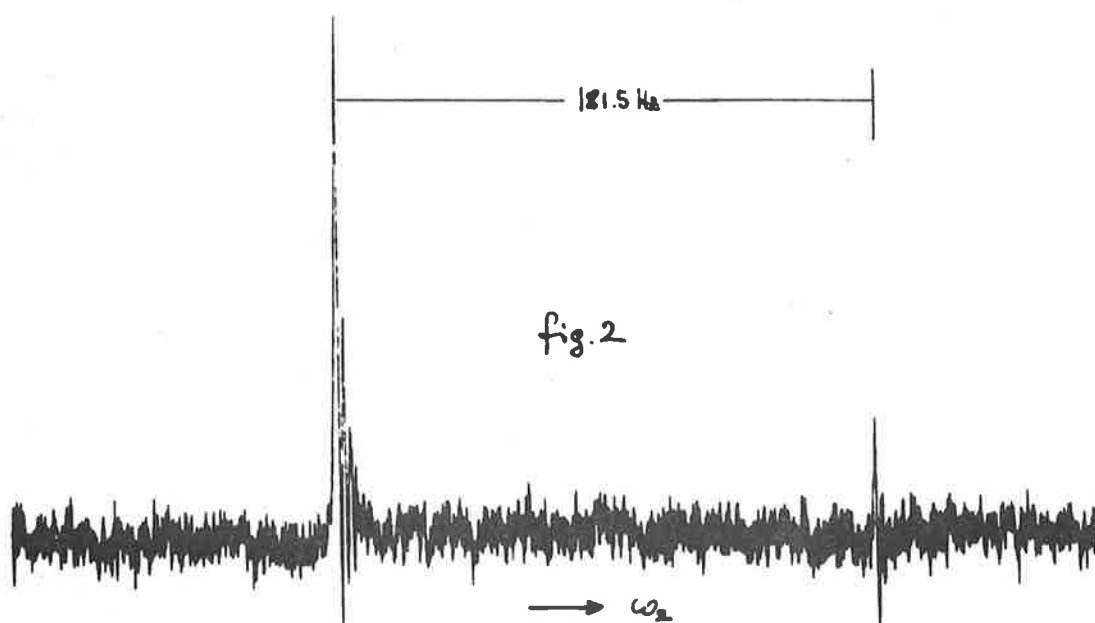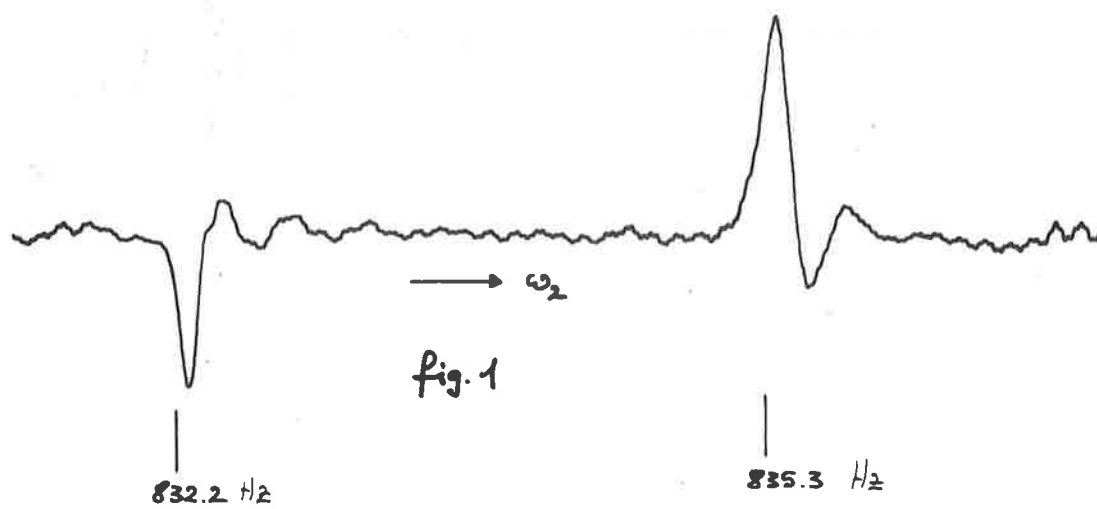
Yours sincerely,

E. Lippert   D. Ziessow

References:

(1) H. C. Torrey, Phys. Rev. 76, 1059 (1949)
(2) D. Ziessow, E. Lippert, J. Mol. Struct, in press
(3) J. A. Feretti, R. Freeman, J. Chem. Phys. 44, 2054 (1965)

fig. 1

832.2 Hz   835.3 Hz

181.5 Hz

fig. 2

181.5 Hz

fig. 3
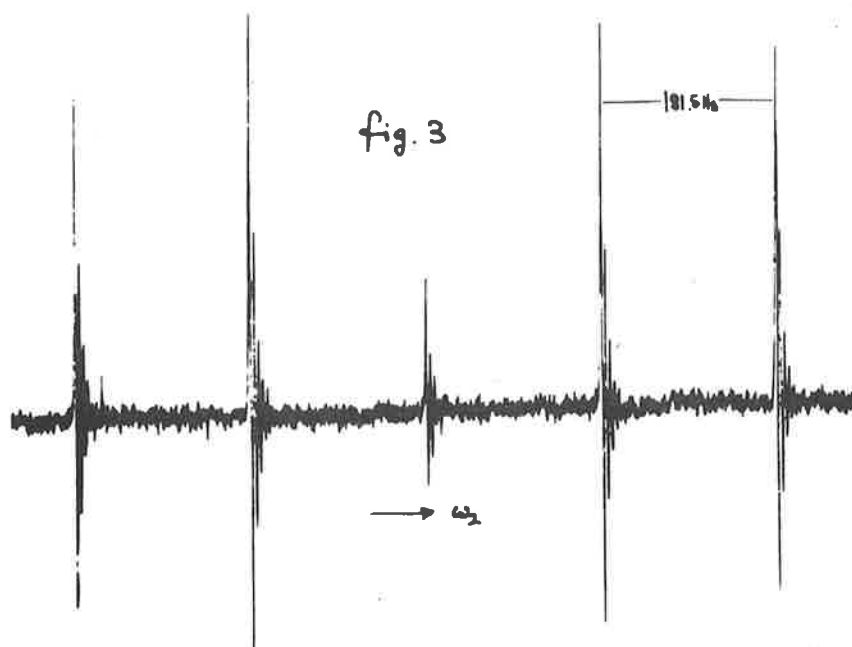
IOWA STATE UNIVERSITY
of Science and Technology
AMES, IOWA 50010

Department of Chemistry

June 28, 1968

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

Dear Barry: Super Stabilizer Protection

There are many advantages to leaving an internal-lock
spectrometer locked on to a standard sample when in a standby
condition, especially with a Varian 14 kilogauss magnet as
subject to uncycling by transients as ours is. However, a
power failure can lead to a 100 volt surge at the open-cir-
cuited stabilizer pickup coil terminals. With a system
resistance of about 1000 ohms the resulting surge current
would do the sensitive galvanometer movement no good at all,
as many have found to their cost.

Taking advantage of the high forward resistance of a
silicon diode at low voltages, we have connected a pair of
silicon diodes (any type with a surge rating of >100 Ma) in
parallel back-to-front configuration across TB-1, 1 and 2
of the Varian V-3506 Super Stabilizer. This limits the surge
voltage to less than 600 mV, a factor of 20 less, with no
detectable effect on the performance of the HR-60+ spectro-
meter (an HR-60 with a home-made lock circuitry). This
circuit has also been fitted to our new HA-100 with no
degradation of performance and has been proved in several
unscheduled shutdowns.

Sincerely,

Roy W. King

RWK/ld

AMERICAN MEDICAL ASSOCIATION/EDUCATION AND RESEARCH FOUNDATION/535 N. DEARBORN ST./CHICAGO, ILL. 606

INSTITUTE FOR BIOMEDICAL RESEARCH

DAN W. URRY, PH.D
ASSOCIATE MEMBER

July 1, 1968

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

Dear Barry:

Enclosed is the ad which we would like to place in your NMR Newsletter.

Position available beginning September 1968 for a postdoctoral
fellow to work on the Varian HR-220 superconducting NMR
spectrometer. Studies will be directed toward molecular
systems of biological interest with emphasis on proteins.

Contact Dan W. Urry, Institute for Biomedical Research
535 North Dearborn, Chicago, Illinois 60610, or phone
(312) 527-1500 ext. 509.

With best regards,

Dan

Dan W. Urry, Ph.D.