Illinois
Institute of
Technology
N — M — R
Newsletter

Illinois   Texas

Institute of   A
                              &
Technology   M

Nuclear   University

Magnetic ————————→   Nuclear

Resonance   Magnetic

Newsletter   Resonance

                            Newsletter

        During the month of August 1968, this Newsletter
and the undersigned will undergo the change in geography
indicated in the following address, to which all Newsletter
contributions and other correspondence should be sent after
10 August 1968:*

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

        This Newsletter will continue without interruption
or changes in policy as a result of this move. The Newsletter's
new name will be as indicated above, in the absence of any more
swinging alternatives, the call for which is hereby sounded.

                            Bernard L. Shapiro
                            2 June 1968

* Until 10 August 1968, all enquiries, contributions, etc.,
   should still be mailed to: Dr. Bernard L. Shapiro
                               Department of Chemistry
                               Stanford University
                               Stanford, California   94305

המכניון - מכון טכנולוגי לישראל

TECHNION — ISRAEL INSTITUTE OF TECHNOLOGY

הפקולמה לכימיה
DEPARTMENT OF CHEMISTRY

Haifa   May 5th, 1968

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

Dear Dr. Shapiro,

      The deuteron magnetic resonance of C_6D_6 dissolved in
the nematic liquid crystalline phase has previously been reported,
a doublet being observed.[1] We have measured the width of these lines,
using time averaging (C-1024 attachment) to improve signal to noise.
From the line width and the doublet splitting we have attempted to
estimate T_1 and T_2 using the Redfield equation. The perturbing
Hamiltonian is written[2]

$$H_1(t) \;=\; \sum_m F^{(0)}\, D^{(2)}_{om}(t)\, A^{(m)}(I)$$

where $F^0(0) \;=\; -V_{zz}eQ/h[4I(2I-1)]\, A^{(m)}(I)$ are spin operators,
and $D^{(2)}_{om}$ the Wigner matrices. The time dependence is in the $D^{(2)}_{om}$. In
the liquid crystal we cannot perform a complete spherical average over the
Euler angles, but rather we assume that alignment of the molecular is
governed by the probability factor $\exp(-\lambda\cos^2\theta)$, where θ is the angle
between the C_6 axis of the C_6D_6 molecule and the direction of this axis
for perfect ordering.[3] We derive values of $\tau_c = 2.1 \times 10^{-8}$sec. and
$T_1 = 4.5 \times 10^{-3}$sec., compared to $T_2 = 3.4 \times 10^{-4}$sec. as estimated from
the linewidth.

                   Yours sincerely,

                      A. Loewenstein

                      Y. Egozy

                      B.L. Silver

References

(1) Rowell, Phillips, Melby and Panar - J.Chem.Phys., 43, 3442 (1965).
(2) Slichter - "Principles of Magnetic Resonance," Harper and Row,
     New York, 1963.
(3) Glarum and Marshall, J.Chem.Phys. 46, 55 (1967).

CHIMIE ORGANIQUE PHYSIQUE

FACULTÉ DES SCIENCES
UNIVERSITÉ DE NANTES

38, Bd Michelet, - 44 - NANTES
B. P. 1044
Tél. (40) 74-50-70

Nantes, le 29 Mars 1968.

<u>Sign determination of allenic geminal
coupling constant from double quantum
spectrum.</u>

Professeur B.L. Shapiro
Department of Chemistry,
Stanford University,
<u>Stanford</u> California 94305.
U.S.A.

Cher Dr. Shapiro,

La grandeur et le signe de la constante de couplage entre
protons alléniques geminés ont fait l'objet de prévisions théo-
riques (1) (2) et une valeur de 9,0 Hz a été déterminée dans le
11 diméthylallène (2).

Dans la cétone deutériée $CH_3CO \overset{(B)}{CH} = C = \overset{(A)}{CHD}$ préparée par
M.M. Gaudemar et Couffignal (3) ce couplage atteint 15,0 Hz.

Nous en avons déterminé le signe par observation du spectre
à deux quantas.

Trois transitions à deux quantas sont théoriquement prévisi-
bles en résonance protonique pour un système ABX dans lequel
X=D a le spin 1. Elles ont pour fréquences $\dfrac{\nu_A + \nu_B}{2}$ et
$\dfrac{\nu_A + \nu_B}{2} \mp \dfrac{J_{AD} + J_{BD}}{2}$. Nous les avons effectivement observées
(Varian A 60 A) pour une irradiation $\dfrac{\gamma H_1}{2\pi} \simeq 2$ Hz et nous avons
utilisé la technique de modulation proposée par S. Yatsiv et
A.D. Cohen-D.H. Whiffen pour accroître l'intensité.

/....

Les 3 signaux étant séparés par des distances égales à la demi-somme des valeurs $J_{H_A D}$ et $J_{H_B D}$ mesurées sur le spectre à un quantum, nous en déduisons que $J_{H-\underset{\|}{C}-D}$ et $J_{H-C=C=C-D}$ donc $J_{H-\underset{\|}{C}-H}$ et $J_{H-C=C=C-H}$ sont de mêmes signes. Le couplage $J_{H-C=C=C-H}$ étant négatif (S.L. Manatt - D.D. Elleman, E.I. Snyder - J.D. Roberts) $J_{H-\underset{\|}{C}-H}$ est lui aussi négatif conformément aux prévisions théoriques de Pople et Bothner-By.

Bien cordialement.

M.L. MARTIN.   G.J. MARTIN.

(1) J.A. Pople et A.A. Bothner-By, J. Chem. Phys. 42 - 1339 - 1965.
(2) E.L. Allred D.M. Grant et W. Goodlett, J. Am. Chem. Soc. 87 - 673 - 1965.
(3) Laboratoire de Synthèse Organométallique - Faculté des Sciences de Paris.

ABBOTT LABORATORIES. SCIENTIFIC DIVISIONS

NORTH CHICAGO. ILLINOIS 60064

April 19, 1968

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

Dear Dr. Shapiro,

LONG-RANGE HYDROXYL COUPLING

Recent publications describing long-range -OH to-H couplings (1)(3) prompt us
to report an interesting example we have encountered. In the previous work
(1) a $J_{H-2,OH-1}$ long-range coupling of 0.7 Hz was noted in α-D-glucose and not
in the β-isomer. Similar couplings were noted in other pyranoses. The authors
generalize by saying that -OH long-range couplings of pyranoses in chair confor-
mations appear between, and only between, the protons of an axial hydroxyl group
vicinal to an axial proton.

α-D-glucose

β-D-glucose

γ-1

γ-2
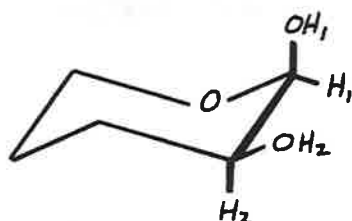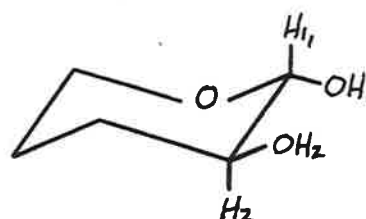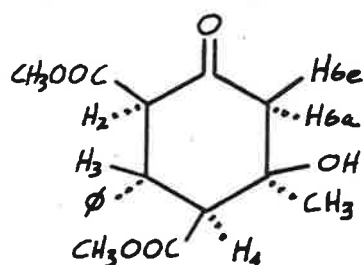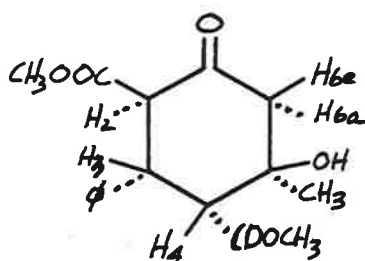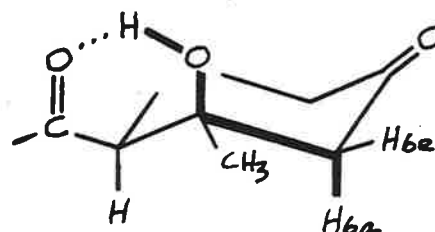
γ-1

We recently examined the 100 MHz spectrum of γ-1 (3-phenyl-5-methyl-5-hydroxy-2,
4-dicarbomethoxycyclohexanone) kindly supplied by Dr. Charles A. Kingsbury at
the University of Nebraska, and noted an interesting long-range coupling
($J_{H-6,OH-5}$ = 2.5 Hz) in CDCl3 solution. The conformation of the molecule is as
shown above as indicated by strong intramolecular hydrogen-bonding in its IR
spectrum. The larger magnitude of our coupling reflects the sterically locked

conformation of γ-1 since Jochims has noted that the size of the coupling constant must depend on the statistical weight of the rotational isomer of the hydroxyl group properly sterically oriented for a long-range coupling. Substituents at C-2,3 and 4 are all equatorial as indicated by the large vicinal couplings ($J_{H-2,H-3}$ = 12.5 Hz; $J_{H-3,H-4}$ = 12.5 Hz).

Assignment of the coupling to a specific proton at C-6 was based on analogy with previous examples in the literature. The C-6 methylene group describes an AB system ($J_{H-6a,H-6e}$ = 14.5 Hz) showing the characteristic multiplets centered at 2.69 and 2.52 ppm. The long-range coupling is clearly shown on the higher field multiplet. Cognizant of Jochims work and following the "W conformation" rule observed by many authors, the upfield multiplet was assigned to the axial proton.

Evidence that in this case the axial proton resonates at higher field was gained by examining γ-2, the C-4 epimer of γ-1, where the 4-carbomethoxy group is now axial. In this compound both 1,3-diaxial protons exhibit a downfield shift (H-2:3.69 to 4.60 ppm; H-6a:2.69 to 3.32 ppm). It is not unreasonable then to assume that in γ-1, the C-6 equatorial proton being coplanar with the C-2 carbomethoxy group has been deshielded relative to the C-6 axial proton which is not coplanar with either carbomethoxy group.

Although this assignment is not the one which would be predicted by the recent work of Karabatsos and others (2) which showed that "... protons α to the carbonyl in cyclohexanones resonate at lower magnetic fields when axial than when equatorial", we feel the effect of nearby carbomethoxy groups makes this a non-ideal case in which the general rule fails.

No evidence for long-range coupling has been found in γ-2; however, a $J_{H-4,H-6e}$ coupling of 2.0 Hz has been noted. Further work in this system is in progress.

(1) J. C. Jochims et. al., Tetrahedron Letters, #44, 4363 (1967).
(2) G. J. Karabatsos et. al., J. Am. Chem. Soc., 89, 5067 (1967). and references therein.
(3) C. W. Schoppee, Tetrahedron Suppl., 8, II, 471 (1966).

Sincerely,

Richard S. Egan
NMR Laboratory, D-407

msg

THE WEIZMANN INSTITUTE OF SCIENCE

REHOVOT · ISRAEL

ISOTOPE DEPARTMENT

רחובות · ישראל

מחלקת איזוטופים

April 24, 1968

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

Dear Dr. Shapiro,

The deuteron magnetic resonance (DMR) of solutions of
paramagnetic ions has received almost no attention since the
earlier work of Laukien and Noack [Z. Physik, 159, 311 (1960)].
A reconsideration of this matter, however, shows that the use
of DMR may lead to a better and detailed understanding of the
processes of nuclear relaxation in these systems and, in
addition to data derived from proton and oxygen-17 studies,
may provide new and important information on the rate constants
and mechanisms of hydrogen exchange, on the electron-nuclear
hyperfine coupling constants, and on the electron relaxation
times.

Owing to the smaller by a factor of 6.5 magnetogyric ratio
of the deuteron its line-width will be smaller by a factor of
42.5 than that of the proton and this will lead to an overall
improvement of spectral resolution by a factor of 6.5, if PMR and
DMR spectra were obtained in the same field. This is very
important for resolving signals of nuclei in the vicinity of
paramagnetic ions or for measuring isotropic shifts in conditions
of fast-exchange.

Another important feature becomes apparent in cases where
$T_{2m}^{-1} \gg \Delta\omega_m$, T_{2m} and $\Delta\omega_m$ being the relaxation time and isotropic
shifts of a nucleus in the coordination sphere. In this case
the "excess" relaxation is given by $1/T_{2p} = P_m/(T_{2m} + \tau_m)$.
Thus, since $T_{2m}^D > T_{2m}^H$, the contribution of T_{2m} to the observable

.. / 2

- 2 -

"excess" deuteron relaxation will be greater than to that of protons. The correlation time for T_{2m}^{-1} is often the electron relaxation time and DMR may serve as an effective probe for studying electron-spin relaxation.

We have taken advantage and used DMR in our studies of aqueous solutions of vanadyl(IV). We were able to obtain for the first time the temperature dependence of the electron relaxation time by NMR. The results are in good agreement with the theoretical predictions of Kivelson, Wilson, and Atkins [J. Chem. Phys., 44, 154, 169 (1966)].

Yours sincerely,

Jack Reuben   Daniel Fiat

JR/sa

From the Dean
Professor A. R. Katritzky

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

1st April, 1968

Dear Dr. Shapiro,

Coupling Constants and Pauling Electronegativity

In a recent paper Castellano (1) has established a relationship between the coupling constants $J_{2,3}, J_{2,4}, J_{2,5}$ and $J_{2,6}$ in a variety of N-substituted pyridine derivatives and the Pauling electronegativity index of the first atom of the N-substituent. No example was included, however, of a substituent with nitrogen as the adjacent atom.

In the course of other work we have had occasion to determine the N.M.R. parameters for two compounds of this type (I, II) and are able to record that the appropriate J_2 values fit convincingly on the straight line graphs obtained by Castellano for the other substituents (Figs 1-2). No correlation was found for the $J_{3,4}$, $J_{3,5}$ and $J_{4,5}$ values, again in agreement with the earlier paper.

In the case of the 3-aminocarbonyl derivative (III) the agreement was not as good as with the unsubstituted compounds especially for $J_{2,4}$ as expected in view of the known (2) effect of mesomeric electronegative substituents on bond orders, and hence on coupling constants.

(I)

(II)

(III)

CONH$_2$

N$^+$

N$^+$

N$^+$

NH$_2$

NHCOMe

NHCOOEt
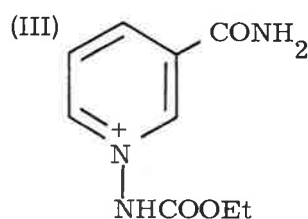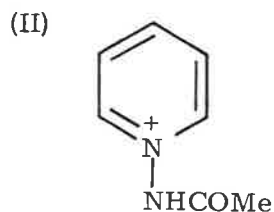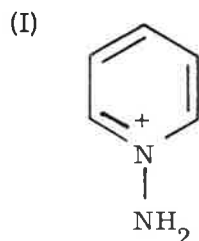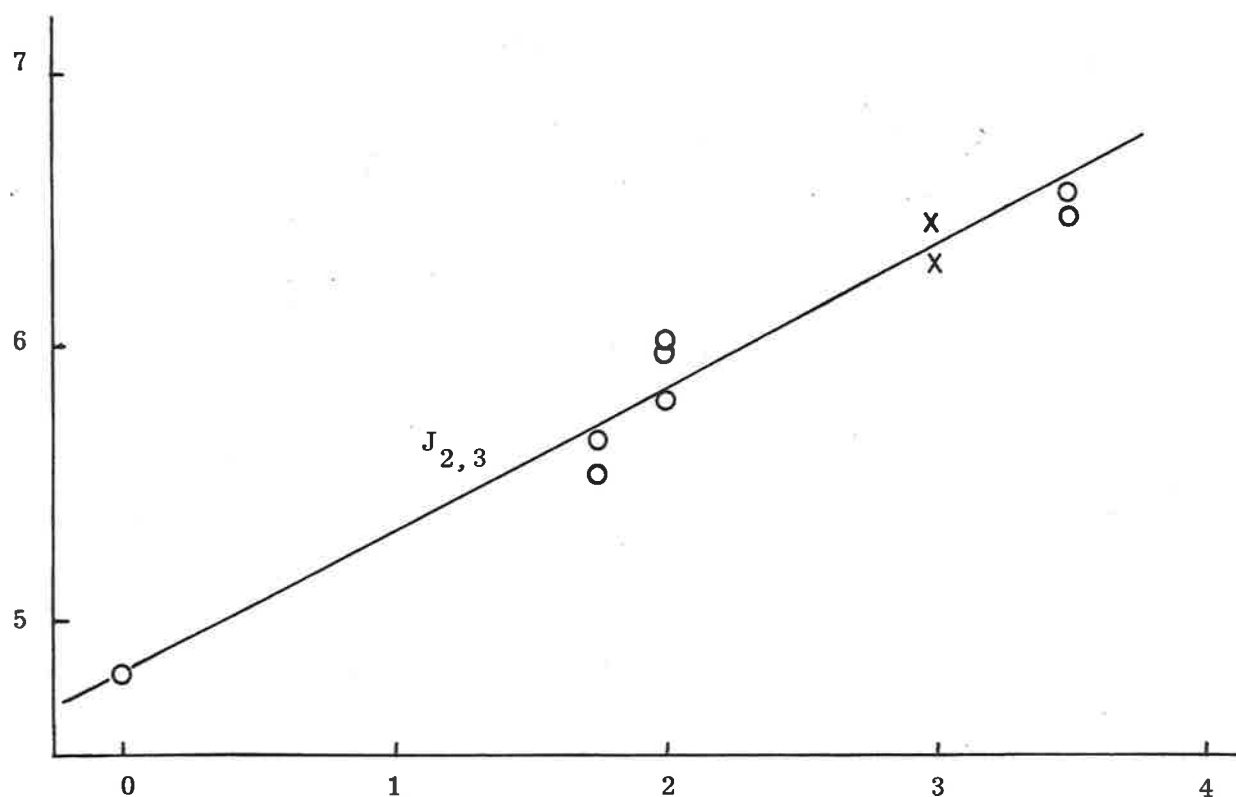
Figure 1. Plot of $J_{2,3}$ versus the Pauling Index: O, from ref. 1; X, our results
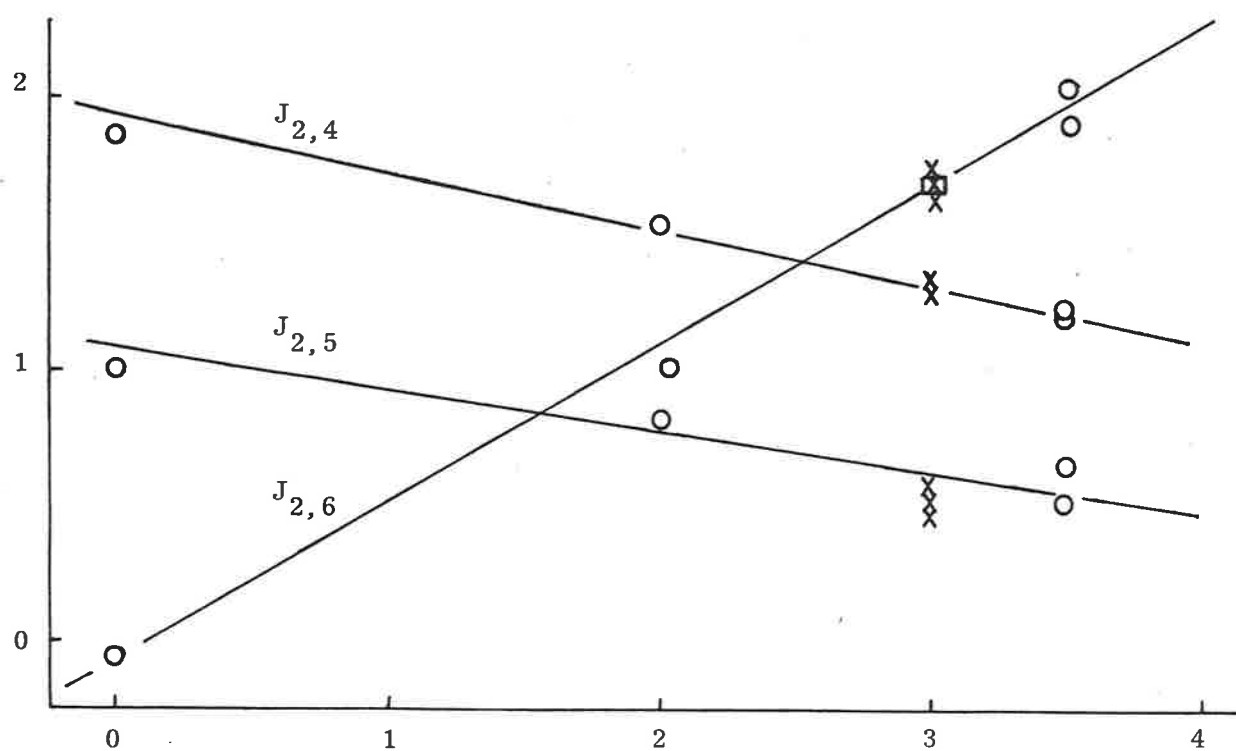
Figure 2. Plots of $J_{2,4}$, $J_{2,5}$, and $J_{2,6}$ versus the Pauling Index:

O, from ref. 1; X, our results; □, $J_{2,4}$ for 3-$CONH_2$ compound

The values for the parameters shown in the table were obtained from spectra taken in D_2O solution on a Perkin-Elmer R10 (60 Mc./s) or Varian HA-100 (100 Mc./s) instrument, and analysed using the LAOCOON least-squares fit program (3).

TABLE
τ values

Compound	CH_3	CH_2	H_2	H_3	H_4	H_5	H_6
I	-	-	1.23	1.23	1.61	1.97	1.97
II	-	-	1.10	1.10	1.26	1.75	1.75
III	8.61	5.53	0.42	-	0.78	1.51	-0.70

H_2

Compound	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{2,6}$	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$
I	6.47	1.29	0.44	1.65	7.86	1.85	0.44	7.86	1.29	6.47
II	6.31	1.35	0.56	1.76	7.78	1.69	0.56	7.78	1.35	6.31
III	-	1.71	0.53	1.70	-	-	-	8.31	1.24	6.43

References

(1)   S. Castellano and R. Kostelnik, J. Amer. Chem. Soc., 1968, 90, 141.

(2)   P. F. Cox, J. Amer. Chem. Soc., 1963, 85, 380.

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

Yours sincerely,

E. Lunt   A. R. Katritzky

University College of Swansea

Department of Chemistry

Professor C H Hassall PhD ScD FRIC
Professor and Head of Department
Professor J H Purnell BSc PhD MA PhD
Professor of Physical Chemistry

SINGLETON PARK   SWANSEA
TEL SWANSEA 25678

3rd May, 1968.

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

Dear Barry,

N.M.R. parameters for fluorinated pyridines

Apologies for the delay in sending my subscription.
As usual, your reminder caught me on the hop, with several
topics on the boil, but few in a state of completion.

With fluoro-aromatics currently the subject of much
n.m.r. activity, my results for various fluorinated pyridines
may be of interest. Without the facility of ^{14}N decoupling,
the coupling between the two α nuclei is impossible to measure
accurately. However, the remainder of the spectrum provides
all other parameters, which are listed in the Table.
2-fluoropyridine has been previously analysed by Brugel[1], whose
results are slightly modified by the more accurate analysis at
100 Mc/s. The first-order nature of the spectrum prevents
relative signs being determined, but from the almost complete
analysis of 2,6-difluoro pyridine, J_{HF} ortho appears to be <u>negative</u>
as found in 2-fluoropyrazine[2], i.e. opposite to the sign of J_{HF}
ortho in fluorobenzenes. In the more strongly coupled
3-fluoropyridine, however, the best computer fit with both ^1H and
^{19}F spectra is with J_{HF} ortho (αβ) and J_{HF} para both <u>positive</u>, the
latter being the larger coupling. The effect of the nitrogen atom
is therefore strikingly illustrated with $J_{1F} = 0.66$ c/s and $J_{3F} = 8.79$ c/s.

Another interesting feature in these compounds is J_{HF} meta, which ranges from ca 0 c/s to 8.3 c/s depending on the environment of the nuclei. The results given in the Table have been refined using several versions of LAOCÒON, with the aid of Graham Griffin of this Department. Further work is in progress in the examination of various difluoropyridines, in order to follow up the trends observed in the monofluoro series.

I hope this contribution will keep me solvent for a few more months.

      With best wishes.
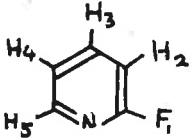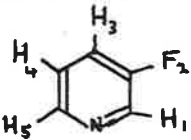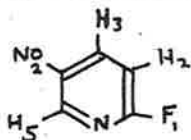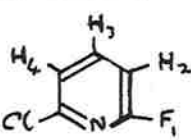
        Yours sincerely,

        W. A. Thomas

1. W. Brügel, Z. Electrochem, 1961, 66, 159.

2. R. H. Cox, I.I.T.N.N. 1968, 113, 13.

Table: Chemical Shifts and Coupling Constants in Fluorinated Pyridines

Compound				
W_1	-	853.80	-	-
W_2	699.80[a]	-	751.54	656.80[c]
W_3	784.04	740.79	889.74	758.87
W_4	721.65	727.05	-	704.31[c]
W_5	826.64	845.85	921.73	-
J_{12}	- 2.63[b]	+ 0.66	- 2.96	- 2.61
J_{13}	+ 8.19	+ 2.99	+ 6.41	+ 8.10
J_{14}	± 2.49	+ 0.63	-	± 2.42
J_{15}	~ 0.8	< 0.5	~ 0	-
J_{23}	+ 8.18	+ 8.79	+ 8.87	+ 7.99
J_{24}	+ 0.83	+ 4.83	-	+ 0.64
J_{25}	+ 0.81	+ 1.97	+ 0.49	-
J_{34}	+ 7.16	+ 8.46	-	+ 7.78
J_{35}	+ 2.14	+ 1.32	+ 2.84	-
J_{45}	+ 4.88	+ 4.62	-	-
RMS error in) line positioning)	0.056	0.058	1st order	1st order

(a) chemical shifts in c/s from TMS.
(b) coupling constants in c/s, with probable signs given.
(c) assignments of H_2 and H_4 based on Brügel's results for 2-fluoro- and 2-chloro-pyridine.

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

April 29, 1968

Professor Bernard Shapiro
Chemistry Department
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Dr. Shapiro:

Adaptation of function generator and op amp to operate HA100 from C1024.

Taking a rather dismal view of the prospect of repairs which would be required
if we continued using the C1024, Time Averaging Computer, with the HA100 NMR
system in the manner provided by Varian, we were looking for a way to generate
the sweep frequency electronically and save on transmissions and slidewires.
The original design called for the sweep to be generated by the HA100 recorder-
movement, with the external trigger for the CAT being generated by a micro-
switch at the left limit of the recorder. This necessitates wear on both the
transmission and slidewires which should be unnecessary.

Any function generator operating at a reasonable input level and supplying
sufficient output would have worked for this application, but we chose the
Wavetek Model 115 (Model 112 would have contained the minimum operational
features but the ability to operate in Phase Lock mode may be important in
some other application). The DC Ramp was taken from J8-2 (Ramp Out) on the
back of the Computer. About 5 db. of attenuation was required on the Wave-
tek input. The output was applied to J1307 (Sweep Out) on the back of the
Lock Box (V4354) and the Sweep Oscillator Tuned Net circuit card in the Lock
Box was removed.

The computer could be triggered in Offset-NMR Trigger mode on any signal of
sufficient voltage except the lock signal (normally TMS). The Sweep Oscil-
lator attenuator and recorder amplitude was adjusted to near the minimum
voltage required to trigger.

Operated in this manner, a high degree of signal coherence was obtained.
However, since the CAT supplies a positive going ramp, spectra were swept
from lower to higher frequency. By various tricks, such as read-out with
recorder travelling right to left, the spectra could be obtained in the
correct direction. Occasionally, though, "ringing" would occur and it
would be on the high frequency of the signal.

By the introduction of an inverting Operational Amplifier in the Wavetek
input, we obtained a negative going ramp. The Op Amp used, although others
would probably work, was Analog Devices Model 114C. The Operational Ampli-
fier and associated components were installed on a card and the card added

to the Wavetek. The power for this circuit (5 ma. $\times \pm 6$ v.) was stolen from
the Wavetek with no ill effects. The diagram shows the final version of the
modification.

The signal coherence obtained is most satisfactory. Shown is the read-out of
a signal stored over 100 sweeps and the ringing is, essentially, unperturbed.
This is the quartet of ethanol in Varian Reference Sample, the spectrometer
is locked on TMS and the computer is triggered on chloroform.

Best regards.

Sincerely yours,

Curtis A. Glass, Chemist
Physical-Chemical Properties Investigations
Cereal Properties Laboratory

100 scans
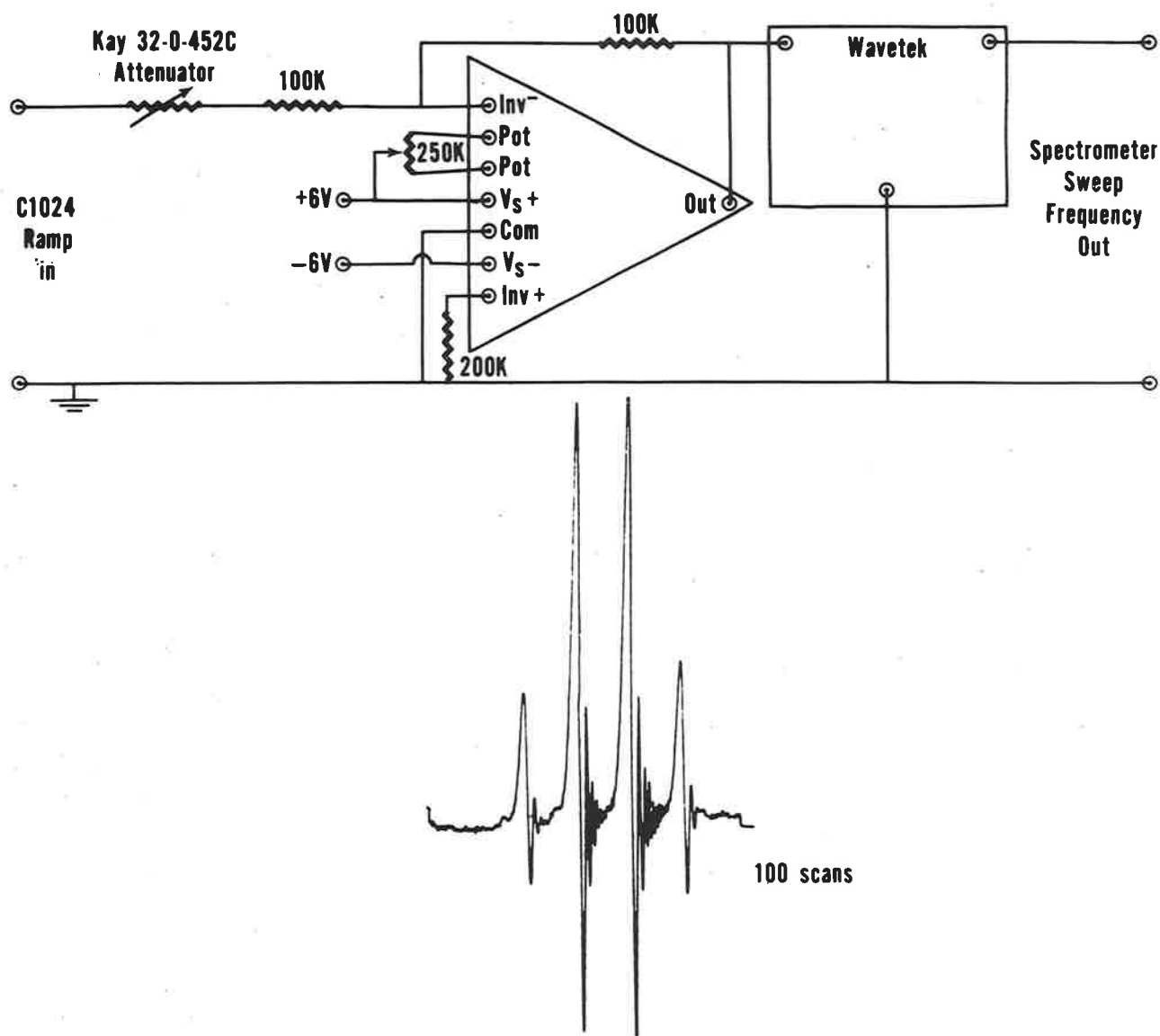
IBM

2670 Hanover Street
Palo Alto, California 94304
415/327-2300

International Business Machines Corporation

May 7, 1968

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

Dear Barry:

Due to several factors, progress on the program to carry automatic analysis of high resolution spectra (IITNMR 107, 63) has been almost non-existent since the last time I received the blue reminder.

Work has resumed, however it will still be some time before the entire program will be ready for distribution. I thought that in the interim some readers might be interested in the availability of the initial step of the program, viz., the automatic decomposition of the spectrum. As those who have used DECOMP know, it is somewhat cumbersome due to the requirements for scaling, making initial estimates of peak parameters, and the usual necessity of making more than one pass when working with more complicated groups of peaks.

The automatic decomposition is much easier to use, reduces the number of computer runs and thus elapsed time by a considerable factor, although the total amount of computer processing time is not necessarily reduced.

Input consists of a few parameters, such as the maximum number of peaks in the curve, threshold, title, etc., and the raw digital data composing the spectrum. A subroutine has been added which uses the Savitsky and Golay (Anal. Chem. 36, 1627 (1964)) smoothing routine to smooth the data points. Two input parameters allow the use of an n point smoothing operator m times, if desired. The spectrum is then shifted and scaled, and the discrete groups are separated by the cutoff points where the curve dips below the threshold value. Initial estimates of the peak positions and intensities are also calculated at the same time by using peak

Dr. B. L. Shapiro   -2-   May 7, 1968

maxima and the input line halfwidth or standard digital peak height, depending upon whether a Lorentz or experimental line shape is chosen. Each of these groups are then decomposed by DECOMP in the usual manner; however, if the fit is not better than a certain criterion, chosen by the user, an additional line is added to the group and the decomposition is repeated with the additional line. This is repeated until the improvement gained by additional lines is not better than a certain value (also adjustable by the user). As mentioned above, an entire curve can be done with a minimum of input, since the data and program are read into the computer only once. Elapsed time is also reduced since only one "turn around" on the computer is required for each spectrum, however the maximum time limit should be set carefully since one may be letting himself in for the use of a large amount of computer time if the limits for the fitting decisions are not correct. It is more satisfactory to set these limits so that the fits are somewhat less than perfect since it is difficult to choose fitting criteria which find an optimum fit without wasting time on trivial improvements when the spectrum is being run for the first time. This could probably be reduced with experience using a given spectrometer under standardized sets of operating conditions.

The program is written in FORTRAN and I have been using an IBM 1800 for most of the debugging. A description and listings will be available in about a month.

<div style="text-align:center">

Sincerely yours,

Ted

T. R. Lusebrink

</div>

TRL:bis

Suggested title: Availability of Program for Automatic Spectrum Decomposition.

Southern Illinois University

CARBONDALE, ILLINOIS 62901

Department of Chemistry

May 10, 1968

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

Nonequivalence and Lack Thereof In 2-Halo-dimethylaminomethylferrocenes

Dear Barry:

One of us has reported previously on diastereotopic protons[1] in the spectra of certain 2-substituted dimethylaminomethylferrocenes.[2] These spectra all possessed extraordinarily large differences in chemical shift for the H_A and H_B protons. We have now observed the diastereo-topic protons in some 2-halo-dimethylaminomethylferrocenes (halogen = Cl, Br, I) in a variety of solvents (cf. Table). In at least one solvent, all of the 2-halo compounds exhibited a singlet for the methylene protons.

$CH_2 N(CH_3)_2$

X

Fe

$X = Cl, Br, I$
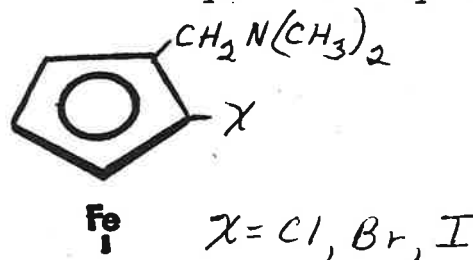
The data would seemingly argue against a simple steric effect as a cause of geminal magnetic nonequivalence in these systems, since one would have expected (perhaps naively) the 2-iodo compound to have exhibited the largest δ_{AB}. Separate analysis of each of the methylene protons and postulation of a contact interaction of the halogen with that proton time-averaged in an exo position has led to a correlation with observed data.

Sincerely,

D. W. Slocum

D. W. Slocum

T. R. Engelmann

T. R. Engelmann

DWS/je

Table I

Differences in Chemical Shift (cps) of the[1]
Methylene Protons of the 2-Halo-DMAMF's $(Ia\text{-}c)$
as a Function of Solvent and Substituent

Solvent	Substituent(X) =	Cl	Br	I
CCl_4		S^a	S^a	S^a
$CDCl_3$		9.6	3.9	S^a
C_6H_6		14.2	12.3	8.9
$C_6H_5CH_3$		12.9	10.8	7.2
CH_3CN		11.5	8.9	S^a
DMSO-d_6		S^a	S^a	S^a

a) S refers to singlet.
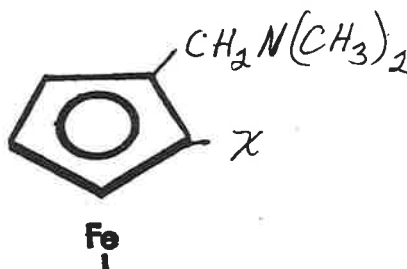
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE

NATIONAL INSTITUTES OF HEALTH
BETHESDA, MD. 20014
AREA CODE 301   TEL: 656-4000

May 8, 1968

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

Dear Barry:

We have been doing heteronuclear double resonance studies (principally $^1H\{^{15}N\}$)
by means of a General Radio Model 1164A frequency synthesizer attached to our
HR-60, which has been modified with a homemade internal lock system. The ultimate
frequency source for the synthesizer is a GR-1160P3 Standard Frequency Oscillator.
In addition to providing the perturbing RF, the synthesizer has a constant frequency
output of 30 MHz, which is amplified and fed to the second stage of the V-4311
transmitter. Thus the 60 MHz output of the V-4311 is locked to the perturbing fre-
quency.

The field/frequency lock is based on the original Anderson-Freeman concept, with the
error signal directed to the flux stabilizer but not to the RF unit. In addition
we have adopted Baker's suggestion (IITNMR 108, 27) and added a solid state amplifier
and additional coils on the magnet. Most of our internal lock error signal goes to
this new amplifier, but we have found it desirable to retain the super stabilizer
as well. The overall lock system works well with a measured maximum short-term
fluctuation of about 0.08 Hz. However, that may result partly from instabilities
in the GR-1107A audio oscillator used to provide the observing side-band frequency.

For heteronuclear decoupling we amplify the variable frequency out of the frequency
synthesizer with a modified Heathkit Model DX-60 RF amplifier. This gives more than
enough power to remove one bond ^{15}N-H couplings ($\sim$ 80 Hz).

We have also installed a Wilmad spinner on our A-60 probe. The spinning, particu-
larly at non-room temperature, is greatly improved over the old Varian spinner. We
have not, however, tried the new type Varian spinner.

If any readers would like further information on any of the instrument modifications,
Bob Bradley or I will be glad to supply details.

Best wishes.

Sincerely,

Ted

Edwin D. Becker

TITLE: Use of GR Frequency Synthesizer with HR-60; Wilmad Spinner on the A-60

University of Notre Dame
College of Science
Notre Dame, Indiana 46556

Department of Chemistry

May 13, 1968

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

Dear Barry:

"A New Era for DNM Resonators?"

Many people have been seriously concerned about the general unreliability of rate and activation parameters obtained by dynamic NMR studies (DNMR). I became acutely aware myself of just how discouraging the situation really is while writing a review article on DNMR methods and their applications for Vol. 3 of "Topics in Stereochemistry" (to appear in August 1968). Although the number of workers that calculate their values by complete line-shape fitting is steadily increasing (in my opinion a significant step towards eradication of the bad reputation DNMR has acquired in the past), the vast majority of the studies are still being done on very simple spin systems. For reasons to be mentioned below I believe one should rather (and deliberately) choose reasonably complex spin systems whenever the molecule under study permits such a choice.

What one needs for doing this is a general theory and a computer program that can handle any complex spin system exchanging intra- or intermolecularly between an arbitrary number of chemical environments. Taking up an idea suggested some time ago by Charles Johnson (JCP $\underline{41}$, 3277 (1964)), I have recently developed such a theory (paper submitted to JCP) and I should now like to give a brief summary of its main features.

It is advantageous to formulate a general theory of line shapes in NMR in the framework of the Liouville representation of quantum mechanics rather than in the Hilbert space representation. If one writes down the state vector ρ in a composite Liouville representation (the elements of ρ are defined as the renormalized density elements of the primitive state vectors of the individual molecules or nuclear configurations) and projects all operators into this composite Liouville space, the equation of motion simply reads $d\rho/dt = \mathcal{M}\,\rho$, where the complex non-Hermitian magnetization operator $\mathcal{M}$ may be broken up into $\mathcal{M} = -i\mathcal{L} + \mathcal{R} + \mathcal{X}$. The Liouville operator $\mathcal{L}$ has elements $L^k_{\mu\nu,\kappa\lambda} = 2\pi[H^k_{\mu\kappa}\delta_{\nu\lambda} - H^k_{\lambda\nu}\delta_{\kappa\mu}]$, the representation of the relaxation operator $\mathcal{R}$ becomes equal to Redfield's matrix, and for the exchange operator $\mathcal{X}$ one finds for the intramolecular case

$$X_{\mu_r\nu_r,\,\kappa_s\lambda_s} = \delta_{\mu\kappa}\,\delta_{\nu\lambda}\left[-\delta_{rs}\sum_{t(\neq r)}K_{rt} + (1-\delta_{rs})K_{sr}\right] \qquad (1)$$

and for intermolecular exchange

$$X_{\mu_r u_r,\,\nu_r v_r;\,\kappa_s x_s,\,\lambda_s y_s}$$

$$= \left[d^{-1}\delta_{\mu\nu}\delta_{\kappa\lambda} - \delta_{\mu\kappa}\delta_{ux}\delta_{\nu\lambda}\delta_{vy}\right]\delta_{rs}\sum_{t(\neq r)}K_{rt} + n_s^{-1}\delta_{uv}\delta_{xy}(1-\delta_{rs})K_{rs} \qquad (2)$$

where the K_{rs} are the first-order or pseudo-first-order rate constants. The Greek indices in Eq. (2) refer to the spin basis functions of the exchanging group of nuclei and the Latin indices to the non-exchanging group; d denotes the dimension of the Hilbert sub-subspace of the exchanging group and n_t is the dimension of the Hilbert sub-subspace of the non-exchanging group of nuclei in molecule t.

For the unsaturated steady-state line shape the equations may be further contracted into a number of smaller Liouville subspaces. To make a long story short, the computational procedure reduces to the problem of transforming a number of complex non-Hermitian and in general non-symmetrical matrices to Jordan canonical form (which is usually diagonal in practice). The total amount of information may eventually be contracted into two complex vectors, a radiofrequency-independent "shape vector" and a "spectral vector" which is a trivially simple function of the radiofrequency. The real and imaginary parts of these vectors lend themselves to a transparent physical interpretation. The absorption line shape is simply obtained as the negative real part of the scalar product of these two vectors.

As an example the attached Figure reproduces the line shapes for a three-proton system with $\nu_A = 19.6$, $\nu_B = 22.9$, $\nu_C = 52.7$, $J_{AB} = 12.3$, $J_{AC} = 7.3$, $J_{BC} = -17.7$ cps and $T_2^{eff} = 0.8$ sec in which A and B undergo mutual exchange. For comparison the spectra for the AB system derived from the ABC by omission of the non-exchanging C nucleus are also shown. Obviously the ABC spectra contain a great deal more dynamic information. One might say that a whole series of "coalescence points" is being observed for different values of K. In complex spectra such as these the sensitivity is therefore more evenly distributed over the accessible range of rate constants. People interested in reliable results might in the future want to avoid the excessively simple spin systems and switch to model compounds for which the spectra do not collapse into a single line in the fast-exchange limit.

The computer program (called DNMR) will be made available to the general public later this year via QCPE (for those who don't know: that's the Quantum Chemistry Program Exchange at Indiana University, an informal organization rather similar to the IITNMR except for the important difference that to remain a member in good standing you are not obliged to be permanently pregnant).

Sincerely yours,

Gerhard

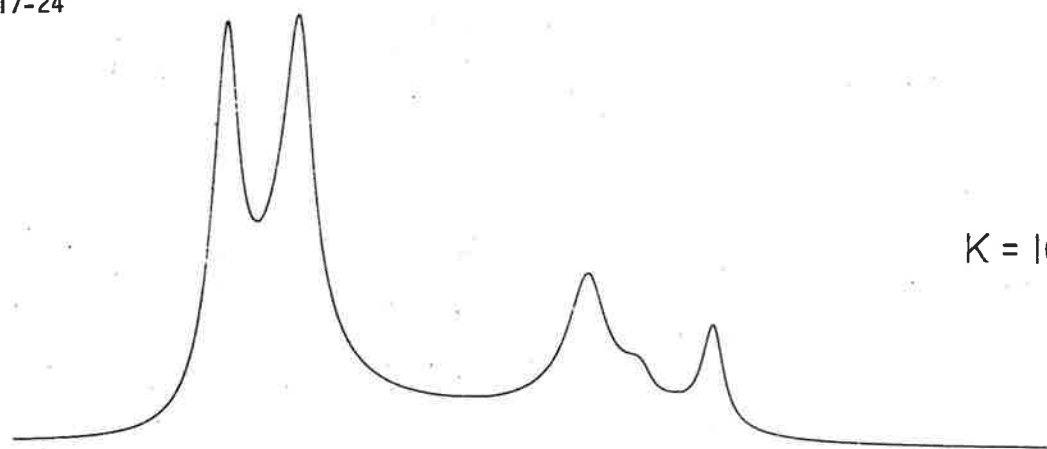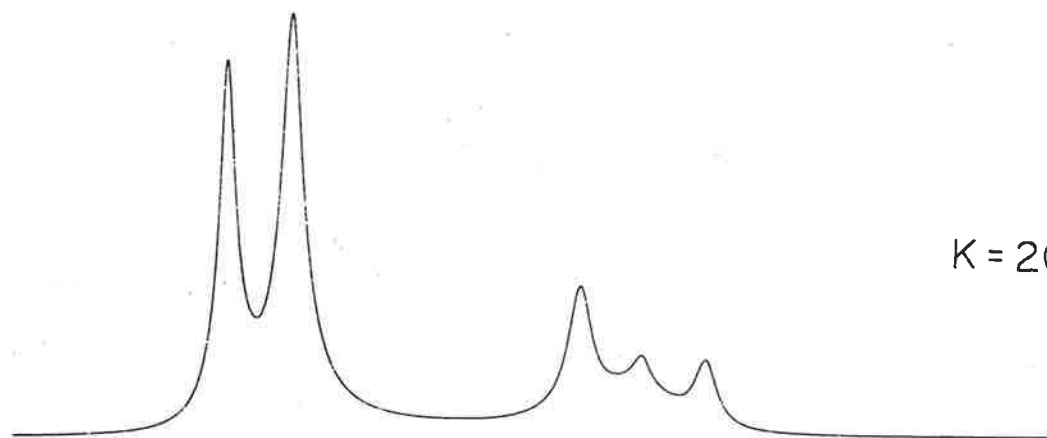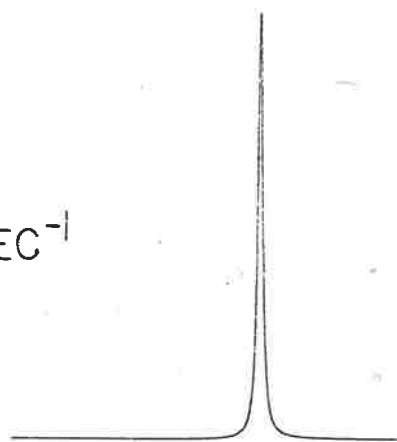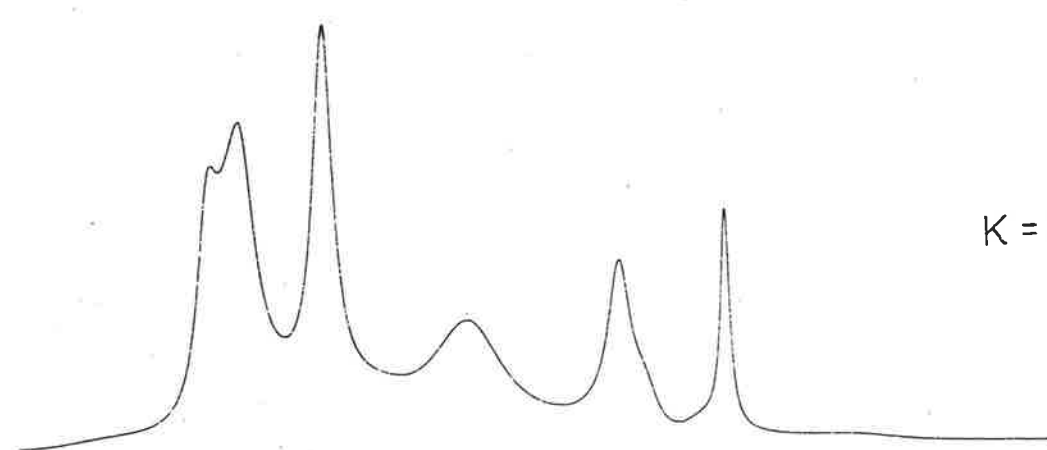Gerhard Binsch
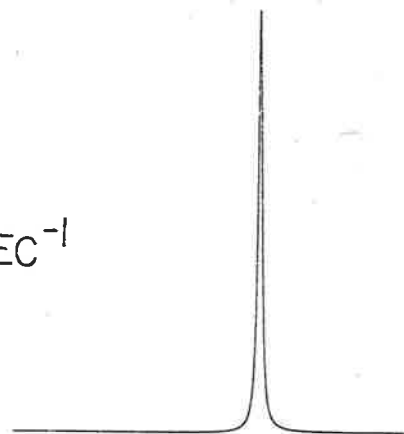Assistant Professor of Chemistry

GB:mm

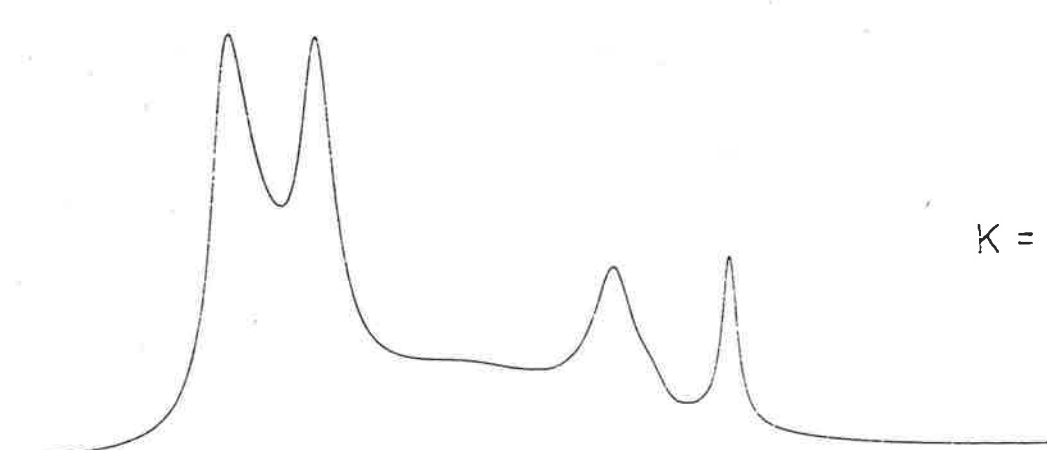P.S. Sorry about the somewhat excessive length of this letter. I promise to be excessively brief on my next delivery.

117-23

K = .1 SEC⁻¹

K = 2 SEC⁻¹

K = 5 SEC⁻¹

K = 10 SEC⁻¹

117-24

K = 100 SEC^{-1}

K = 200 SEC^{-1}

K = 20 SEC^{-1}
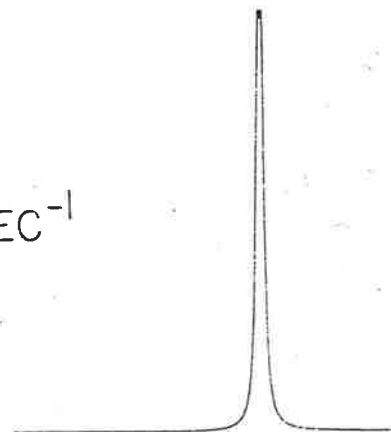
K = 50 SEC^{-1}
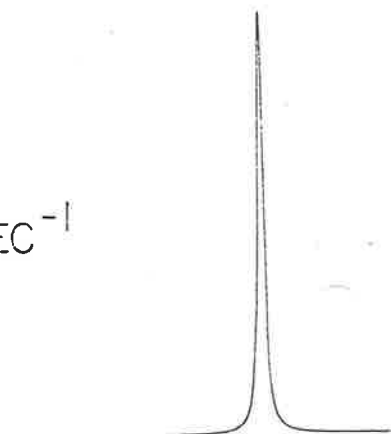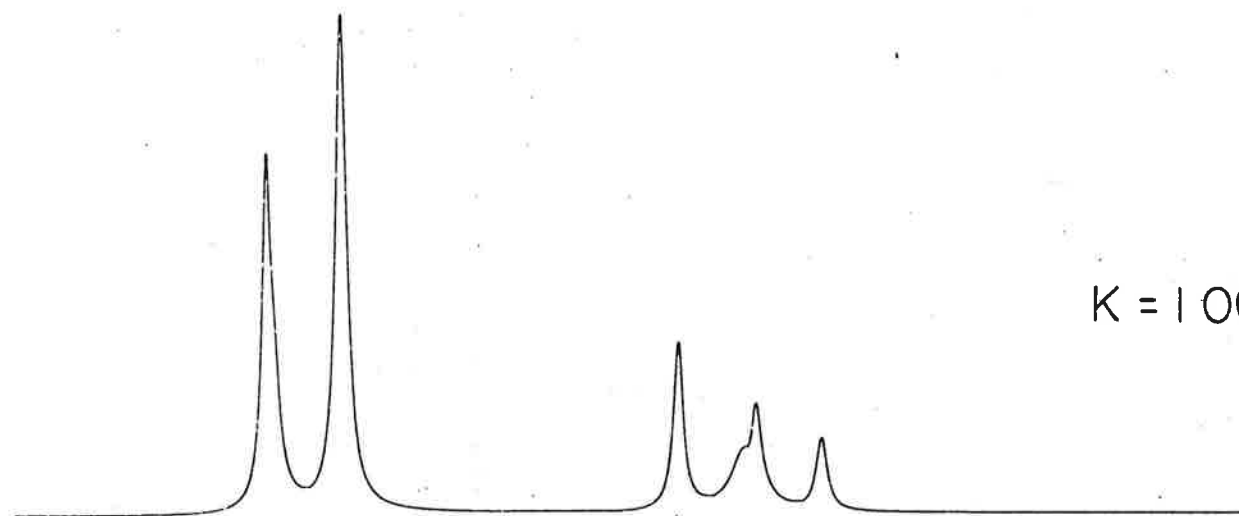
K = 1 000 SEC^{-1}

K = 10 000 SEC^{-1}

0   50   CPS   0   20

117-25
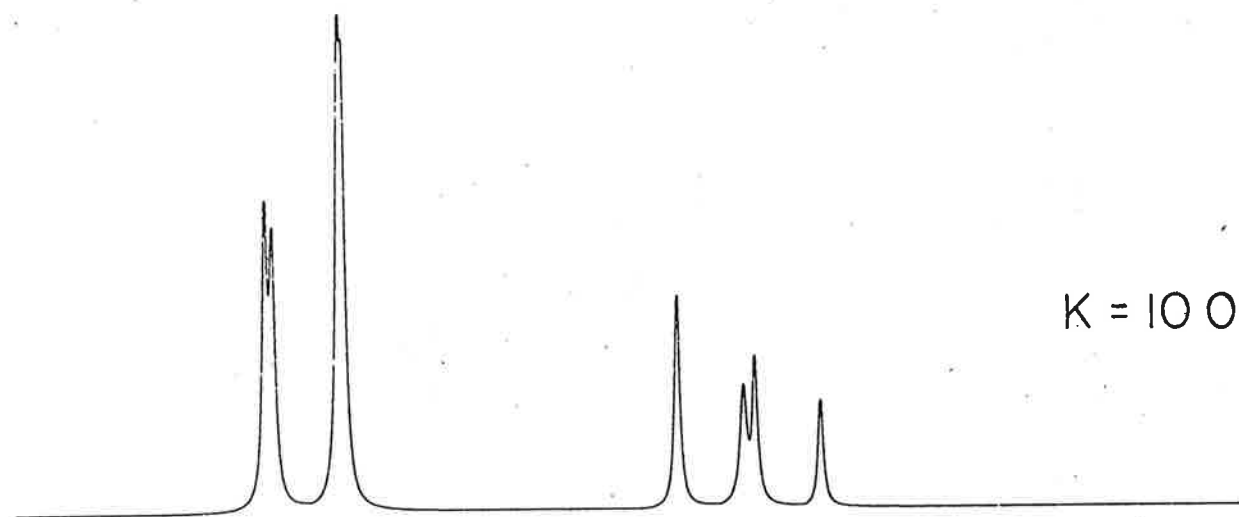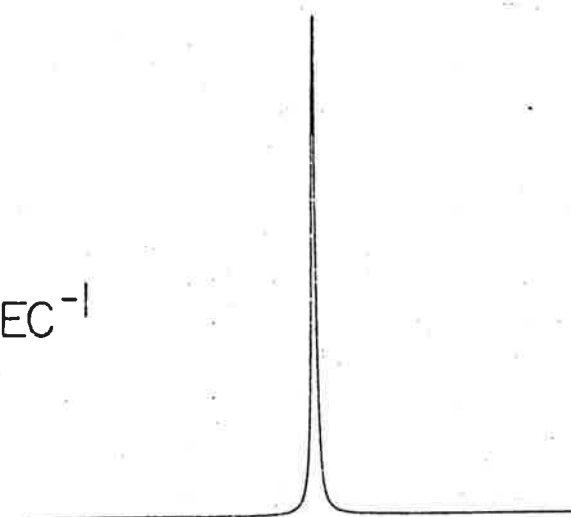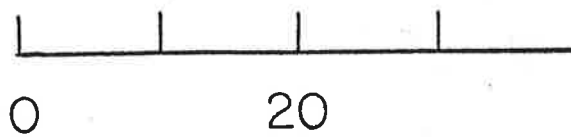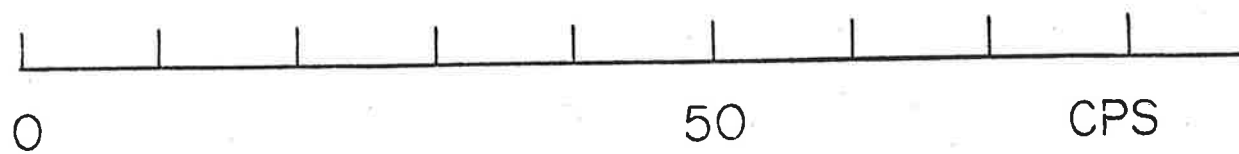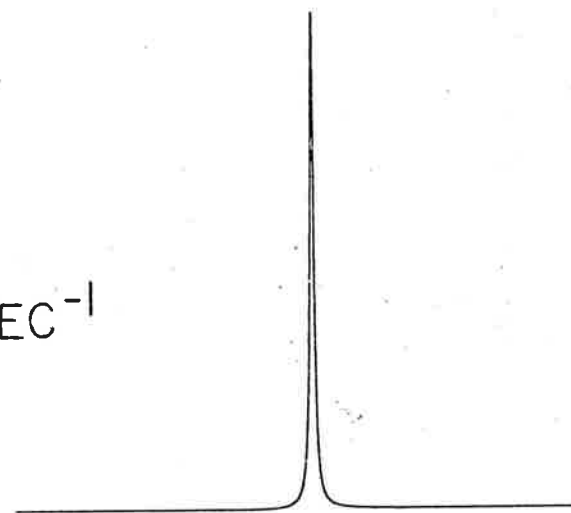
NAVAL RESEARCH LABORATORY
WASHINGTON. D.C. 20390

IN REPLY REFER TO:

Correcting line width for magnet inhomogeneity

Common practice when reporting line widths measured by c.w. techniques has been to subtract from all observed line widths a correction for the magnet inhomogeneity. Typically, the minimum observable line width in the particular study is taken to be the correction factor. (The correction for modulation broadening is not under discussion here.)

In our work with the N^{14} resonances of aliphatic nitro compounds, we observe line widths in some cases of only a few Hertz. Because we are using 5 mm samples in the HA-100 magnet, our inhomogeneity line width for a reference sample such as acidified NH_4NO_3 approaches 1 Hz for the lines of the ammonium ion quintet. In order to determine the effect of magnet inhomogeneities, we introduced through the X and Y shims controlled line broadening, using a known line of ca 1 Hz line width as a measure of the broadening. We were careful to keep line shapes symmetrical and to avoid saturation. Our results are as follows:

"Resolution" (Hz)	Observed N^{14} line width (Hz)		
	$MeNO_2$	$(CH_3)_2CClNO_2$	$\diagup^{-NO_2}$
1	19	32	128
9	20	--	--
15.5	27	--	--
23	34	44	136

These results, while only preliminary, are disconcerting in view of the amount of data in the literature in which a simple minimum observable line width correction has been applied.

C. F. Poranski, Jr.

W. B. Moniz

EASTMAN KODAK COMPANY

ROCHESTER 4, NEW YORK

May 13, 1968

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

Dear Dr. Shapiro:

Here is a subscription contribution: <u>NMR Difference Spectrum Showing Co(II)-Polypeptide Specific Interaction</u>.

We have begun to study the high resolution proton spectrum of polypeptides in solution from both the standpoint of protein spectral analysis and conformational determination. We are reasonably far along with the job of understanding a good deal of the spectrum of gelatin - a fairly complicated polypeptide. Most of this work will be reviewed at the Toronto IUPAC Symposium but I would like to describe a novel bit of our results here.

As is inevitably the case when doing proton nmr in (even D_2O) aqueous solution, we were hampered by the obscuring aspect of the HDO peak (which hides most of the α-CH's). While we are attempting exhaustive deuteration, etc., it occurred to us that we might be able to make use of the very large (water proton) contact shift (to low field) we have observed in previous studies of aqueous Co(II) solutions. We calculated that $\sim 0.1\underline{M}$ $CoCl_2$ would produce an adequate shift and perhaps not be expected to alter, too seriously, the peptide.

The HDO peak did indeed move as expected, revealing the α-CH= peaks. In addition, however, we noted some revealing changes in (primarily) the methylene region of the gelatin spectrum. Brief contemplation of possible interacting side chains suggested the carboxyl-bearing aspartic acid and glutamic acid segments as the most likely candidates. We had previously studied Co(II)-aspartic acid solutions and knew that complexes formed in water, yielding resonances for the ligand protons which were shifted thousands of Hz. to low field.

We have "measured" the <u>difference spectrum</u> which is shown in the accompanying figure. The comparison with aspartyl (β-CH_2=) and glutamyl (β+γ-CH_2=) resonance components (obtained from the respective homo-polypeptide solutions and normalized to the proper area for gelatin composition) is very gratifying. It is evidence that, assuming such complex formation <u>does</u> occur, we have made a good estimate of the aspartyl and glutamyl contributions to the spectrum or, conversely, if our knowledge of the gelatin spectrum is accurate,

Dr. Shapiro   -2-   5/13/68

that complex formation of Co(II) with the free carboxyl side
chains does occur. Previous work on gelatin-transition metal-
ion interaction[1] considered only somewhat generalized com-
plexing by the peptide backbone.

1. Bello, Biochemistry $\underline{2}$, 276(1963).

                              Sincerely,

                              Philip I. Rose
PIR/ES   Research Laboratories
Encl.

100 MHz.
----- 10% bone gelatin in D_2O
——— with 0.1 $\underline{M}$ Co^{++}
•—•—• difference spectrum
///// expected contribution of asp.+glu.
in absence of $Co(II)$ complex

$H_0 \rightarrow$ (ppm) with respect to HDO at 45 °C

17-29
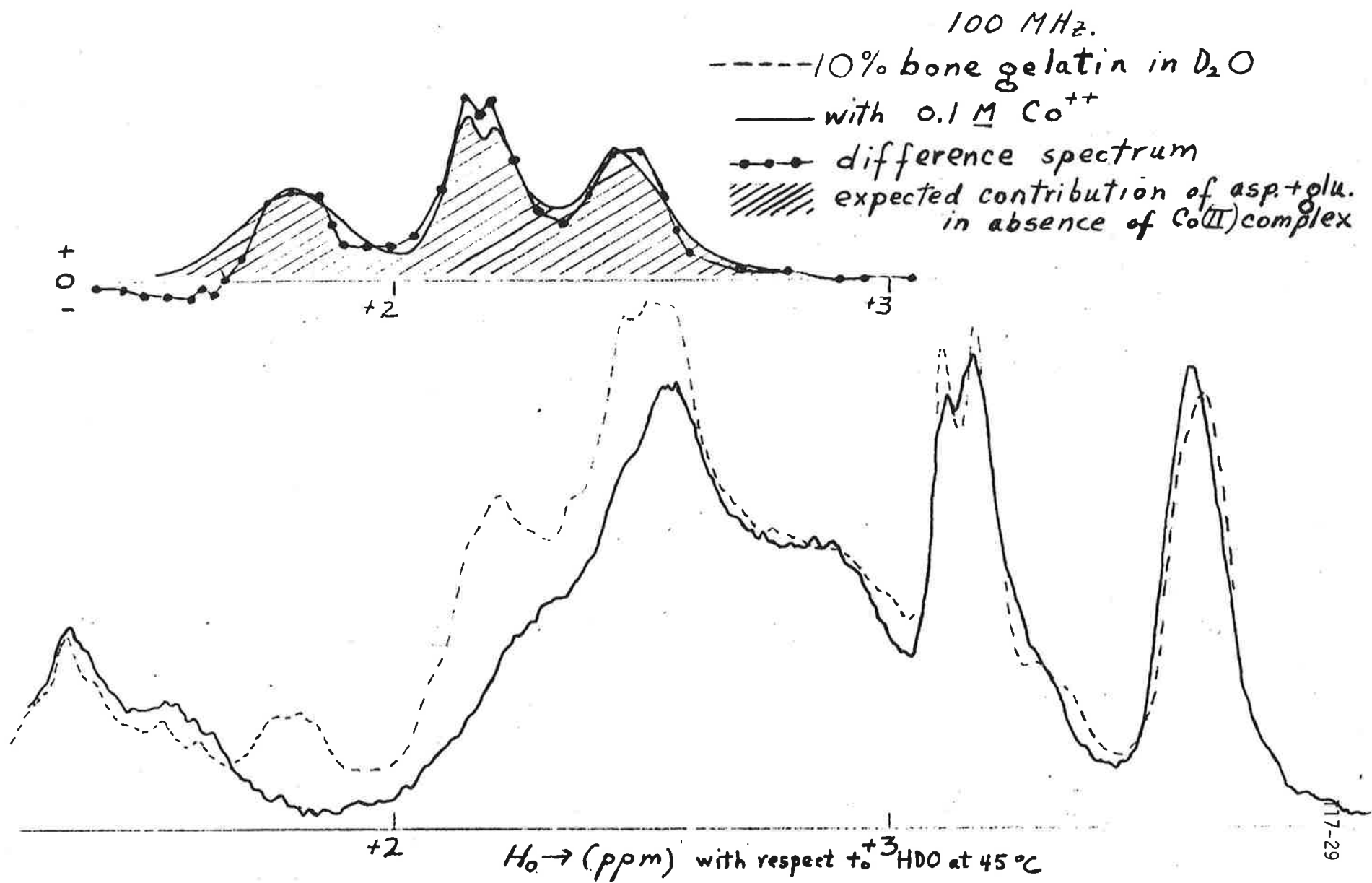
COMUNITA EUROPEA
DELL'ENERGIA ATOMICA
La Commissione
CENTRO COMUNE DI RICERCA

EUROPÄISCHE
ATOMGEMEINSCHAFT
Die Kommission
GEMEINSAMES FORSCHUNGSZENTRUM

Magnetic Resonance

EURATOM
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DE L'ENERGIE ATOMIQUE
La Commission
CENTRE COMMUN DE RECHERCHE

EUROPESE GEMEENSCHAP
VOOR ATOOMENERGIE
De Commissie
GEMEENSCHAPPELIJK CENTRUM
VOOR ONDERZOEK

Ispra, May 13th, 1968

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

Oriented Allene

Dear Barry:

    I realize that it is very late again but it seems
that your date line has changed too, since you moved
to California.

The spectrum of allene taken in a eutectic mixture of
nematic phases at $34^\circ C$ consists of twelve symmetrically
arranged lines. It can easily be analysed by assuming
a hamiltonian which commutes with D_{2d}. This proofs that
the two methylene groups are perpendicular to one another
with the protons occupying the corners of a square when
projected into a plane perpendicular to the C=C bonds.
Two lines are split into doublets due to the scaler
interaction of the protons across the molecule. The
spectrum has been computer simulated using the infrared
data of Maki and the motional constant : $c_{3z^2-r^2}= 0.22768$.
With a pseudo dipolar coupling of -11.8 Hz for the
interaction between the CH_2-groups we get the following
dipolar coupling: 941.9 Hz within and -164.1 Hz between
the methylene groups. The figure shows the result of a
sign variation for J. The proper fit is obtained assuming
J and D both negative. The ratio of the interproton
distances is 0.4778 as compared to 0.4719 from IR
measurements. The corresponding values for the CH angel

- 2 -

are 120.4° and 118.2°.

Yours sincerely,

H. Spiesecke
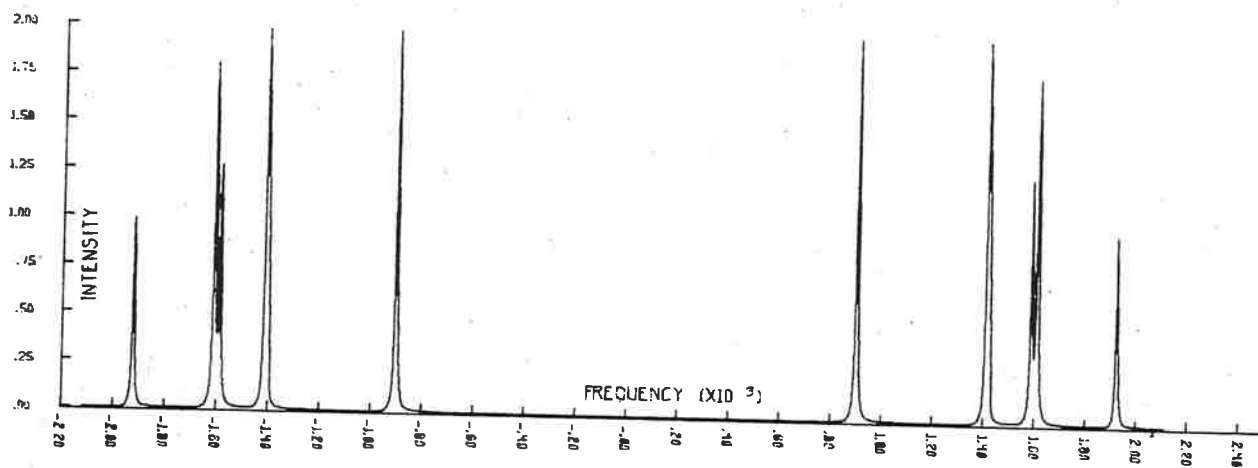
ALLENE NO 1   J POSITIVE

ALLENE NO 1   J NEGATIVE

CZECHOSLOVAK ACADEMY OF SCIENCE
INSTITUTE OF ORGANIC CHEMISTRY AND BIOCHEMISTRY,

FLEMINGOVO NÁM. 2
PRAHA 6

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

Prague, May 15th, 1968

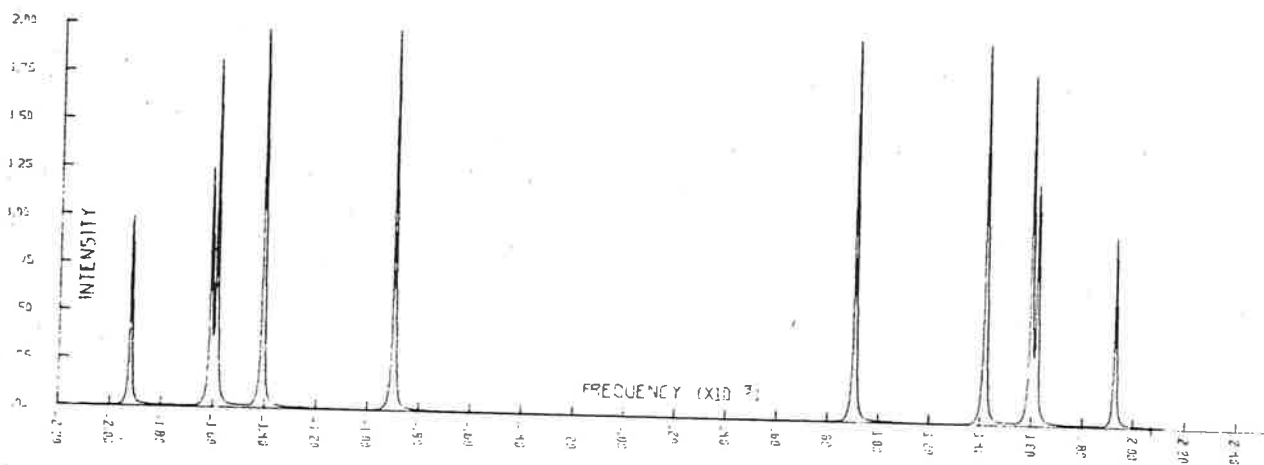**Long-range couplings in some guaianolide derivatives containing cyclopentadiene system**

Dear Professor Shapiro,

Thank You very much for the reminder. In this time I am dealing with many various topics in solving of structural problems of natural compounds and I am unable to send you some "NMR-specialities". Because of lack of time I am sending you some data about long-range couplings in two following compounds without further discussion. These data are obtained by first-order analysis of the 100-Mc-spectra with use of frequency-swept decoupling experiments and I think they may be interesting for structural determinations.

$J_{2,15} = J_{3,15} \simeq 0$

$J_{6,15} \cong 1,7 \ Hz$

$J_{3,6} \cong 2,1 \ Hz$
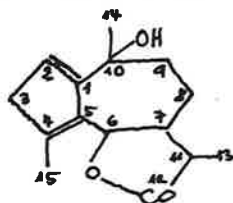
$\tau_3 = 7,17$

$\tau_2 = 3,97$
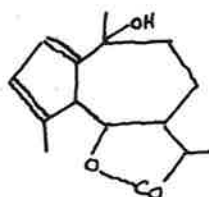
$J_{3,15} \cong 1,35 \ Hz$

$J_{2,5} = J_{3,5} \cong 1,3 Hz$

(all data in $CDCl_3$-solution)
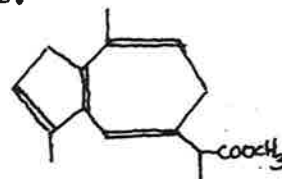
$J_{2,15} \cong 2,0 \ Hz$

$J_{3,15} \cong 1,5 \ Hz$

$J_{2,6} \cong 1,1 \ Hz$

$J_{9,14} \cong 1,5 \ Hz$

$J_{8,14} \cong 0,7 \ Hz$

$J_{6,11} \cong 0,6 \ Hz$

$\tau_2 = 6,89 \quad \tau_3 = 4,02$

$\tau_6 = 3,78 \quad \tau_9 = 5,01$

Yours sincerely

Ž.Šámek

Help!! I need for some special measurements a small ammount of 2-fluoro-4,5-dichlorophenol. I will be very greatefull for any ammount. Thanks!

St 214 632 65

UNIVERSITY OF SOUTH FLORIDA

TAMPA, FLORIDA 33620

AREA CODE 813: 988-4131

DEPARTMENT OF CHEMISTRY

May 15, 1968

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

Re: Structure of $Al(BH_4)_3-6NH_3$

Dear Barry:

We were very interested in Paul Lauterbur's recent report in Inorganic Chemistry[1] on the trimethylamine adduct of $Al(BH_4)_3$. Cal Maybury here has long been interested in aluminum borohydride and its derivatives and we are now in the midst of a study of the ammoniates of this compound as well as the ammoniates of several of the boron hydrides.

Unlike the amines, which generally appear to form simple adducts or symmetic cleavage of boron hydrides to form amine-boranes, the action of NH_3 generally results in an unsymmetrical cleavage. In the particular care of $Al(BH_4)_3-6NH_3$, which we have been studying for some time, the ^{11}B resonance shows a low-field triplet and a higher-field quintet in almost exactly the same positions as observed for the diammoniate of diborane[2] except that the area of the triplet is only half that of the quintet in this case. This is strong evidence for a structure like $AlH_2(NH_3)_4^+, 2BH_4^-$ for the ammoniate and this seems to be borne out by the chemical evidence and proton spectrum in which the bond ammonias and the BH_4^- quartet are nicely apparent. We are investigating a number of related compounds with ammonia and primary amines and will report shortly on the systematics of these systems.

Plan to be in Palo Alto this summer with the AC_3 and hope to see you.

Sincerely yours,

Jeff C. Davis, Jr.
Associate Professor

JCD*aw

[1] Inorg. Chem. **7**, 1025 (1968)
[2] J. Chem. Phys., **32**, 952 (1960)

National Chemical Research Laboratory

of the South African Council for Scientific & Industrial Research

NCRL

OF THE CSIR

Telegrams NAVORSCHEM
Telephone 74-6011

cc/31/N M R.

| Our file | Our letter | Your file | Your letter | **P.O. Box 395, Pretoria** |

<u>AIR MAIL</u>

15. MAY 1968

Prof. B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
<u>CHICAGO</u>, Illinois 60616,
<u>U.S.A.</u>

Dear Prof. Shapiro,

<u>NMR Spectra of Oxazoline Derivatives</u>

We have recently recorded and analysed the NMR spectra of the oxazoline derivatives I-III.

	R =
I	methyl
II	phenyl
III	o-nitro-phenyl
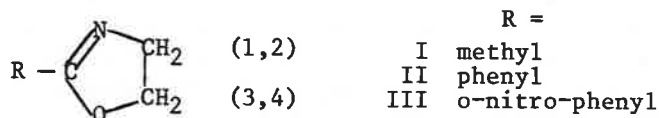
60 MHz spectra were of the deceptively simple A_2B_2 type but at 100 MHz we were able to resolve lines 10 and 11* and to detect the two low-intensity lines 9 and 12. The spectrum of the methyl derivatives illustrates these points. The high field portion is complicated by a homo-allylic coupling of 1.4 Hz between the methyl and the N-methylene groups via the C=N double bond. We could not determine the geminal couplings as it was impossible to identify transitions 5 and 8 unambiguously. The results are summarised in the following table.

	I	II	III
$\tau_{1,2}$	6.205	5.957	5.947
$\tau_{3,4}$	5.788	5.601	5.590
$\Delta\nu$	41.7	35.6	35.7
$^3J_{13}$	10.37	10.40	10.14
$^3J_{14}$	8.54	8.62	9.04
$\left\vert ^2J_{12}\right\vert - \left\vert ^2J_{34}\right\vert$	5.62	6.70	6.44

Both vicinal couplings are relatively large but similar values have already been reported for other five-membered rings. From literature values one would expect geminal couplings of 15-17 Hz (J_{12}) and 8-10 Hz (J_{34}). Thus the difference between the two geminal couplings found (5.6 - 6.7 Hz) is as predicted.
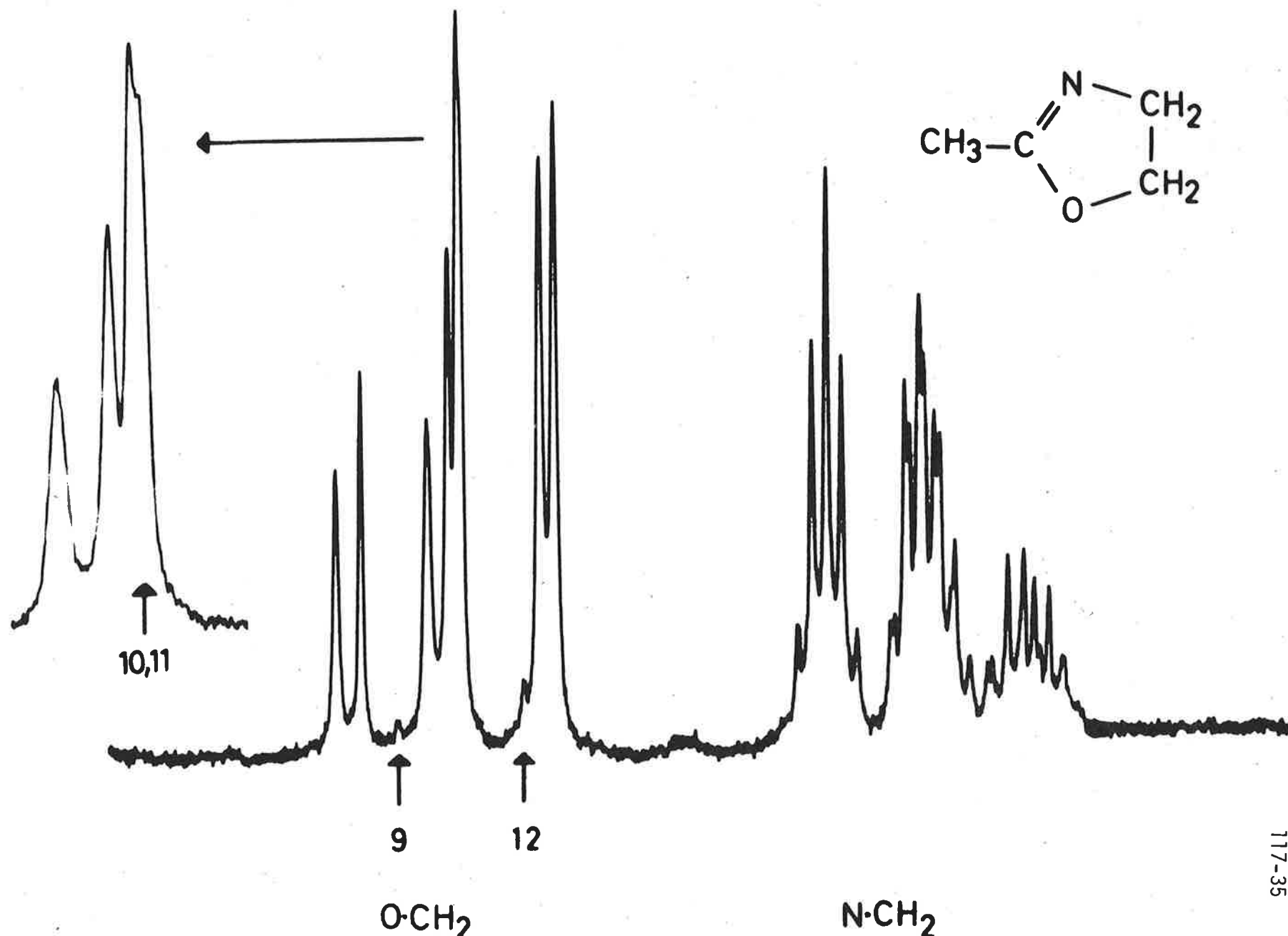
Yours sincerely,

K. Pachler

K. Pachler
SENIOR RESEARCH OFFICER
CHEMICAL PHYSICS GROUP
NATIONAL CHEMICAL RESEARCH LABORATORY

---

*The numbering is as in Pople, Schneider, Bernstein: High-resolution Nuclear Magnetic Resonance, McGraw-Hill (1959), p. 144.

KGRP/SC

10,11

9

12

$O \cdot CH_2$

$N \cdot CH_2$

$CH_3 - C \overset{N - CH_2}{\underset{O - CH_2}{\diagdown}}$

117-35

ORGANISCH-CHEMISCHES
INSTITUT
DER UNIVERSITÄT ZÜRICH

8001 Zürich, Rämistrasse 76
Telefon 34 24 50

Direktion: Prof. Dr. H. Schmid

May 20, 1968

Prof. B.L. Shapiro
Department of Chemistry
Stanford University
Stanford, California

" Hindered Internal Rotation in Mono- and Di-protonated Pterines "

Dear Barry:

In the course of our proton NMR studies on pteridines we have
found that FSO_3H is an excellent solvent for this class of comp-
ounds and far superior to CF_3COOH. However double protonation
must be taken into account. 2-Amino-4-oxo-3,4-dihydropteridine (I)
("pterine") forms the following cations:
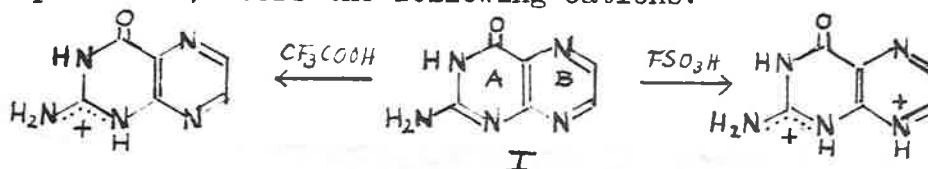
It is interesting to measure the barrier to internal rotation
around the $C(2)-NH_2$ bond and to see how such values depend on
the additional protonation in ring B. Here are some of our res-
ults obtained at 100 MHz from the NH_2- and $N(CH_3)_2$ signals resp-
ectively. E_a has been calculated from an analysis using several
line shape parameters.

	solv.	conc.	T_c (°C)	E_a (±2 kcal/mole)
I	CF_3COOH	0.3 m	28	12
		0.1	40	11
II	CF_3COOH	0.2	55	10
III	CF_3COOH	0.1	55	16
	FSO_3H	0.1	125	20

Whereas the amidinium group in I and II has values for E_a of
10-12 kcal/mole, the dimethylamino compound III shows an exp-
ected increase to 16 kcal/mole. Additional protonation of III
at N(8) in ring B again increases the barrier to 20 kcal/mole.
This seems to indicate a charge effect which results from a
Coulomb repulsion and causes a shifting of the positive charge
of the amidinium system on to the exocyclic nitrogen atom.
Hereby the π-bond order of the $C(2) \rightleftharpoons N(CH_3)_2$ bond is increased
which is directly reflected in the barrier to internal rotation.
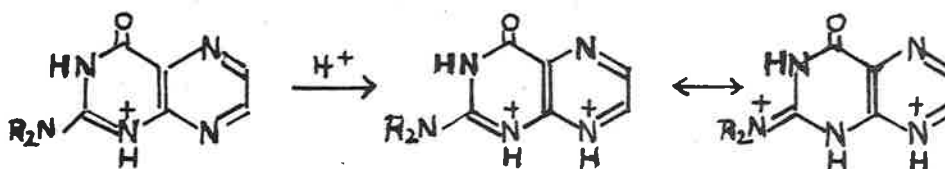
Other studies on pteridines in our laboratory include correl-
ations of basic pk_a-values and π-electron densities with
methyl proton chemical shifts in mono-methyl-substituted pter-
idines. A paper is prepared for Helv. Chim. Acta.

Best wishes,

Prof.W.v.Philipsborn

Dr.A.Dieffenbacher

Dr.D.Wendisch in Firma

FARBENFABRIKEN BAYER AG

Ing.-Abt. Angewandte Physik 10

Postanschrift: Bayer · 509 Leverkusen

		TELEGRAMME	Farbfabrik Leverkusen		

Professor Dr.B.L.Shapiro,

Department of Chemistry,

Stanford University,

Stanford, California 94305

U.S.A.

Ihre Zeichen	Ihre Nachricht	Unsere Zeichen	Telefon-Durchwahl	LEVERKUSEN-Bayerwerk
		Wec/Ko	Lev. 30 ...7458	den 20.5.1968

Sehr geehrter Herr Professor Shapiro!

Vielen Dank für die Mahnung, wieder einen Beitrag für die IIT-NMR-Newsletters zu liefern. In Zusammenhang mit Strukturaufklärungen an verschiedenen Produkten, die durch photosensibilisierte C_4-Cycloadditionen von Chlorolefinen an Indene erhalten wurden (s.W.Metzner, Tetrahedron Letters 1968, 1321; W.Metzner u. K.Morgenstern, Ang.Chem. 80, 366 [1968] ; W.Metzner u. W.Hartmann, Chem.Ber. 101, im Druck), untersuchten wir die NMR-Spektren von einer größeren Anzahl von 2.3-Benzo-bicyclo [3.2.0] -hepten-(2)- und -heptadien- (2.6)-Derivaten. Wir analysierten die Spektralbilder der alicyclischen Protonen bei 100 MHz unter Benutzung des Computerrechenprogramms LAOCOON II und konnten so die entsprechenden Strukturen der Isomeren aufklären. In einzelnen Fällen konnten die Strukturen direkt aus den 220 MHz-Spektren geschlossen werden. Die gesamten Ergebnisse werden in Kürze publiziert (D.Wendisch und W.Metzner, Chem.Ber. in Vorbereitung). Als Beitrag möchte ich hier einige durch Computerrechnung erhaltene Werte für Kopplungskonstanten in Inden-Chlorolefin-Cycloaddukten mitteilen (s.S. 2 und 3).

Titel: Kopplungskonstanten von Protonen des alicyclischen Vierringes in einigen Bicyclo [3.2.0] -hepten-(2)-und-heptadien-(2.6)-Derivaten.

Mit freundlichem Gruß

(Dr.D.Wendisch)

FARBENFABRIKEN BAYER AG

- 2 -
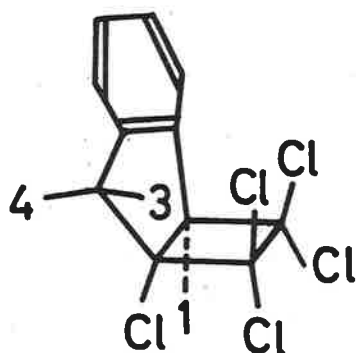
$J_{12} = 8,32 \pm 0,08$ Hz

$J_{23} = 1,37 \pm 0,06$ Hz

$J_{24} = 8,86 \pm 0,08$ Hz
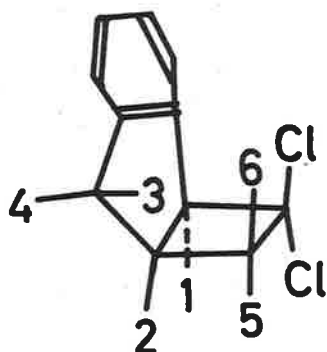
$J_{12} = 7,96 \pm 0,24$ Hz

J_{23} = Wert innerh.d.Fehler-
grenze

$J_{24} = 9,09 \pm 0,27$ Hz

$J_{25} = 8,14 \pm 0,30$ Hz

$J_{26} = 7,24 \pm 0,27$ Hz

$J_{56} = (-)14,63 \pm 0,26$ Hz
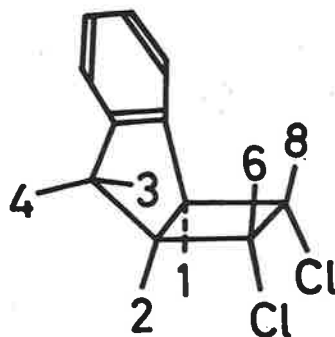
$J_{12} = 7,53 \pm 0,23$ Hz

$J_{18} = 5,12 \pm 0,18$ Hz

$J_{23} = 2,55 \pm 0,17$ Hz

$J_{24} = 12,30 \pm 0,26$ Hz

$J_{26} = 6,41 \pm 0,25$ Hz

$J_{68} = 7,27 \pm 0,22$ Hz
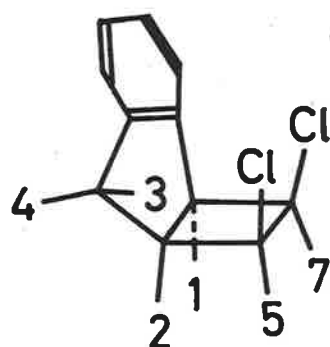
$J_{12} = 6,67 \pm 0,13$ Hz

$J_{17} = 7,38 \pm 0,14$ Hz

$J_{23} = 0,99 \pm 0,12$ Hz

$J_{24} = 9,05 \pm 0,14$ Hz

$J_{25} = 7,29 \pm 0,15$ Hz

$J_{57} = 7,46 \pm 0,13$ Hz

13894/7

FARBENFABRIKEN BAYER AG

- 3 -
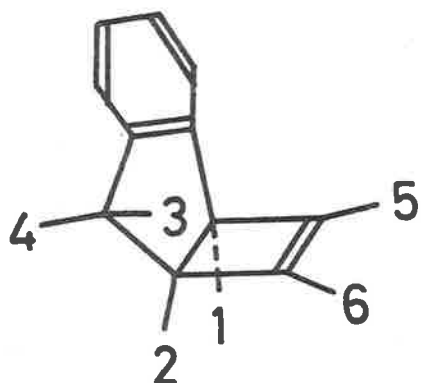
$J_{12} = 3{,}70 \pm 0{,}55$ Hz

$J_{23} = 2{,}25 \pm 0{,}41$ Hz

$J_{24} = 4{,}50 \pm 0{,}70$ Hz

$J_{56} = 3{,}49 \pm 0{,}47$ Hz
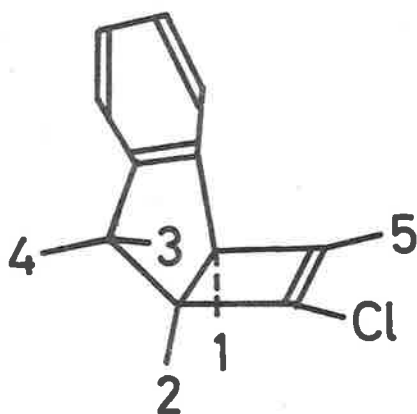
$J_{12} = 3{,}30 \pm 0{,}24$ Hz

$J_{23} = 3{,}11 \pm 0{,}23$ Hz

$J_{24} = 7{,}14 \pm 0{,}24$ Hz
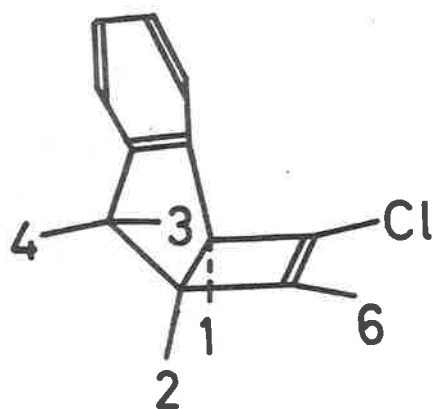
$J_{12} = 3{,}39 \pm 0{,}16$ Hz

$J_{23} = 1{,}79 \pm 0{,}24$ Hz

$J_{24} = 8{,}73 \pm 0{,}22$ Hz

NORTH CAROLINA STATE UNIVERSITY | AT RALEIGH

SCHOOL OF PHYSICAL SCIENCES AND APPLIED MATHEMATICS

DEPARTMENT OF CHEMISTRY
BOX 5247   ZIP 27607

May 21, 1968

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

T-60 For Routine NMR

Dear Barry,

We have just added to our nmr facilities (HA-100 and DP-60) by the purchase of a Varian T-60 spectrometer and thought other readers might be interested in our experience (The instrument has been in operation for over three months here at State).

First of all, the permanent magnet has removed just about all of the routine maintenance worries. Our biggest headaches are now the pen and keeping sufficient paper on hand. The instrument has been ON in an air conditioned instrument room apart from our other spectrometers and has required a minimum of attention. One breakdown (the only one) was caused by an electrical short in the probe connector and was quickly remedied by Varian engineers.
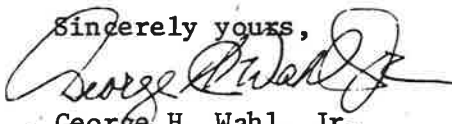
Secondly, everyone, undergraduates, graduate students, and faculty have been using it night and day, unsupervised and with little instruction. The spin decoupler (Frequency Sweep) is the easiest possible. The integrator when carefully used, is unsurpassed.

Thirdly, we are cautioning people about quoting precise chemical shifts since the error involved is as yet unclear. Drift is sometimes a problem, 2-3 Hz within the time required to complete a spectrum. However, at other times reproducibility is well within specs ($\pm$1 Hz per spectrum).

The requirement of storing samples in a heated chamber (35°C) in the instrument for a few minutes prior to running a spectrum has been used to advantage. Specifically, we have stored samples in this chamber (at the same temperature as the probe) and periodically run the spectrum. In this way, we were able to obtain some rough kinetic data without completely tying up the instrument.

Please credit this to the "account" of Dr. Charles G. Moreland.

Sincerely yours,

George H. Wahl, Jr.
Assistant Professor

GHW/jd

DEPARTMENT OF THE AIR FORCE

AIR FORCE MATERIALS LABORATORY (AFSC)

WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

REPLY TO
ATTN OF: MAYH/Roger E. Rondeau/255-2280

2 1 MAY 1968

SUBJECT: NMR Analysis of 1-Methylbenzotriazole

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

Dear Dr. Shapiro:

1. In a recent attempt toward analyzing the ABCD spectrum of the title compound, we invoked simple Hückel Molecular Orbital computations in the hope of gaining information regarding the ordering of the chemical shifts of the four aromatic protons. This was done to expedite a judicious selection of "ball park" parameters for line fitting purposes.

2. We were aware of previous fruitless attempts at correlating electron densities with chemical shifts in some nitrogen heterocyclics (A. H. Gawer and B. P. Dailey, J. Chem. Phys., <u>42</u>, 2658, 1965). Nevertheless, we hoped to obtain at least some qualitative guidelines from the HMO computations of this particular compound.

3. From the MO results shown here
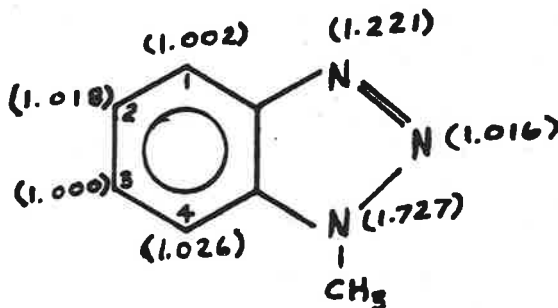
where the parenthetic numbers are the electron densities (based on 1.00 for benzene) one would be tempted to predict the following relative positions: $\nu_1 \simeq \nu_3 > \nu_2 > \nu_4$, with proton 4 being at highest field.

4. However, this is not so. Here are the refined parameters which were eventually extracted via LAOCOON III (with no help from HMO):

$$J_{1,2} = \pm\ 8.338\ \pm\ .076$$

$$\nu_1 = 475.811\ \pm\ .026 \qquad J_{1,3} = \pm\ 1.021\ \pm\ .085$$

$$\nu_2 = 434.789\ \pm\ .047 \qquad J_{1,4} = \pm\ 0.633\ \pm\ .085$$

$$\nu_3 = 439.435\ \pm\ .060 \qquad J_{2,3} = \pm\ 6.965\ \pm\ .051$$

$$\nu_4 = 442.315\ \pm\ .068 \qquad J_{2,4} = \pm\ 0.852\ \pm\ .054$$

$$J_{3,4} = \pm\ 8.358\ \pm\ .045$$

5. The above data were obtained from lines from six spectra (3 up, 3 down). Twenty-seven observable lines were matched with an rms error of 0.087.

Sincerely,

Roger E. Rondeau

ROGER E. RONDEAU
Exploratory Studies Branch
Materials Physics Division
AF Materials Laboratory

AMERICAN MEDICAL ASSOCIATION/EDUCATION AND RESEARCH FOUNDATION/535 N. DEARBORN ST./CHICAGO, ILL. 60610

INSTITUTE FOR BIOMEDICAL RESEARCH

DAN W. URRY, PH.D
ASSOCIATE MEMBER

May 22, 1968

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

Dear Barry:

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

> Position availably for research assistant to work on Varian
> HR220 superconducting NMR spectrometer. Duties include sample
> preparation, recording of spectra, and general care and main-
> tainance of the NMR system. Studies will be directed toward
> those molecular systems of biological interest. Familiarity
> with NMR spectroscopy and bachelor's degree desired. Write
> Dan W. Urry, Institute for Biomedical Research, 535 North
> Dearborn, Chicago, Illinois 60610 or phone (312) 527-1500 Ext.
> 509.

With best regards,

Dan W. Urry, Ph.D.

DWU:lz

JOURNAL OF MAGNETIC RESONANCE

May 24, 1968

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

NEW JOURNAL

Dear Barry:

Your readers may be interested in the appearance of a new bimonthly publication, the Journal of Magnetic Resonance, the first issue of which is scheduled for January, 1969. The Journal will include papers dealing with nuclear resonance, electron resonance, and related fields. They will be varied in content, covering a range from theory, through apparatus and methods, to correlations of results.

The response of individuals in the NMR and EMR communities to invitations to serve on the Editorial Board has been quite gratifying, and we have succeeded in gathering as members quite an eminent group of scientists from several countries. The first few issues will consist principally of invited papers, but we will consider submitted manuscripts at any time. Of course, authors must realize that a paper received now will not appear until the first part of 1969, although our aim is to achieve a publication time of three to four months after operation is under way.

I should be pleased to send copies of the directions for authors as well as information about the scope of the Journal to anyone who will write to me for them. Subscription information should be obtained from the publishers, Academic Press. Present plans are for a rate of $25 per annual volume, with a "personal-use" rate of $15.

Cordially yours,

Wallace

Wallace S. Brey
Editor

Dr.Heinz Dürr

Institut für organische Chemie

der Universität des Saarlandes

Germany

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

Ringinversionen von substituierten Benzo-cycloheptatrienen

Sehr geehrter Dr.Shapiro,

Kürzlich fanden wir eine einfache Synthese von substituier-
ten Benzo-cycloheptatrienen(1). Dies veranlasste uns,die Tempe-
raturabhängigkeit der noch wenig untersuchten NMR-Spektren von
Benzo-cycloheptatrienen zu studieren. Deshalb wählten wir die
7H-Benzo-cycloheptatriene 1,2 und 3, die in der Reihe 1, 2 und 3
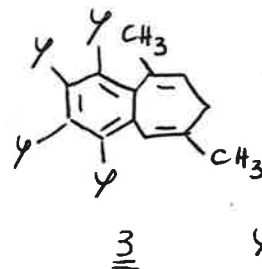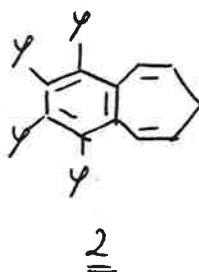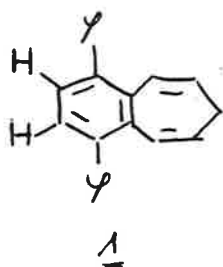
zunehmend substituiert sind und die daher einen Aufschluss über
den Effekt steigender Substitution auf die Energiebarriere
zwischen den beiden Konformeren A und B der 7H-Benzo-cyclohepta-
triene geben sollten. Zur Untersuchung der Ringinversion wur-
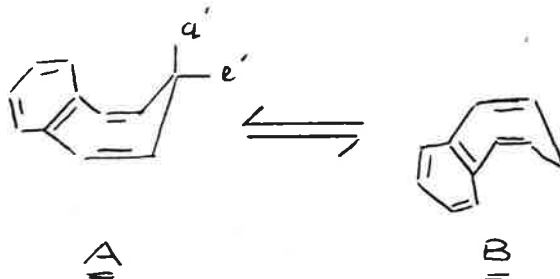
Dürr   — 2 —

de die Temperaturabhängigkeit des Methylen-Signals von $\underline{1}$, $\underline{2}$
und $\underline{3}$ gewählt. Dieses Methylen-Triplett spaltet bei Cyclohep-
tatrien bei -143° (Koaleszenztemperatur T_c)(2) in zwei getrennte
Signale auf, während bei Dibenzo-Verbindungen T_c bei mittleren
Temperaturen liegt(3).
        Die NMR-Spektren bei 37° weisen folgende Signale auf:
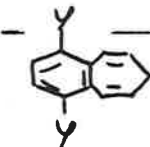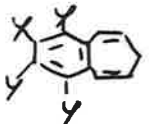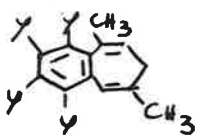
$\underline{1}$: (CS_2:$CFCl_3$ = 1:1)
τ(ppm)   : 2.61   2.73   3.62   4.17   7.54
Multiplizität; J(Hz):   s   s   d;(10) dopp.t t(7)
                                                  (10;7)

$\underline{2}$: (CS_2:$CDCl_3$:$CFCl_3$ = 1:1:1)
τ(ppm)   : 2.87   3.17   4.20   3.67   7.54
Multipl.;J(Hz):   s   s   dopp.t d(10)   t(6.5)
                                    (10;6.5)

$\underline{3}$: (CS_2)
τ(ppm)   : 2.89   3.20   4.01   4.16   7.62   8.06   8.76
Mult.; J(Hz):   s   s   q(1.5) t,q   d(7.5) d(1.5) s
                                      (7.5;1.5)

Die Tieftemperaturspektren wurden in einem Varian A 60 Spek-
trometer gemessen(Tieftemperaturzusätzgerät: V 6057 mit zwei
Kühlwendeln), wobei Temperaturen bis -106° erreichbar waren.
Die Substanzen $\underline{1}$-$\underline{3}$ waren auch bei diesen Temperaturen noch
vollkommen gelöst. Untersucht wurde im einzelnen die Veränderung
des Methylen-Tripletts von $\underline{1}$ und $\underline{2}$, sowie die des -Dubletts in
$\underline{3}$. Der Versuch, das Signal der Methylengruppe von $\underline{3}$ durch Spin-
Entkopplung in ein Singulett umzuwandeln und dadurch die Ana-
lyse zu vereinfachen, misslang.

Tab.1

Verbindung	$\tilde{\tau}_{CH_2}$ (ppm)	Verschwinden d. Multiplettstrukt. bei °C	T_c(°C)	k_c (sec^{-1})	$\Delta G^{\neq}$ (kcal/Mol)
	7.53	- 84	$<$ -102	$\sim$ 89	$<$ 8,2
	7.54	- 70	$\cong$ -106	$\sim$ 89	$\cong$ 8,0
	8.06	- 66	$<$ -96	$\sim$ 89	$<$ 8,5

Dürr   — 3 —

Der Koaleszenzpunkt wurde für die CH_2-Gruppe bei 1 und 3

nicht erreicht; die beginnende Verbreiterung unter Verlust der
Multiplettstruktur ist in Tab. 1 angegeben. Lediglich für 2

konnte die beginnende Aufspaltung T_c annähernd bestimmt wer-
den. Aus diesem Grunde konnten auch keine exakten Δv- und
J_{AB}-Werte(3) für die quasi-axialen(a') und die quasi-äquato-
rialen(e') CH_2-Protonen bestimmt werden. Deshalb wurde nach
der von Anet(2) angewandten Näherung:

$$k_c = \frac{\pi}{\sqrt{2}}\Delta v \quad (sec^{-1}),$$

die streng nur für AX-Systeme
gilt, verfahren. Als Δv wurde
aus analogen Verbindungen ein
Mittelwert zwischen Δv-Cycloheptatrien = 80 Hz(2) und Δv-1-
Methoxy-2.3.4-triphenyl-6.7-benzo-cycloheptatrien(4,5) = 14
Hz von $\Delta v \cong 40$ Hz angenommen und damit wurden die in Tab. 1
angegebenen k_c- und $\Delta G^{\neq}$-Werte berechnet(3).

Die erhaltenen Näherungswerte, zeigen (der $\Delta G^{\neq}$-Wert von 8 kcal/
Mol zusammen mit den sehr tief liegenden T_c-Werten) dass in den

7H-Benzo-cycloheptatrienen 1-3 die Ringinversion durch die

Substitution des Benzolrings nicht wesentlich erschwert wird.
Aus den T_c-Werten von 1,2 und 3 kann man jedoch entnehmen,

dass mit steigender Phenylsubstitution ein schwächer negatives
T_c auftritt, d.h. die Ringinversion wird durch die Phenyl-

kerne im Benzolring geringfügig behindert. Der Einfluss ist
aber wesentlich geringer als bei direkter Phenylsubstitution
des Cycloheptatrienringes(3).

                                mit freundlichen Grüssen

                                (H.Dürr)

1) H.Dürr und G.Scheppers, Angew.Chem. im Druck.
2) F.A.Anet, J.Amer.chem.Soc. 86, 458 (1964) und F.R.Jensen und
    L.A.Smith, ibid. 86, 956 (1964).
3) Eine sehr gute Literaturübersicht geben: W.Tochtermann,
    G.Schnabel und A.Mannschreck, Liebigs Ann.Chem. 705, 169 (1967).
4) W.Tochtermann, G.Schnabel und A.Mannschreck, Z.Naturforsch.
    21 b, 897, (1966).
5) H.Dürr, Z.Naturforsch. 22 b, 786 (1967), ergibt ebenfalls
    $\Delta v_{CH_2} \cong 40$ Hz.

MERCK SHARP & DOHME

RESEARCH LABORATORIES

May 25, 1968

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

Re: Imidazole-Phosphate Interaction

Dear Barry:

Dee Meadows in this laboratory has recently observed that only one of the
four C-2 histidine (His) peaks of RNase is shifted downfield (ca. 30 cps) in
the presence of saturation levels of 3'-CMP at acid pH.[1,2] The peak which
shifts has been assigned to His-119.[3] Shifts of this magnitude and direction
are usually associated with H-bond formation. In water hydrophobic (stacking)
interactions (upfield shifts) are commonly observed between purines and
pyrimidines,[4,5] although selective Watson-Crick H-bonding has been reported
in DMSO.[6,7] In order to test my conjecture that the downfield shift of the
C-2 peak of His-119 beyond its normal maximum downfield shift when fully
protonated was due to H-bond formation with the nucleotide phosphate moiety,
imidazole (Im) was titrated with H_3PO_4 in DMSO.

The accompanying curve shows the results obtained. The C-2 Im proton absorbs
to higher field in DMSO than in D_2O due to greater bulk diomagnetic shielding.
$CHCl_3$ in solutions at the extremes of the range used (zero and 20 M ratio
H_3PO_4) retained the same chemical shift (852 cps) indicating no bulk suscepti-
bility change. The residual DMSO methyl peak shifted 7 cps downfield indi-
cating solvent H-bond formation with phosphate. The overall chemical shift
difference for the C-2 proton in DMSO was 138 cps, 46 cps greater than the
difference in D_2O. 94 cps is a normal value for the acid titration of the
Im group in His.[8,9] In water the shift results from intramolecular deshielding
due to aromatization of the ring on protonation, and should be independent
of solvent. Thus Im and phosphate associate in DMSO, and the Im of His-119
may perform a similar function in the nucleotide binding site of RNase.

Dr. Bernard L. Shapiro
Stanford University
May 25, 1968

These studies are being extended to other solvents and amino acid derivatives since it appears that certain non-aqueous solvents may be model environments for the binding sites (clefts) of enzymes.[10]

Sincerely yours,

Jack Cohen

Jack S. Cohen

JSC:ras
Att.

References:
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3. D. Meadows, O. Jardetzky, R. Epand, M. Ruterjans and H. Scheraga, P.N.A.S., in press.
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7. R.R. Shoup, H.T. Miles and E.D. Becker, Biochem. Biophys,Res. Comm. 23, 194, 1966.
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9. D. Meadows, J. Markley, J. Cohen and O. Jardetzky, P.N.A.S. 58, 1307, 1967.
10. D.C. Phillips, P.N.A.S. 57, 484, 1967.

TITRATION OF IMIDAZOLE WITH H_3PO_4
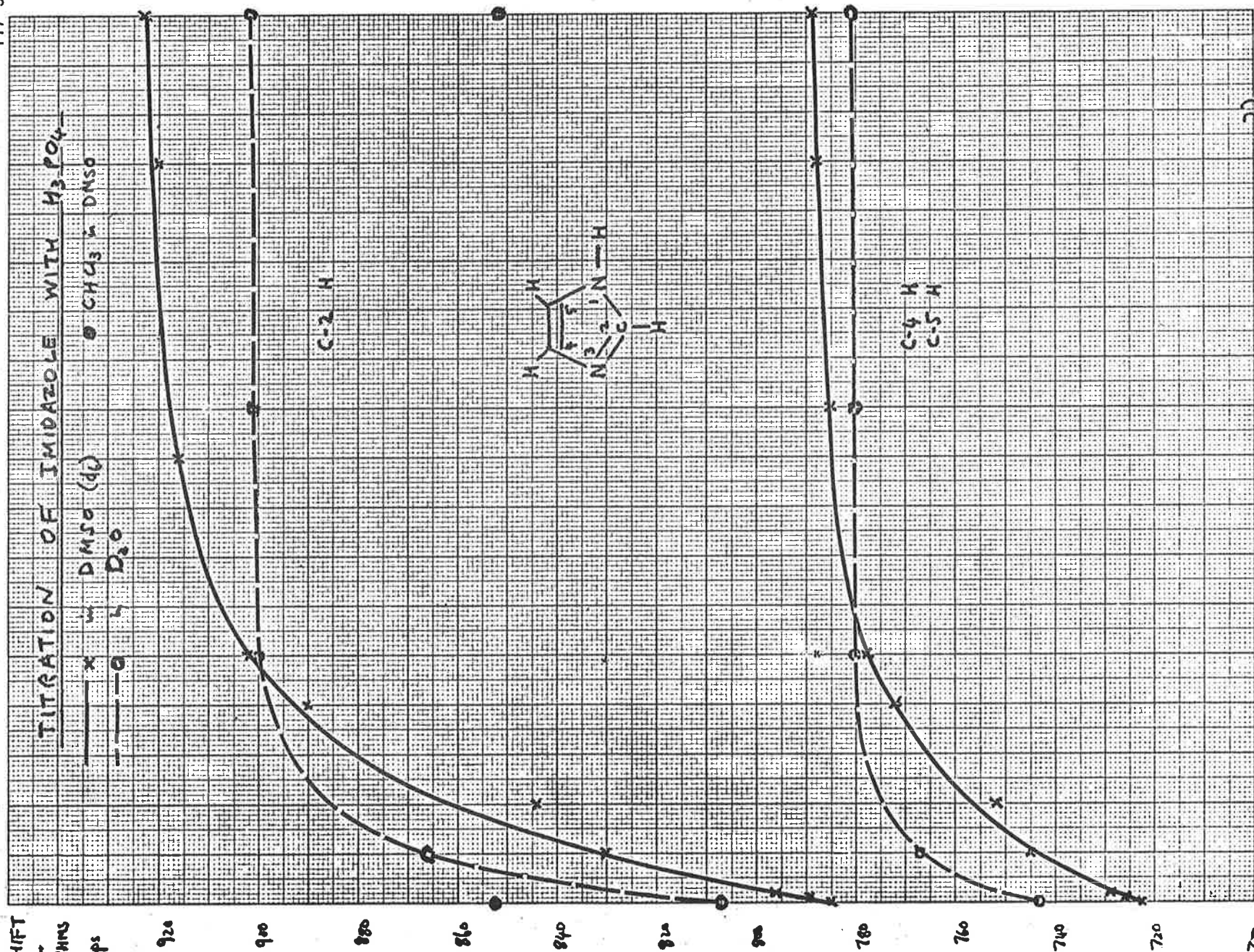
CHEMICAL SHIFT δ_{HMS}

x —— in DMSO (d_6)
o - - - in D_2O
● CH_3 in DMSO

C-2 H
C-4 H
C-5 H

MOLAR RATIO H_3PO_4/Im.

117-51

Dow THE DOW CHEMICAL COMPANY

P. O. BOX: MIDLAND, MICHIGAN 48640

May 8, 1968

Dr. Bernard L. Shapiro
Chemistry Department
Stanford University
Palo Alto, California   94300

RE: Solvent effects on the P^{31} - H^1 spin-spin coupling con-
      stant and chemical shift in dimethylphosphite

Dear Dr. Shapiro:

Please include the following in the IIT NMR newsletter and
credit it to the subscription of Dr. J. P. Heeschen, Chemi-
cal Physics Research Laboratory, 1603 Building, The Dow
Chemical Company, Midland, Michigan, 48640.

In an effort to obtain information on the factors that in-
fluence changes in spin-spin coupling constants and on the
nature of the interaction between phosphites and various
hydrogen donor molecules, a study of the PH coupling con-
stant and chemical shift in dimethylphosphite, $(OCH_3)_2P(O)H$,
in various solvents has been made.

The results of this study are presented in Table I. Both
specific association effects and bulk solvent medium effects
are observed. There is no good correlation between the
coupling constant and dielectric constant as has been ob-
served for geminal HH couplings. The PH coupling constant
is greatest in solvents which can form hydrogen bonds to
the phosphoryl oxygen. The difference between the smallest
and largest observed PH coupling affected by the solvents
studied is 46.6 hz. This is the largest observed difference
in couplings yet reported.

We also wish to note that it appears that the effect of
solvents on the PH coupling in diphenylphosphine also in-
creases in the same manner as observed for dimethylphos-
phite. This may indicate that the signs of the PH coupling
constant are the same in these two molecules.

Dr. Bernard L. Shapiro
May 6, 1968
Page 2

We are currently studying solvent effects in a series of
similar molecules as well as on the effects of metal ion
complexation to dimethylphosphite and tetramethylphos-
phoramide. The results and interpretations will be pre-
sented later.

Sincerely yours,

Robert T. Iwamasa
Chemical Physics Research Laboratory
1603 Building

csk

TABLE I

Solvent	ϵ	$|J_{PH}|$ cps	$-\delta$ cps (rel. int.TMS)
1. Cyclohexane	2.0	687.7	-393.4
2. Toluene	2.4	688.4	-382.1
3. Benzene	2.3	688.5	-383.5
4. Carbondisulfide	2.6	689.5	-394.6
5. Nitrobenzene	32.2	690.8	-410.3
6. d_6-Acetone	19.8	691.2	-401.8
7. Pyridine	12.3	691.2	-409.9
8. Hexamethylphosphor- amide		692.0	-397.7
9. N,N-dimethylacetamide		692.1	-406.2
10. Carbontetrachloride	2.2	693.2	-397.5
11. Acetonitrile	37.0	693.6	-401.5
12. 1,4 dioxane	2.2	693.8	-397.7
13. Methylenechloride	9.1	694.0	-403.0
14. Nitromethane	35.0	695.9	-399.4
15. Acetaldehyde	22	696.0	-401.0
16. Dimethylphosphite(1)		696.6	-404.7
17. d-Chloroform	4.6	697.7	-406.0
18. Cyclohexanol	15.0	701.2	-404.0
19. Benzaldehyde	18.0	701.3	-409.4
20. tert-Butanol		704.0	-404.0
21. $CH_3OCH_2CH_2OH$		707.4	-404.3
22. Ethanol	24.0	708.0	-407.0
23. Methanol	33	709.9	-404.6
24. Water	80	726.3	-416.7
25. Trifluoroacetic acid		734.3	-430.9

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

Dear Prof. Shapiro,

Shielding of Methyl Groups in Alkylbenzenes

We have recently been applying NMR to the quantitative and qualitative
study of mixtures of alkylbenzenes. Amongst many model compounds (supplied
by Dr J.R. Nooi of this laboratory) has been the series of 1- to 6-phenyl-
dodecanes. Measurements were at 100 MHz on 50% solutions in CCl_4. Considera-
tion of the chemical shift of the methyl absorptions relative to the distance
from the phenyl group produced the result shown in the figure.

Number of carbon atoms between methyl
and phenyl groups
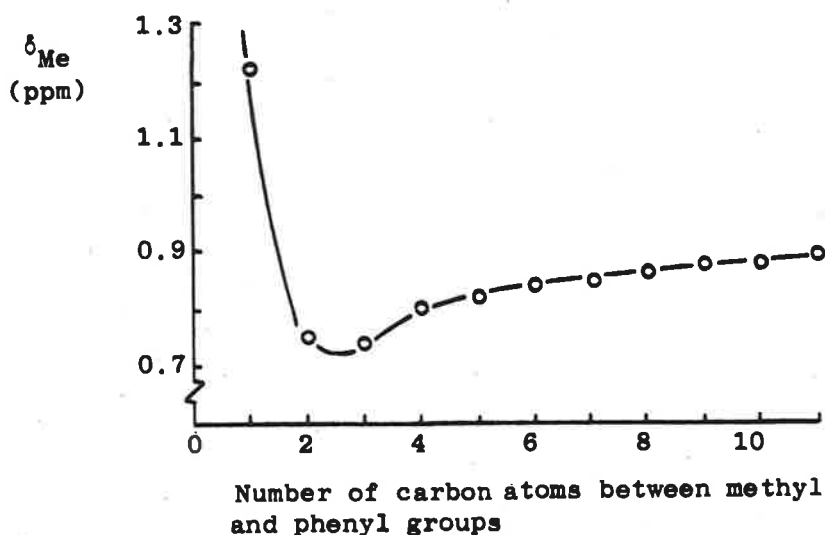
The δ-value for an abscissa of zero would come from toluene, at
~ 2.3 ppm. The minimum can be explained when it is realised that, with
increasing length of the alkyl chain, for propyl (abscissa 2 in the
figure) is it first possible to position the methyl group above the
aromatic ring. Consequently the methyl will spend a part of its time
in this region of shielding resulting from the ring current. With the
longer chain lengths this possibility for the methyls becomes more remote.
The effect is somewhat analogous to the results observed (Waugh and
Fessenden, J. Am. Chem. Soc. 79, 846 (1957)) for the 1,4-polymethylene-
benzenes. It is, however, perhaps surprising that chemical shift differences
were still measured for methyls 10 and 11 carbon atoms distant from the
benzene ring. We are at present studying the quantitative aspects of these
results and those of many other such models.

Yours sincerely,

D.J. Frost

J. Barzilay

Unilever Research Laboratory
Vlaardingen (The Netherlands)

INDIAN INSTITUTE OF TECHNOLOGY KANPUR
KANPUR. U. P, INDIA.

PHYSICS DEPARTMENT
Phys/BDNR/IITK-68/

May 28 1968

Professor B.L. Shapiro
Department of Chemistry
Stanford University
STANFORD, Calif.
U.S.A.

Short title: Effect of inhomogeneity in relaxation
studies by Double Resonance.

Dear Professor Shapiro,

Thank you for the reminder. We have just completed
the analysis of relaxation effects in the steady-state
double resonance spectra of the ring protons in 2,6-dibro-
moaniline(AB_2) in which we have noticed that the effect
of inhomogeneity of the applied magnetic field plays a
rather crucial role. As has been pointed out by Freeman
and Anderson[1] the contribution of inhomogeneity to the
linewidth is different for different transitions in a
double resonance spectrum. This enters the density-matrix
formalism in the following way: The lineshape in this
formalism is a Lorentzian with a full width at half height
given by $R_{\alpha\alpha'\alpha\alpha'}=(1/T_2)_{\alpha\alpha'}$. The peak height, which one
wants to use for comparison with experiment, is proportional
to

$$(I_+)^2_{\alpha\alpha'}[(\tilde{\chi}+\sigma_0)_{\alpha'\alpha'}-(\tilde{\chi}+\sigma_0)_{\alpha\alpha}]/R_{\alpha\alpha'\alpha\alpha'}$$

(for the case of strong irradiation) where $(I_+)_{\alpha\alpha'}$ is the
matrix element of I_+, and $(\tilde{\chi}+\sigma_0)_{\alpha\alpha}$ is the diagonal element
of the stationary part of the spin density matrix in the
rotating frame[2]. The inhomogeneity can now be added to the
problem by the method suggested by Abragam[3]. A detailed
consideration shows that, if the shape of the magnetic
field is also assumed to be Lorentzian with a certain width
ΔH_0, the peak height will be given by

$$\frac{(I_+)^2_{\alpha\alpha}[(\tilde{\chi}+\sigma_0)_{\alpha'\alpha'}-(\tilde{\chi}+\sigma_0)_{\alpha\alpha}]}{R_{\alpha\alpha'\alpha\alpha'}+(\Delta\omega)_{\alpha\alpha'}(\text{Inhomogeneity})+(\Delta\omega)_{\alpha\alpha'}(\text{other causes})}$$

where the denominator now includes all sources of linewidth including relaxation, inhomogeneity, instability etc. The first term has to be calculated on the basis of a chosen relaxation mechanism. The inhomogeneity contribution can be computed from a plot of the frequency $\omega_{\alpha\alpha'}$ Vs. the "frequency-offset" of irradiation[1]. The last term is a small constant factor which may be assumed to be the same for all transitions. The denominator in the above expression is just the observed linewidth[1]. The theoretical relative intensities should therefore, be calculated by dividing the numerator, computed for a particular relaxation process, by the observed linewidth rather than by $R_{\alpha\alpha',\alpha\alpha'}$. A comparison with the experiment would then lead to more accurate conclusions. Further details of this work are being written up and would be available pretty soon.

Yours sincerely,

(B.D. Nageswara Rao)

(Anil Kumar)

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2. B.D. Nageswara Rao, Phy. Rev., 137, A 467, (1965)

3. A. Abragam, Principles of Nuclear Magnetism, Chap. III page 50, Oxford University Press, (1961)

UNIVERSITY of BRISTOL

School of Chemistry,
University of Bristol,
Cantock's Close,
BRISTOL 8,
England.

31st May, 1968.

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

Dear Dr. Shapiro,

Shifts in Trimethylphosphine Complexes

We have been studying the pmr spectra of an extensive series of trimethylphosphine and trimethylarsine complexes with Pd(II), Pt(II) and Au(I). The shifts (see Table) seemed to be showing a regular trend with halide until we measured the gold compounds where there is very little change in shift and this is in the reverse direction to that of the other complexes.

	τ_{Me}	$^2J_{PH}$	$^3J_{PtH}$	$\tau_{Me}(Cl)-\tau_{Me}(I)$
$Pt_2Cl_4(Me_3P)_2$	8.46	12.5	35.8	
$Pt_2Br_4(Me_3P)_2$	8.38	12.1	35.9	−0.24
$Pt_2I_4Me_3P)_2$	8.22	11.6	38.4	
$[Ph_4P][PtCl_3.Me_3P]$	8.54	11.7	30.7	
$[Ph_4P][PtBr_3.Me_3P]$	8.42	11.5	31.1	−0.34
$[Ph_4P][PtI_3.Me_3P]$	8.20	11.1	33.7	
trans $PtCl_2(Me_3P)_2$	8.54	7.6[†]	21.2	
" $PtI_2(Me_3P)_2$	8.18	7.5[†]	23.1	−0.36
cis $PtCl_2(Me_3P)_2$	8.26	11.5	35.6	
" $PtBr_2(Me_3P)_2$	8.20	11.3	36.1	−0.15
" $PtI_2(Me_3P)_2$	8.11	10.9	36.1	
$AuCl.Me_3P$	8.39	11.2		
$AuBr.Me_3P$	8.39	11.3		+0.02
$AuI.Me_3P$	8.41	11.1		

[†] $|^2J_{PH} + {}^4J_{PH}|$

This and the lower change in σ in the cis complexes is explained if it is a cis halide that causes the shift whilst a trans halide has little or no effect. This system also fits the results of Shaw et al [1] for similar octahedral compounds. These changes in shift are of the same magnitude as those caused by exchanging X and phosphine (e.g. going

from cis to trans isomers). If the change reflected an equivalent change in the bonding of the phosphine, then we must conclude that cis halides have a large effect on such bonds. This is opposed to all previous experience on square planar systems so some other explanation must be found.

The most obvious is a direct interaction through space. Since the nearest approach of a proton to the Pt-X is about 2.6 Å and the halide is likely to be near to this point along the axis (2.4 to 2.7 Å) such an interaction is quite feasible. Further, the size of the shift caused by replacing Cl by I decreases in the order $(Me_3P/Pd) > (Me_3P/Pt) \sim (Me_3As/Pd) > (Me_3As/Pt)$ in agreement with the likely order of the distance of H from the M-X axis.
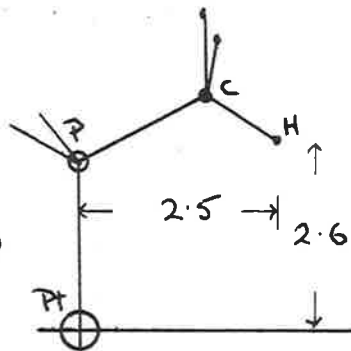
Thus the situation is similar to that of the methyl groups in CH_3CH_2X[2] where the 'neighbour anisotropy' effect has been used to explain the shift of .5p.p.m. to lower field on changing Cl to I (after removal of electronegativity effects). The spread of the effect over nine protons in our case should be compensated by the shorter H-X distance and the greater angle subtended by H to the M-X axis. As this angle is near to 90°, the shift should be lower field as observed. Relation of this case to the hydrogen halides also suggests that the neighbour anisotropy effect is a satisfactory explanation of the results for these complexes.

Yours sincerely,

R. J. Goodfellow

R. J. Goodfellow.

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ORGANISCH-CHEMISCHES INSTITUT
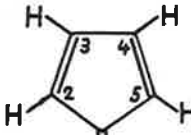DER UNIVERSITÄT

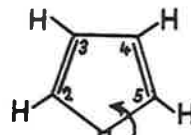Albrecht Mannschreck, Ulrich Koelle

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

^{1}H,^{1}H Coupling Constants in 6-Dimethylaminofulvenes

Dear Professor Shapiro:

We have analyzed the spectra[1] of $\underline{1}$ and $\underline{2}$. Close agreement between experimental curves and plots of results from FREQINT IV (A.A.Bothner-By) was obtained with the following parameters[2]:

$\tau_2 = 3.63$	$J_{23} = \underline{5.08}$ cps
$\tau_3 = 3.54$	$J_{24} = 2.05$ cps
$\tau_4 = 3.33$	$J_{25} = 2.10$ cps
$\tau_5 = 3.78$	$J_{34} = 2.50$ cps
	$J_{35} = 1.30$ cps
Solvent: $CDCl_3$	$J_{45} = \underline{5.50}$ cps

$\tau_2 = 3.72$	$J_{23} = \underline{4.58}$ cps
$\tau_3 = 3.88$	$J_{24} = 1.90$ cps
$\tau_4 = 3.66$	$J_{25} = 2.10$ cps
$\tau_5 = 3.50$	$J_{34} = 2.48$ cps
	$J_{35} = 1.38$ cps
	$J_{45} = \underline{4.55}$ cps
$\tau_6 = 2.81$	$J_{26} = 0.00$ cps
	$J_{36} = 0.00$ cps
	$J_{46} = 0.85$ cps
Solvent: CD_3CN	$J_{56} = 0.45$ cps

The assignments given are based on other fulvenes[3] and on the fact[2,4] that the 2- and 5-positions in $\underline{2}$ are deuterated in CH_3OD. We do not yet know whether the dimethylamino group points towards

H-2 or H-5. The parameters given by Crabtree and Bertelli[5] for $\underline{2}$ essentially agree with ours; in addition, our spectrum yields J_{46} and J_{56}, as it is better resolved than the published one[5].

We did not succeed in getting the parameters for both fulvenes in the same medium, because the solvent-dependence of τ is unfavourable. Literature data[3] for other systems support the view that the differences in J_{23} and J_{45} between $\underline{1}$ and $\underline{2}$ are not due to solvation. The coupling constants in the azafulvene $\underline{1}$ are similar to those in normal fulvenes (e.g. $J_{23} = J_{45} = 5.17$ cps in 6.6-diphenylfulvene[3]), whereas J_{23} and J_{45} in $\underline{2}$ show some tendency towards the smaller vicinal coupling constants in cyclopentadiene anions (e.g. $J = 3.23$ cps in the indenyl anion[3]). Therefore, delocalization of π electrons in the ground state (see arrows in formula $\underline{2}$) seems to be decreased by the aza nitrogen in $\underline{1}$. This conclusion is consistent with dipole moment measurements[6], investigations of internal rotation[4], formylation[6] and deuteration[2,4] experiments.

Sincerely yours,

Albrecht Mannschreck

Ulrich Koelle

---

1) Measured at 100 Mcps by Dr.J.C.Jochims and Miss G.Taigel, Heidelberg.
2) A.Mannschreck and U.Koelle, Chem.Ber., to be published (preprints available).
3) W.B.Smith, W.H.Watson, and S.Chiranjeevi, J.Am.Chem.Soc. 89, 1438 (1967) and references cited therein.
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INSTITUT FÜR ORGANISCHE CHEMIE DER TECHNISCHEN HOCHSCHULE BRAUNSCHWEIG

PROF. DR. PHIL., DR. MED. h. c. H. H. INHOFFEN

Dr. Gisela Brockmann

Dr. Hans Brockmann jr.

33 BRAUNSCHWEIG
SCHLEINITZSTRASSE
Tel. Hochschule 4781
Durchwahl Institut 4782225
Vorwahl 0531

29. Mai 1968

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

Sehr geehrter Herr Professor Shapiro!

Bestimmung der relativen Konfiguration durch induzierte Konformationsänderung.

Bereits Woodward [1] zeigte, daß sich Chlorine in δ-Stellung leicht substituieren lassen; es gelingt zum Beispiel das δ-Wasserstoffatom in **1** elektrophil durch Deuterium oder Chlor zu ersetzen. Daß wirklich das δ-Wasserstoffatom substituiert wurde, folgerte man aus dem Fehlen des Methin-protonen-Resonanzsignals bei höchsten Feldstärken, das auf Grund theoretischer Überlegungen dem δ-Proton zugeordnet wurde [2]

Im Zusammenhang mit anderen Substitutionsreaktionen wurden am hiesigen Institut verschiedene δ-Chlor-chlorine hergestellt und ihre NMR-Spektren gemessen. Im Vergleich zu den Chlor-freien Verbindungen treten in den Spektren einige charakteristische Veränderungen auf, die besonders ausgeprägt an den chemischen Verschiebungen des 1-Methylgruppen-Signals und der 8-Wasser-stoff-Resonanz zu erkennen sind (Tabelle). Damit scheint uns die Konstitution der δ-Chlor-chlorine unabhängig von obigem Argument [1,2] bestätigt zu sein.

Eine weitere Beobachtung läßt auf die relative Stereochemie an C-7 und C-8 schließen. Nimmt man an, daß wie durch meso-Methylgruppen in peripher substituierten Porphyrinen [3] die
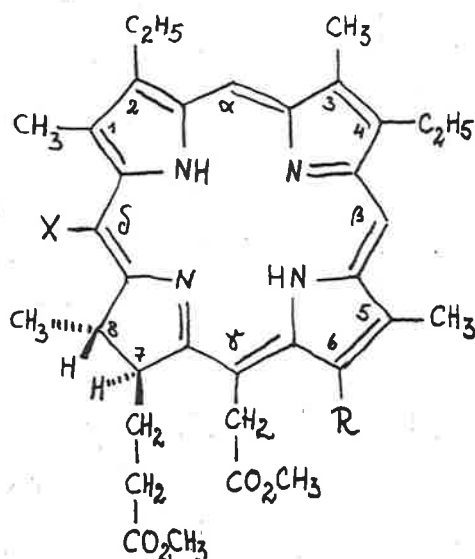
1 X = H; R = H   4 X = Cl; R = H

2 X = H; R = CO₂CH₃   5 X = Cl; R = CO₂CH₃

3 X = H; R = COCH₃   6 X = Cl; R = COCH₃

Tabelle: NMR-Spektren in CDCl₃ (0.05 m)
Chemische Verschiebung in ppm.

Protonen	1	4	2	5	3	6
8-H	4.49	4.91	4.37	4.85	4.39	4.86
7-H	4.71	4.59	4.39	4.29	4.41	4.28
1-CH₃	3.38	3.56	3.31	3.52	3.32	3.51
3-CH₃	3.35	3.34	3.27	3.27	3.28	3.27
5-CH₃	3.61	3.56	3.55	3.52	3.53	3.48
8-CH₃	1.71	1.58	1.73	1.64	1.72	1.61

Planarität des Macrocyclus auch durch ein δ-ständiges Chlor-
atom aufgehoben wird, und sich die dem meso-Substituenten be-
nachbarten Pyrrol- bzw. Dihydropyrrolenin-Ringe aus der Ebene
des Moleküls herausdrehen, so läßt sich die diamagnetische
Verschiebung der Signale der 8-Methylgruppe und des 7-Wasser-
stoffatoms nur dadurch erklären, daß diese auf der gleichen
Seite des Dihydropyrrolenin-Ringes stehen. Durch die Einführung
eines δ-Chlorsubstituenten und den damit verbundenen Übergang
des Moleküls aus einer weitgehend planaren in eine nicht
planare Konformation werden die 8-Methylgruppe und das

7-Wasserstoffatom dem paramagnetischen Entschirmbereich des Ringstromes weitgehend entzogen, während das 8-Proton stärker in den paramagnetischen Entschirmbereich hineingedreht wird.

Die abgeleitete trans-Konfiguration der Wasserstoffatome an C-7 und C-8 wurde erstmals von Fischer [4] vermutet und steht im Einklang mit Ergebnissen, die man durch oxidativen Abbau von Chlorophyll-Derivaten [5,6] sowie durch Interpretation der Kopplungskonstante $J_{7,8}$ in den NMR-Spektren von Phäophorbiden erhalten hat [7].

Wenn auch das Resultat unserer Untersuchungen nicht neu ist, so kann doch das Prinzip der Bestimmung von relativen Konfigurationen durch induzierte Konformationsänderung auch bei Verbindungen angewendet werden, bei denen sich keine Möglichkeiten zur Konfigurationsbestimmung auf Grund von Kopplungskonstanten bieten.

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6) H.Brockmann jr., Angew.Chem. 80, 233 (1968); Angew. Chem. internat.Edit. 7, 221 (1968).
7) G.L.Closs, J.J.Katz, F.C.Pennington, M.R.Thomas u. H.H.Strain, J.Amer.chem.Soc. 85, 3809 (1963).

Mit vorzüglicher Hochachtung

Ihre

Gisela Brockmann

Hans Brockmann jr

Bell Telephone Laboratories

Mountain Avenue, Murray Hill, N. J. 07974   Telephone 201-582-3000

May 31, 1968

DR. BERNARD L. SHAPIRO
Department of Chemistry
Stanford University
Stanford, California 93405

Dear Dr. Shapiro:

I would like to briefly discuss our use of the HA-100 in
solid state studies. The relative errors in any field
dependent measurement (e.g. shielding anisotropy) are re-
duced by going to higher fields. In our work the solid
state resonances were observed directly in the absorption
made at the output of the V-4311 unit. No audio modulation
was used. The field sweep was gained by applying a suitable
(i.e. linear and stable) ramp voltage at the field control
input to the magnet power supply (in place of the super-
stabilizer). Since solid state resonances are quite weak
due to their breadth, the C-1024 time averaging computer
was employed. The ramp voltage of the C-1024 served as a
suitable field control input. The V-4311 output at J314
was connected to the analog input. Sweep number, rate and
width were adjusted according to resonance width, saturation
conditions, etc.

This technique has been applied to shielding anisotropy studies
of fluorine containing compounds. We have some data on solid
XeF_2 and other fluorine compounds which we hope to publish soon.
(The 100 to 94 MHz conversion went quite smoothly).

Since discussion of chemical shift scales seems in vogue these
days, I would also like to insert a few comments. Based on
some work on gaseous HF at Wisconsin, Professor C. D. Cornwell
and I have developed what we think is a very adequate absolute
shielding scale for fluorine nuclei. Most of the compounds
placed on the scale are gaseous but we have included liquid CCL_3F
to enable liquid measurements to be tied in. This work will be
published soon in the Journal of Chemical Physics.

Sincerely,

D. K. HINDERMANN

MH-1519-DKH-MS

Title: I) Solid State Studies with the HA-100;II) A Fluorine

Absolute Shielding Scale.

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

Division of Chemistry and Chemical Engineering

May 29, 1968

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

Dear Barry:

Noise Decoupling. ^{13}C Spectra of Cholesterol

The development of practical noise decoupling procedures by
Roy Johnson has led us to investigate extension to ^{13}C spectra of
complex organic molecules where splittings associated with strong
proton-proton couplings result in poor signal-to-noise ratios. Selec-
tive proton decoupling (a la David Grant) can relieve the situation but
is exceedingly tedious and wasteful of spectrometer time. The prob-
lem is illustrated by Figure 1 which shows a 1000-scan spectrum of a
1.1 M solution of cholesterol in CS_2 over a 1000-Hz sweep width.

Noise decoupling with the hookup shown in Figure 2 using about
a 300-Hz bandwidth dramatically improves the cholesterol spectrum
as can be seen in Figure 3. We can distinguish 26 out of 27 separate
carbon resonances and our next job will be to find out which are which.
Similar spectra have been easily obtainable of terpenes (pinenes and
squalene) and sugars (sucrose).

With all good wishes,

Very truly yours,

Jack

John D. Roberts

Frank

Frank J. Weigert

JDR:FJW/bi

Cholesterol – 1.1 M in CS_2 – without
decoupling – 1000 scans
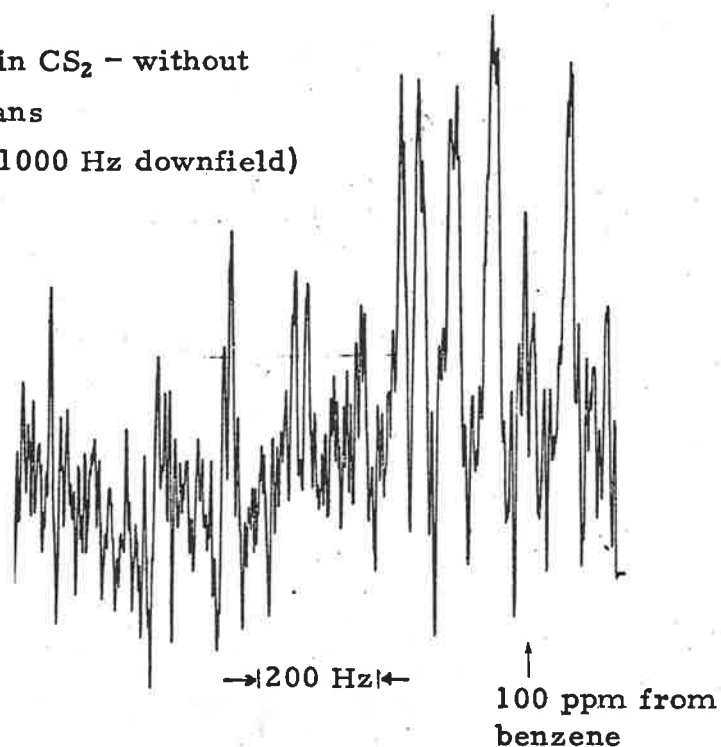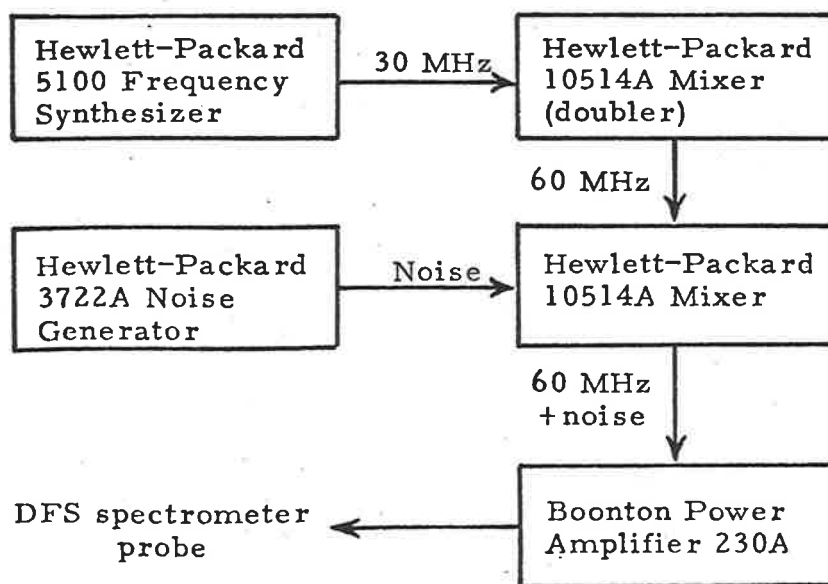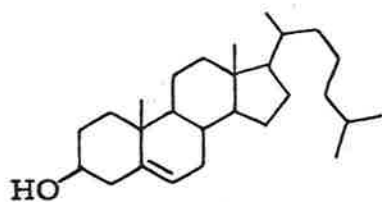(the 2-vinyl carbons 1000 Hz downfield)

→|200 Hz|←

100 ppm from
benzene

Figure 1.

Figure 2.

Cholesterol – 1.1 M in CS$_2$ – 1000 scans
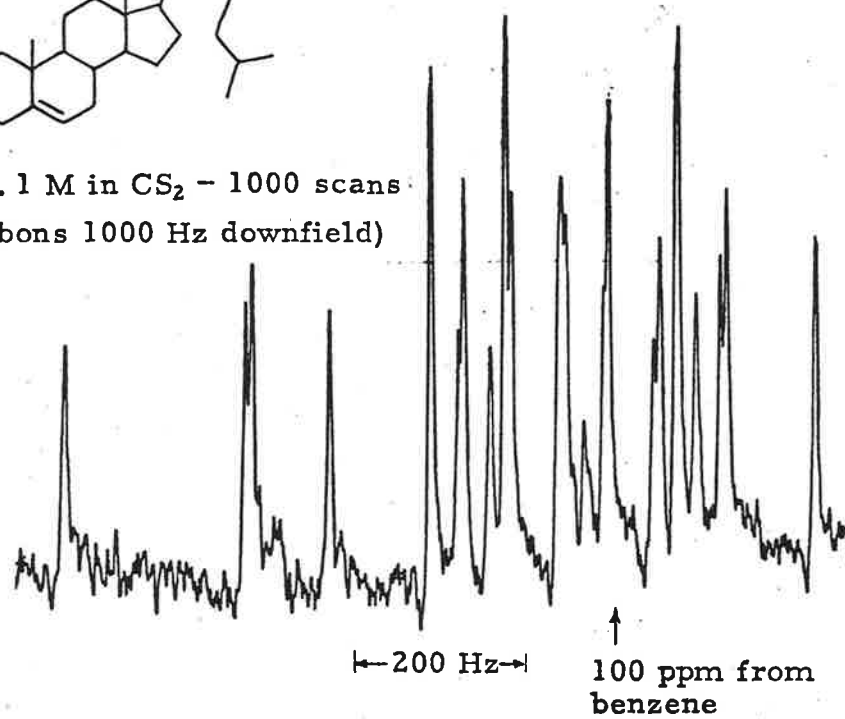(the 2 vinyl carbons 1000 Hz downfield)

|←200 Hz→|

100 ppm from
benzene

Figure 3.

Deadline Dates: No. 118: 2 July 1968   <u>PLEASE NOTE</u>!
                 No. 119: 6 August 1968

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

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<u>O V E R</u>

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