Texas
A & M
University
N – M – R
Newsletter

No. 136
JANUARY , 1970

CSIRO

DIVISON OF PLANT INDUSTRY

P.O. BOX 109, CANBERRA CITY, A.C.T., 2601, TELEPHONE 4-0455 — TELEGRAMS CORESEARCH CANBERRA

WPAP:IVS.
Refer.:

12th November, 1969.

<u>DNMR Down Under</u>

Dear Professor Shapiro,
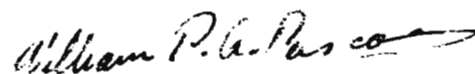
      I would like to start this letter by thanking the authors of DNMR, Daniel A. Kleier and Gerhard Binsch, for very kindly supplying me with a copy of their program.

      Unfortunately as we are not endowed with a 65K Univac, it became necessary to reduce the core requirements to suit our humble Control Data 3600 which has a 32K core with Drums And Display. The net available core under standard operation is about 24K.

      The total number of cards to change is small (about 60). The changes may be done in two stages. The first will reduce the program by 4600 words and if a RANDOM ACCESS DRUM is used a further reduction of 4600 words is achieved. The extra time is only 2 secs in 1 minute. All this is only necessary of course if it is required to calculate the larger configurations.

      A copy of the changes will be available from either of us.

Sincerely yours,

(W.P.A. Pascoe)

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, AUSTRALIA

W.P.A. Pascoe,
C.S.I.R.O.,
Canberra. A.C.T. Australia.

11th November, 1969.

The following changes to DNMR will reduce the core requirements from 29814 to about 20600 words.

In main program,

```
        COMPLEX (delete CR,CL,EIG) (insert LAMBDA(48))
        COMMON/EIVEC/ (change to A,QQNV,LAMBDA)
add     DIMENSION TEXT(10)
    1   CALL STADAT(TEXT)
        CALL ALLMAT(NT,K)
delete  CALL CONVEC(K,NT)    EQUIVALENCE (CR(1,1),A(1,1))
        CALL SPECT(J,TEXT)


        SUBROUTINE STADAT(TEXT)

        SUBROUTINE ALLMAT(M,KS)
        COMPLEX (delete CR,CL,EIG) (reduce H array to (2,2))
        COMMON/EIVEC/ A,HL,LAMBDA
        COMMON/TEM/ H
delete  DO 19 I=1,N    insert  CALL WDRUM(66,A,4608,0)
        DO 19 J=1,N            500 IF (UNIT,66)  500,501
     19 H(I,J)=A(I,J)          501 CONTINUE
```

The above change uses a RANDOM ACCESS DRUM to write out the A matrix.

delete cards between 38 and 40 and insert the following,

```
        38 DO 56 L=1,NCAL
           IF (N.EQ.2) GO TO602
           CALL RDRUM (66,HL,4608,0)
        600 IF (UNIT,66) 600,601
        601 CONTINUE
           IF (N.NE.2) GO TO 603
        602 HL(1,1) = H(1,1)
           HL(1,2) = H(1,2)
           HL(2,1) = H(2,1)
           HL(2,2) = H(2,2)
        603 CONTINUE
           DO 40 I=1,N
        40 HL(I,I)=HL(I,I)-LAMBDA(L)
change
        53 VECT(J)=HL(J,N1I)*VECT(N1I+1)+VECT(J)
           CALL NVRT(M,KS)
```

W.P.A. Pascoe,
C.S.I.R.O.,
Canberra, A.C.T. Australia.

Page 2

```
        SUBROUTINE NVRT(N,KS)
change dimension statments to the following,
        COMPLEX QQNV(48,48),TEMP(48,48),P(48),Q(112),D(112),CRS(48)
        COMMON/EIVEC/TEMP,QQNV,LAMBDA
        COMPLEX TFR,CLS,LAMBDA (48)
        COMMON/VECT/Q,D
        COMMON/VEC/ V(112),POV(112)
CONVEC is divided and incorporated with NVRT.
        NT = N
        KM = KS
        K1 = 1
        KK = KS - 1
    505 CRS(K1) = CMPLX(0.,0.)
        DO 506 LA = 1,NT
        LAK =LA+KK
    506 CRS(K1) = CRS(K1)+V(LAK)*TEMP(LA,K1)
        KS =KS + 1
        K1 =K1 +1
        IF(K1.LE.NT) GO TO 505
```

```
NVRT
delete
        TEMP(I,J) = Q(I,J)
change QNV to QQNV
balance of CONVEC
        M1 = 1
        MM = KM - 1
    501 CLS = CMPLX(0.,0.)
        Q(KM) = CMPLX(0.,0.)
        DO 502 NU = 1,NT
        NUK = NU + MM
    502 CLS = CLS + POV(NUK) * QQNV(M1,NU)
        Q(KM) = CRS(M1) * CLS
        D(KM) = LAMBDA(M1)
        KM = KM + 1
        M1 = M1 + 1
        IF (M1.LE.NT) GO TO 501
        RETURN
        END
```

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AREA CODE 203 348-7331

October 24, 1969

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

Dear Barry: <u>The Structure of a Streptothricin Type Antibiotic</u>

     I'm afraid that most of our work during the past few months has utilized NMR in fairly straightforward fashion. In conjunction with continuing work on antibiotics by Dr. D. Borders at our Lederle Laboratories, we have used NMR extensively to determine the structure of LLAC541 (I), a new antibiotic of the streptothricin class, as well as other related compounds. As far as we are aware, no NMR investigations of these types of antibiotics have been reported. The coupling constant data supported the stereochemistry of the hexosamine and streptolidine rings, indicated in Figure 1. A rather high vicinal coupling of 14.8 H_3 was noted for the two axial-axial oriented protons a & b. This work will be published shortly.
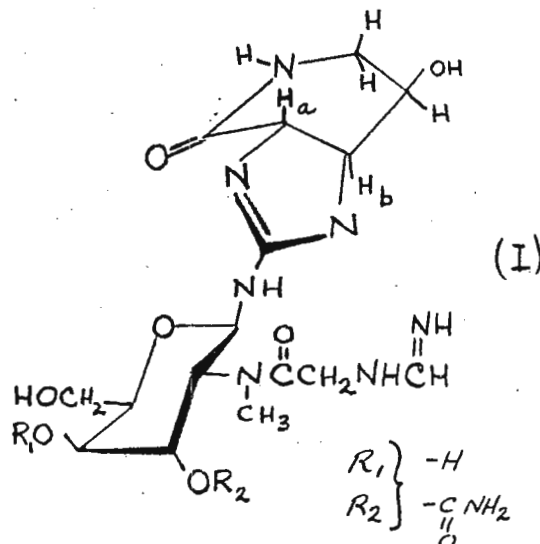
Very truly yours,

John Lancaster

John E. Lancaster, Group Leader
Nuclear Magnetic Resonance Group
Research Service Department

pps

NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20390

IN REPLY REFER TO:

6110-531:WBM:vmg
8 December 1969

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

Dear Barry:

MO Calculations of Quadrupole Coupling Constants

Betsuyaku [1] has recently shown that the nitrogen net p-orbital populations calculated for nitrite ion by the LCAO-MO-CNDO method [2], when used in the quadrupole coupling constant expression derived by Cotton and Harris [3], yield values for the coupling constants in very good agreement with those determined experimentally.

We have performed similar CNDO/2 calculations [4] on CH_3NC and HCN, and have found that there is poor agreement between the calculated and experimental coupling constants for these compounds. To make matters worse, the calculated e^2qQ for MeNC is larger than that calculated for HCN:

$|e^2qQ|$ (MHz)	HCN	MeNC
calc.	0.725	3.345
exp.	4.58	0.48

We doubt that the well-known sensitivity of the calculations to geometry can be responsible for such large discrepancies, and are inclined to suspect that the parameters may require adjustment for nitrogen in the triply-bonded (sp) state.

Sincerely,

W. B. MONIZ
C. F. PORANSKI, Jr.
NMR Spectroscopy Section
Chemistry Division

1. H. Betsuyaku, J. Chem. Phys. **50**, 3117 (1969)
2. Pople, Santry, Segal, J. Chem. Phys. **43**, S129, S136 (1965); **44** 3289 (1966)
3. F. A. Cotton and C. B. Harris, Proc. N.A.S. (U.S.) **56**, 12 (1966)
4. J. L. Ragle, R. Gentzler and P. A. Clark, QCPE 144, obtained from QCPE, Indiana Univ., Bloomington, Indiana

varian /analytical instrument division
25 route 22/springfield/new jersey/07081/201 376—6620

December 3, 1969

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

Dear Barry,

Scope Display for the T-60

Sometimes it is convenient to tune the magnetic field of the
T-60 while observing an nmr signal on a scope rather than using
the existing NSBO or lock level indicator. While there does exist
an optional accessory which provides this facility, anyone with
an appropriate oscilloscope can build his own for the cost of a
SPST switch and a 20 k potentiometer. Whatever scope is used, it
must be capable of providing an external linear sawtooth (from the
internal sweep circuit) without being overloaded internally. This
sawtooth is used to synchronously sweep the magnetic field and the
horizontal axis of the scope. The 20 k pot provides an independent
control for the field swept, and the SPST switch returns the spectro-
meter to recorder control without having to turn off the scope.

The scope we used was an Hp Model 120B (standard on the HA-100).
The schematic below shows the modification as discussed for the
horizontal axis. The vertical input to the scope is taken directly
from the standard "Signal Out" jacks at the side of the T-60. With
the scope switched to an internal sweep rate of approximately 100
milliseconds/cm, nmr signals may be conveniently monitored while
electrically shimming the magnetic field.

Hp Model 120B Scope Manual
Figure 5-8 Sweep Generator
(Scope Circuit)

Varian Model T-60 Manual
Recorder Publ. No.87-121-719
(Recorder Circuit)

Sweep Current Source (Part of
Schematic 87-121-722 (J205)

(NEW)

50K

X5

4000

1000

X1

S102

Sweep
Magnifier

Sweep
Output

20K

SPST

Common

E205

3

1

8

9

2
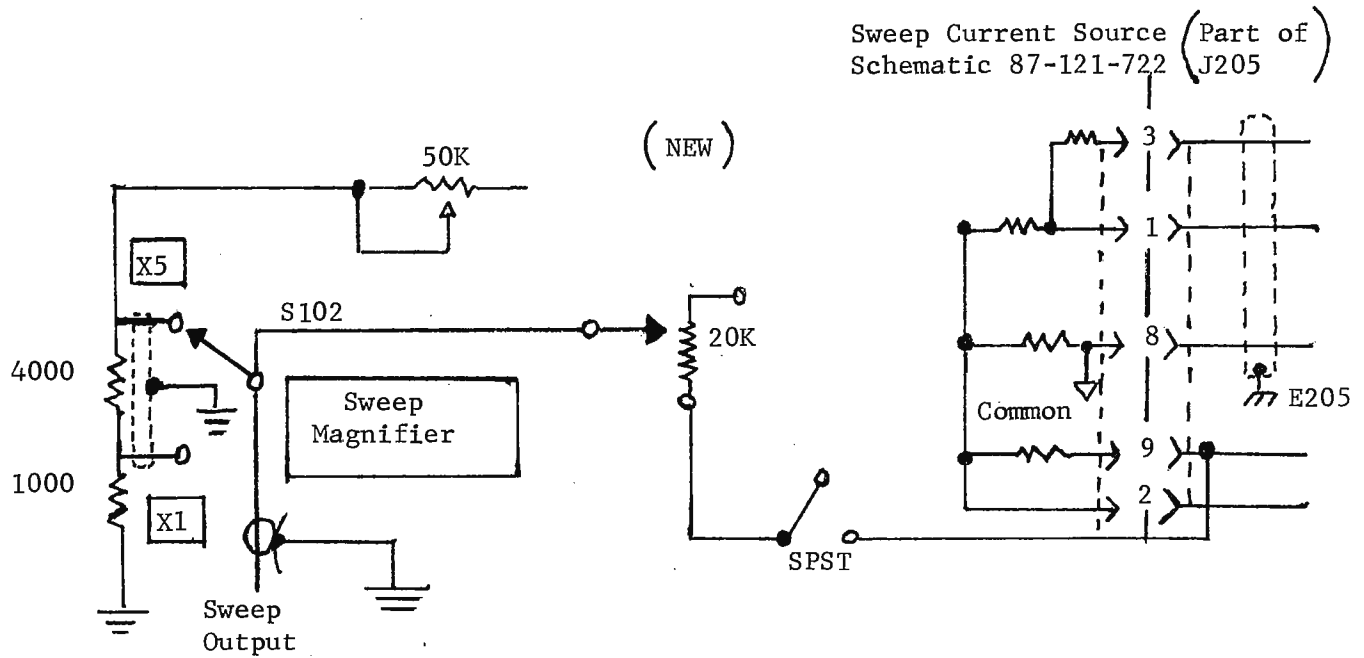
Yours Sincerely,

Michael H. Gross
Applications Scientist

William Hatfield
Service Engineer

NATIONAL CHEMICAL RESEARCH LABORATORY

OF THE SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

Telephone 74-6011   Telegrams **NAVORSCHEM**

P. O. Box 395

OUR FILE   YOUR FILE   **PRETORIA**

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

Dear Prof. Shapiro,

Rotational Isomerism in Ethylene Glycol and 2-Fluoro-ethanol

An NMR study of the solvent dependence of 1,2-disubstituted ethanes may yield information on vicinal coupling constants and on rotational isomerism[1]. We have extended our investigations to ethylene glycol and 2-fluoro-ethanol, two compounds which are supposed to exist as gauche isomers only[2]. Small but significant solvent effects on the vicinal couplings were observed and attributed to changes in the relative rotamer populations (see Table). The gauche populations (ng) in the Table were obtained using Abraham's equations[3], which relate the vicinal couplings in the individual rotamers to the electronegativity of the substituents.

TABLE

Ethylene Glycol				2-Fluoro-ethanol			
Solvent	J	J'	ng	Solvent	J	J'	ng
Et_3N	6.06	4.42	.79	$CHCl_3$	5.97	2.48	.95
CH_3COCH_3	6.16	4.13	.82	neat	5.98	2.44	.95
CH_3CN	6.16	3.71	.86	D_2O	6.00	2.25	.97
D_2O	6.25	3.56	.88				

The relatively small proportion of trans isomer found in 2-fluoro-ethanol does not necessarily contradict previous IR results since it is apparently difficult to detect an isomer population of 5% by IR. However, the results on ethylene glycol are obviously in disagreement with conclusions drawn from other investigations, but one has to bear in mind that in this case IR measurements are hampered by the presence of various inter- and intramolecularly hydrogen bonded species, while dipole moments, governed by the larger OH bond dipole, reflect a rotation around the C-O bond rather than the C-C bond.

Please address all correspondence to the Director.

Thus NMR spectroscopy could be a very powerful tool in the study of rotational isomerism, being more sensitive and more selective than other techniques, <u>provided</u> one is able to obtain reliable values for the vicinal couplings in the individual rotamers.

Yours sincerely,

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

References:

1. Abraham, Cavalli, Pachler, Mol. Phys. <u>11</u>, 49 (1966).

2. Buckley, Giguére, Canad. J. Chem. <u>45</u>, 397 (1967).
    Wyn-Jones, Orville-Thomas, J. Mol. Structure <u>1</u> 79 (1967).
    Buckley, Giguére, Yamamoto, Canad. J. Chem. <u>46</u>, 2917 (1968).

3. Abraham, Nato Summer School on NMR Spectroscopy, Coimbra, Portugal (1968).

KP/EW

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DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

December 8, 1969

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

Dear Barry:

RE: F^{19} Lock for C^{13} on an HA-100

Some of your readers who have HA-100's with 25.1 MHz rf units might be interested in recent modifications we have made on our system for ^{13}C. After three years of struggling with $^{13}CS_2$ locks[1] we decided to try for a more convenient technique, and worked out the internal ^{19}F lock system shown in the accompanying figure. Vic Bartuska and Tom Nakashima have done nearly all of the work on this project.

The internal ^{19}F lock circuit is based upon a single-coil that is wound concentrically about the 25.1 MHz receiver coil of the Varian insert for 8mm tubes. Using a "magic T" bridge and FET preamps, this provides adequate signals for the 94.1 MHz V4311 unit. The basic frequency (provided by a 15.678 MHz crystal in the original Varian configuration) is derived from appropriate mixing and division of signals available at the HP5110A Synthesizer Driver. From the front of the attached HP5100A Synthesizer a variable 6.28 MHz signal is taken as a basic frequency that replaces the crystal in the 25.1 MHz rf unit. This permits the ^{13}C centerband to be placed in any region desired to resonate ^{13}C nuclei in the field fixed by the ^{19}F lock (usually a capillary of CF_3CO_2H).

The V-4354A unit was modified so that the ^{19}F control signal and ^{13}C analytical signal pass through entirely separate components. Proton decoupling uses a slightly modified Varian V3512-1 unit.

All of the individual modifications or circuits have previously been used individually in closely analogous systems.[2,3] The impressive frequency stability of the system makes it ideal for high-precision measurements and for CATing.

With best regards from Ronnie,
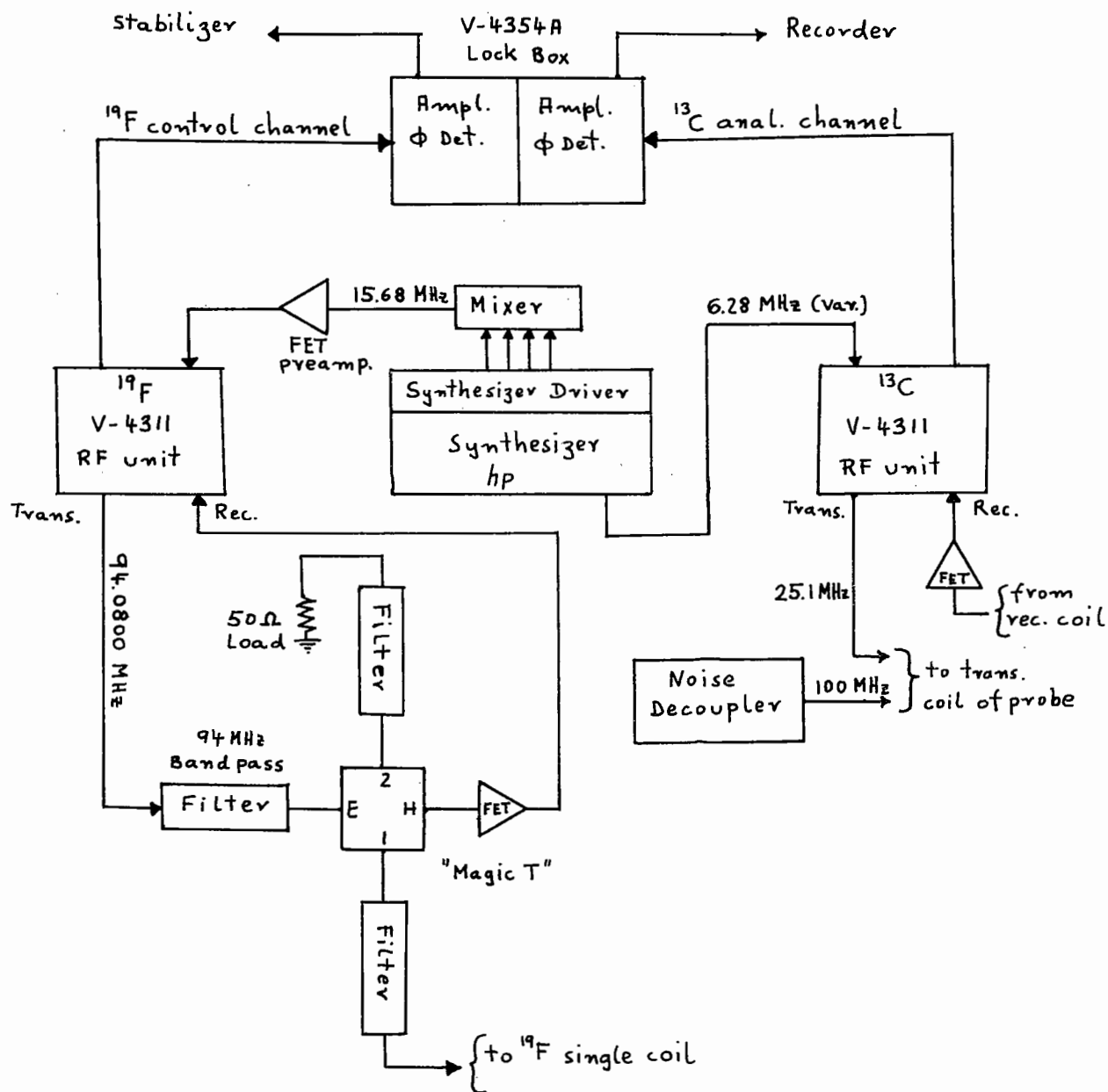
Gary

Gary E. Maciel

GEM:scb

References

1. G. E. Maciel, IIT NMR Newsletter, No 98, p. 34 (1966).
2. D. D. Elleman and S. L. Manatt, Abstracts of 8th ENC, Pittsburgh, 1967.
3. M. P. Klein and D. E. Phelps, Rev. Sci. Inst., 38, 1545 (1967).

Stabilizer ← V-4354A Lock Box → Recorder

^{19}F control channel → | Ampl. φ Det. | Ampl. φ Det. | ← ^{13}C anal. channel

15.68 MHz — Mixer — FET preamp.

6.28 MHz (var.)

Synthesizer Driver

Synthesizer hp

^{19}F V-4311 RF unit

^{13}C V-4311 RF unit

Trans. Rec.

Trans. Rec.

94.0800 MHz

25.1 MHz

FET {from rec. coil

50 Ω Load

Filter

Noise Decoupler — 100 MHz {to trans. coil of probe

94 MHz Band pass

Filter — E | 2 | H — FET

1

"Magic T"

Filter

{to ^{19}F single coil

Dec. 9, 1969

Dr. Bernard L. Shapiro
Texas A & M University
College of Science
College Station, Texas   77842
ATTN: TAMU NMR

Title: HR 220 sweep modification
Dear Dr. Shapiro:

Enclosed please find an HR 220 modification procedure which I trust will
serve as my reinstatement to the TAMU NMR newsletter.

Our HR 220 has been bubbling along happily now for many months and we are
quite pleased with its overall performance. We have had no difficulty
routinely exceeding specifications as the instrument appears to be conser-
vatively rated in the best Varian tradition.

A minor inconvenience,however, is encountered when controlling the oscil-
loscope readout from the SS 100 console. Since no attempt has been made
to logically interface the SS 100 readout with the scope z-axis, consi-
derable manual manipulation of scope controls is necessary each time one
switches from computer driven to instrument driven scope display or vice
versa. The enclosed circuit, which is quite simple and can be built for
under $20, reduces this procedure to moving the z-axis switch from
1 v/cm to 2 m sec/cm corresponding to the time (20 m sec) necessary for
one sweep through memory.

The simplification is brought about by making the HR 220 scope sweep
signal equivalent to the SS 100 scope sweep signal and is accomplished
by breaking the line at J 305 M of the V-4356 sweep unit and inserting
the adaptation circuit between this point and scope output J 304. The
range pot is adjusted to give a 10 cm. trace with the scope z control in
the 1 v/cm position. The z-axis is then centered and zero is adjusted
so that the trace does not shift when going from HR 220 to SS 100 display.

This circuit was constructed on a 1½ by 3 inch card and mounted in the
V-4356 chassis to the right of J 302. Access holes were drilled so that
zero a nd range could be adjusted after the instrument reaches nominal
operating temperature.

Sincerely,

Dennis E. Wisnosky
Electronics Research
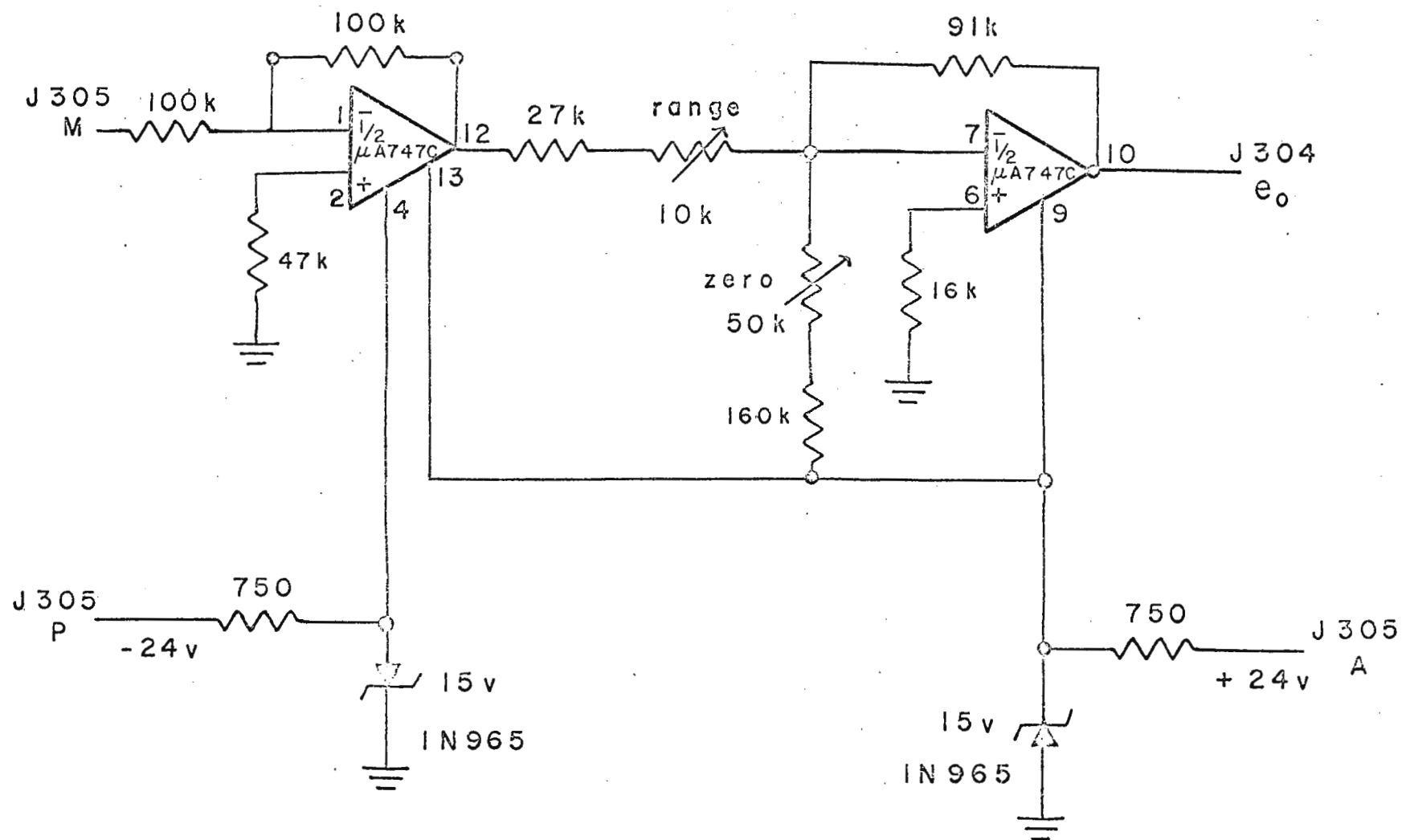
Monsanto

December 12, 1969

Prof. Bernard L. Shapiro
Texas A&M University
College of Science
College Station, Texas 77843

Dear Barry:

We offer the following contribution under the class of "partly explained mysteries". If any readers can offer a more complete explanation, we would like to hear from them, either directly, or in a future issue of your esteemed newsletter, which we hope to continue receiving.

^{31}P NMR OF METHYL ETHYLENE PHOSPHITE: AN APPARENT ANOMALY

The 60 $\overline{M}$ Hz proton spectrum of methyl ethylene phosphite has been analyzed by Haake, McNeal, and Goldsmith[1], who concluded that envelope conformation II (see Fig. 1) is favored over I and made tentative peak assignments on that basis. Moreover, they used the vicinal hydrogen-hydrogen coupling constants as evidence for preferring two equivalent twist-envelope conformations, one of which is approximated as III. They were unable to rule out the possibility of rapidly interconverting conformations, however.

We have had occasion recently to measure the 40.5 $\overline{M}$ Hz ^{31}P NMR spectrum of freshly distilled, neat methyl ethylene phosphite. Under low resolution we observed a rather broad multiplet centered at -131.4 ppm from H_3PO_4. (Previously reported shifts are -132.4 and -131.6[2].) The intensity ratios approximated the 1, 3, 5, 5, 3, 1 expected from observation of the six most intense peaks of a pseudo-first order eight-fold multiplet arising from coupling of the P to seven nearly equivalent protons. Under higher resolution (see Fig. 2) we found this spectrum to be made up of more than 40 individual peaks of less than 0.5 Hz width, arranged in a clearly assymetric multiplet. The assymetry initially suggested to us that methyl ethylene phosphite at room temperature might be locked into two or more non-equivalent conformations which were not rapidly interconverting and in which the ^{31}P chemical shifts of the phosphorus nuclei differ slightly. Since this was not apparent from the previously published proton work[1], we subjected the spectrum to more diligent scrutiny and were able by inspection to decompose it into three simpler multiplets. These were a major symmetrical multiplet of at least 36 peaks, and two superimposed lower intensity quartets, one displaced to lower field by 0.07 ppm and one displaced to higher field by 0.15 ppm (see Fig. 2).

Prof. Bernard L. Shapiro
Page 2
December 12, 1969

Although we have not attempted a complete and detailed study, including rigorous repurification of the sample and all the obvious possible temperature, decoupling, ^{13}C, and solvent experiments, the present observations are sufficient in themselves to define a mystery. The two independent quartets which contribute to the overall spectrum could logically arise from impurities, and this should be ruled out first. We are unable, however, to conceive of any hypothetical structures which would be expected to have a ^{31}P chemical shift nearly identical to the cyclic five-membered ring phosphite and yet give rise to only simple quartets with the 10 Hz splitting expected from coupling of a single methoxy group with the phosphorus without evidence of other H-P coupling of any kind. The chemical shifts of known and expected impurities are nearly all several ppm removed from this region of the phosphorus spectrum, which is rather unique for trivalent phosphorus, particularly cyclic five-membered ring phosphites[2]. If the two quartets do not arise from impurities, but from stable conformational isomers, the same absence of additional H-P coupling is equally puzzling. Could rapid torsional oscillation along the C-C bond effectively decouple proton-phosphorus spin coupling in one conformational isomer and not in another?
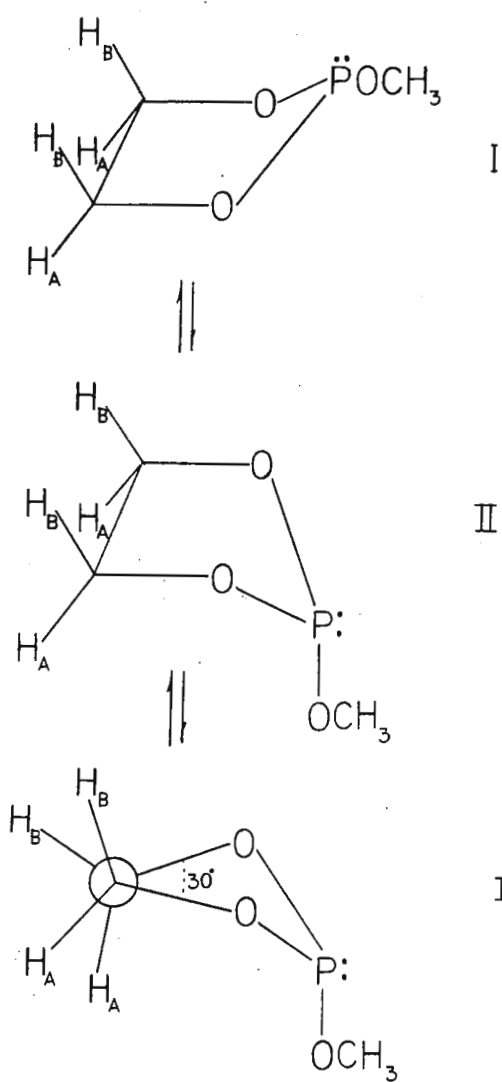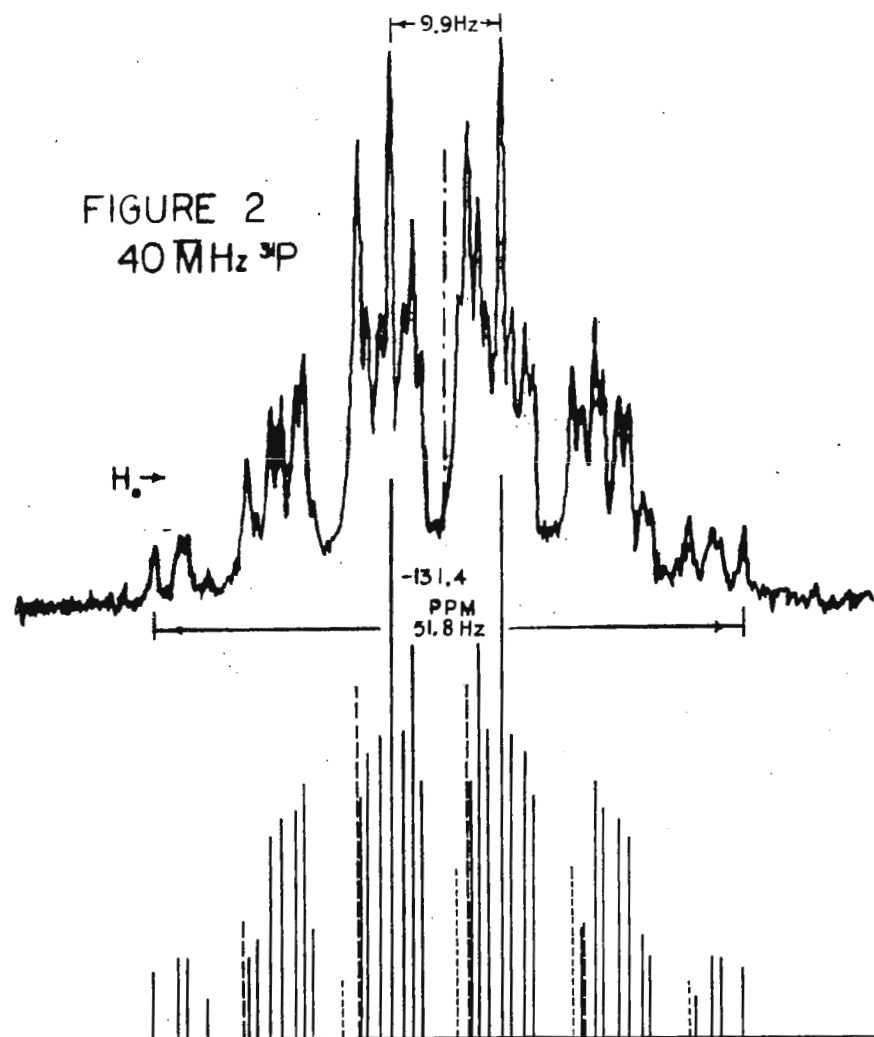
Sincerely,

M. M. Crutchfield

C. W. Heitsch

/cm
Attachment

References:

(1) P. Haake, J. P. McNeal, and E. J. Goldsmith, J. Am. Chem. Soc., 90:3, 715 (1968).

(2) M. M. Crutchfield, et al., TOPICS IN PHOSPHORUS CHEMISTRY, Vol. V, Interscience Publishers, 1967, p. 264.

FIGURE 1

I

II

III

FIGURE 2
40 MHz ³¹P

9.9Hz

H.→

-131.4
PPM
51.8 Hz

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969-0100
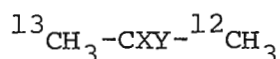Phone 332-3200
Area Code 617

Department of Chemistry

December 16, 1969

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

Dear Barry:

Our studies of substituent effects on four-bond HH couplings in propanic fragments established that, in molecules of the type

$$^{13}CH_3-CXY-^{12}CH_3$$

as the combined electronegativity of X and Y increases, $^4J_{HH}$ also increases. We were therefore rather surprised when we began to look at the methylene-methyl coupling in some neopentane derivatives:

$$(CH_3)_3C\ CH_2X.$$
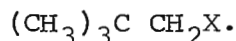
Since the couplings are quite small, we've been forced to estimate their magnitudes by lineshape analysis. Some preliminary results (shown below) indicate a substituent dependence opposite to that in the propane derivatives! Clearly (and significantly), what

X	E_X	$^4J_{HH}$
H	1.9	+0.35*
Cl	3.2	$+0.15 \pm 0.03$
OH	3.5	$+0.05 \pm 0.03$
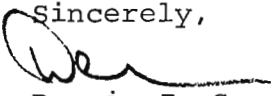
*H. Dreeskamp, <u>Z. Phys. Chem. (Frankfurt am Main)</u>, <u>59</u>, 321 (1968).

happens to the coupling constant depends not only on whether electrons are added to or removed from the carbon chain, but <u>where along the chain the perturbation occurs</u>. We are actively pursuing this intriguing observation.

Best wishes to all.

Sincerely,

Dennis J. Sardella
Assistant Professor

DJS/beb

Short Title: An Unusual Substituent Effect on $^4J_{HH}$, or
"Pornography is Question of Geography".

SHELL DEVELOPMENT COMPANY

A DIVISION OF SHELL OIL COMPANY

1400-53rd STREET
EMERYVILLE, CALIFORNIA 94608

December 16, 1969

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

Dear Professor Shapiro:

As part of our interest in the high resolution proton magnetic resonance spectra of paramagnetic transition complexes, we have attempted to exploit the very large non-linear expansion of the chemical shift scale due to proton-electron coupling to monitor rapid intramolecular ligand rearrangements.

Our most recent experiments have yielded estimates of the rate of intramolecular optical racemization of some "labile" octahedral cobalt(II) compounds. To date nothing is known about the kinetics and mechanisms of such inversions in cobalt(II) complexes.

Thus in the chelate bis(acetylacetonate)-(4,7-dimethyl-1,10-phenanthroline)-Co(II) the two acetylacetonate methyl groups are magnetically non-equivalent. In the process of optical inversion, these two methyl groups are interchanged (although not necessarily in a one-to-one ratio). In analogous diamagnetic compounds, this non-equivalence of the methyl groups has yielded chemical shift differences of ~0.1 ppm. In our cobalt chelate, this paramagnetic shift difference is ~40 ppm! As the two spectra in the figure illustrate, at high temperature only an average acetylacetonate methyl signal is observed, which clearly splits at low temperatures. Addition of excess ligand precludes intermolecular ligand exchange as a source of the averaging.

Standard analysis of the linewidths in the limit of slow inversion yields a first order rate constant ~5 x 10^6 sec^{-1}, with E_a ~13 kcal mole. Preliminary analysis of the origin of this sizable magnetic non-equivalence between the methyl groups which allows the detection of this kinetic process indicates that a strong dipolar coupling between the protons and the highly anisotropic electronic moment is responsible. Furthermore, such sizable magnetic non-equivalence between the two sides of a symmetric bidentate ligand, A-A, appears to be a general property of complexes of structural formula $Co(A-A)_2(B-B)$. Preprints are available to those interested.

Sincerely yours,

Gerd N. La Mar

Title: Rapid Intramolecular Ligand Rearrangements in Paramagnetic Complexes.

Dear Barry; Please credit to our subscription. Merry Xmas. Charlie
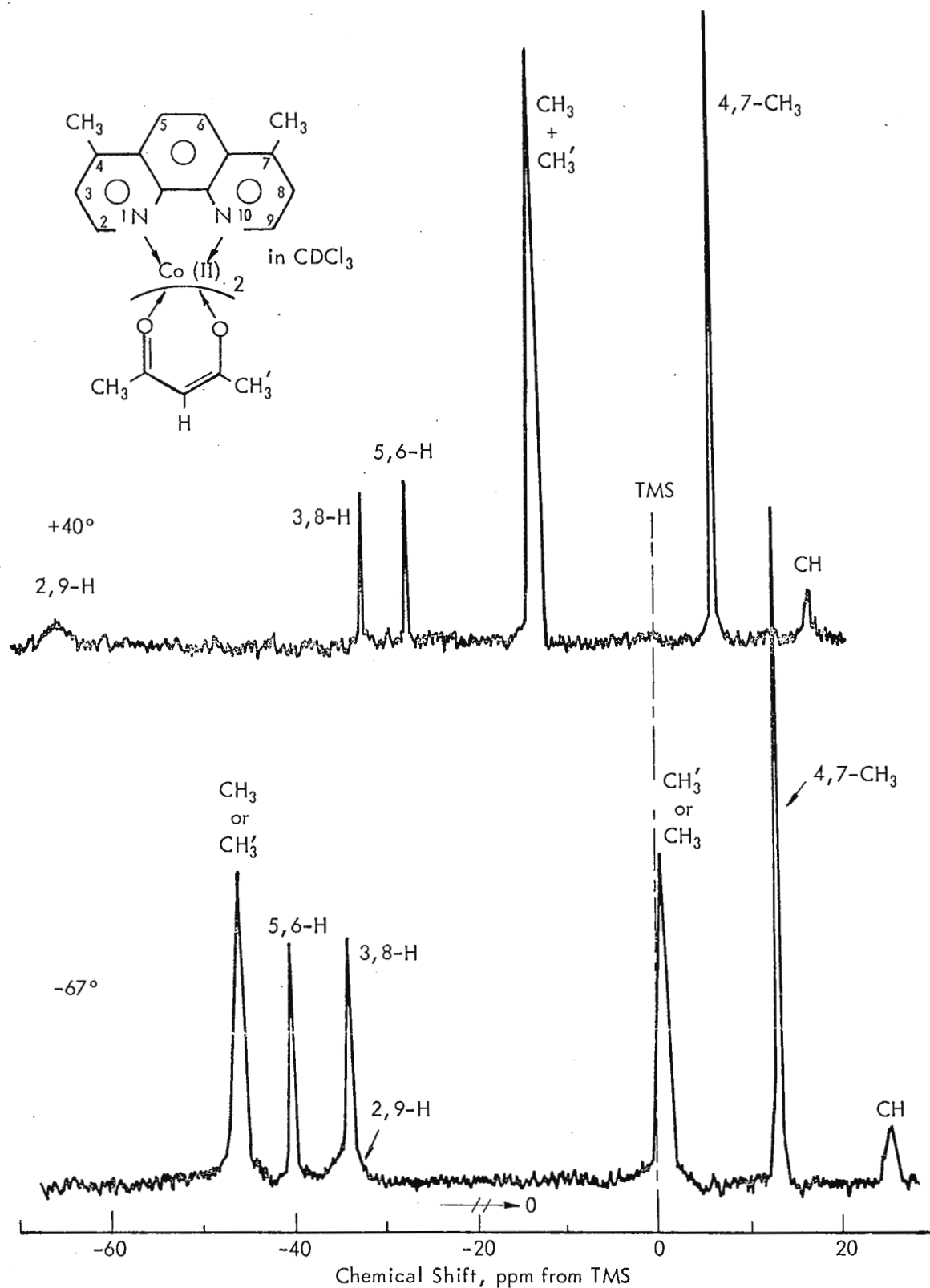
PROTON NMR TRACES OF Co (AA)$_2$ (4,7-PHEN) IN CDCl$_3$ IN THE LIMIT OF
FAST (+40°) AND SLOW (-67°) ENVIRONMENTAL AVERAGING

MONASH UNIVERSITY

P.O. BOX 92,
CLAYTON. VICTORIA. AUSTRALIA

TELEGRAMS:
MONASHUNI. MELBOURNE

DEPARTMENT OF   CHEMISTRY

TELEPHONE:
544 0611

17th December, 1969.

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

Title: Long recovery time after saturation by high power magnetic resonance.

Dear Barry,

Isolated as we are in Australia, we hope you will understand that the perturbation induced by the International Symposium on Magnetic Resonance in August has taken some time to die away. The most direct result of such a long relaxation time is that we have nothing of our own to contribute.

However, the Monash Department is now large enough to provide a steady flow of interesting compounds, some of which involve novel, or at least unusual, features in their n.m.r. spectra. For example the spectrum of ethyl 2-(1-methyl-3-indolyl)-pyruvate shows an interesting long range coupling to the enol proton, maximized, no doubt, by favourable geometry. The observed parameters are ($CDCl_3$, 60 MHz):
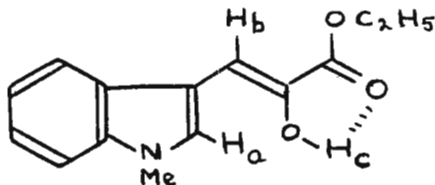
δH_a 7.83 $J_{ab} = 0.6\ H_z$

δH_b 6.97 $J_{bc} = 1.6\ H_z$

δH_c 6.25 (lost on D_2O exchange)

We are indebted to Dr. R.F.C. Brown and Mr. P. Newman of this department for the above example, but we will take the subscription credit just the same! We will write and tell you about our own things when we have stopped nutating wildly.

Best wishes for 1970

Ian D Rae

Ian D. Rae

Michael L. Heffernan

Michael L. Heffernan

PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA 47907

December 18, 1969

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

Dear Dr. Shapiro,

Charge Calculations, Dianions and Paramagnetic Ring Currents.

In the course of a study with Professor L. M. Jackman we
became interested in trying to develop an empirical model for
the calculation of charge induced shifts in aromatic systems.
Our study was based on the Buckingham equation for charge
effects and used a range of nitrogen heterocycles to establish
the empirical relationship. The equation obtained was

$$\Delta \sigma_i (ppm) = 11.75 \sum \frac{\Delta q_j \cos \theta_{ij}}{X_{ij}^2} - 34 \times 10^{-6} \left(\sum \frac{\Delta q_j}{R_{ij}^2} \right)^2$$

where $\Delta \sigma_i$ is the charge induced shift for proton i caused by the
system of charges Δq_j around the proton (all shifts and charges
relative to benzene) X_{ij}, R_{ij} and θ_{ij} are defined in the figure
below.
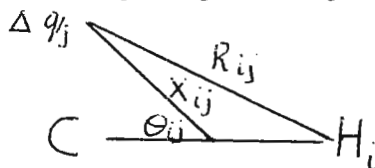
This equation calculated the shifts of 117 protons covering a
range of 4 ppm with a mean deviation of 0.18 ppm. The calcula-
tions were then extended to determine the shifts in several
aromatic carbanions and carbonium ions with moderate success
and also to the estimation of the effect of the alkali metal
cation on carbanion shifts in ion paired systems. Two manu-
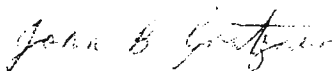scripts covering this work are currently in preparation.

100

CENTENNIAL 1869·1969

We then pressed our luck too far and tried to calculate the shifts for the aromatic dianions recently reported by Lawler[1]. The results were very poor (see Table) with differences of as much as 2.9 ppm between observed and calculated shifts, with the calculated shifts generally being too low. This observation combined with the knowledge that these dianions are $4n\pi$ electron systems suggested the possibility that paramagnetic ring currents might be the cause of the discrepancy. An attempt was made to calculate the ring currents in these systems using the Hall, Hardisson, Jackman[2] SCF method. These calculations yielded the values shown in the table which are obviously far too high, but at least they do show that a paramagnetic current is possible in these ions and that the ring current effects tend to parallel the differences between observed and calculated values. No allowance was made for bond alternation in the calculations and this should serve to diminish the paramagnetic current.[3]

There are obviously many possible conclusions that can be drawn from the results discussed here, our aim has been to present one possible treatment and invite comments from your readers. We are planning to try to measure the magnetic susceptibilities of a couple of these ions to provide some experimental justification for these ideas (possibly even a scaling factor for the calculated values).

Please count this contribution towards Dr. Muller's subscription.
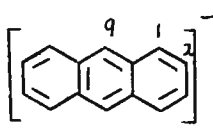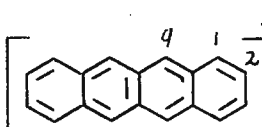
Yours sincerely,

John B. Grutzner

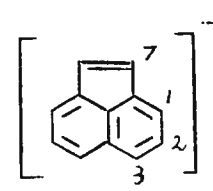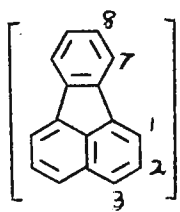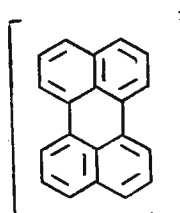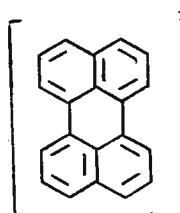John B. Grutzner

JBG:mf

1. R. G. Lawler and C. V. Ristagno, J. Am. Chem. Soc., 91, 1534, (1969).

2. G. G. Hall, A. Hardisson and L. M. Jackman, Tetrahedron, 19 (Supp. 2), 101 (1963).

3. J. A. Pople and K. G. Untch, J. Am. Chem. Soc., 89, 4811 (1967).

	Proton	δ_{obs}^{a}	δ_{calc}^{b}	$\delta_{obs} - \delta_{calc}$	δ_{RC}^{c}	ΔX_{calc}
anthracene dianion·Li⁺	1	3.91	2.25	1.66	-7.15	
	2	3.02	2.24	0.78	-6.07	225.5
	9	5.34	2.43	2.91	-9.20	
tetracene dianion·Na⁺	1	2.81	1.51	1.30	-2.08	
	2	2.62	1.74	0.68	-1.52	100.9
	9	4.27	1.53	2.74	-3.56	
acenaphthylene dianion·Na⁺	1	2.77	2.63	0.14	-0.58	
	2	2.23	2.21	0.02	-0.93	5.3
	3	3.94	2.57	1.37	-0.89	
	7	2.81	3.00	-0.19	+1.84	
fluoranthene dianion·Na⁺	1	2.46	2.12	0.34	-0.43	
	2	2.23	1.81	0.42	-0.96	
	3	4.00	1.90	2.10	-0.96	-18.7
	7	0.38	1.07	-0.69	2.28	
	8	1.21	1.91	-0.70	2.16	
perylene dianion·Na⁺	1	2.28	1.31	0.97		
	2	1.34	1.47	-0.13		
	3	2.40	1.95	0.45		

(a) Reference 1, relative to benzene in ppm.

(b) Using equation in text and VESCF charge densities.

(c) Calculated using procedure in reference 2, the benzene value is 2.35 from these calculations.

DEPARTMENT OF THE AIR FORCE

AIR FORCE MATERIALS LABORATORY (AFSC)

WRIGHT-PATTERSON AIR FORCE BASE. OHIO 45433

REPLY TO
ATTN OF AFML/MAYH/R. E. Rondeau/52280   19 December 1969

SUBJECT Another Modification of LAOCN3-LAOCNP

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

Dear Dr. Shapiro:

Mr. Hughey Rush, who wrote the technical report describing a plotting routine for LAOCOON II (NMRN 108-26), spent his two-week reserve duty tour with me last summer. During that time he streamlined his 75-card subroutine and incorporated it in LAOCN3.

When used with Castellano and Bothner-By's LAOCN3, the output consists of the usual printout followed by a printed stick plot of the calculated spectrum. Also, the line identification numbers are printed along the frequency axis. Therefore, not only can the calculated spectrum be seen at a glance but the calculated line numbers can also be directly transferred to matching experimental frequencies. In the iterative part of LAOCN3, the "best fit" spectrum is also plotted.

Modification of the main program is minimal. Data input format is unchanged. The plotting option is simply punched on the second data card - after the minimum intensity option.

A listing is available upon request.

Sincerely,

Roger E. Rondeau

ROGER E. RONDEAU
Exploratory Studies Branch
Materials Physics Division

STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY 07030

Department of
Chemistry and Chemical Engineering

December 18, 1969

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

Factor Analysis of Solvent Effects in NMR

Dear Prof. Shapiro,

We have been applying Factor Analysis in an attempt to decipher the nature of solvent effects in NMR. Preliminary work on simple substituted methanes, dissolved in a variety of solvents, leads us to believe that only three factors are involved. Since only three factors are required we decided to rotate the resulting vectors from the analysis into three solvent vectors: acetonitrile, carbon tetrachloride and methylene bromide. Resulting equations are listed below:

$$\delta^i_{CH_3CN} = 1.0016f_1 - .0038f_2 + 0.0022f_3$$

$$\delta^i_{CH_2Cl_2} = 0.0806f_1 + 0.7150f_2 + 0.2070f_3$$

$$\delta^i_{CHCl_3} = -0.0458f_1 + 0.8169f_2 + 0.2300f_3$$

$$\delta^i_{CCl_4} = -0.0018f_1 + 1.0041f_2 - 0.0022f_3$$

$$\delta^i_{CS_2} = 0.0064f_1 + 1.1281f_2 - 0.1394f_3$$

$$\delta^i_{CH_2Br_2} = -0.0010f_1 + 0.0090f_2 + 0.9922f_3$$

$$\delta^i_{CH_3I} = 0.5613f_1 - 0.2237f_2 + 0.6527f_3$$

$$\delta^i_{CH_2I_2} = -0.1092f_1 - 1.1972f_2 + 2.2946f_3$$

$$\delta^i_{CHBr_3} = -0.2562f_1 - 1.1972f_2 + 2.2946f_3$$

Prof. Bernard L. Shapiro
Texas A & M University

In these equations $\delta^i_{CH_3CN}$ is the chemical shift of solute i in acetonitrile.

$$f_1 = \delta^i_{CH_3CN} \; , \; f_2 = \delta^i_{CCl_4} \; , \; \text{and} \; f_3 = \delta^i_{CH_2Br_2}$$

The success of this choice is illustrated in Table I attached, which is self-explanatory. Furthermore, with three factors the Factor Analysis scheme allows us to predict gas phase chemical shifts from solution measurements. These results are shown in Table II.

Sincerely yours,

Paul H. Weiner

Edmund R. Malinowski

/jef
Attachment

Table II. Test of Gas Phase Chemical Shifts as a Solute Factor Using three Factors in the Rotation Matrix

Solute	δ_g (predicted)	δ_g (experimental)	diff.
CH_3Cl	168.2	-	-
$CHCl_3$	427.1	427.3	-0.2
CH_3Br	147.1	146.9	0.2
CH_2Br_2	285.5	285.0	0.5
$CHBr_3$	406.8	406.9	-0.1
CH_3I	118.5	119.0	-0.5
CH_2I_2	227.6	-	-
CHI_3	301.5	-	-
CH_2ClBr	297.7	-	-

Table I. Comparison of Calculated and Experimental Chemical Shifts of Substituted Methanes

S O L U T E S

Solvents	CH_4 Exp.	CH_4 Pred.	CH_3CN Exp.	CH_3CN Pred.	CH_2ClCN Exp.	CH_2ClCN Pred.	CH_2Cl_2 Exp.	CH_2Cl_2 Pred.	$CHClBr_2$ Exp.	$CHClBr_2$ Pred.
CH_3CN	12.1	--	117.6	--	256.8	--	326.9	--	449.7	--
CH_2Cl_2	12.1	13.7	118.0	119.4	248.2	247.5	319.8	319.5	434.5	434.0
$CHCl_3$	12.7	13.8	120.0	118.8	246.1	245.7	317.4	317.9	432.1	431.0
CCl_4	13.8	--	17.4	--	244.2	--	317.1	--	430.2	--
CS_2	13.3	13.6	114.8	116.1	242.8	241.9	313.9	315.0	427.9	427.5
CH_2Br_2	13.8	--	122.7	--	252.3	--	321.2	--	435.4	--
$CHBr_3$	15.2	14.3	127.3	124.6	253.0	252.3	321.8	320.9	433.0	433.3
CH_3I	12.9	12.7	122.9	119.8	255.3	254.2	322.5	322.2	439.6	440.4
CHI_2	15.1	13.8	128.8	128.1	257.3	258.5	323.5	321.7	434.9	434.9
Exp. Range of Data	3.0		14.0		15.0		13.0		21.8	
Aver. Error		0.9		1.7		0.7		0.8		0.5

Institut für Physikalische Chemie   51   Aachen, den 3.12.69
der Rheinisch-Westfälischen
Technischen Hochschule   Templergraben 59
                                   Fernruf 422/2770
                                   Telex   832 704

1. Mitteilung

zum 7. Kolloquium über Kernresonanz-Spektroskopie in
Aachen

In der Zeit vom 13. bis 17.4.1970 findet im Institut für
Physikalische Chemie der Rheinisch-Westfälischen Techni-
schen Hochschule das 7. Kolloquium über Kernresonanz-
Spektroskopie statt.

Hauptthema des Kolloquiums:

     "Kernresonanz-Spektroskopie an natürlichen und
      synthetischen Hochpolymeren".

Eine vorläufige Vortragsübersicht liegt bei.

Interessenten wollen sich bis zum 15. Januar 1970 auf
beiliegendem Formblatt vorläufig anmelden.

Die Teilnehmergebühr beträgt DM 60,-.

Für Studenten, Diplomanden und Doktoranden, die keine
planmäßigen Assistenten sind, beträgt die Teilnehmerge-
bühr DM 10,-.

Das endgültige Programm wird allen Teilnehmern Mitte
Februar 1970 zugesandt.

(R. Kosfeld)

2 Anlagen
——————————

Vortragsübersicht
Anmeldeformular

Vortragsübersicht

Dr. K. Bergmann
Ludwigshafen

Untersuchung von Beweglichkeiten
in Polymeren durch NMR

Dr. F.A. Bovey
Murray Hill (USA)

High Resolution NMR of Polymers

Prof. Dr. Cantow
Freiburg

Kettenstruktur und Kinetik der
Polymerisation, untersucht durch
NMR

Prof. Dr. H. Fischer
Zürich, Schweiz

ESR-Untersuchungen an Hochpoly-
meren

Prof. Dr. E. Forslind
Stockholm

NMR-Untersuchungen an Zellulose

B. Groß
Aachen

Spin-Echo-Untersuchungen an
Polymeren

Dr. J. Guillot und
Dr. Pham Quang Tho
Villeurbanne, Frankreich

Sequenzlängenverteilung in
Copolymeren

Prof. Dr. H.J. Harwood
Akron (USA)

Problems Concerning Copolymer
Structure

Prof. Dr. W. Holzmüller
Leipzig

Neuere Ergebnisse auf dem Gebiet
der Platzwechseltheorie

Dr. E. Klesper
Zürich, Schweiz

Sequenzlängenverteilungen,
untersucht durch NMR

Dr. R. Kosfeld
Aachen

Relaxationserscheinungen und
Linienbreitenphänomene bei NMR-
Spektren

Prof. Dr. P. Laslo
Princeton (USA)

Solvent Effects in High-Resolu-
tion NMR

Dr. W.D. Phillips
Wilmington

NMR-Studies in Biopolymers

Prof. T. Shimanouchi
Tokio, Japan

Conformations fo Polymers as
revealed by Infrared Spectroscopy

Prof. W.P. Slichter
Murray Hill (USA)

NMR-Studies of Solid Polymers

Name (nicht ausfüllen)	Eingangsdatum	Nr.

Vorläufige Anmeldung zur Teilnahme am 7. Kolloquium über Kernresonanz-Spektroskopie (Aachen, 13. bis 17. April 1970)

Ich werde voraussichtlich am 7. Kolloquium über Kernresonanzspektroskopie teilnehmen:

Name, Vorname: _____

Titel: _____

Institut/Firma: _____

Adresse: _____

_____

Ich werde ein/kein Quartier benötigen.

Ich bitte weitere Anmeldeformulare zu senden an: _____

_____

Datum:

(Unterschrift)

Glaxo

Glaxo Research Ltd, Greenford, Middlesex

Telephone: 01-422 3434
Telegrams: Glaxotha, London
Telex: 22134
Code: New Standard, Bentleys

Please address reply to: Dr. J.E. Page

12th December, 1969.

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

Dear Professor Shapiro,

Trifluoroacetic acid as low-field lock for
routine HA-100 proton spectra and
2,5-dichlorothiophene for wide-temperature
range locks

For routine HA-100 proton spectra that need to be
recorded under standard operating conditions, we prefer
to lock on the low-field carboxyl proton signal of
trifluoroacetic acid (TFA) instead of the high-field
signal of TMS. The TFA is dried by addition of 10% of
TFA anhydride and sealed in a capillary tube; the drier
the sample, the further down-field is the lock. The lock
is, depending on solvent, between 1090 ($CDCl_3$) and 1250 Hz
(C_5D_5N) below TMS in the solution in which the capillary is
immersed; a full 1000 Hz sweep is thus practicable. A
saturated solution of trichloroacetic acid in TFA anhydride
gives a slightly lower down-field lock, permitting a 1100 Hz
sweep, which is useful for observing low-field NH groups; the
lock is, however, weaker and more oscillator power is needed.

In setting up the HA-100 spectrometer for a day's work, we
use a sealed sample tube containing TFA, a little TMS and
sufficient acetone to give three peaks of roughly equal height
on the oscilloscope using HR mode. When locked on TFA , the
acetone peak is useful for checking inter alia line-shape and
sensitivity. Lock-transference either to a working sample or
between samples fitted with sealed TFA capillaries is immediate,
allowing only for probe-leakage nulling.

The great advantage of the TFA method is that for
measurements on solutions in normal deuterated or proton-free
solvents, the same routine procedure can be used to "lock"
the instrument. Each solution, as in A-60 operation, contains
only a trace of the relevant reference compound. Solutions in

Contd./

proteopyridine (not deutero) are locked on the lowest-field band of pyridine, the TFA capillary signal being too close to that of pyridine to be satisfactory; rather surprisingly, good resolution is obtained. For measurements on TFA solutions, sealed TFA capillaries are unnecessary and are in fact undesirable; the instrument can "jump lock" between the signals due to the sealed and to the inevitably damper unsealed TFA solutions.
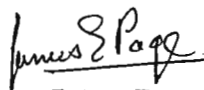
A few Hz drift, relative to the recorder chart, occurs until the sample and TFA capillary have attained probe temperature. Nevertheless, by the time normal instrumental adjustments have been made, stability is usually adequate.

In order to zero on TMS or its equivalent, the manual oscillator frequency must be adjusted to between about 3590 Hz (CDCl$_3$) and 3750 Hz (C$_5$D$_5$N). This range is not attained by the built-in manual oscillator, but we have extended the range of our spectrometer by modifying it to permit the substitution of an external oscillator (cf. R.J. Goodfellow, IIT NMR Newsletter, 1967, 101, 52). The oscillator of our machine may be switched either through an attenuator to the V4354A or coupled to the probe, via a transformer, for precise impedance matching when spin-decoupling. When the V4354A is modified in this way, the manual oscillator level switch, S1303, and the signal monitor switch are in circuit with the external oscillator, the output of which is adjusted to give 1 v. peak-to-peak on the oscilloscope; S1303 is then operated normally. To avoid loss of lock, it is expedient to work in the field-sweep mode; this allows for large changes in the external oscillator frequency. In spin-decoupling, using frequency sweep, the range of the built-in manual oscillator is sufficient to set on the chart almost any band upfield of the lock; zeroing on TMS is unnecessary and the external oscillator is free for double-irradiation.
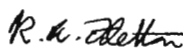
The precision coaxial capillary tubes supplied by the Wilmad Glass Co. (Cat. No. 520) are suitable for holding the TFA mixture. They fit inside Varian sample tubes, but unfortunately each capillary is only 7" long and so does not project beyond the open end of the sample tube. 8" Capillaries, which were specially supplied by the Wilmad Glass Co., proved to be more satisfactory. Spinning side-bands are sometimes (particularly for D$_2$O spectra) troublesome. However, fast spinning is possible, since the capillaries damp vortex formation.

With reference to Drs. H. Maltz and D.J. Sardella's suggestion (TAMU NMR Newsletter, 1969, 127, 2) to use t-butylbenzene for wide temperature range locks (-58° to + 169°), we wish to mention that we have used 2,5-dichloro--thiophene (-40° to +161°); it gives a signal at about 𝜏3.3, which does not obscure the high-field region.

Yours sincerely,

J.E. Page   R.A. Fletton   G.F.H. Green

Eidg. Technische Hochschule
Laboratorium
für Physikalische Chemie
Zürich

ZÜRICH,
Universitätstrasse
Tel. (051) 32 73 30

December 17, 1969

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

ANOTHER APPLICATION OF NOISE IN NMR: "NOISE RESONANCE"

Dear Barry,

Is it possible to improve Fourier transform spectroscopy or is
it the optimum method with respect to sensitivity? - There is
one possibility which has some advantage compared with conven-
tional Fourier spectroscopy. Particularly, it is able to produce
a better sensitivity for the same resolution, in principle. We
like to call it "Noise Resonance" or "Stochastic Resonance".

In noise resonance, the sample is excited with random noise.
The response of the spin system will again be noise (wanted noise
+ unwanted noise) and the crosscorrelation function between the
input noise and the output noise just gives the Fourier transform
of the conventional absorption mode spectrum. In contrast to
noise decoupling, it is no double resonance experiment, no de-
coupling occurs under appropriate conditions. With its broad-
band excitation of resonance it is completely analogous to Fourier
spectroscopy. The instrumental requirements are obvious, a means
to generate and modulate noise onto an rf carrier and a means to
crosscorrelate and Fourier-transform the data. Both problems are
easily solved with a computer (Varian 620i) which generates a
binary random sequence for excitation of the sample.

What is the real advantage of this method? In Fourier spectroscopy,
the resolution requirements demand a long interval between pulses,
but best sensitivity is achieved with closely spaced pulses. This

discrepancy does not exist in noise resonance. It produces a
sensitivity equal to the optimum achievable one with conventi-
onal Fourier spectroscopy but without deterioration of resolu-
tion. There are some further advantages with respect to power
consumption.

An actual spectrometer output of noise and its Fourier transform
are shown in the attached figure. Here, not the crosscorrelation
function was computed but simply the power spectrum of the
spectrometer output, which is equivalent to $(v^2 + u^2)^{1/2}$, is
plotted. Some of the basic ideas of this experiment are due to
Wes Anderson.

Sincerely yours,

Richard

Richard R. Ernst

STOCHASTISCHE RESPONSE VON $(CH_3CH_2)O$

SPEKTRUM
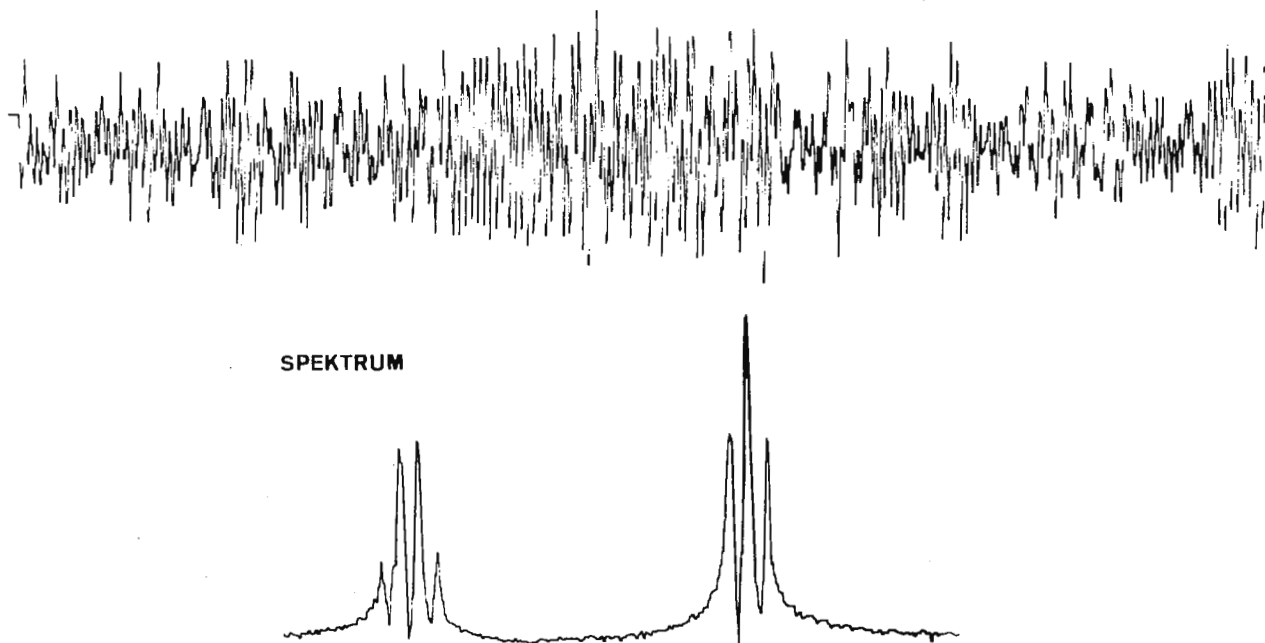
# CHEMICAL CENTER

PHYSICAL CHEMISTRY 2

Lund, December 18, 1969

KID/AiL

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

Internal rotations in an enamine: large positive entropies of
activation

Dear Professor Shapiro:

In the course of our investigations of hindered internal rota-
tion in enamines, we have studied the following compound (I),
which at room temperature was found
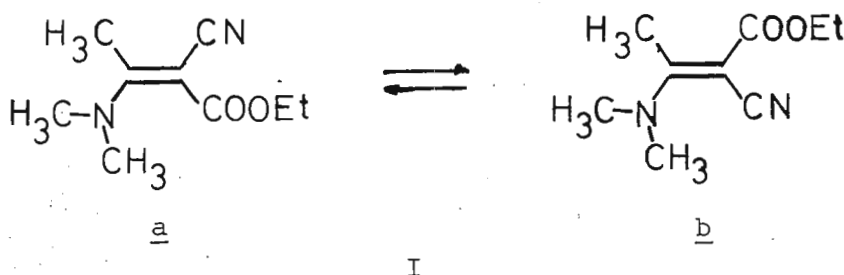
to undergo a rapid equilibration between the isomers a and b.
From a complete lineshape analysis of the dimethylamino proton
spectrum (Fig. 1) it was possible to evaluate the activation
parameters for the hindered rotations around the $N-C$ bonds in
the two isomers, as well as the corresponding data for the
isomerization around the $C=C$ bond. A virtually temperature-
independent isomer ratio (a/b or b/a) of 1.30 was observed.
One can see from the Table below that the activation parameters
for the rotations around the $N-C$ and $C=C$ bonds are of the
same order of magnitude, which indicates a significant delocali-
zation of the π-electrons.

/cont./

THE LUND INSTITUTE OF TECHNOLOGY

Rotation	$\Delta H^{\ddagger}$ kcal/mole	$\Delta F^{\ddagger}$ $298°K$ kcal/mole	$\Delta S^{\ddagger}$ e.u.
N – C [a)]	14.88±0.21	10.75±0.35	13.9±2.0
N – C [a)]	15.36±0.28	12.99±0.43	8.2±2.4
C = C [a)]	13.78±0.14	14.82±0.21	-3.5±1.2
C = C [b)]	14.10±0.17	14.73±0.25	-2.1±1.4

The error limits given in the Table were calculated assuming only random errors.

a) Evaluated from the spectrum of the diemthylamino protons.
b) Evaluated from the spectrum of the $C=C-CH_3$ protons.

The observation of large positive entropies of activation for the N-C rotations (also found for other enamines[1,2]) was at first sight quite a surprise, especially in view of the slightly negative value found for the C=C rotation and the fact that $\Delta S^{\ddagger}$ values close to zero are obtained for simple amides[3,4]. However, since the rate data for the three internal rotations have all been evaluated from the exchange broadening of the $N-CH_3$ signals, we believe that the observed differences in $\Delta S^{\ddagger}$ are significant. Furthermore, since it is sometimes assumed that $\Delta S^{\ddagger}$ for internal rotation should be zero[5], comments on possible sources of our large positive entropies of activation are welcome.

Sincerely yours,

Kjell-Ivar Dahlqvist

References

1. K.-I. Dahlqvist and S. Forsén, Acta Chem. Scand. In press.
2. K.-I. Dahlqvist, S. Forsén and M. Nilsson. To be published.
3. P.T. Inglefield, E. Krakower, L.W. Reeves and R. Stewart. Molec. Phys. _15_ 65 (1968).
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5. G. Binsch, In E.L. Eliel and N.L. Allinger (Eds.) Topics in Stereochemistry, Interscience, New York 1968, Vol. 3, p. 97.
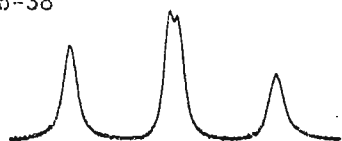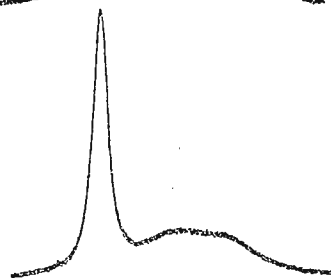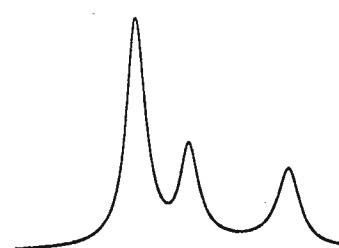
$T_1 = 1.00 \cdot 10^2$ sec.
$T_2 = 1.00 \cdot 10^2$ sec.
$T_3 = 1.00 \cdot 10^2$ sec.
$t = -65.0$ °C
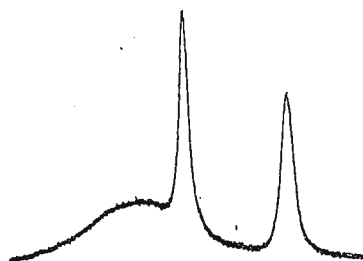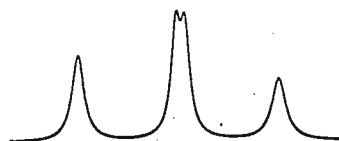
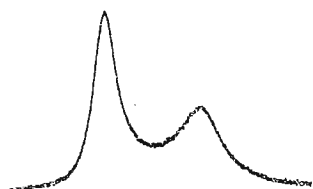$T_1 = 2.50 \cdot 10^{-2}$ sec.
$T_2 = 1.65$ sec.
$T_3 = 1.76 \cdot 10^1$ sec.
$t = -42.7$ °C
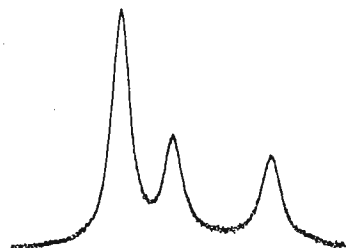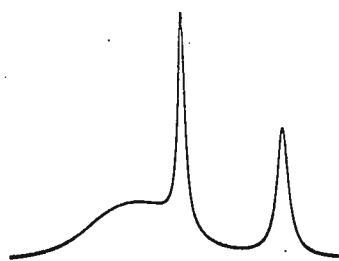
$T_1 = 2.60 \cdot 10^{-3}$ sec.
$T_2 = 1.65 \cdot 10^{-1}$ sec.
$T_3 = 2.27$ sec.
$t = -27.2$ °C

$T_1 = 5.60 \cdot 10^{-4}$ sec.
$T_2 = 3.20 \cdot 10^{-2}$ sec.
$T_3 = 4.82 \cdot 10^{-1}$ sec.
$t = -14.9$ °C
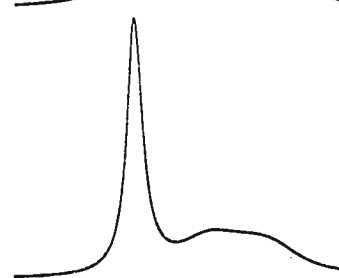
$T_1 = 1.43 \cdot 10^{-4}$ sec.
$T_2 = 8.00 \cdot 10^{-3}$ sec.
$T_3 = 1.30 \cdot 10^{-1}$ sec.
$t = -2.1$ °C
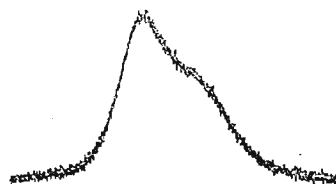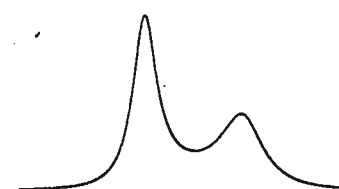
$T_1 = 4.10 \cdot 10^{-5}$ sec.
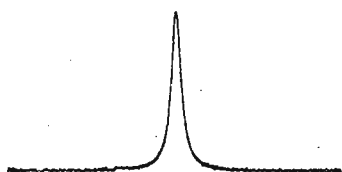$T_2 = 2.10 \cdot 10^{-3}$ sec.
$T_3 = 4.38 \cdot 10^{-2}$ sec.
$t = +10.3$ °C

$T = 1.00 \cdot 10^{-6}$ sec.
$T = 1.00 \cdot 10^{-6}$ sec.
$T = 1.00 \cdot 10^{-6}$ sec.
$t = +47.1$ °C

UNIVERSITY OF MARYLAND

COLLEGE PARK, MARYLAND 20742

DEPARTMENT OF CHEMISTRY

30 December 1969

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

Wide-band Audio Frequency
Phase-Shifter; Postdoc Position

Dear Dr. Shapiro,

The use of a synchro resolver to shift the phase of audio frequencies is certainly not new to NMR (Noggle, Rev. Sci. Instr. 35, 1166 (1964), Gutowsky et al, Rev. Sci. Instr. 39, 805 (1968)) but neither of the resolvers used seems generally available. We have used a Kearfott R931-43E (available from American Relays Electronics Division, 39 Lispenard Street, New York, N.Y. 10013 for $21.50) for phase-shifting over a wide frequency range. We found that tuning the output portion of the resolver was sufficient to keep the output voltage reasonably constant with change in frequency. The frequencies at which no change in amplitude occurs with phase shift are shown along with the nominal values of the tuning capacitance. For other frequencies in the range indicated, there is of course some change in amplitude as the phase is shifted, but it is tolerable for our purpose which is providing a drive for the X-axis of a scope.

We have funds for a postdoctoral appointment to work on the NMR of solids starting as soon as possible and I would be interested in hearing from anyone who is interested.

Sincerely yours,

Gerald Ray Miller
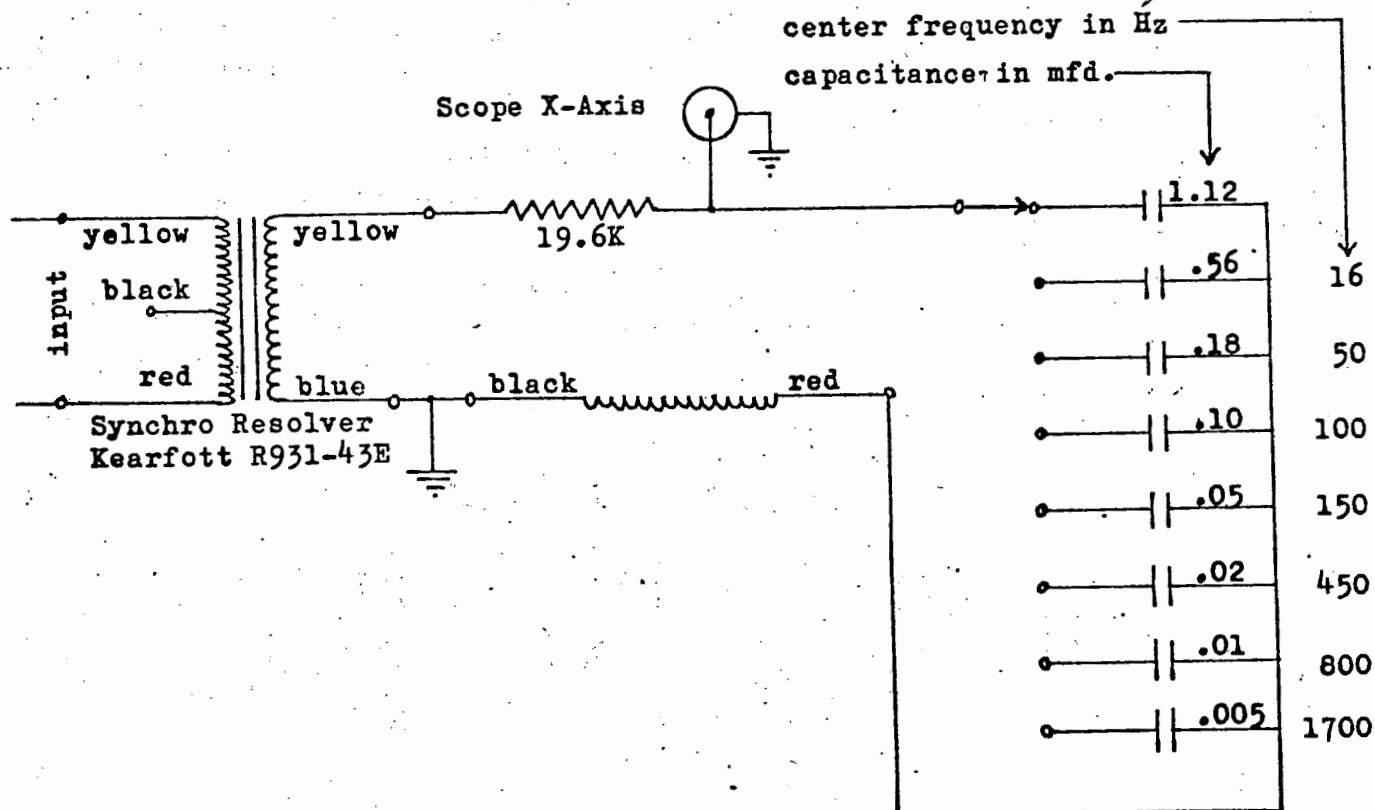
Dr.Horst Kessler
Chemisches Institut der Universität
D 74 Tübingen
Wilhelmstrasse 33

December 21, 1969

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

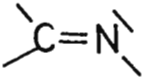Steric Effect on Isomerisation of C-N and C-S Double Bonds
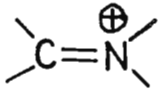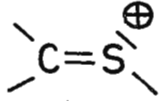
Dear Dr. Shapiro,

Large groups in ortho position of N-aryl-imines (for instance in
N-aryl-guanidines I) cause an increasing rate of isomerisation (1).
This is a proof of the inversion mechanism ("lateral shift" mechanism)
on the imino nitrogen, in which a linear transition state is
involved (the hybridisation of the nitrogen atom changes from sp^2 to
sp). A rotation about double bonds should be hindered by large
groups in ortho position. Therefore we synthesized the pentamethyl-
aryl-guanidinium salts II in which no inversion is possible because
there is no lone electron pair. The variable temperature NMR spectra
of these compounds show hindered rotations about the three CN bonds
a,b and c. The free enthalpies of activation $\Delta G_c^{\ddagger}$ of the rotation
about the partial CN-double bond c were calculated at the coalescence
temperature in the usual manner. The bond c is in β position to the
aromatic ring as it is the corresponding CN double bond in the guani-
dines I. The $\Delta G_c^{\ddagger}$-values of II increase with increasing size of R as
it is expected for the rotation case (table).
The low temperature spectra of the thiuronium salts III show four
signals for the N-methyl-groups: the rotation about both CN bonds
and the isomerisation on the CS partial double bond has to be "slow".

I   II   III   IV
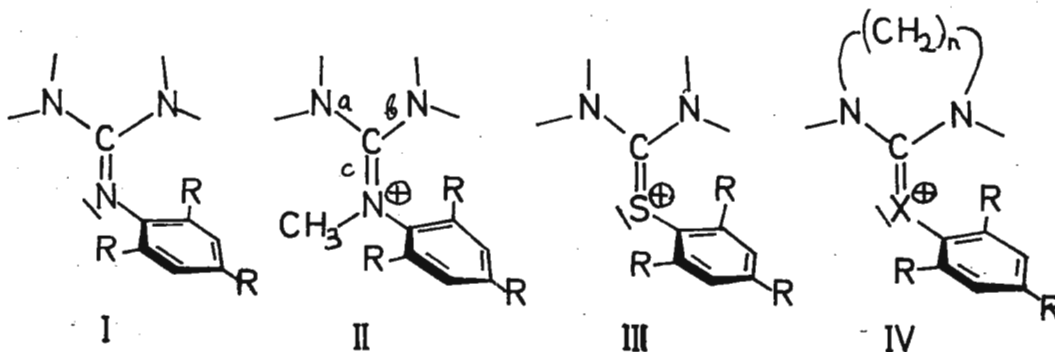
At room temperature a singlet for these signals is observed. The calculated free enthalpies of the CS bond isomerisation are shown in the table.

Table: Steric effect on isomerisation of CN and CS double bonds[a]
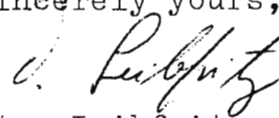
bond	$\diagdown C = N \diagdown$		$\diagdown C = \overset{\oplus}{N} \diagup$		$\diagdown C = \overset{\oplus}{S} \diagdown$	
mechanism	inversion		rotation		rotation	
compound	I		II		III	
R	T_c	$\Delta G_c^{\neq}$	T_c	$\Delta G_c^{\neq}$	T_c	$\Delta G_c^{\neq}$
H	-35	12.1	29	15.0	-83	9
CH_3	-24	12.6	147	21.1	-64	10
C_2H_5	-37	11.9	180	22.9		
$i-C_3H_7$	-47	11.4	>200	>24	-29	12

a) T_c = temperature of coalescence [in $^{\circ}C$]; $\Delta G_c^{\neq}$ free enthalpy of activation at the coalescence point [in kcal/mole].

The increasing values of $\Delta G_c^{\neq}$ with increasing size of R is an argument against the atom inversion of the sulfur and gives evidence for the <u>rotation</u> mechanism in the sulfur compounds III. The observed effect is smaller than in II as it can exspected by going from the larger sulfur atom to the smaller nitrogen atom.

Our results on the corresponding oxygen compounds (uronium salts) are in progress. More complete datas will be obtained by studying the cyclic compounds IV (X= N,S,O).

Sincerely yours,

H. Kessler

Horst Kessler

D. Leibfritz

Dieter Leibfritz

References

(1) H.Kessler, Angew.Chem.<u>79</u>, 997 (1967) Internat.Ed. 977;
    H.Kessler and D.Leibfritz, Tetrahedron in press

IMPERIAL CHEMICAL INDUSTRIES LIMITED

NOBEL DIVISION | Telephone: Stevenston 2140

Research Department | Telex: 77370

Nobel House, Stevenston, Ayrshire |

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

Your ref:

Our ref: JSG/CG

Date: 22nd December, 196?.

Dear Professor Shapiro

Restricted Rotation in Certain Silanes

We have recently been examining some monosubstituted methyl silanes on the Perkin-Elmer R10 instrument. Working with the normal scale-factor of 6 cycles/division we found a splitting of the methyl peak with allyltrimethyl silane (Fig. 1) which, on expansion of the scale twelvefold (scale factor $\frac{1}{2}$ cycle/division), we were able to show, by integration, that the three CH_3 groups are not equivalent, one being in a different environment to the other two.

This prompted us to make up a Stewart model of the molecule and it was immediately obvious that the 'bent' nature of the allyl group prevents free rotation about the CH_2-Si bond. Two of the CH_3 groups flank the $CH=CH_2$ group, the third being spatially distant from the allyl group.

This suggested that other silanes should show a similar effect and acetoxyltrimethyl silane (Fig. 2) does indeed show a much wider splitting of the methyl absorption, again in the ratio of 2:1.

There does seem to be an anomaly here though; we would have expected that proximity to the allyl or acetoxy group would have brought the signal due to the adjacent two CH_3 groups further downfield that the single CH_3 absorption whereas the reverse is the case. We are still working on this problem and hope to publish some of our results shortly.

Yours sincerely,

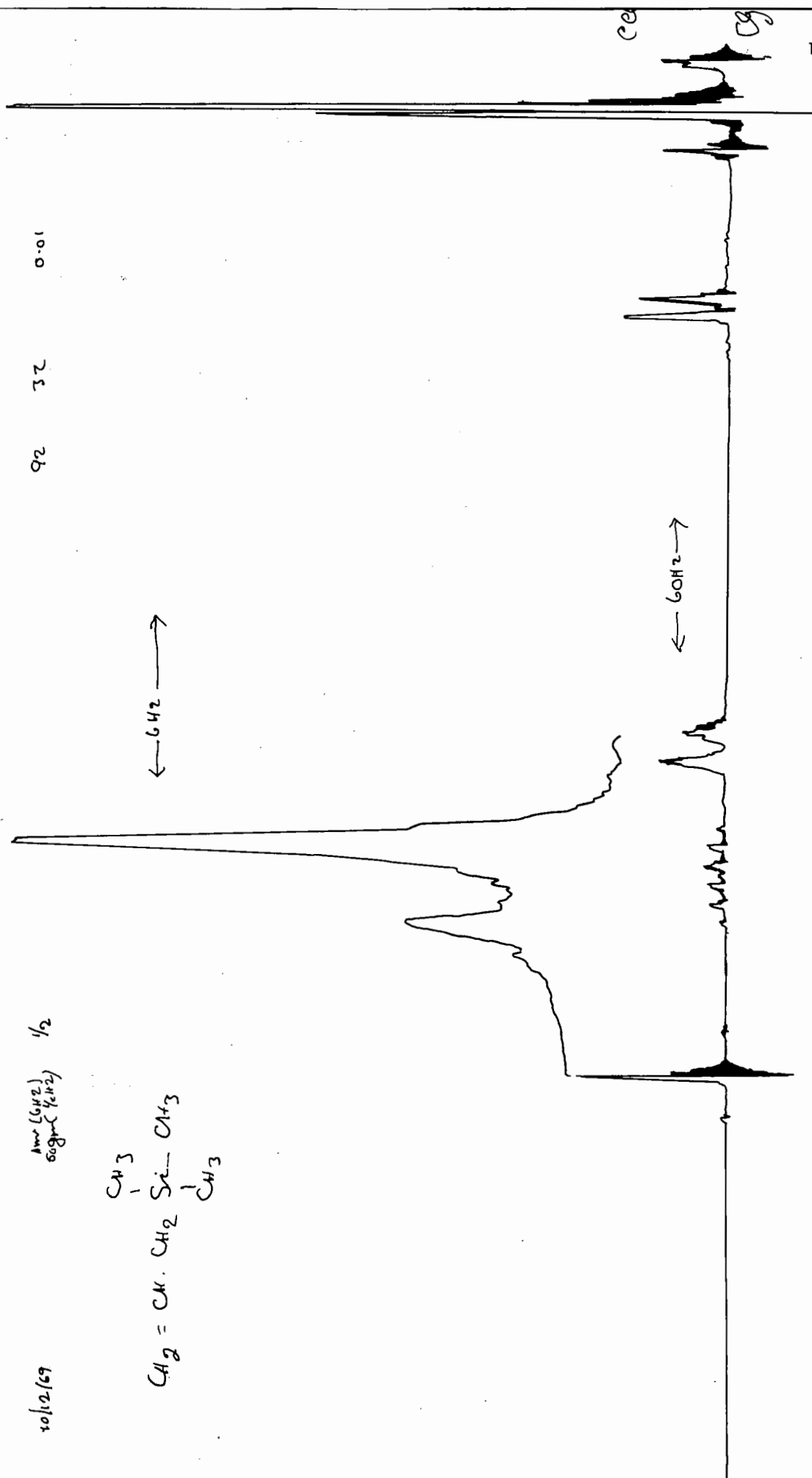10/2/69
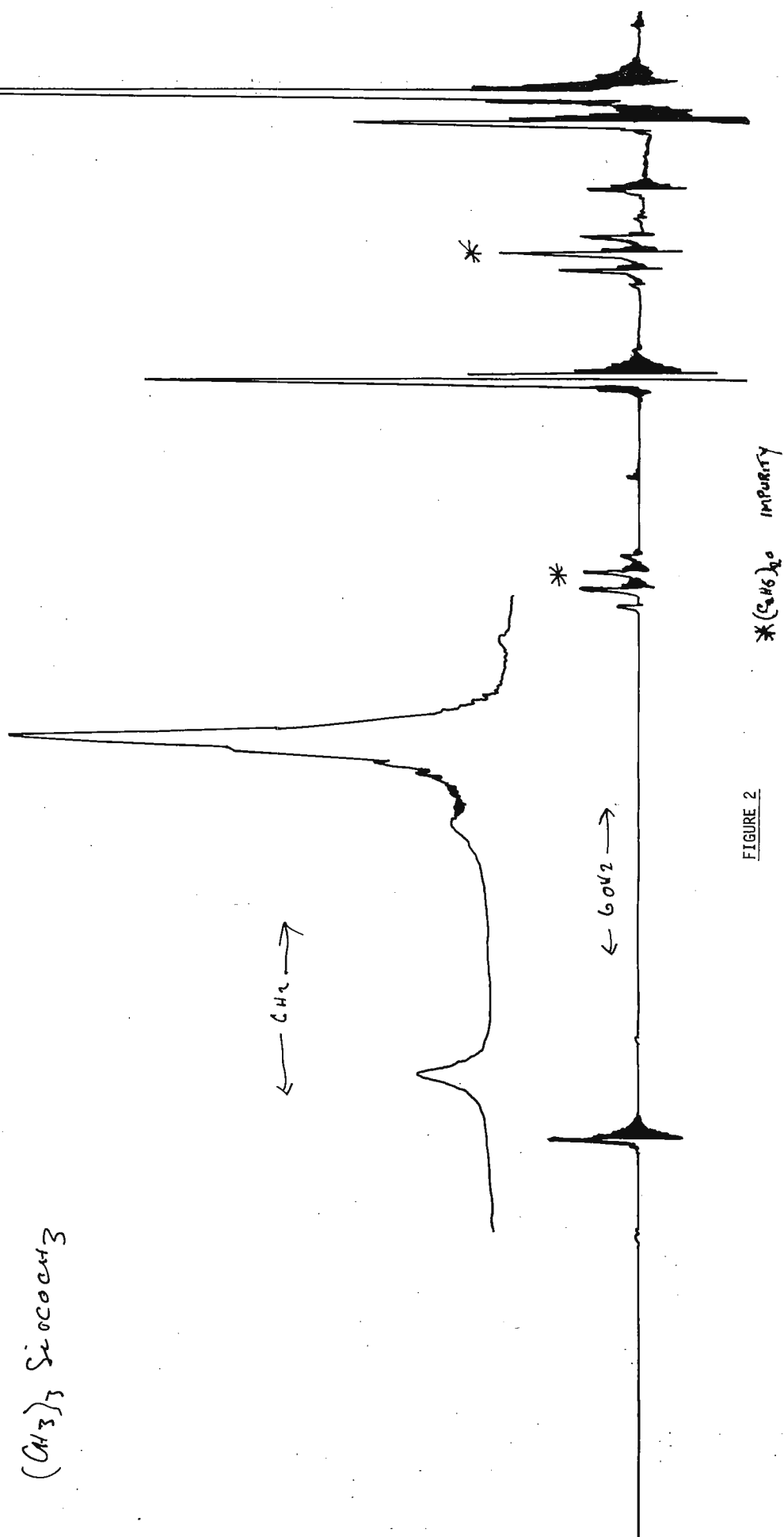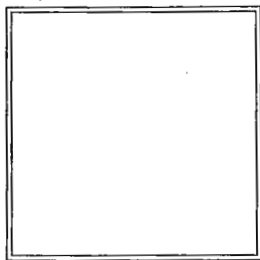
$CH_2 = CH \cdot CH_2 \, Si - CH_3$
with CH_3 and CH_3

$\frac{\int\!\!\sim (6Hz)}{60gr\!\sim (\frac{1}{4}CH_2)}$ $\frac{1}{2}$

92   72   0.01

← 6Hz →

← 60Hz →

FIGURE 1

$(CH_3)_3 Si OCOCH_3$

FIGURE 2

$*(C_4H_6)_{2o}$ IMPURITY

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

December 30, 1969

Professor Bernard L. Shapiro
Texas A&M University
Department of Chemistry
College Station, Texas 77840

Dear Barry:

Computer Time-Averaged ^{13}C-Indor

We have been using ^{13}C Indor for some time in our studies of stable
carbonium ions at low temperatures (in cases as low as -150°).
Time-averaging has proved to be a helpful and time-saving technique.
Many of the systems we studied were obtained in concentrations too
low to observe either the ^{13}C-H satellites or the one percent ^{12}C-H
main peak enhancement upon satellite decoupling. Our general setup
is a Varian HA-100 spectrometer and a Monsanto Model 3100A Frequency
Synthesizer. The C-1024 time-averaging computer is hooked up to the
HA-100 in the usual way, except the voltage ramp is used to drive the
frequency synthesizer giving, in our case, sweep ranges in the 25.1 MHz
region. The C-1024 is internally triggered for the desired number of
passes.

We have succeeded in obtaining ^{13}C-Indor spectra from "invisible"
satellites as also described recently in TAMU-NMR NEWSLETTER #135
by Dr. Dreeskamp. The method is also advantageous in observing
^{12}C-H peak enhancement. Rapid sweeping of the 25.1 MHz region
(150 Hz/sec) gives satisfactory results. This is especially important
where unstable species are being observed, but also results in sub-
stantial time-saving as a general method. Maintaining homogeneity
for long periods of time at low temperatures is difficult, but neces-
sary in observing main peak enhancement. Time-averaging rapid sweeps
enables one to stop at frequent intervals, observe what has been
compiled in the CAT, remaximize the homogenity, and continue with
no loss of information.

Best regards,

Yours sincerely,

Richard D. Porter

George A. Olah

Professor G. A. Olah
Department of Chemistry
Area Code 216 · 368-3623

STANFORD UNIVERSITY
STANFORD, CALIFORNIA

DEPARTMENT OF CHEMISTRY

31 December 1969

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

Re: Relaxing with an HA-100

Dear Barry:

In our laboratory we have been measuring proton
NMR relaxation times by a $T_{1\rho}$ method. The technique
was described by Solomon[1] and Meiboom[2], and recently
Sykes[3-5] has successfully employed this method for
the study of the rates of exchange of inhibitors from
enzymes. Sykes' experiments were performed with Varian
HR-100 and HR-60 spectrometers.

The technique involves adiabatic rapid passage
into the center of a (dispersion mode) resonance. This
aligns the magnetization along the rf field, H_1, and
the magnetization relaxes along H_1 with a time constant,
$T_{1\rho}$. $T_{1\rho}$ equals T_2 under appropriate conditions. In
addition, Sykes has shown that T_1 may be obtained from
the variation of the amplitude of the response as a
function of the time spent off resonance. The method
is quite sensitive, relatively simple, and particularly
useful for obtaining relaxation times of individual res-
onances in reasonably complex spectra.

However, the method requires that the sweep be
exactly into the center of resonance and with the HR
instruments the adjustments for drift can become tedious.
The logical alternative is to use a field-frequency
locked instrument. The problem here is that the dis-
persion mode must be used for the measurements. With

Professor Bernard L. Shapiro   -2-
31 December 1969

our Varian HA-100 this requires a phase shift in the
analytical signal section since in its usual config-
uration the spectrometer puts out only an absorption
mode signal. We modified our instrument by simply
replacing card 910872 with card 911636 in the "lock
box".

To do the adiabatic sweep we use a voltage con-
trolled oscillator (MF Electronics, 118 E. 25th St.,
N.Y., model no. 301-2501-10-1001) in place of the sweep
oscillator of the HA-100.[6] Fig. 1 shows a schematic of
the input to the voltage controlled oscillator. The
output of the voltage controlled oscillator is plugged
into J1307 (sweep osc. out) of the lock box. In addi-
tion, card 910868 in the lock box must be pulled.

The pots are adjusted so that the spectrometer
sits close to resonance. The 10K pot is then adjusted
so that when switch 1 is closed the spectrometer goes
off resonance 50-100 Hz. The switch is opened and the
40K pot is again adjusted to bring the spectrometer close
to the center of resonance and the trimmer pot (2K) is
used to place the spectrometer exactly on resonance.
Switch 2 allows one to choose the direction of the jump
off resonance to avoid the problem of sweeping through
a nearby resonance. Closing switch 1 puts the spectro-
meter off resonance and opening it makes the oscillator
sweep adiabatically back into resonance with a time
constant determined by the RC circuit. This time con-
stant is usually about 0.05 - 0.1 sec. The output of
the spectrometer is recorded on a fast response recorder.
No filtering is used. We have found that best results
are obtained when the lock signal lies far away from
the signal of interest.

T_1 is obtained by progressively varying the time
off resonance $t \gg T_1$, then a plot of $\ln(A_\infty - A_t)$ vs.
t has slope T_1.*

Professor Bernard L. Shapiro   -3-
31 December 1969

   A prime advantage of $T_{1\rho}$ with a field-frequency
locked system is the possibility of time averaging the
signal. To this end, we have constructed a rather
pedestrian, but effective switching set-up. A syn-
chronous motor, appropriately geared down, drives a
wheel to whose face is bolted a lucite disc. The disc
is programmed with notches along the edge. Micro-
switches for starting the C-1024 sweep and for switch-
ing on and off resonance are poised so that they are
activated by the notches as the wheel rotates. The
CAT is run in the ext. trig. mode and its sweep is
started by a momentary short to the ext. trig. jack
through one of the micro-switches. The other micro-
switch replaces switch 1 of Fig. 1. Programs for
either T_2 or T_1 or both are easily constructed from
the lucite. The period of rotation is variable in
our set-up so that a wide range of relaxation times
can be accommodated. Fig. 2 shows a single absorption
mode scan of 0.005 M sodium succinate in D_2O and also
the $T_{1\rho}$ decay obtained from 9 accumulations in the CAT.

   We hope this communication may prove useful to
TAMUNMR newsletter readers and that it will get us off
the hook until the next pink letter day.

                              Yours sincerely,

                    Paul G. Schmidt   Thomas R. Krugh

PGS:TRK:mc

Professor Bernard L. Shapiro   -4-
31 December 1969

* We have learned that Dr. Brian Sykes has designed a
set-up similar to the one we describe here for obtain-
ing $T_{1\rho}$ and T_1. In a paper describing the set-up, he
discusses in detail the requirements for adiabatic
sweep with regard to rf power levels, sweep rates and
relaxation times. The paper should appear shortly in
Rev. Sci. Instruments.

1.   I. Solomon, Compt. Rend., 248, 92 (1959)

2.   S. Meiboom, J. Chem. Phys., 34, 375 (1961)

3.   B. D. Sykes, J. Am. Chem. Soc., 91, 949 (1969)

4.   B. D. Sykes, Biochem., 8, 1110 (1969)

5.   B. D. Sykes and C. Parravano, J. Biol. Chem., 244,
     3900 (1969)

6.   D. J. Matter, G. D. Norman, and J. J. Katz, IITNMR
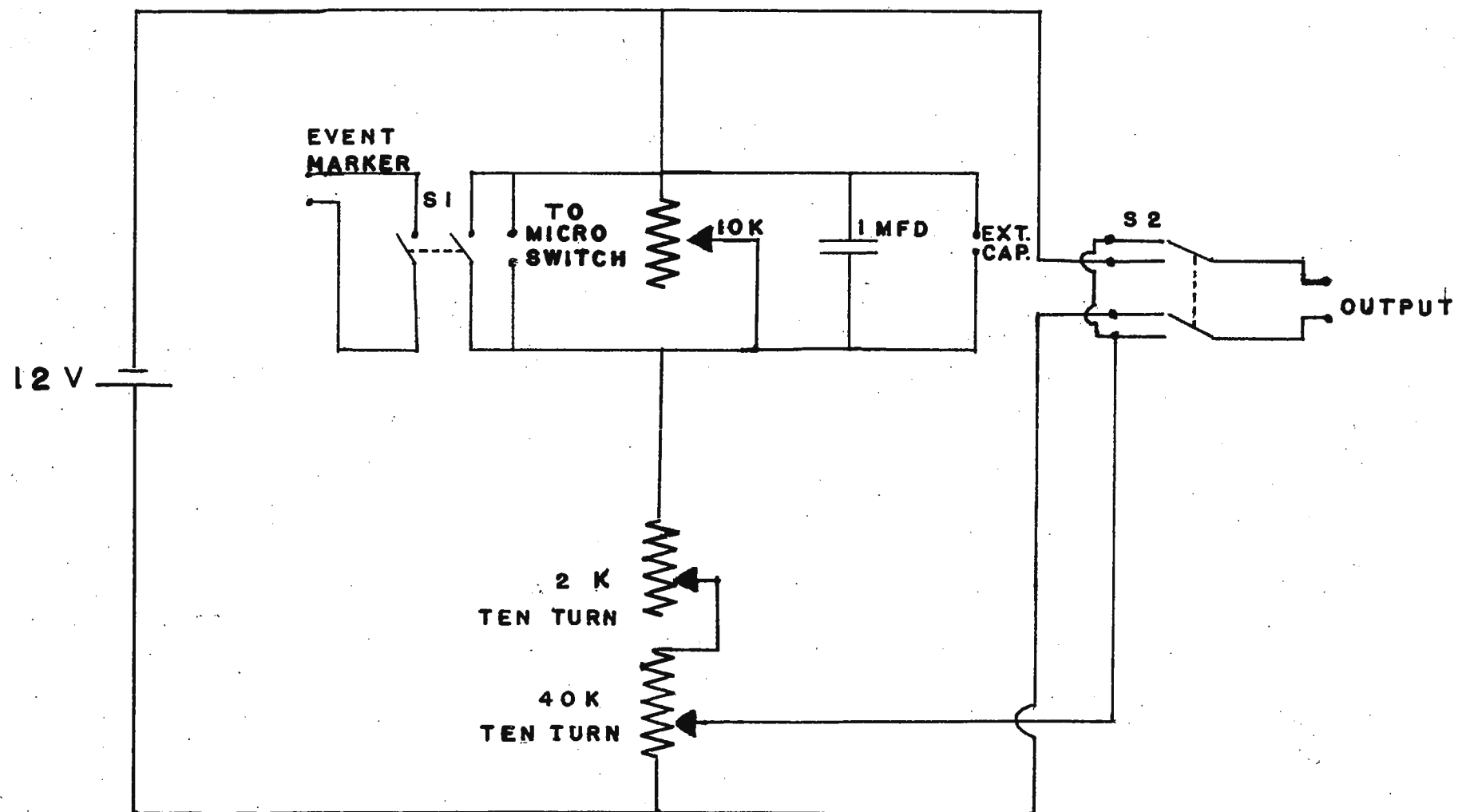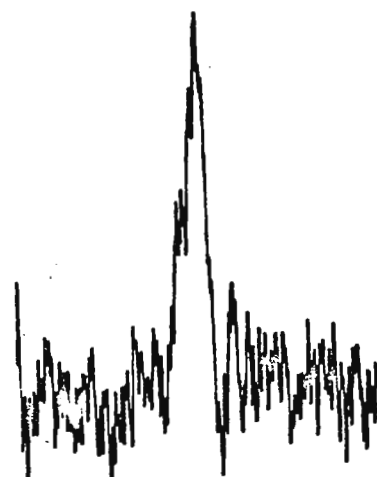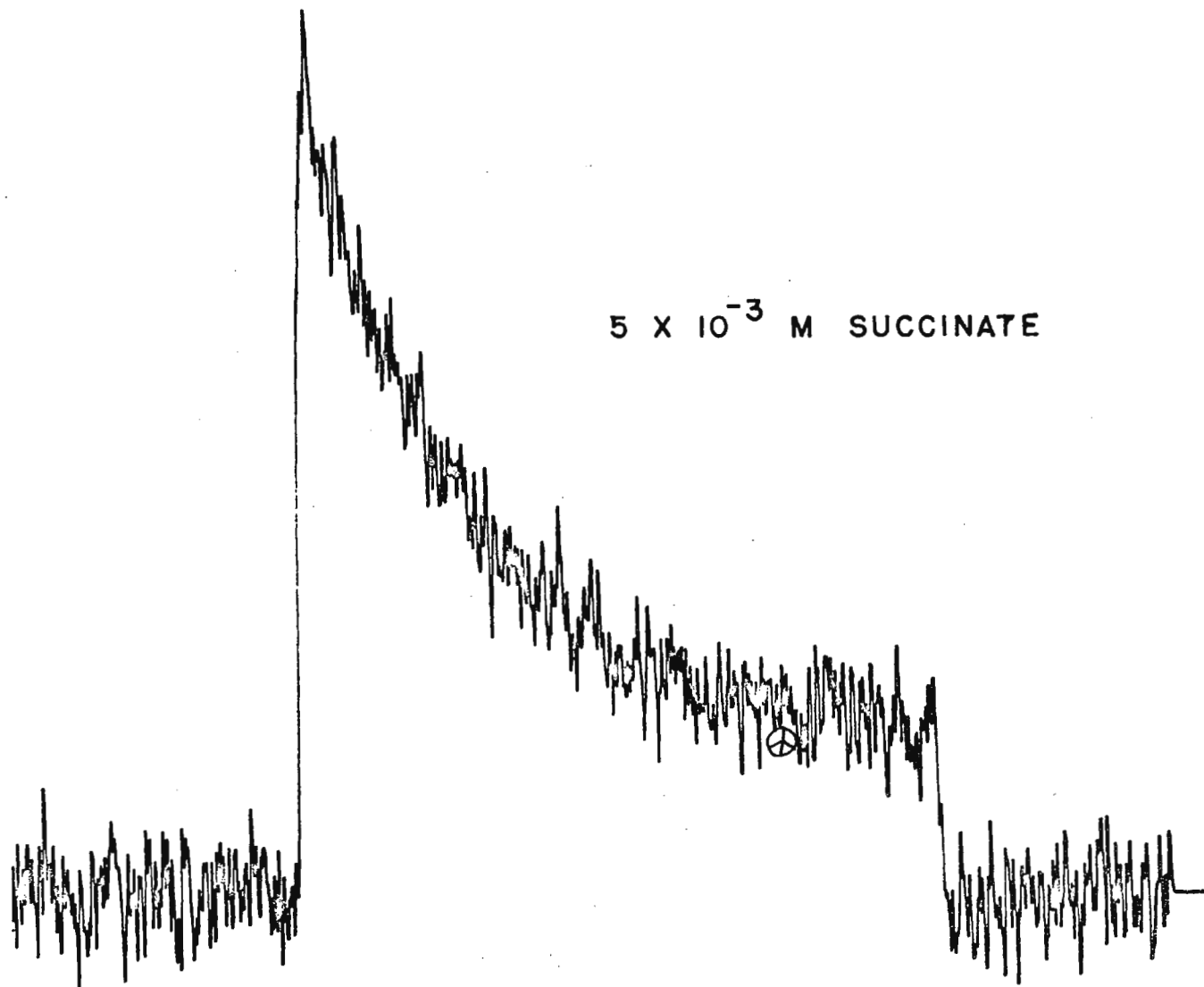   Newsletter, 93, 52 (1966)

FIG. 1.

5×10^{-3} M SUCCINATE

SINGLE SCAN

9 ACCUMULATIONS OF $T_{1\rho}$ DECAY

FIG. 2.

136-51

December 31st 1969

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

More Cautionary Tails

Dear Barry,

In Fourier transform NMR, there are several factors that may introduce frequency-dependent phase shifts of the signal and thus cause the ratio of absorption mode to dispersion mode to vary across the spectrum. For example, an insufficiently strong rf pulse will cause a spread of the phases of individual magnetization vectors as they begin their free precession, or an incorrectly-timed start of the data acqisition process after the pulse will introduce a phase shift that is strongly frequency-dependent.

Although such phase errors can be satisfactorily corrected, there is a strong temptation to sidestep the problem entirely by calculating and displaying the absolute value of the transverse magnetization, $(u^2 + v^2)^{1/2}$ instead of the traditional v mode (absorption) signal. There are dangers in such a procedure.

The most evident artifact of the absolute value display is perhaps the least serious -- much longer tails on each side of the line caused by the slower decrease of the resonance denominator as a function of the offset $\Delta\omega$:

$$v = \gamma H_1 M_0 T_2/(1 + \Delta\omega^2 T_2^2) \qquad (u^2 + v^2)^{1/2} = \gamma H_1 M_0 T_2/(1 + \Delta\omega^2 T_2^2)^{1/2}.$$

More insidious problems arise when two lines overlap, since the resultant line profile is no longer the sum of the two overlapping components (as in the conventional v mode) due to interference of the dispersion-mode components which tend to cancel in the region of overlap. For only moderate degrees of overlap, where the absorption-mode display would show negligible effects, the absolute value plot exhibits line displacements and intensity variations. However the main indictment of the absolute-value display must be made when a weak line falls in the tail of a strong line, for then the weak line appears to have the dispersion-mode shape -- the very problem the trick was designed to circumvent.

This behavior can be likened to the detection of the absolute-value signal in a simple diode detector. A tail from a strong nearby resonance will introduce a second signal component that will bias the diode detector, and since this component is predominantly in the dispersion phase and is relatively constant in amplitude across the profile of the weak line, it has the effect of converting the simple diode detector into a phase-sensitive detector adjusted for a dispersion-mode display. Another way to visualize this is as the interference between the dispersion-mode component on one side of the weak line and the strong (almost uniform) dispersion background from the nearby resonance.

Figure 1 illustrates this effect. It shows the calculated profile of two overlapping Lorentzian lines with intensity ratio 10:1 for both the absolute-value mode (upper traces) and the conventional v mode (lower traces). Note the tendency for a dispersion-like shape of the weaker line in the absolute-value plot. The effect persists for surprisingly large separations. A practical illustration is provided by part of the carbon-13 spectrum of Vitamin A acetate obtained by the Fourier transform technique (Figure 2). The line at 133 ppm (assigned to the CH_2O carbon) is seen to exhibit considerable dispersion-like character in the absolute-value plot owing to interference from the strong resonance from nearby dioxane solvent, whereas in the absorption-mode display such interference is negligible.
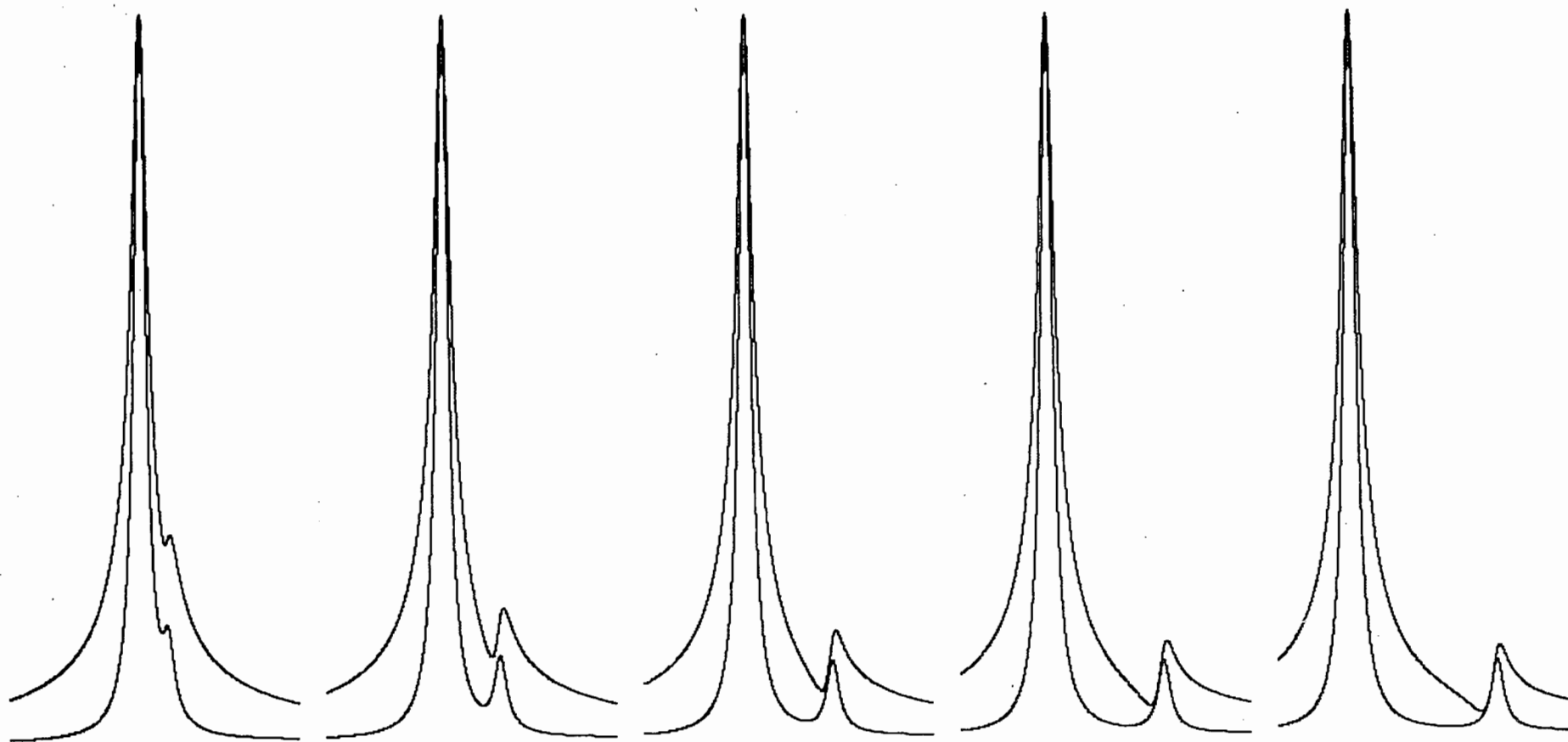
Happy New Decade,

Ray

Figure 1. Computed line profiles of two overlapping Lorentzian lines with intensity ratio 10:1. The horizontal scale represents 100 units of frequency, the full width of each line is 5 units and the separation of line centers increases in equal steps from 10 to 50 units. The absolute-value plot (upper traces) is compared with the traditional v mode plot (lower traces) with the same baseline zero. Note the much longer tails and the apparent frequency shifts and intensity changes in the absolute value display. Note in particular the dispersion-mode character of the weak line at intermediate separations.
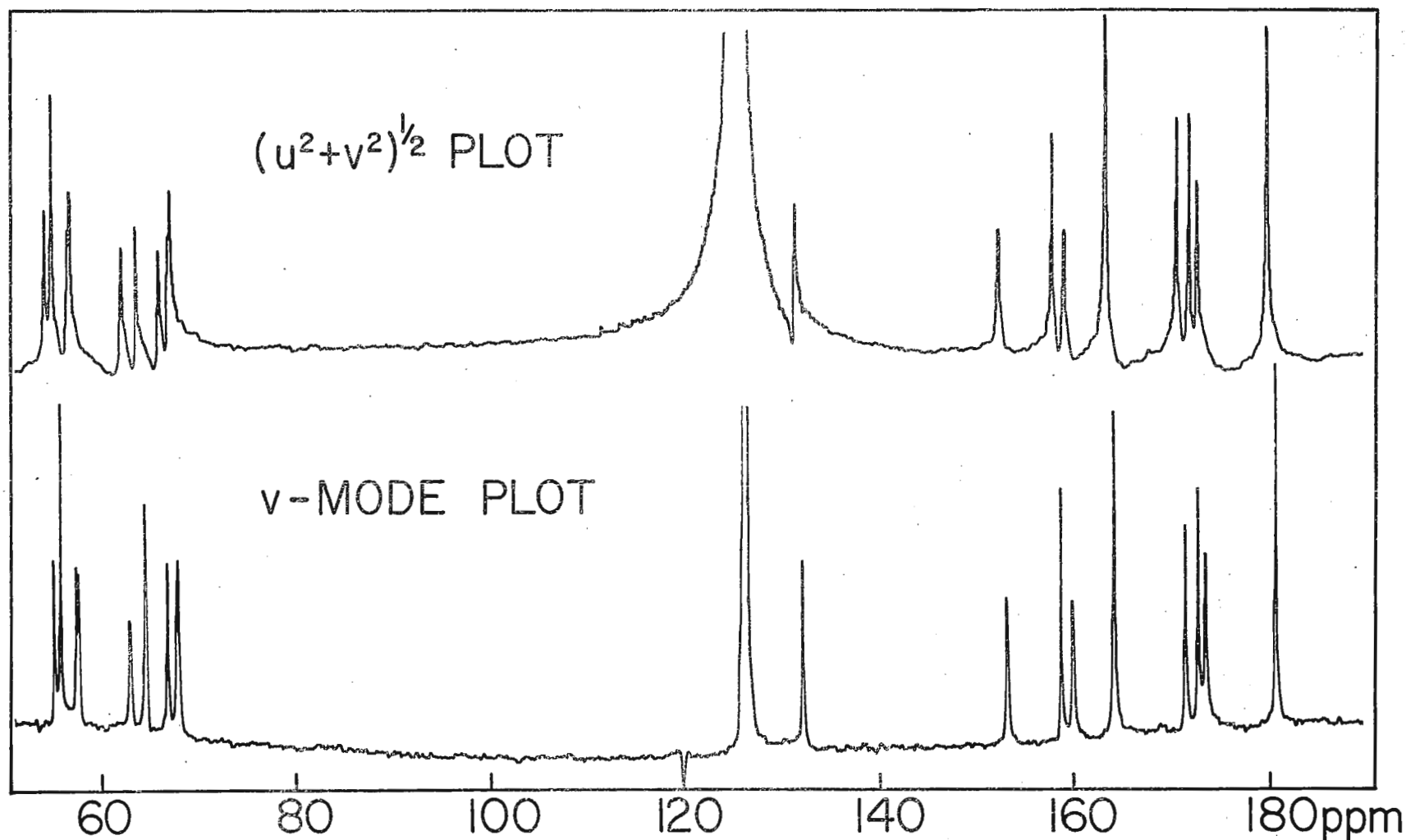
Figure 2.   Comparison of the absolute-value mode with the conventional absorption-mode display for a portion of the carbon-13 spectrum of Vitamin A acetate in solution in dioxane.   The spectra were obtained in about 17 minutes on an HA 100-15 spectrometer by the Fourier transform technique with the usual proton noise decoupling.   The CH_2O carbon resonance near 133 ppm exhibits the most marked effects of interference from the nearby dioxane solvent resonance in the absolute-value mode, having a lineshape resembling that of a dispersion signal.   Other more distant lines still show detectable distortion of the line shape.

UNIVERSITY OF FLORIDA
GAINESVILLE, 32601

DEPARTMENT OF CHEMISTRY

December 30, 1969

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

Dear Barry: Subjects: Advanced Workshop; News Items

        Some of your readers may be interested in knowing of the
Second Advanced Workshop and Seminar in NMR which we will be conducting
in Gainesville during the week of April 6, 1970. The five days of the
Workshop will include lectures on the more mathematical aspects of NMR
and on recent developments in techniques and in instrumentation. The
workshop is designed for persons with some experience in NMR who wish
to build up their background of principles and theory. For those who
wish experience in high-resolution spectral analysis, there will be
opportunity for practice with the IBM 360/65 computer. We hope also
to have our XL-100 instrument in operation in the laboratory by the
time of the Workshop. The group of participants will be limited so that
each person will have adequate opportunity for individual instruction.

        Among the lecturers and staff for the program will be
Rex Richards, J. M. Anderson, Frank Anet, Roy King, R. W. Kreilick, and
Charles Moreland. Some of the topics to be emphasized include the use
of computers in spectral analysis, relaxation effects in high resolution
spectroscopy, NMR spectra of free radicals, use of spectrometers with
superconducting magnets, spectroscopy of ^{13}C, ^{11}B, ^{31}P, and ^{19}F, molecular
conformation, and dynamic nuclear polarization.

        Those who wish more information or application blanks should
write to me at the address on the letterhead.

        On the subject of short courses, meeting, and symposia concerning
magnetic resonance, I should like to invite others who are planning such
events to publicize them by listing them in the column "Announcements and
News Items" which the Journal of Magnetic Resonance is now carrying. Our
current production schedule requires a lead time of eight to ten weeks
before the first of the month in which the item is to appear in the
Journal, although we hope to be able to reduce this somewhat a bit later on.
It would seem particularly valuable to announce symposia or sessions which,
because they are parts of larger meetings, might be missed by some of those
active in magnetic resonance. Either a phone call (904-392-0520) or a letter
to me will suffice to have the information included in the Journal.

                            Cordially yours,

                            Wallace

                            Wallace S. Brey, Jr.
                            Professor of Chemistry

WSB/ewh

THE OHIO STATE UNIVERSITY
DEPARTMENT OF CHEMISTRY
140 W. 18TH AVENUE
COLUMBUS, OHIO 43210
December 31, 1969

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

<u>Frequency Sweep on HA-100</u>

Dear Barry:

Frequency sweep on Varian HA systems is limited in the available sweep widths, the range of frequency in which one may sweep and the fact that all sweeps start at 2500 Hz minus whatever is available from the sweep offset. Furthermore the stability and linearity of the Varian sweep are less than desirable.

To alleviate the above problems what we have done is to replace the Varian sweep system with a voltage controlled oscillator, Wavetek #114 whose frequency is linear with the voltage. This oscillator has a reasonably flat output over a wide frequency range. The voltage which drives it is swept by means of the recorder sweep pots in conjunction with the dividing network shown in Figure 1. In this way we can set the recorder sweep for any frequency difference from 10 Hz to a maximum of 8 KHz (4 KHz above and below the lock). This arrangement is very useful for ^{19}F resonance where the spectra can be swept in increments of 8 KHz using, if necessary, different lock signals. At frequencies beyond 4 KHz from the lock it is hard to maintain lock.

Two switches which disable the manual and sweep oscillators, respectively, have been installed behind the 4354 lock box. They are ahead of the amplitude control on the front panel. A BNC was added to feed an external sweep signal into the lock box. Note also, as is common practice, an external frequency can be fed into the manual oscillator jack allowing any lock frequency to be selected. A third switch, three poles, two positions, and a three terminal jack was installed on the recorder frame. In this way we can switch between the Varian and the Wavetek sweep options.

Our Varian HA 100 spectrometer is now routinely run with the Wavetek sweep.
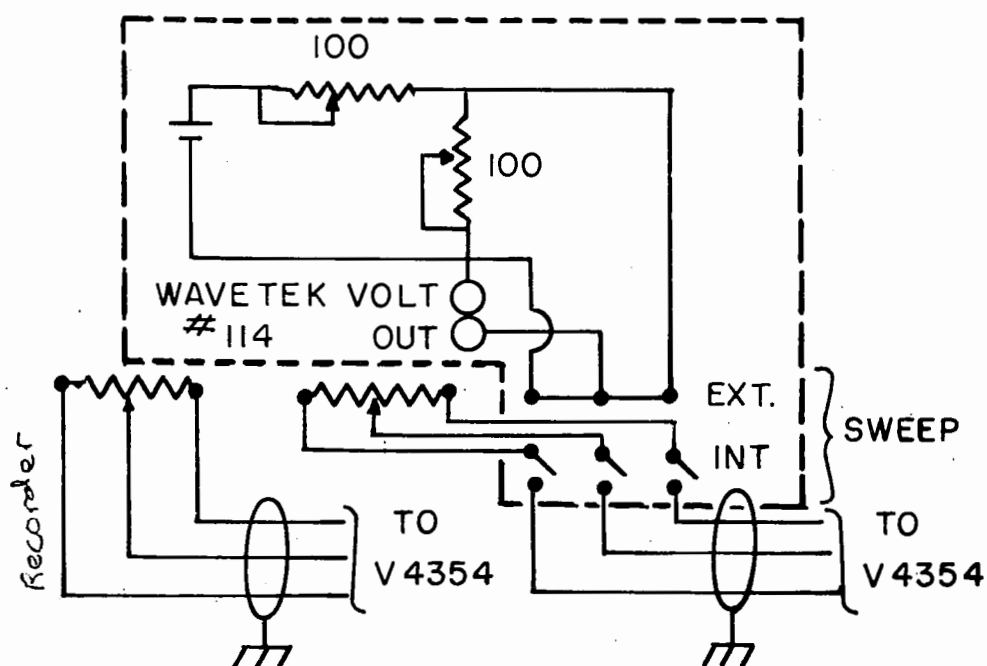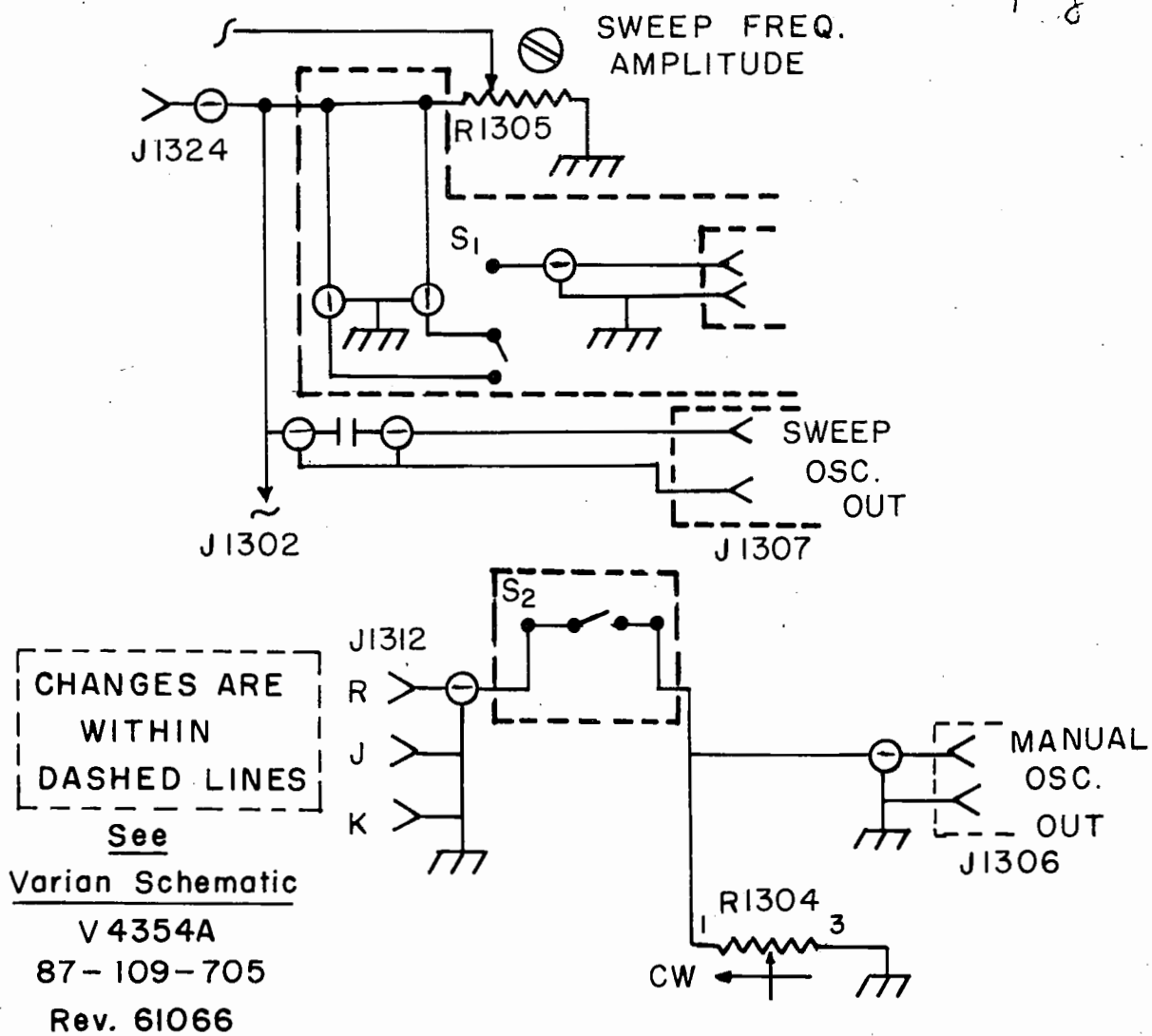
Sincerely yours,

Gideon Fraenkel,
Professor of Chemistry.

GF:cm
incl

Fig 1.

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY   December 31, 1969

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

Dear Barry:

IBM 1620-II For Sale

We would like to advertise the fact that our IBM 1620-II
is for sale and immediately available. This is the computer
on which we have been running all our NMR analyses. We have a
very extensive library of programs. Of particular interest is
our 7-spin version of LAOCOON II. The computer has been under
maintenance contract which we understand can be extended at the
option of the purchaser. The system includes a Calcomp plotter
and 1311 disk drive.

Anyone interested in obtaining further details should contact
me, preferably by phone.

                                        J. H. Goldstein
                                        Professor of Chemistry
                                        Office Phone
                                        404-377-2411 Est. 7527
                                        Home Phone
                                        404-636-4814

Description of 1620-II System

(Prices given are current IBM list Prices)

1620-II	CPU	$ 32,010
1289	Floating Point	13,335
3340	Disk Adapter	6,210
5515	Paper Tape Adapter	1,210
4627	Index Registers	8,000
1625	40K Core Storage	76,630
1311-III	Disk Drive	27,895
1621-I	Paper Tape Reader	8,390
1624	Paper Tape Punch	1,360
1626	Plotter Controller	4,850
1627	Plotter	4,560
1316	Disk Packs (total of 7)	3,430
		$187,880
F-1620	Off-line Flexowriter for 1620	3,525
	6-Drawer Cabinet for Disks	250
		$191,655

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TAMU NMR Newsletter

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