Texas
A
M &
University
N – M – R
Newsletter

No. 147
DECEMBER, 1970

All Newsletter correspondence, etc., should be addressed to:

November 6, 1970

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

<u>Interaction of Aromatic Protons with Methoxyls in
Ortho Position</u>: Expected and Unexpected Effects.

Dear Professor Shapiro:

During the study of the mold pigment elsinochrome A (I), we have made some
observations which may be of general interest.

The compound has been proven[1a,b] to be the rapidly equilibrating tautomeric
system Ia ⇄ Ib. In its nmr, the signal from one of the two pairs of methoxyls,
unequivocally identified as (c), is reproducibly ~ 20% shorter than those from
(d) and (g), the latter two signals being of equal heights. The effect is
accentuated at lower temperature (Δ = ~ 66% at -60°), and disappears when
the nuclear protons (a) are replaced by Br (see Fig. 1). All three signals:
(c), (d), and (g), integrate precisely for 3 protons.

Compound I forms two dimethyl ethers[1a]: V, derived from Ia, and VI, derived
from Ib. In both, the signals from methoxyls adjacent to the nuclear protons
(a), i.e. (c) in V, (c) and (f) in VI, are shorter than the other methoxyl and
-CO-CH$_3$ signals, which are of equal heights (see Table I).

Similar shortening of signals from methoxyl <u>ortho</u> to aromatic protons, compared
with reference signals from methoxyls without free ortho positions, has been
observed in a number of simple aromatic model compounds: 2,3,4-trimethoxy-
benzaldehyde (II), 2,3-dimethoxyphenol (III), and apiol (IV).

Ia: R = H
V: R = CH$_3$ (e)

Ib: R = H
VI: R = CH$_3$ (f)

II

III

IV
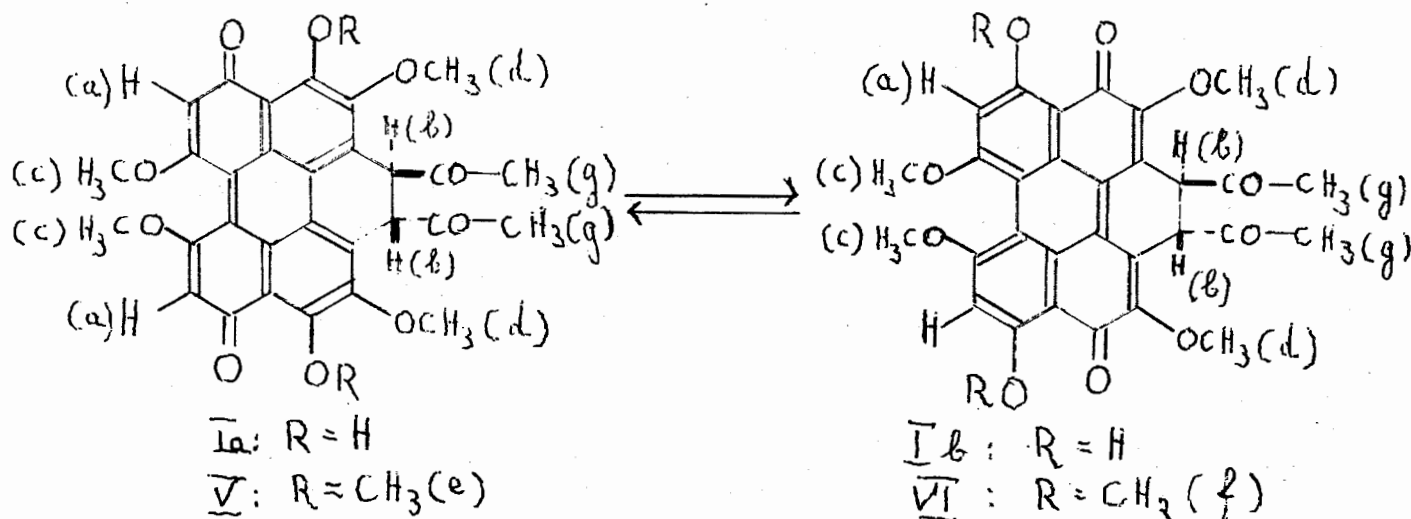
In these cases, the shortening seems to be due entirely to long-range coupling between aromatic and methoxyl protons; it disappears on decoupling, which leads to equalization of the heights of the methoxyl signals (in the case of compound III, an unexplained small difference, $\sim$ 3%, persists). Long-range coupling of this kind has been demonstrated recently.[2]

In I, V, and VI, this long-range coupling is likewise present, and accounts for $\sim$ 50% of the difference in peak-heights (see Table I). However, the remaining half is uninfluenced by decoupling, and must be due to some other cause, which appears to be specific for I, V, and VI; presumably, it is this residual effect which is responsible for the increase of the peak-height difference at low temperature. Integration of the decoupled spectra shows no nuclear Overhauser effect. NOE in the reverse direction has been demonstrated[1b]: increase of the integrated area of (a) on irradiation with the frequency of (c) in I and with those of (c) and (f) in VI. In the NOE of I, the half-band width of (a) decreases, in spite of the increase in integrated area--good evidence for the participation of long-range coupling.

Table I
Ratio of CH_3O Peak Heights

COMPOUND	NORMAL	DECOUPLED
I	73%	89%
II	78%	$\sim$100%
III	73%	97%
IV	86%	$\sim$100%
V	78%	90%
VI	71%	82%

This specific effect seems difficult to rationalize. One tentative interpretation, suggested to us by Dr. J. A. Ferretti, is based on the presence of magnetic non-equivalences in I, if there should be spin-spin coupling between the (a) protons. (Such a 7-bond coupling seems plausible in view of 7-bond couplings of $\sim$ 0.5 Hz in some dienes.[3]) In this $A_3A_3'XX'$ system decoupling might leave "residual splittings" (cf. Anderson and Freeman[4]), hence provide a major line with a peak intensity less than expected.

We would welcome comments and suggestions.

Yours sincerely,

Ulrich Weiss

E. A. Sokoloski
Laboratory of Chemistry
National Heart and Lung Institute

Karl H. Weisgraber and U. Weiss
Laboratory of Physical Biology
National Institute of Arthritis
and Metabolic Diseases

National Institutes of Health, Bethesda, Maryland 20014

REFERENCES

1. a) R. J. J. Ch. Lousberg, C. A. Salemink, U. Weiss, and T. J. Batterham, J. Chem. Soc. C, 1219 (1968); b) R. J. J. Ch. Lousberg, L. Paolillo, H. Kon, U. Weiss, and C. A. Salemink, J. Chem. Soc., in press.

2. H. Angad Gaur, J. Vriend, and W. G. B. Huysmans, Tetrahedron Letters 1999 (1969); R. W. Crecely, K. W. McCracken and J. H. Goldstein, Tetrahedron 25, 877 (1969); L. M. Jackman and S. Sternhell, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, New York, 2nd Ed., 1969.

3. P. Albriktsen, A. V. Cunliffe and R. K. Harris, J. Magn. Res. 2, 150 (1970).

4. W. A. Anderson and R. Freeman, J. Chem. Phys. 37, 85 (1962).
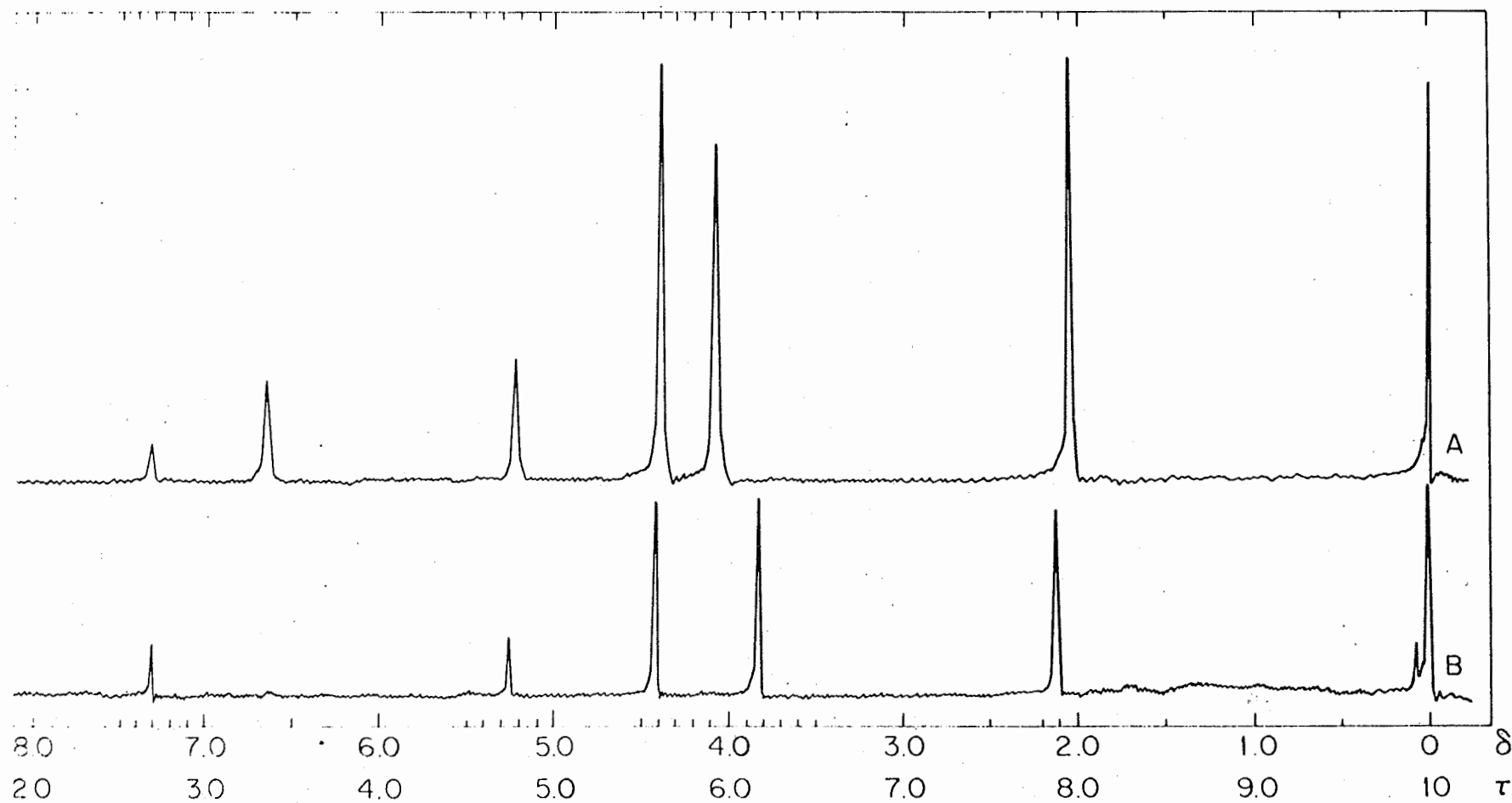
Figure 1:

Spectra of I (upper curve) and dibromo-I (lower curve); cf. Fig. 3 of Ref. 1A. $CDCl_3$, TMS as internal standard. Peaks shown (from left): $CHCl_3$; (a); (b); (d); (c); (g). The upfield shift of (c) on bromination is one of the arguments for assignment of peaks.

PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA 47907

October 21, 1970

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

Dear Dr. Shapiro,

Deuterium NMR on the XL-100-15 with the CAT.

Recently (TAMUNMR 142-26) Brey and Block reported a method for
obtaining deuterium nmr spectra with the XL-100-15. We have also used
this method, but have found that sensitivity is a major problem. In
order to alleviate this difficulty, we have constructed a circuit that
interfaces the CAT with the XL-100 and allows accumulation of the signal
displayed on the scope – the deuterium lock signal in this particular
instance.   After careful adjustment of the drift, we have been able
to accumulate up to 100 25 second scans using HR mode. The scanning
ramp of the CAT is used to drive the linear sweep coils; sweep widths
are set by the sweep width control of the linear sweep module, sweep
times are provided by the CAT, or more conveniently from the recorder
as in the conventional time, averaging operation. Additional amplifica-
tion of the signal may be selected. The circuit is shown on the
following pages and may be constructed for about $100. A full descript-
ion of the circuit and its operation is available on request.

As an example of the use of this circuit we recently ran a sample
of bicyclo [4.2.1] nona-2,4,7-triene (D_2) for Dr. J. Berson at Yale.
The spectrum shown below was the sum of 10 50 second scans on a 180 mg
sample with $CDCl_3$ and $(CD_3)_2C=O$ as references.
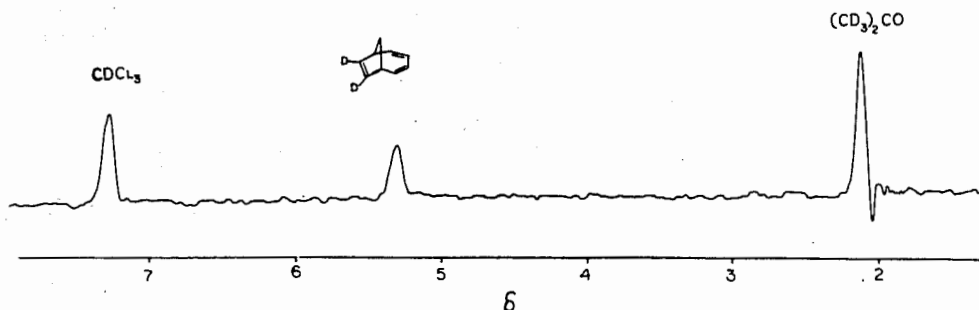
Please credit this contribution to Dr. Muller's subscription.

Yours sincerely,

Robert E. Santini   John B. Grutzner

JBG:ch

C₁
R₁₄
S₂
TRIGGER OUTPUT
A₆
R₁₅
R₁₆
C₂
R₁₇

R₂₀ R₂₁ R₂₂ R₂₃
R₁₉
S₃
R₁₅
OUTPUT FROM NMR TO SCOPE
A₇
TO C-1024 INPUT
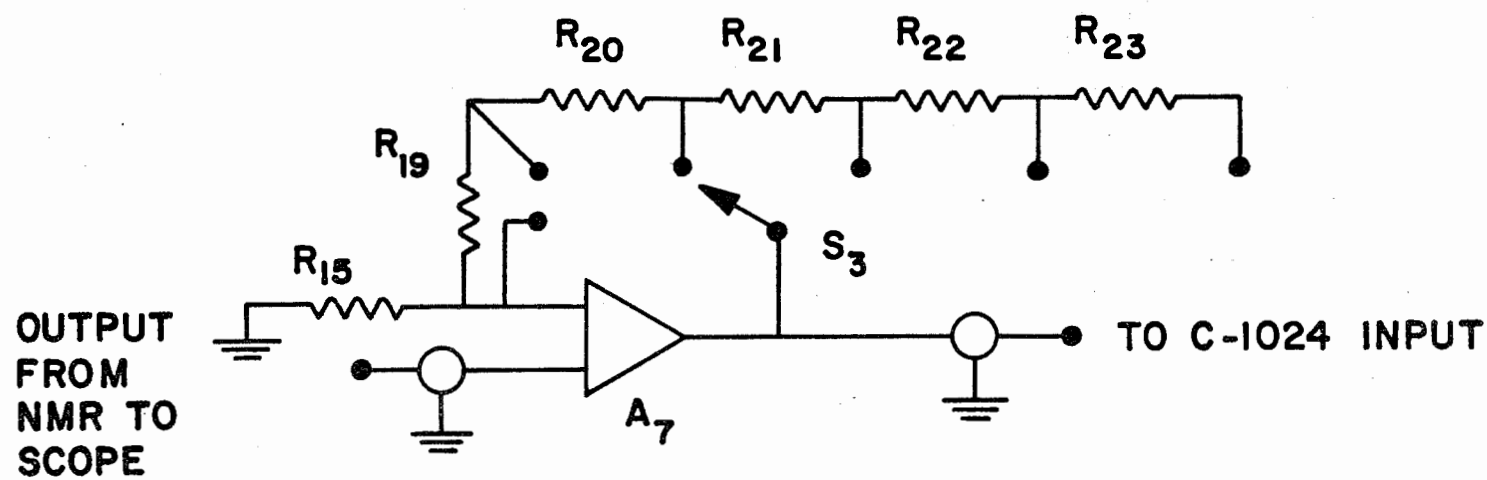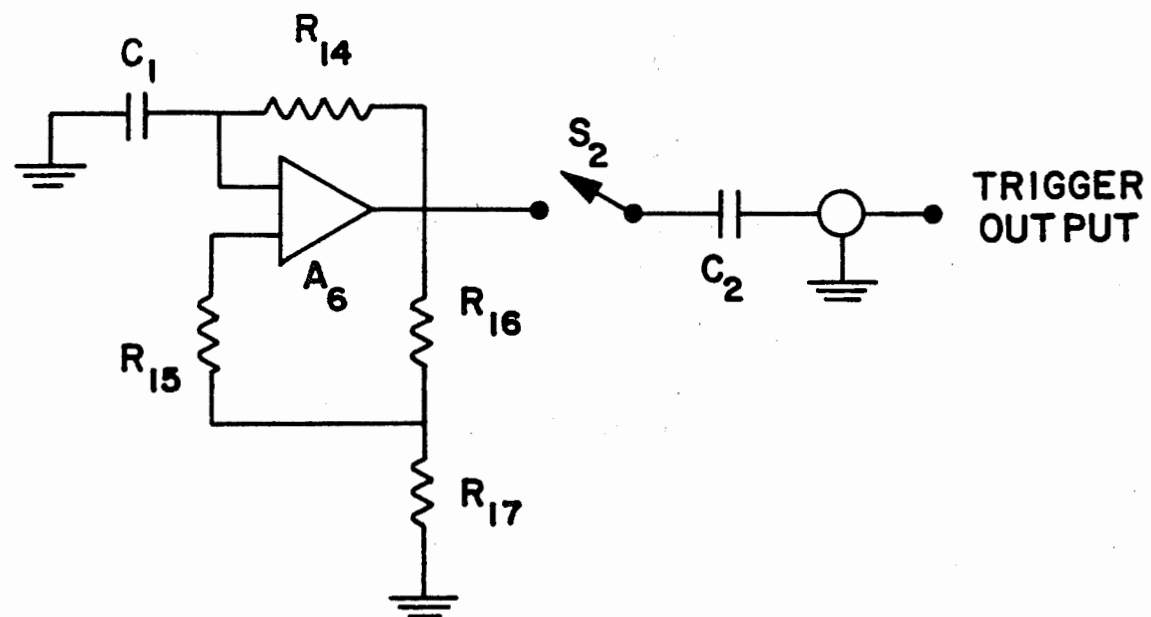
MODIFICATIONS TO LINEAR SWEEP UNIT
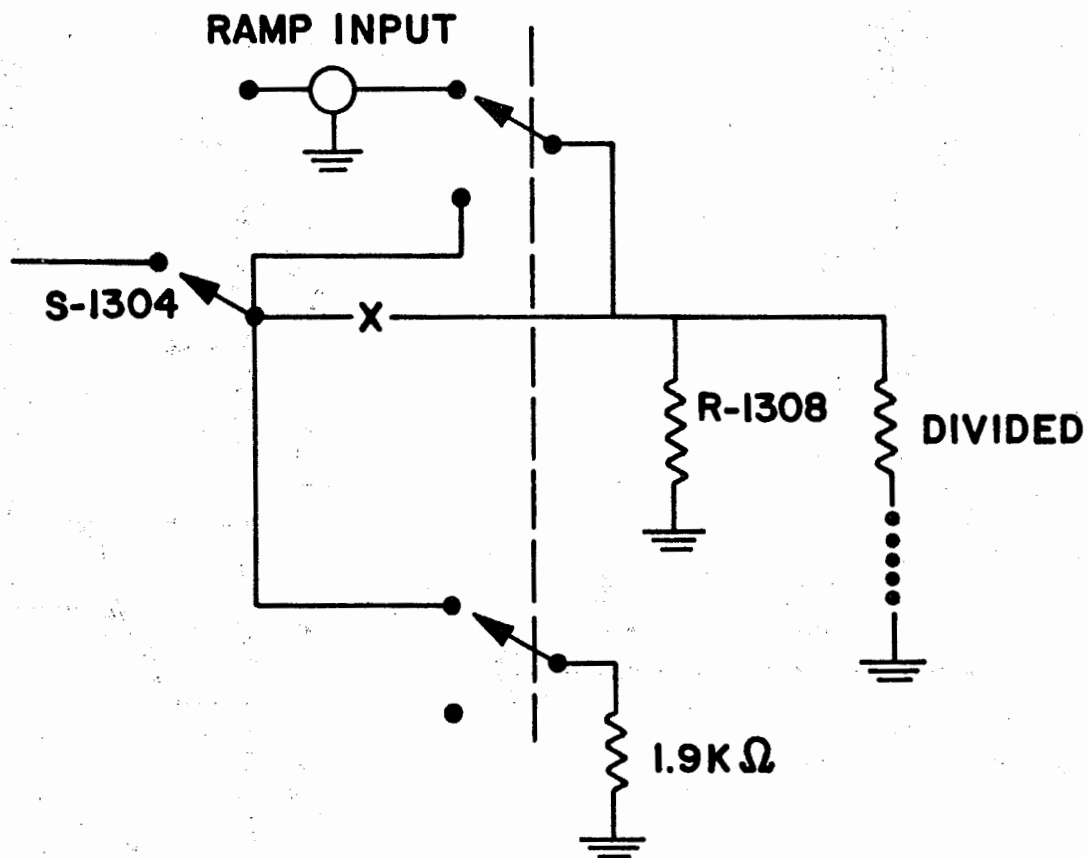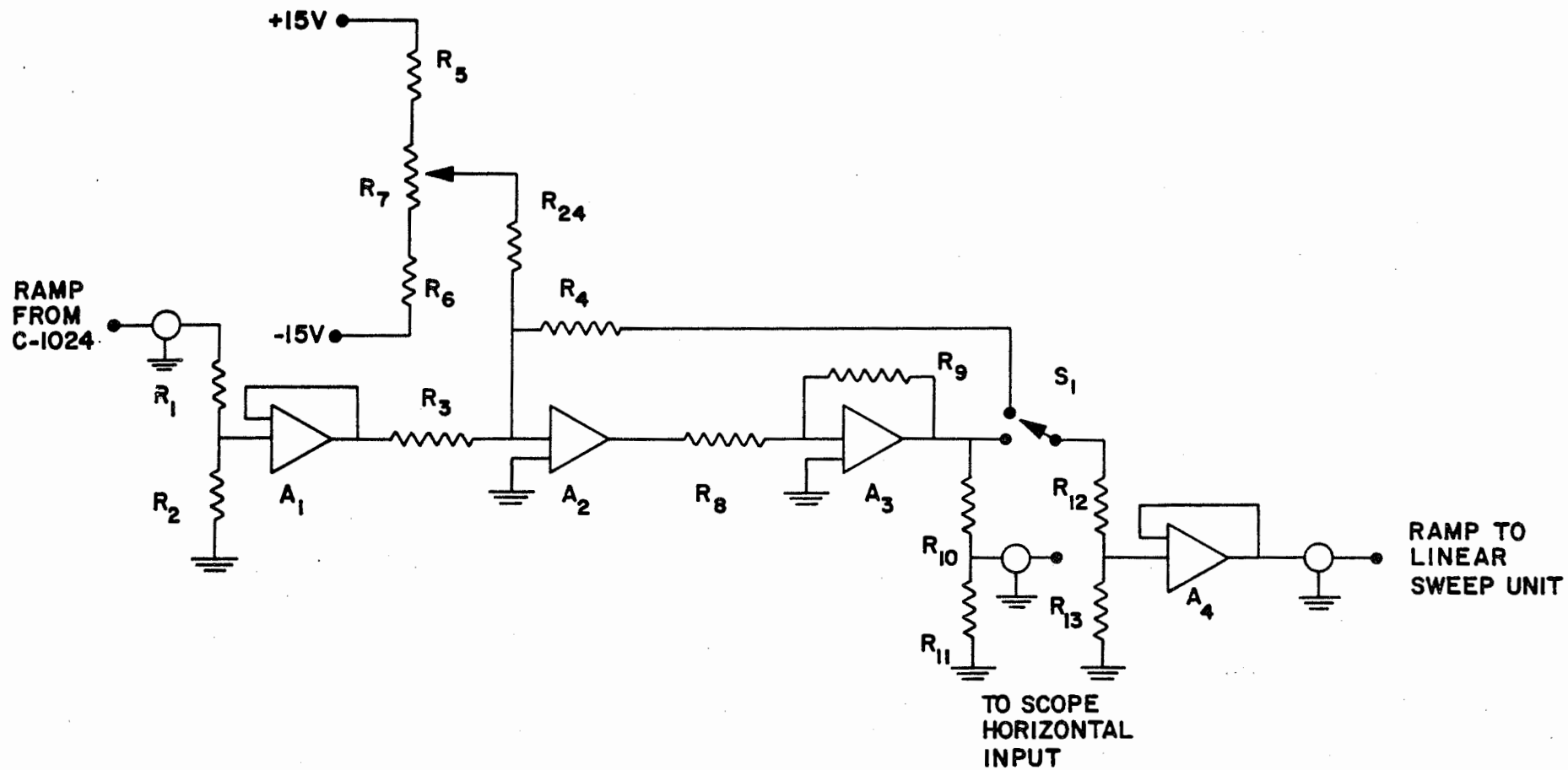
RAMP INPUT

S-1304

X

R-1308

DIVIDED

1.9K Ω

X = BREAK

RAMP FROM C-1024

+15V

R_5

R_7

R_24

R_6

-15V

R_1

R_2

A_1

R_3

R_4

A_2

R_8

R_9

A_3

S_1

R_10

R_11

R_12

R_13

A_4

TO SCOPE HORIZONTAL INPUT

RAMP TO LINEAR SWEEP UNIT

147-7

CHIMIE ORGANIQUE PHYSIQUE

Nantes, le 27 OCTOBRE 1970

Professeur Bernard L. SHAPIRO

Department of Chemistry
Texas A.M. University
College Station - Texas 77843

Hindered rotation about C-N bonds in ureas and thioureas

Cher Professeur Shapiro,

Par une étude conformationnelle à très basse température (< - 100°C), nous avons mis en évidence la rotation empêchée autour des liaisons C-N dans les urées CH_3 NH - CO - NH - R (R = H, CH_3). Parallèlement, les thiourées correspondantes ont été examinées en vue de compléter l'étude comparative des systèmes carbonyle-thiocarbonyle.

Le calcul, par étude des formes de raies, des durées de vie τ en fonction de la température, donne accès aux paramètres d'activation.

Dans la N-méthylurée, les valeurs de T_c et de ΔG^* (T_c) sont de 153° K et environ 7,5 Kcal/mole. En raison des difficultés techniques propres à ce domaine de températures, la détermination des valeurs de Ea , ΔH^* et ΔS^*, est imprécise.

.../...

.../...

   - Dans le cas de la N-méthylthiourée, nous observons à T_C = 285° K (± 3) la coalescence relative à l'isomérie de rotation autour de CH_3 NH $\frown$ CS :
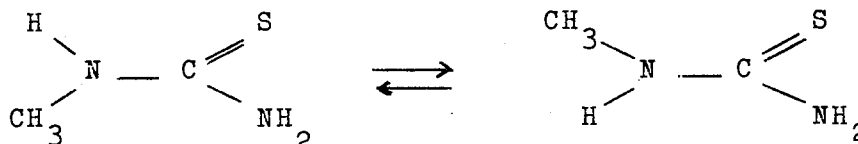
$\Delta G^*(T_C)$ = 15,1 Kcal/mole (±0,2) - ΔH^* = 15,07 Kcal/mole (±2)

ΔS^* = - 0,14 u.e. - Ea = 15,7 Kcal/mole (±2).
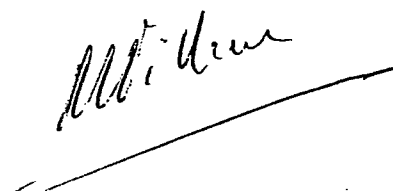
   A plus basse température se manifeste l'isomérie de rotation autour de - CS $\frown$ NH_2 :

T_C = 203°K (±3) - $\Delta G^*(T_C)$ = 10,2 Kcal/mole.(±0,2)

   Comme pour les amides et vinylogues d'amides, le remplacement de C=O par C=S s'accompagne d'un accroissement important de ΔH^*.

   Veuillez croire, Cher Professeur Shapiro, à nos sentiments cordiaux.

M.L. FILLEUX-BLANCHARD   G.J. MARTIN.

JEOLCO (U.K.) LIMITED

JEOLCO HOUSE GROVE PARK COLINDALE LONDON NW9 Telephone 01-205 6376/9 Telex 28350

Professor B. L. Shapiro,   AID/2346/PJB/PAT
Texas A. & M. University,
College of Science,
College Station,
Texas 77843,
U.S.A.   28th October, 1970.

Dear Professor Shapiro,

Easier Decoupling on the C60HL with almost no Modification

Ron Dean has very kindly passed on to me your blue note, so please accept this letter as our contribution from Jeolco (U.K.) Limited.

In the past, two methods of homonuclear spin decoupling have been used on the C60HL and its predecessors: frequency sweep and field sweep using a fixed decoupling frequency. The former method takes rather longer as it requires a change from the normal field sweep mode of operation to the frequency sweep mode, while the latter is only satisfactory if the location of both signals is known before decoupling. The method now proposed has neither of these disadvantages, as it uses the synchro-track technique (i.e. a field sweep measurement is performed, but the decoupling frequency is swept together with the field, so that the decoupling condition is always maintained). The only modification required is to disconnect (and insulate) lead 8 from terminal block TM 3201 at the back of the VF amp unit. This permits the variable frequency oscillator to be switched on during external lock field sweep operation. The frequency should then be adjusted to 4 KHz. with the pen at 0 ppm on the chart, and the sweep control set to field/frequency. (This adjustment may be performed using the zero beat if a counter is not available).

After a normal field sweep spectrum has been recorded, decoupling is achieved by the following procedure:-

1. Adjust the fixed frequency modulation to approx. 2-2.
2. Reduce the RF gain (1 or 2).
3. Increase the RF level ($\sim$10 dB).
4. Turn sweep control to field/frequency if not already selected.
5. Put pen over signal to be decoupled.
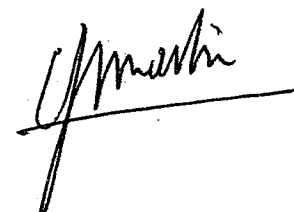6. Turn on sweep generator and set modulation to $\sim$5-6.
7. Adjust frequency offset to give 4 KHz.*
8. Record decoupled signal (some phase correction may be required).

*If a counter is not available, subtract the frequency read on the chart, and perform fine adjustment by observing zero beat on the pen.

The enclosed spectra are of the old favourite trans-crotonaldehyde and also 1% ethyl benzene, decoupled by the synchro-track method. Originally, I was going to send some ^{13}C results, but I think this decoupling method will be of more use to your readers.

                                        Yours sincerely,

                                        DR. P. J. BEYNON

Enclosures

DIRECTORS T TAKEUCHI B A J. KOBAYASHI LL B T KAMEWARI B.Sc   PARENT COMPANY JAPAN ELECTRON OPTICS LABORATORY COMPANY LIMITED TOKYO JAPAN
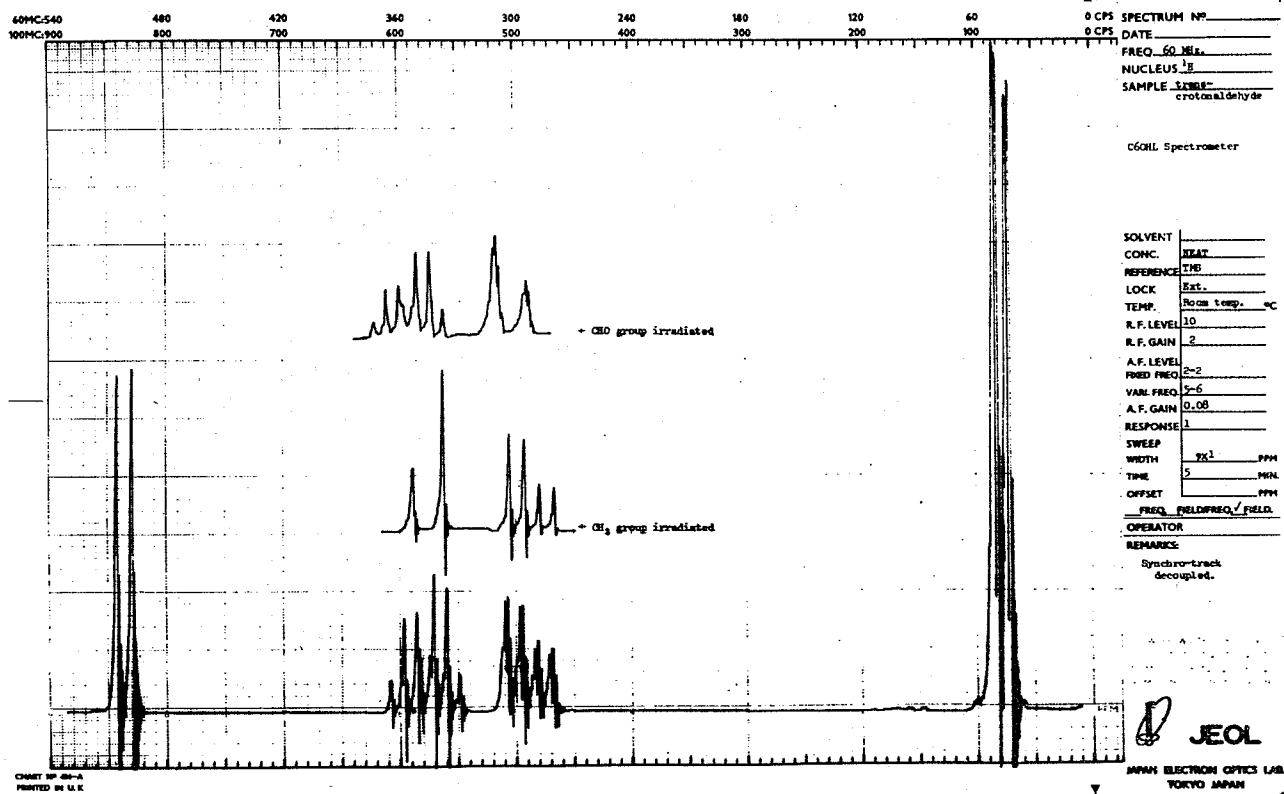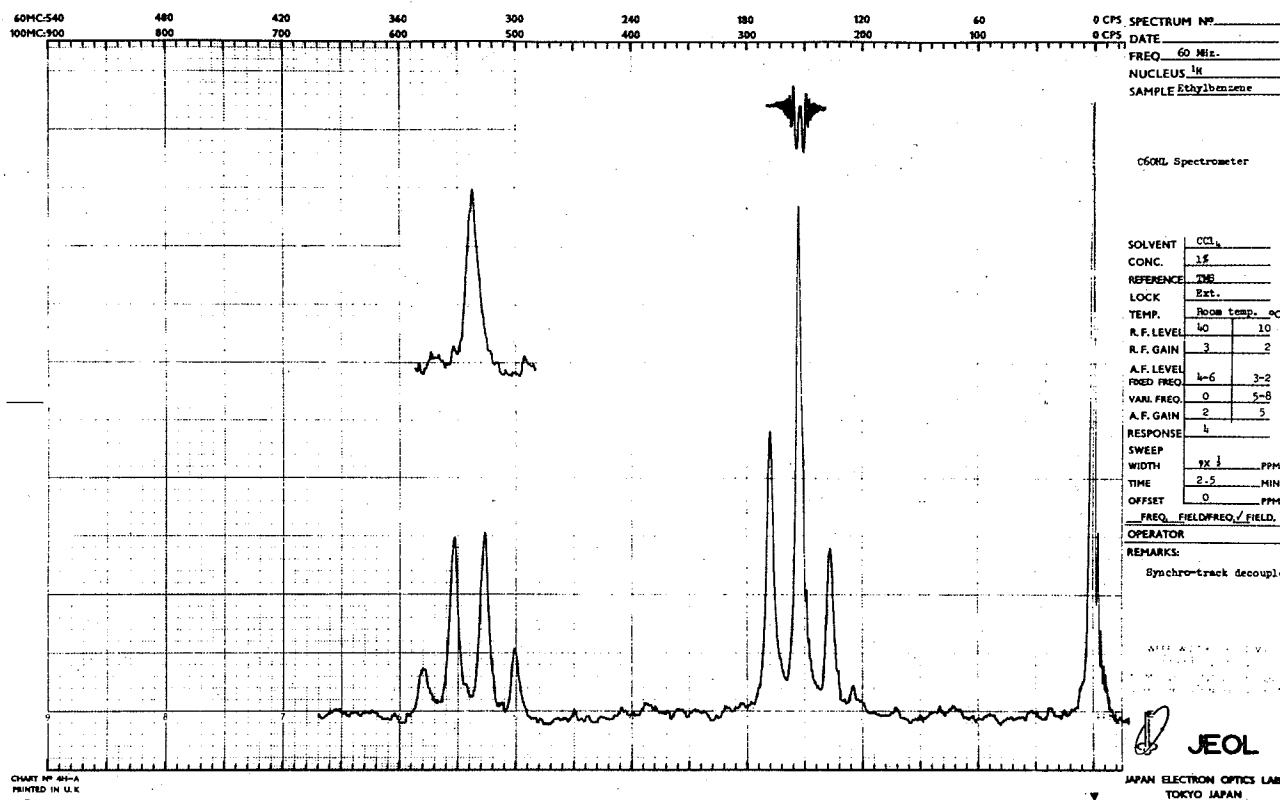
STANDARD OIL COMPANY

⟨INDIANA⟩

NAPERVILLE TECHNICAL CENTER, BOX 400, NAPERVILLE, ILLINOIS 60540

October 30, 1970

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

Dear Barry:

First we would like to call your attention to our new address. The spec-
troscopy group is now part of Standard Oil (Indiana) Research Department
whereas previously it was part of American Oil, the petroleum division.
Our new laboratory is about 30 miles west of Chicago.

While moving into the new building we have recently (April 1970) received
a new spectrometer, the Bruker HFX-90/7-12/14. The 12/14 designation in-
dicates the intermediate size magnet. So far we have encountered the
usual difficulties in setting-up the spectrometer. Particularly we have
found utility requirements quite important and this may be of interest to
Newsletter subscribers.

First, the raw water temperature, as well as pressure, are critical. Al-
though a temperature of less than 65°F and a pressure between 60-100 psi.
is specified, we have been operating our system with the water at 59°F
and 47 psi. by having the returning magnet water pass thru a small heat
exchanger. In addition, although Bruker supplies a 200 to 220 VAC trans-
former, we found it to be not completely adequate, requiring small booster
transformers, one on each phase. The voltage level input is quite critical,
but small voltage drifts are not (i.e. we have not needed a large voltage
regulator).

We experienced a 60 cycle beat signal (from TMS) in our HA60-IL. It inter-
ferred with the 1.0 ppm (δ) region when recording ^{1}H-NMR Spectra. The
problem was corrected by isolating the probe from the probe holder with
nylon spacers and using a nylon duplicate of the knurled hand screw that
secures the probe to the holder.
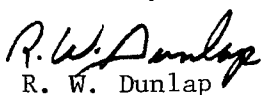
In addition, we would like to pass on a useful aid. We find that the NMR
sample tube caps (cat. no. 15-106) purchased from NMR Specialties, Inc.
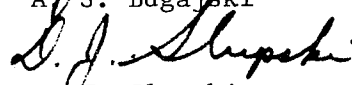
are generally very loose. To correct this situation, we heat the plastic caps to between 95° and 100°C and cool at various rates, depending upon degree of tightness required.

We would also like to mention that Dr. G. Joseph Ray joined us this past June.

Suggested title: New Laboratory; New Bruker HFX-90/7-12/14;
                         60 Cycle Beat in HA60-IL; Sample Tube Caps

                                        Best regards,

B. E. Wenzel   E. M. Banas

G. J. Ray   A. J. Bugajski

R. W. Dunlap   D. J. Slupski

/ch

(ici)

Imperial Chemical Industries Limited

PETROCHEMICAL & POLYMER LABORATORY

P.O. Box No. 11, The Heath, Runcorn, Cheshire

Telephone: RUNCORN 3456   *Trunk Dialling:* OWA 853456   *Telegrams:* MONDIV. RUNCORN
Telex: 62655 ICIMONDIVHQ, RCN

9th November, 1970.

Your Ref.

Our RefMCMcI/AR

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

Dear Dr. Shapiro,

3 years non-stop with a supercon - Liquid crystal studies of some π cyclopentadienyl complexes of Tungsten

We have just completed 3 years of continuous operation of an HR-220 with relatively little trouble. The continuity was broken when, after suffering severe icing-up of the magnet cap and high liquid nitrogen boil off, we discovered a large block of ice inside the dwar and had to warm up the magnet system to room temperature. Over 2 Kg of water were removed from the dewar! I am pleased to say that we are once more back to normal and looking forward to another 3 years continuous operation.

The range of suitable molecules which can be studied by n.m.r. in liquid crystalline solvents is becoming exhausted with little attention having been drawn to organo metallic species. This has been due mainly to the lack of symmetry in these molecules as well as poor stability and solubility in liquid crystalline solvents. A series of which we have been studying are transition metal complexes containing the cyclopentadienyl moiety. It was hoped that by making the right choice of complexes we might determine the angle, out-of-plane, of the cyclopentadienyl protons as well as some symmetry parameters. For the first problem it was necessary to use a transition metal with an isotope of nuclear spin of $\frac{1}{2}$, as well as a large magnetic moment, and so far we have not succeeded. The second part of the problem is continuing and spectra of some Tungsten complexes are shown below. Figure 1 shows the spectrum of cyclopentadienyl Tungsten tricarbonyl iodide oriented in a liquid crystal mixture at 50°C. Analysis of this spectrum shows no $^1H - ^{195}W$ coupling but within the limits of accuracy of the experiment agree with the regular pentagonal geometry of the C.P.D. moiety. Figure 2 is the spectrum of oriented cyclopentadienyl tungsten tricarbonyl hydride. Again no $^1H - ^{195}W$ couplings were observed in the C.P.D. portion of the spectrum but they were

observed in the hydride region. A first analysis of this spectrum shows there to be no symmetry axis along the CPD-W-H axis but that this is an angle of about 127°. Figure 3 is the spectrum of oriented cyclopentadienyl tungsten tricarboxyl methyl. The computed spectrum (figure 4) again shows no ^1H - ^{195}W couplings but contains a great deal of structural information which we hope to extract in the near future. Spectral simmulations were carried out using a LAOCN-II programme modified for 8 spins and to give a plot output.

Yours sincerely,

M.C. McIvor

fig 1

400 Hz
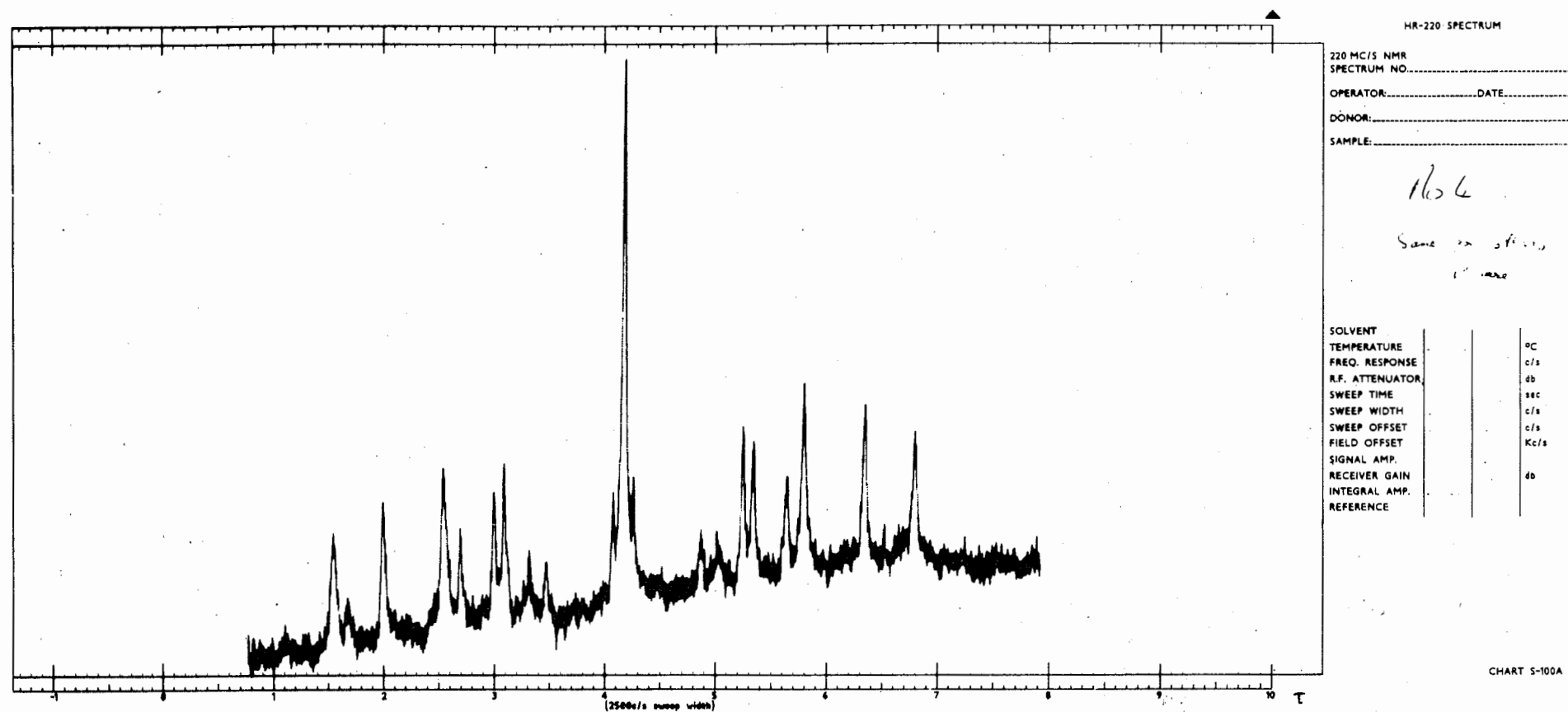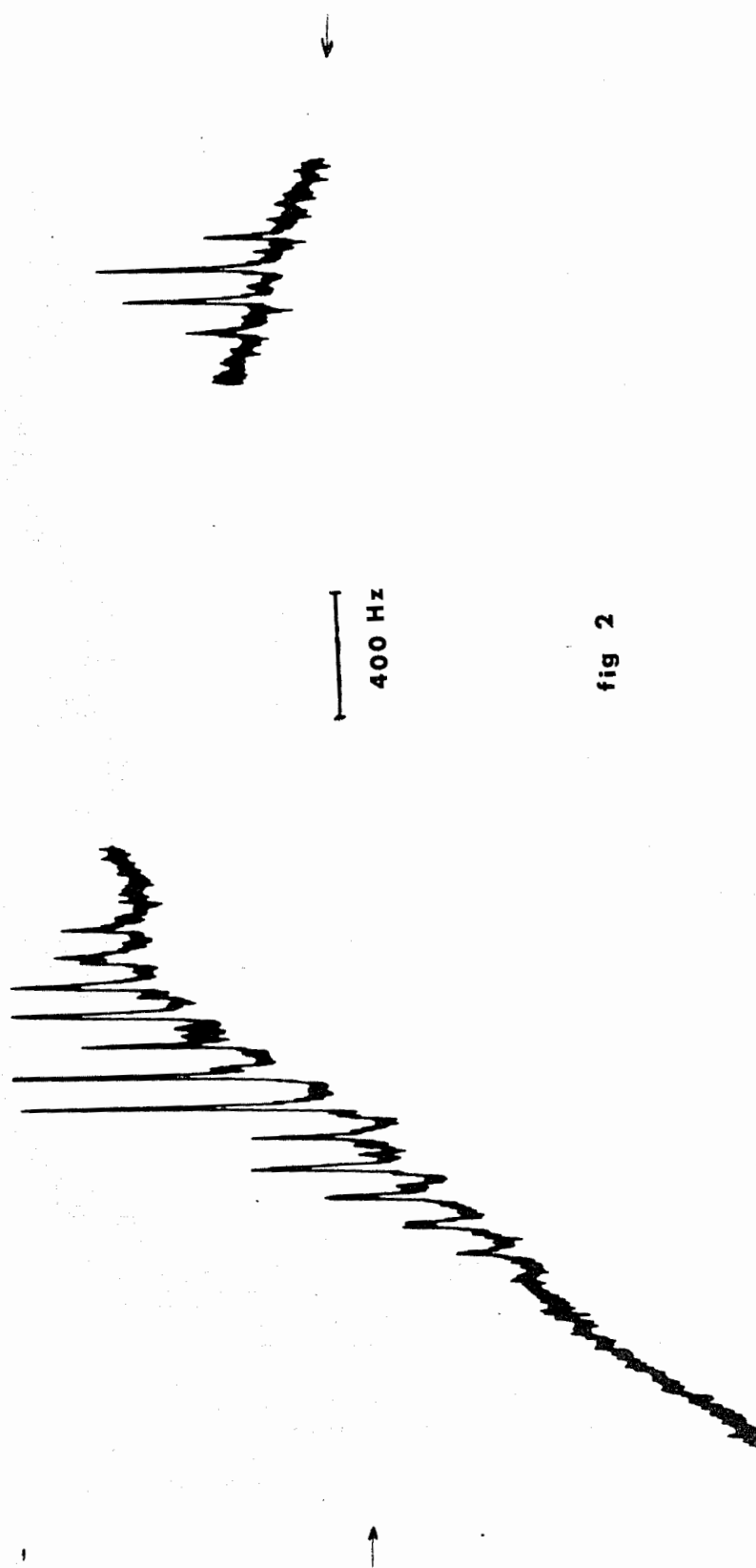
fig 2

fig 3

200 Hz
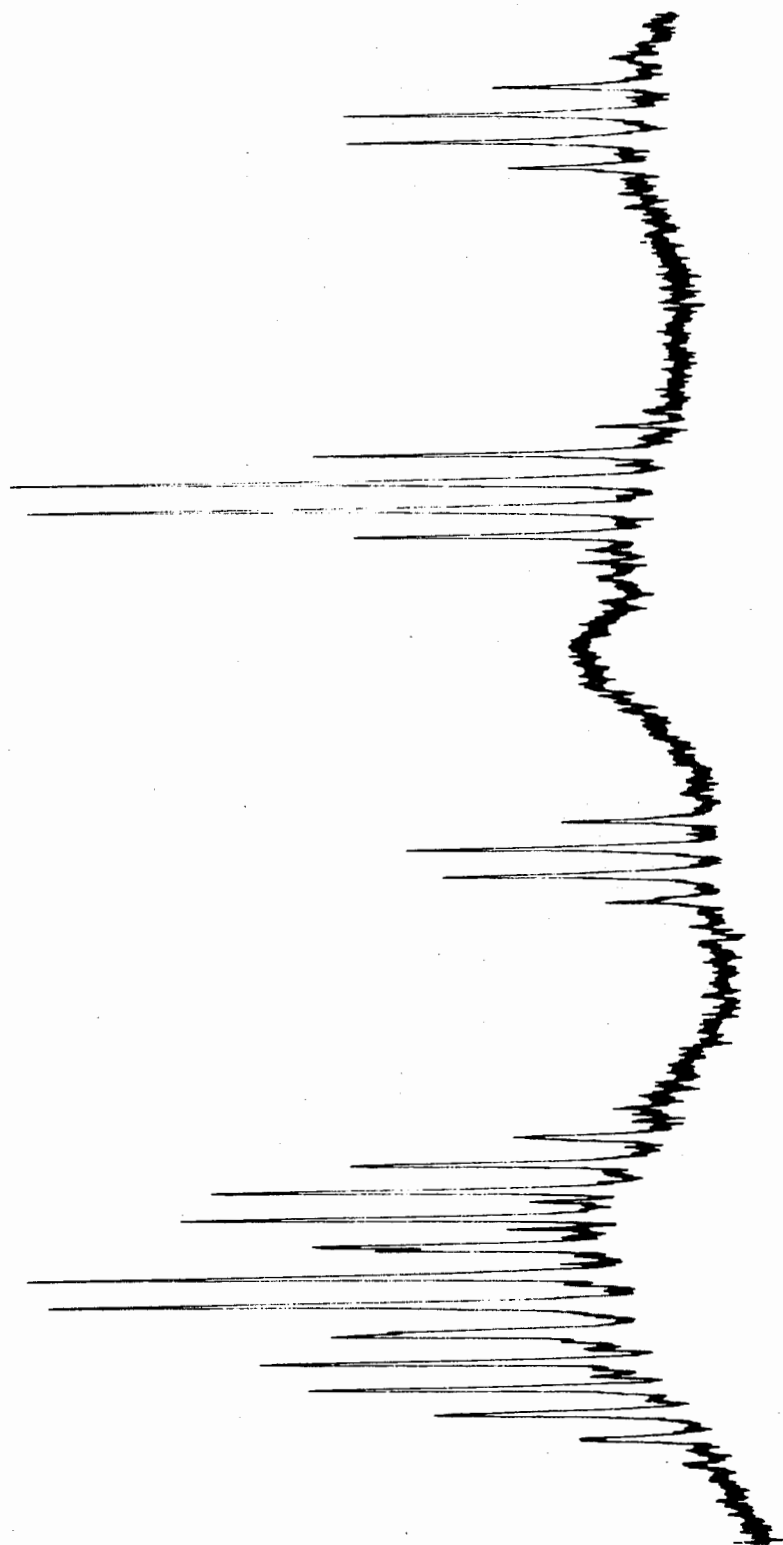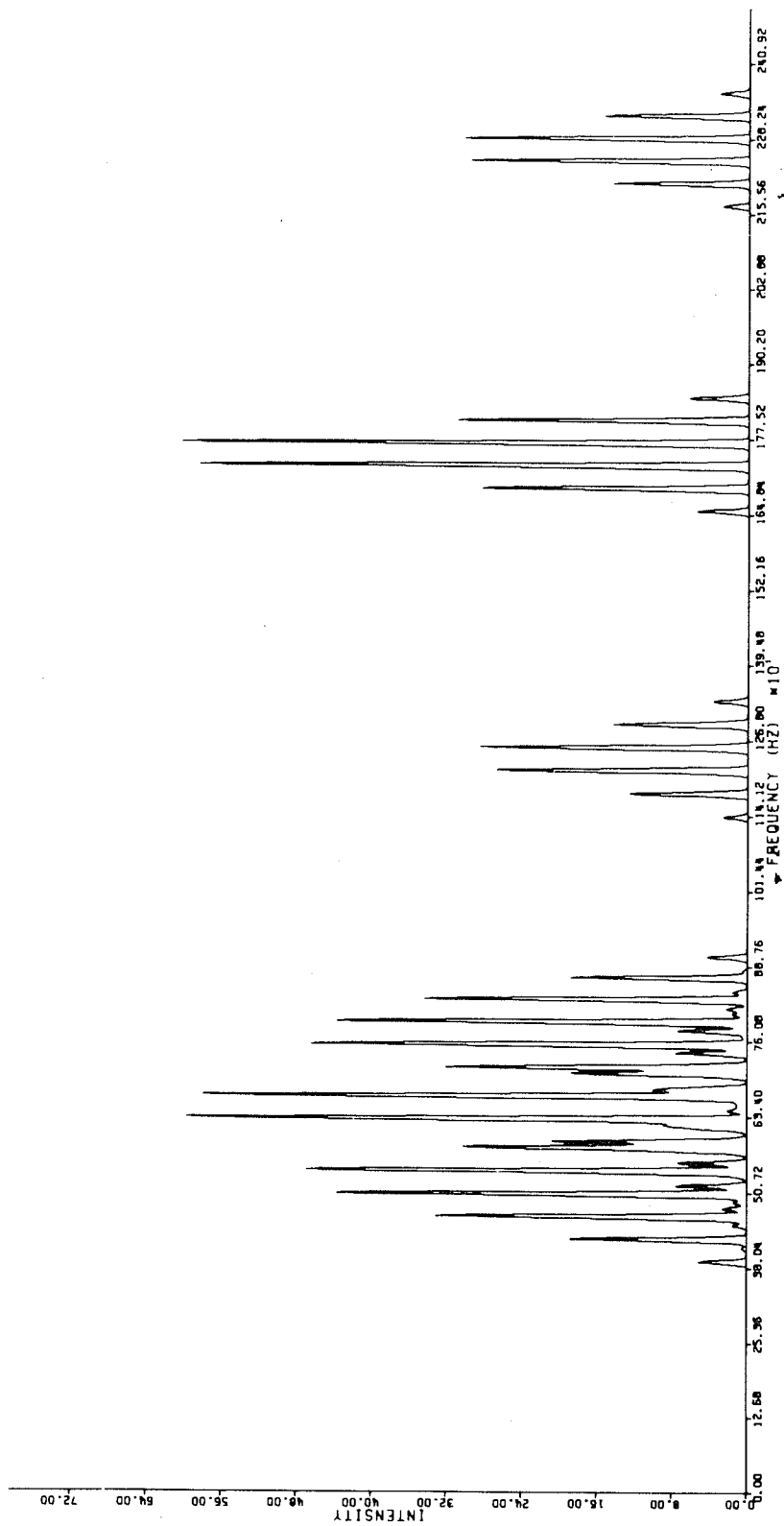
fig 4

Oklahoma State University

Department of Chemistry / (405) 372-6211, Ext. 7215 / Stillwater, Oklahoma 74074

November 12, 1970

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

Dear Dr. Shapiro:

We have developed a simple procedure for the synthesis of iso-phosphindolonium salts from readily available materials. The first recorded PMR values for this family are shown:
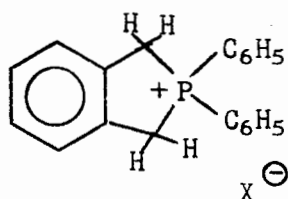
$$J_{PCH} = 10.6, \; X = Br$$

$$J_{PCH} = 10.6, \; X = picrate$$

(In DCCl$_3$)

Reduction in the J_{PCH} value of these compounds from that of many benzyltriarylphosphonium salts is a subject under study.

Short Title: PMR Data for Certain Isophospholindolonium Salts.

Sincerely,

K. D. Berlin
Professor

KDB:wp

YESHIVA
UNIVERSITY

BELFER GRADUATE SCHOOL OF SCIENCE

Amsterdam Avenue and 186th Street / New York, N.Y. 10033 / (212) LOrraine 8-8400

Octobber 12, 1970

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

Pseudorotation in Phosphoranes;
Stereochemistry of Vinyl Phosphates

Dear Barry,

In response to your vicious pink letter I enclose a report
of some interesting NMR work by my colleague I.J. Borowitz. He would
be interested in any response of the readers of TAMU NMR.

For myself, there is unfortunately little to report, except
our recent postulate that "pseudorotation" in phosphoranes takes place
via a non-symmetric dimer, e.g. for PF_5,
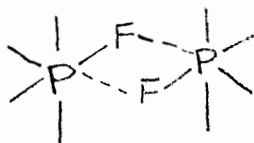
There is a variety of experimental evidence which is consistent with
this dimer-mediated mechanism, or the analogous six-coordinated solvated
complex and we find it inherently more satisfying than the accepted
hypothesis of large vibrational amplitudes, as in the Berry-mechanism.
Alan Cowley and I plan to publish something on this soon.

With best regards,

Yours sincerely,

Jeremy I. Musher

sg

ON THE STEREOCHEMISTRY OF VINYL PHOSPHATES[1]

In many cases the predominant stereochemistry of the vinyl phosphates resultant from α-haloketones and triethyl phosphite (TEP) has

$$(EtO)_2P-O \quad \overset{O}{\underset{\displaystyle Z}{\overset{\displaystyle }{}}} \quad C=C \quad \overset{H_B}{\underset{Y}{}} \quad$$
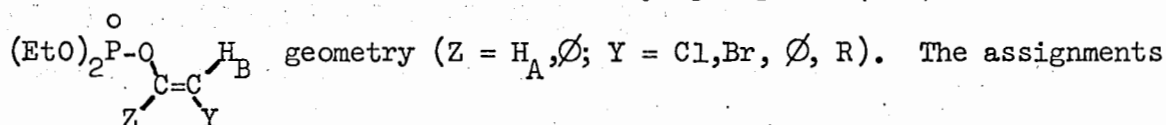
geometry ($Z = H_A, \emptyset$; $Y = Cl, Br, \emptyset, R$). The assignments are based on a combination of nmr spectral effects including: (a) the well known differentiation of cis and trans 1,2 -vinyl protons by their J_{HH} coupling constants wherein $J_{trans} > J_{cis}$: (b) a downfield shift for H_B when cis to phosphate (and little or no effect for a trans H_B) in the presence of $BF_3 \cdot Et_2O$ due to co-ordination of the BF_3 with PO and a resultant decrease of negative charge on the oxygen and (c) an upfield shift for trans H_B (and little or no effect for cis H_B) in changing solvent from CCl_4 to C_6D_6- due to "collision complex" formation. Relevant data is given in Table I. The conclusive case is the reaction of 22 to give 23, proven to be the trans-isomer: $H_B \ J_{AB} = 12 \ H_Z$: "BF_3 shift" -0.26 ppm ; "C_6D_6 shift" minimal (-0.06 ppm). The presence of vinyl halogen as in 25, 26 causes both isomers to give "BF_3 shifts", presumably because the halogen also co-ordinates with BF_3. The major isomer is trans 25, contrary to previous work.[2] The assignment of the H_A and H_B protons in 23,25,26 and the prediction of all of the vinyl proton nmr absorptions in vinyl phosphates was done by our application of method of Tobey[3] with the following assigned values: -1.39 to -1.44 ppm for geminal-phosphate (or phosphinate), +0.30 ppm for cis phosphate and +0.50 for trans phosphate. These values are all about 2/3 of those reported for $-OCOCH_3$.

---

1. I.J. Borowitz, M. Anschel and S. Firstenberg, J. Org. Chem, 32, 1763 (1967).

2. A.R. Stiles et al, J. Org. Chem, 26, 3960 (1961).

3. S.W. Tobey, J. Org. Chem, 34, 1281 (1969).

October 12, 1970

I.J. Borowitz
Belfer Graduate School of Science
Yeshiva University

Table I

The Stereochemistry of Enol Phosphate Formation

Reaction	δ^{Et_2O} (ppm)	$\Delta^{BF_3 \cdot Et_2O}_{Et_2O}$	δ^{CCl_4}	$\Delta^{C_6D_6}_{CCl_4}$
13 ϕ-C(O)-Cϕ(H)Cl $\xrightarrow{TEP}$ 65% **15**	6.42	−0.28	6.33	−0.15
35% **16**	6.79	−0.02	6.69	+0.30
14 ϕ-C(O)-Cϕ(H)Br $\xrightarrow{TEP}$ single isomer **15**	6.40	−0.26	6.315	−0.045
3 ϕ-C(O)-CH$_2$Cl $\xrightarrow{TEP}$ **2**	5.255	−0.265	5.23	−0.27
	5.22	−0.01	5.19	0.00
$\frac{13}{14}$ or $\xrightarrow{EtOP\phi_2}$	6.22	−0.185	6.19	−0.045
18 X = Br $\xrightarrow{TEP}$	5.45	−0.14	5.39	−0.24
19 X = Cl $\xrightarrow{EtO-P\phi_2}$	5.505	−0.145	5.38	−0.32
			5.68	
22 ϕ-C(Br)(H)-CHO $\xrightarrow{(MeO)_3P}$ single isomer **23**	6.37	−0.26	6.32	−0.06
24 Cl$_2$CH-CHO $\xrightarrow{(MeO)_3P}$ 80% **25**	6.26	−0.23	6.14	+0.185
20% **26**	5.70	−0.30	5.605	+0.435

H_B δ 6.32 (d, J = 12 Hz)

H_A δ 7.08 (d, J = 11.5 Hz)

PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL
KLINGELBERGSTRASSE 82 — TEL. 43 04 22
VORSTEHER: PROF. DR. P. HUBER

NEUE NR.
061-44 22 80
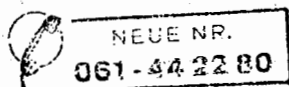
Prof. Dr. P. Diehl
Dr. H.P. Kellerhals
W. Niederberger

Basel, November 12, 1970/ea

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

Texas - 77843

USA

Computer program LEQUOR

Dear Barry,

we have extended the program for oriented spin-systems
LAOCOONOR (Mol.Phys.$\underline{15}$, 333, 1968) for use in cases with groups
of fully equivalent nuclei (total spin formalism).

The capacity of the new program LEQUOR is limited to
cases which do not exceed 7 groups of fully equivalent nuclei
and 16 spin-combinations with 13 submatrices for each combina-
tion. The dimension of a submatrix should not exceed 52.

LEQUOR is consequently applicable to any problem of
7 spins or fewer, to 8-spin systems such as A B C D E F G_2 and
e.g. to 11-spin-systems such as A B C_3 D_3 E_3.

Descriptions of the program and listings are available
upon request.

Sincerely yours,

P.Diehl   H.P. Kellerhals   W. Niederberger

Peter   H.P. Kellerhals

UNIVERSITY OF CALIFORNIA

Professor B. L. Shapiro   November 17, 1970
Department of Chemistry, Texas A and M University
College Station, Texas   77843

Dear Barry:

RELAXATION TIMES IN PHOSPHORUS COMPOUNDS

Your threats of expulsion have finally succeeded.

We are applying the Fourier transform technique of measuring relaxation times
(1) to a number of problems involving P^{31}. Irv Salmeen, who has been a post-doctoral
fellow with me and will be leaving for the Ford Scientific Labs at the beginning of
December, has been measuring T_1 and T_2 for phosphorus-containing molecules. Quite
naturally, adenosine tri-phosphate (ATP) has been examined. He has observed a pH
dependence of the T_1 for each of the three phosphates which exhibit titration-like
curves. The chemical shifts of these three phosphates are known to exhibit a pH
dependence (2) and it is natural to invoke an interaction common to both the relaxation
and chemical shift mechanisms to account for these parallel results. In the absence
of a better choice we are inclined to attribute these results to the spin-rotation
interaction. The temperature depencende of the relaxation rates should help us
establish the contribution of this interaction to the relaxation rates.

We have been using a modification of the Fourier T_1 relaxation method to
measure the T_2's of the individual lines in complex spectra. A Carr-Purcell, Meiboom-
Gill sequence is established. This, of course, evokes a series of echoes which
after Fourier transformation yield the partly (transversally) relaxed spectra. If
the interval between the π pulses is shorter than the time required for the echoes'
to decay into the noise, the decays are artifically truncated. Two effects arise
as a consequence of the interruptions; 1) the transformed spectra will contain lines
artificially broadened and, 2) a number of artifactual features or satellites will
appear in the spectra.

These undesirable features are circumvented by terminating the pulse sequence at
the pulse which evokes the echo to be examined thus allowing it to decay completely.
The trailing half of this terminal echo is accumulated with as many identical passes
as are required to achieve adequate signal-to-noise ratios. The timing is switched
to accumulate the next echo in the sequence, etc.

Although it may be surprising to some, the spectra resulting from these half-echoes
are strikingly similiar to those resulting from the transformation of simple free-
decays following a single pulse.

For simple molecules such as PO_4^{-3}, P_4O_6 and $P(OCH_3)_3$, $T_1 = T_2$ while for more
complex molecules, including ATP, this equality is not found. The extension to addition-
al systems and the interpretation of these findings will, obviously, receive much of
our attention for the immediate future.

Sincerely,

Melvin P. Klein

1. R. L. Vold, J. S. Waugh, M. P. Klein and D. E. Phelps, J. Chem. Phys. _48_, 3831 (1968)

2. M. Cohn and T. R. Hughes, J. Bio Chem., _235_, 3250 (1960)

Monsanto

November 17, 1970

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

Dear Barry:

We are using Fourier Transform ^{13}C nmr techniques in the analysis of
the microstructure of polymers. Fourier transforms have been obtained
of the noise-decoupled, natural abundance, 22.6-MHz ^{13}C nmr free
induction decays of a half dozen different polyelectrolytes, of poly-
acrylonitrile, of styrene-acrylonitrile copolymers, and of some
highly cross-linked polymers. The latter were in the form of semi-
rigid gels rather than true solutions. These polymer systems are not
amenable to study by ^{1}H nmr. However, the wide range of ^{13}C chemical
shifts, the easy removal of all spin-spin interactions by heteronuclear
decoupling, and the absence of severe dipolar broadening of the polymer
lines, permit a detailed ^{13}C nmr analysis of both the structural and
steric configurations of the chains. (Details of these studies will
appear in the January-February issue of Macromolecules.)

Our spectrometer consists of a Bruker HFX-Fabri-Tek 1074-PDP-8/I combination.
The spectrometer has four independent, simultaneously available rf channels,
namely the ^{13}C analytical channel, the ^{19}F lock channel, and two irradia-
tion channels which are presently tuned to ^{1}H and ^{14}N. All of the rf
frequencies are phase-locked. The ^{13}C rf drives a transmitter capable
of producing a 60-watt (into 50 ohms), square-wave pulse with a width
variable between 20 and 200 μsec. Wider pulse widths are used when only
a portion of the ^{13}C nmr spectrum is to be investigated. The pulse
sequence timing is provided by the trigger output of the Fabri-Tek 1074.
Only identical pulses with equal spacing are produced generating repeti-
tive free induction decays. Delays between pulses ranging from 0.1 to
20 seconds have been used. Very short pulse spacings can be used in
obtaining polymer ^{13}C nmr spectra because of the small effective T_2 values
involved. The 1074 is used to sample the receiver output after completion
of the irradiating pulse. The frequency sweep width is changed by
varying the 1074 data sampling rate. A tunable filter between the
receiver and 1074 removes undesired high-frequency components from the
free induction decay. The PDP-8/I is directly interfaced to the 1074
and calculates the Fourier transform using a program written by Fabri-
Tek. Either the amplitude spectrum (the square root of the sum of the
squares of the absorption and dispersion spectra) or the pure absorption
spectrum can be calculated, the latter calculation including a linear
phase correction. Line positions in the transformed spectra are read

Dr. Bernard L. Shapiro
Texas A&M Univ.
College Station, Tex.   - 2 -   November 17, 1970

as channel locations in the 1074 by means of a CRT display.

The optimum sensitivity of the Bruker spectrometer operating in the
pulsed mode is between two and three orders of magnitude greater than
when operating in the CW mode, while the sensitivity of the CW mode
is about five times greater than what I was able to achieve using
an HA-100 in CW ^{13}C nmr studies of polymers two years ago.

An example of the kind of noise-decoupled, natural abundance ^{13}C nmr
spectra of small molecules obtained with the Bruker spectrometer is
shown in the first figure. Here, we are illustrating lineshape and
resolution rather than sensitivity. This is an amplitude spectrum in
which no phase correction has been made. The free induction decay
from the methyl carbon of the propylene glycol has been removed by
filtering and so is not folded back into the narrow width of the
transformed spectrum. The ^{13}C nmr spectra of a 10% (wt/vol) DMSO
solution of polymethacrylonitrile is shown in the second figure. De-
tailed interpretations have not yet been completed. However, the
indicated line assignments in the wide sweep-width spectrum are clear
on the basis of off-resonance decoupling experiments. (The very intense
peak is due to the solvent, and is many times off scale.) The free
induction decay was accumulated in 4 minutes, and the transform required
30 seconds. In a separate experiment, the high-field methyl-carbon
region was expanded yielding the second spectrum of this figure. The
increased resolution was obtained at a cost of about a factor of 30
in the time of data accumulation. Other lines were removed from the
spectrum by filtering before the transform was performed. (Both of these
spectra are amplitude spectra.) The many lines in the methyl-carbon
region of the spectrum of polymethacrylonitrile can be interpreted in
terms of the various steric pentads present in different concentrations
in the chain. That is, the resonance of each methyl carbon is sensitive
to the steric configuration of nearest and next-nearest monomer neighbors
in the chain. This kind of detailed information is not available from
the ^{1}H nmr spectrum of polymethacrylonitrile.

Please credit this contribution to the Monsanto subscription.

Sincerely,

Jake

Jacob Schaefer

rl

Title: Fourier Transform ^{13}C NMR Studies of Polymers
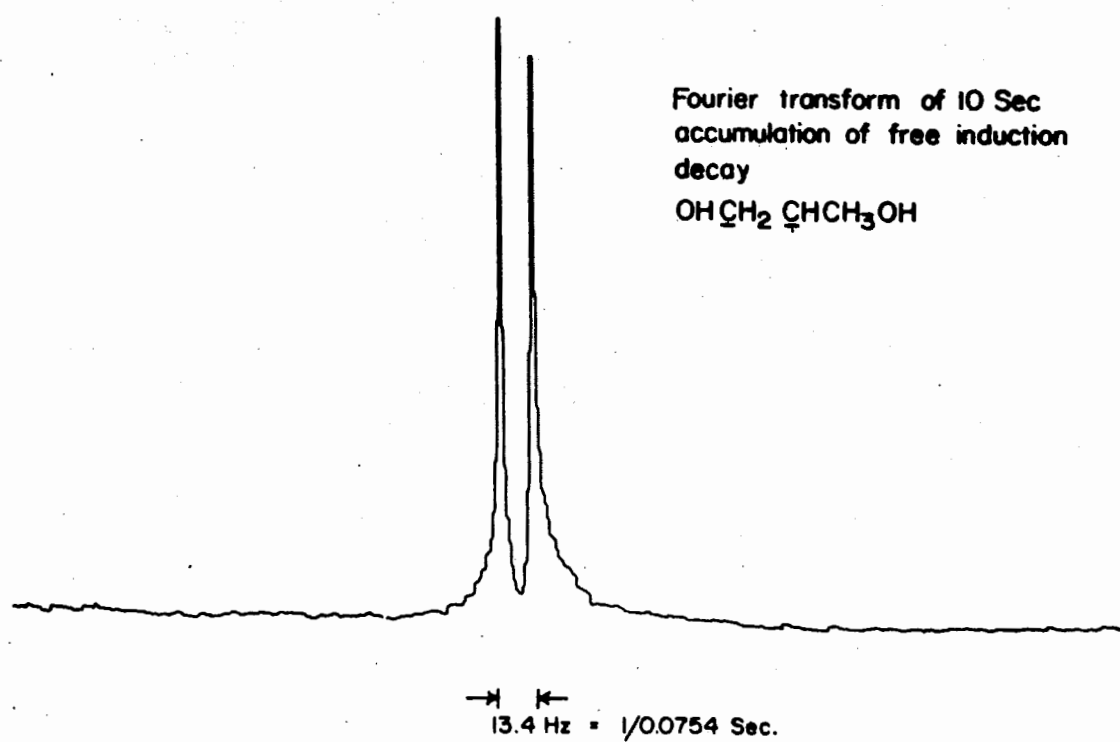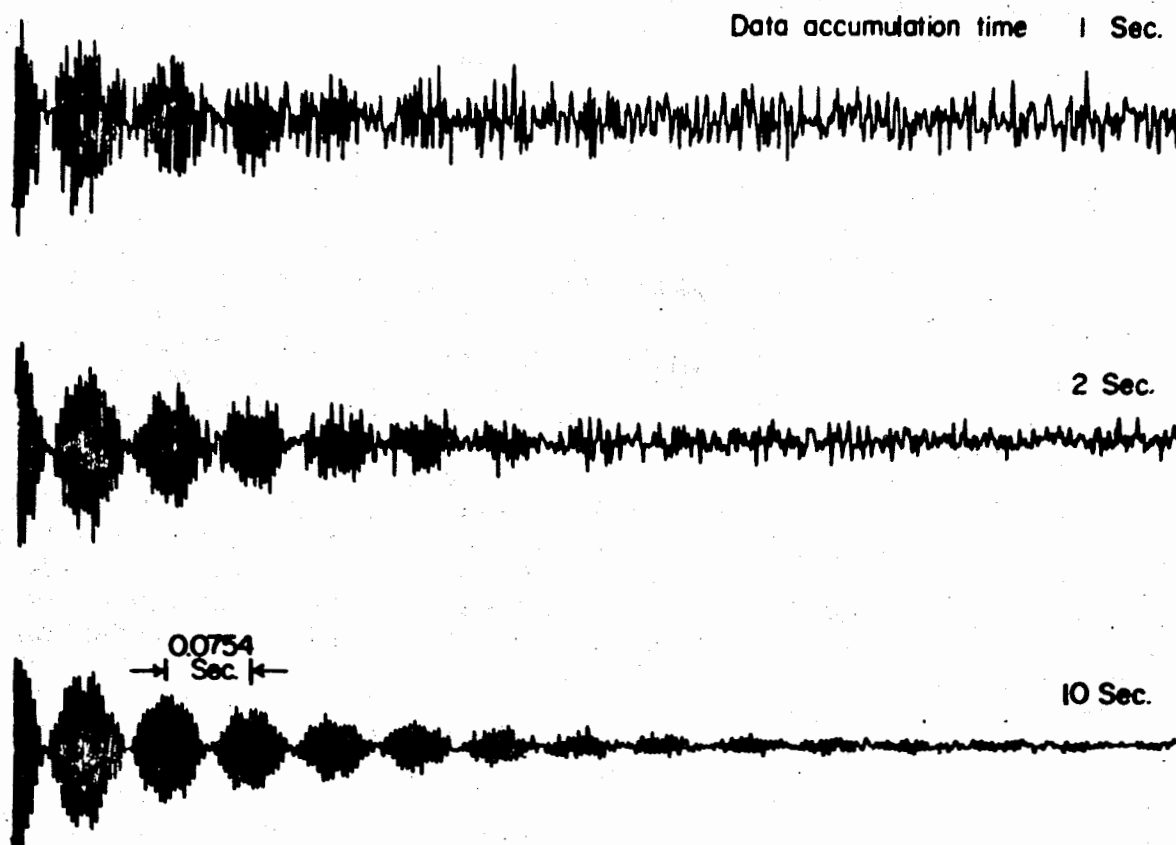
Data accumulation time   I Sec.

2 Sec.

0.0754
Sec.

IO Sec.

Fourier transform of IO Sec
accumulation of free induction
decay

OH CH₂ CHCH₃OH

13.4 Hz = 1/0.0754 Sec.

−CN

−C−

solvent
(DMSO)

polymethacrylonitrile

$+CH_2 \overset{CH_3}{\underset{CN}{C}} \overset{}{\underset{}{}}_x$

−CH₂−

−CH₃

$\xrightarrow{500}$ Hz

Ho→

25 Hz

expanded
−CH₃

←Ho

FACULTÉ DES SCIENCES DE MARSEILLE - SAINT-JÉROME

13 · MARSEILLE (13ᵉ)

TÉL. : 50-31-61
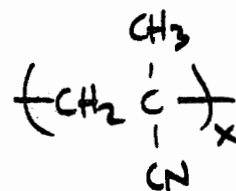
DÉPARTEMENT DE CHIMIE ORGANIQUE
LABORATOIRE DES ORGANOMÉTALLIQUES
PROFESSEUR J. C. MAIRE

Professor Bernard L.SHAPIRO
Department of Chemistry
Texas A-M University
College Station, Texas 77843

FIVE-BOND FLUORINE-SIDE CHAIN COUPLING IN
FLUOROAROMATIC COMPOUNDS

Dear Dr.Shapiro :

Thank you for reminder. As a payement on our subscription here are a few notes on a
study of long range fluorine-proton coupling. In the Nmr spectrum of compound $\underline{1}$ (6) the
signal of the trimethylsilyl group appears as a doublet which is due to five-bond cou-
pling with the ortho-fluorine. A similar coupling has been observed by C.TAMBORSKY and
E.J.SOKOLSKI (J.Organometal.Chem. 1969, $\underline{17}$, 185) in compounds $\underline{2}$, $\underline{3}$ and $\underline{4}$.
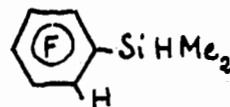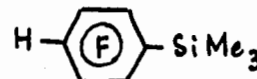
J_{F-Me} =   1,5 Hz   1 Hz   1 Hz   1,5 Hz
              $\underline{1}$ $\underline{2}$ $\underline{3}$ $\underline{4}$

In order to check the generality of the phenomenon we have examined a series of compounds
of the type $\underline{5}$:
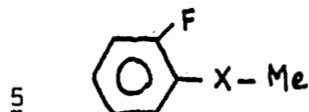
It occurred to us that the size of coupling constant could depend on the presence on the
heteroatom of free electron pairs, or low-lying empty-d orbitals (like 3d orbitals of
silicom atom) available for extended conjugation with the phenyl ring.
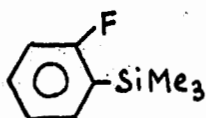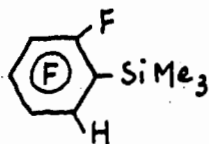Two different cases are to be considered pentafluorophenyl compounds (5F) and simple
o-fluorophenyl compounds (1F). Our results are given in table, together with data from
the litterature. The compounds are listed in order of increasing J_{F-Me} coupling. The
"five bond" or "through space" F-Me coupling is larger in the 5F than in the 1F
series. Moreover it is clear from compounds 1,9 and 10 that for a given heteroatom, con-
jugation increases the coupling constant. In the 1F series a long range coupling is obser-
ved when X is able to enter conjugation with the ring, but does not occur with any of
the other compounds. This observation is in favour of pπ-dπ bonding in trimethylsilyl aro-
matic compounds. Further investigations are on the way.

Sincerely yours.

JC MAIRE

M.DONNIER
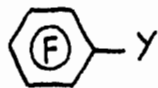
(5F) —Y   (1F)
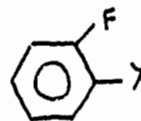
	Y =	J=		Y =	J=
1	Et	0			
2	$-SnMe_3$	0,4			
3	$-SnClMe_2$	0,4 (1)			
4	$\rangle SnMe_2$	0,4 (1)	13	$-CH_2-CH_3$	0
5	$-SMe$	0,7 (2)	14	$-CH(CH_3)_2$	0
6	$- PbMe_3$	1 (3)	15	$-t-Bu$	0
7	$- OMe$	1,1 (4)	16	$-SnMe_3$	0
8	$-PMe_2$	1,2 (5)	17	$CH_2=C-Me$	1,5
9	$CH_2=C-Me$	1,2	18	$-SiMe_3$	1,2
10	$-\underset{O}{\overset{\parallel}{C}}-CH_3$	1,7			
11	$-NMe_2$	1,9 (1)			
12	$-NHMe$	2,6 (1)			

(1) J.BURDON, Tetrahedron, 1965, 21, 1101.

(2) P.ROBSON, MSTACEY, R.STEPHENS, J.C.TATLOW, J.Chem.Soc. 1960, 4754.

(3) L.H.SUTCLIFFE, unpublished result.

(4) I.J.LAWRENSON, J.Chem.Soc. 1965, 1117.

(5) M.G.BARLOW, M.GREEN, R.N.HASZELDINE, H.G.HIGSON, J.Chem.Soc. 1966 (B), 1025.

(6) Y.VIGNOLLET - unpublished result.

UNIVERSITY OF SOUTHERN CALIFORNIA

UNIVERSITY PARK

LOS ANGELES, CALIFORNIA 90007

DEPARTMENT OF CHEMISTRY

November 23, 1970

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

Dear Professor Shapiro:

The title for our initial contribution to the TAMUNMR
Newsletter is <u>Rotational Isomerism in α,β-Unsaturated Acyl
Fluorides</u>. Koster[1] studied the temperature dependence of the
^{1}H nmr spectrum of acryloyl fluoride at temperatures above $-95°$
and concluded from the changes in the three-bond HF coupling
constant that the enthalpy difference between <u>s-cis</u> and <u>s-trans</u>
conformations was 800 ± 250 cal/mole, with the latter conforma-
tion having the lower energy. Subsequently, infrared[2] and
microwave[3] studies have confirmed that the energy difference
between the two forms is small. This is in contrast to the
behavior of most α,β-unsaturated carbonyl compounds, which
generally have a strong preference for the <u>s-trans</u> conformation.
We have found that, at very low temperatures, interconversion
of the two conformations is stopped on the nmr time scale.
The <u>s-trans</u> and <u>s-cis</u> forms are present in a ratio of 76:24
at $-161°$.

s-trans   s-cis
76%   24%
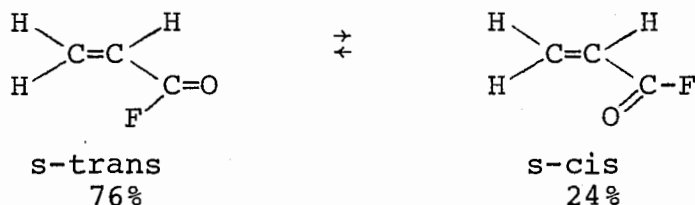
This ratio corresponds to a free energy difference of 0.25 kcal/
mole. The values of Ea and $\Delta G^{\ddagger}$ for rotation about the C-C bond
were 6.06 ± 0.07 and 5.66 ± 0.07 kcal/mole.

The ^{19}F chemical shifts at 94.1 MHz were 3623 and 1548 Hz
downfield from fluorotrichloromethane, the internal standard,
for the <u>s-cis</u> and <u>s-trans</u> conformations, respectively. The fluorine
of the <u>s-trans</u> conformation is coupled ($^3J_{HF}$ = 19.2 Hz) to the
proton separated by three bonds; the corresponding coupling con-
stant for the <u>s-cis</u> form was calculated to be -7.5 Hz, assuming
the ground-state energy difference between these two forms is
invariant with temperature. Crotonyl fluoride, cinnamoyl
fluoride, and p-methoxycinnamoyl fluoride also exhibit <u>cis-trans</u>
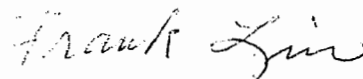
Professor Bernard L. Shapiro
Page Two
November 20, 1970
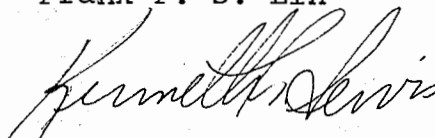
isomerism, and the free energy differences and barriers to rotation have been determined for these compounds.

Sincerely yours,

Frank F. S. Lin

Kenneth L. Servis
Associate Professor
of Chemistry

KLS:jeb

References:
1. D. F. Koster, J. Amer. Chem. Soc., 88, 5067 (1966).

2. G. L. Carlson, W. G. Fateley, and R. E. Witkowski, ibid., 89, 6437 (1967).

3. J. J. Keirns and R. F. Curl, Jr., J. Chem. Phys., 48, 3773 (1968).

UNIVERSITÉ D'OTTAWA

**OTTAWA 2 CANADA**

UNIVERSITY OF OTTAWA

DÉPARTEMENT DE CHIMIE

DEPARTMENT OF CHEMISTRY

November 23, 1970

Professor B. L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station, Texas 78843,
U. S. A.

Substituent Effects on Geminal Couplings
in Allylic Methylene Groups

Dear Barry:

I thought it worthwhile to describe some work just
completed by Bruce Raby for his M.Sc. degree since it will be
several months before it appears in the literature.

Bruce synthesized ten members of the series of general
formula I for the purpose of studying substituent effects on the
geminal coupling constant J_{AB} in the allylic methylene groups.

I
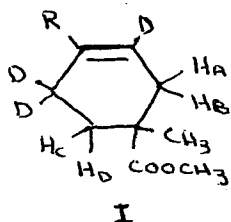
The nmr spectra were measured at 100 MHz during
simultaneous irradiation of the deuterons, and the spectra, which
were first order, gave the parameters listed in Table I.

........2
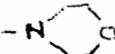
Prof. B. L. Shapiro   - 2 -   November 23, 1970

Table I

Coupling Constants in I (in Hz)

Compound	$-J_{AB}$	$-J_{CD}$		$-J_{AB}$	$-J_{CD}$
R=Cl	17.4	13.3	R=$COHH_2$	18.8	13.4
$OCOCH_3$	17.3	13.3	OCH_3	16.4	13.2
C_6H_5	18.1	13.2	H	17.5	13.2
CN	19.3	13.4	SC_6H_5	17.2[a]	-
$COOCH_3$	19.2	13.3	$-N\bigcirc O$	16.8	13.0

[a] estimated from undeuterated derivative of I.

It can be seen that J_{AB} varies by almost three Hz as R is varied. Changes in J_{AB} do not correlate well with Hammett σ_p values for the R substituents but correlate better when increased weight is given to the resonance effect of the substituents.

These results show J_{Gem} to be more susceptible to the R substituent in this series than in the benzylic system, para-$R-C_6H_5-C-X$.
$$\overset{}{\underset{H_A \quad H_B}{}}$$

In this latter system a large conformational influence of the orientation of the benzene ring in determining substituent effects on J_{Gem} has been observed (R. R. Fraser and R. N. Renaud, Can. J. Chem. in press) and it seems very likely that the substituent effects in allylic CH_2's are also conformationally dependent and those in the table represent the maximum values. (In the cyclohexene ring the π-orbitals of the double bond are within $9°$ of the geometry required for maximum overlap with the anti-symmetric M.O. of the methylene group). Work towards establishing the conformational influence on J_{Gem} in allylic systems is continuing.

Yours sincerely,

Robert R. Fraser

RRF:ae

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

November 20, 1970

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

Dear Professor Shapiro:

Subject: Checking performance of Pulse-Gate for FID

We are trying to get approval for FID-FT gear for protons at 100 MHz
initially and, after increasing our know-how, for C^{13} at 25 MHz.
Judging by the experience of other workers, there are problems related
to proper evaluation of the pulse gear as electronic components. The
supplying companies rely almost wholly on computer output. We may be
driven to using the central computer on a real-time basis to perform
these experiments and need some method of evaluating the pulse gear on
its own.

A number of properties have been suggested as criteria, but the method
of making the necessary measurements is not clear.

Among the properties which should effect performance are: accurate
pulse durations to 1% in the 1 to 10 microsecond range; sharp, square
cut-off of the pulse (To what standard?); reproducible phase relation
of pulse to carrier (To what standard?); and broad band-pass for the
system including the detector.

These seem to be the important considerations but most of them are not
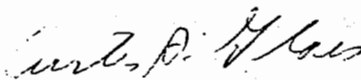easily measured.

We should be happy to receive any comments on this problem from readers.

With best regards.

Sincerely,

David Weisleder, Chemist
Physical-Chemical
  Properties Investigations
Cereal Properties Laboratory

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

NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20390　　IN REPLY REFER TO:

6110-382:CFP:vmg
30 November 1970

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

    A.　High Current Connections in Varian Power Supplies
    B.　Fabri-Tek 1074
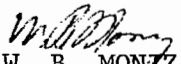
Dear Barry:
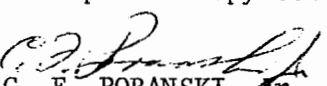
Recently, while trying to locate the source of extreme field insta-bility in our broadline magnet system (9" magnet, V-2503 power supply and Mark 1 Fieldial), we attempted to adjust the Fieldial following the pro-cedure described in the Varian manual. We located the instability at the step in which the field must be reversed, because at this point the field reversing switch jammed when it was activated. When we disassembled the switch we found several of the plastic parts charred and the main assembly broken. We also found that the current carrying cables were quite stiff near the lugs and the insulation starting to crack. The switch and cables (all 7) had to be replaced. This overheating can arise from loose connec-tions, as mentioned in the Varian manual, but in our case may more likely have been due to increased resistance caused by corrosion of the high-current connections since the connections appeared to be quite tight.

We recommend that, in addition to checking the nuts and bolts for tightness, the lugs should be checked for corrosion as evidenced by dis-coloration. If the current cables have to be replaced, the lugs should be soldered on instead of just crimped.

We have received a Fabri-Tek 1074 signal averaging system. In a preliminary arrangement we have used the voltage ramp of the Fabri-Tek to drive a Wavetek 134 sweep generator whose output is used as an ex-ternal sweep frequency for our HA-100 system. We read out on either the HA-100 recorder or an x-y recorder. This setup has been reasonably suc-cessful and will be developed further.

Sincerely,

W. B. MONIZ, Head
NMR Spectroscopy Section

C. F. PORANSKI, Jr.
NMR Spectroscopy Section
Chemistry Division

30 November 1970

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

"Absolute" Signs of J_{HH}'s and J_{HF}'s in Benzenes; Guide for the Blind

Dear Barry,

We apparently went through the entire spectrum of your reminders, as the foot-
note on the far-infrapink letter shows. The present contribution, we hope,
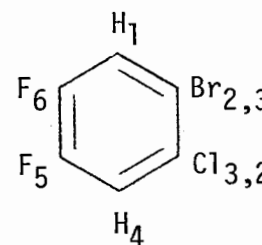will reach you before you cut us off.

This is a sequel to our recently published note [1], part of which was pre-
sented at the Aachen NMR Colloquium last April. We think it gives strong
evidence that all J_{HH}'s as well as ortho- and meta-J_{HF}'s in benzenes are
"absolutely" positive, if one piece of theory is taken as "absolutely" true,
that is, that $^1J_{CH}$'s are absolutely positive. Two other groups of investi-
gators [2,3], working in the area of oriented molecules, have reached the same
conclusion; their auxiliary hypothesis has been one on the orientation of
benzene rings in a strong magnetic field.

We related signs of coupling constants to each other by heteronuclear tickling.
Mr. E. P. Ragelis of our laboratory synthesized a molecule simple enough to
do the necessary tickling experiments, namely, 2-bromo-3-chloro-5,6-difluoro-
benzene. Mr. R. Tschudin of Varian Associates constructed a frequency mul-
tiplier for us so that the 5 MHz standard frequency from the GR frequency
synthesizer could be used to provide a 50 MHz source for driving the doubler
stage of the V-4311 rf unit of the HA-100 [4]. We gratefully acknowledge
the assistance of both gentlemen.

To get oriented in "F-space", that is, to establish an absolutely relative
scale of the F spectrum with respect to H (how was that again?), we tickled
the two AX systems of cis- and trans-1,2-dichlorofluoroethylene (the "guide"
compound mentioned below) and noted at what F frequency the H lines of these
two molecules exhibited the cleanest tickling patterns. This "guide for the
blind" may not be original and fortunately will not be necessary for those
who use spectrometers of the last generation, where all frequencies are derived
from one master oscillator.

Spectra were taken of a 50% solution of 2-bromo-3-chloro-5,6-difluorobenzene
in a 3:1:1 mixture of CCl_3CF_3, TMS and our guide compound (see above). The
parameters of the Table have an r.m.s. error of 0.01_1 Hz and were obtained
by refinement of experimental data through two iterations.

TABLE

$$H_1$$

$$F_6 \quad\quad Br_{2,3}$$
$$F_5 \quad\quad Cl_{3,2}$$
$$H_4$$

$w_1 = 8.77$ Hz $w_5 = 107.14$ Hz

$w_4 = 22.80$ Hz $w_6 = 18.95$ Hz

J_{ij} (Hz)	+0.36	-20.50	+9.46	+9.76	+7.76	+7.47
ij	14	56	16	45	15	46
Type	HH para	FF ortho	HF ortho	HF ortho	HF meta	HF meta

The Larmor frequencies w_i are referred to arbitrary zeros which correspond approximately to the first lines of the H and F spectra respectively.

The absolute character of the signs is based on the fact that ortho-J_{FF}'s are absolutely negative [1]. That the relative signs are

$$^oJ_{FF} \mp, \quad ^pJ_{FF} \pm; \quad ^oJ_{HF} \pm, \quad ^mJ_{HF} \pm; \quad ^oJ_{HH} \pm, \quad ^mJ_{HH} \pm, \quad ^pJ_{HH} \pm$$

has already been established by spectral analysis [5] and by tickling experiments [6].

It would, of course, be desirable to do an experiment similar to ours with a molecule which contains two H's ortho or meta to each other: there is an outside chance that in our particular molecule para-J_{HH} is negative, because para-J_{HH}'s can be close to zero.

[1] E. Lustig and E. A. Hansen, Chem. Commun. 1970, 661.
[2] L. C. Snyder and E. W. Anderson, J. Chem. Phys. 1965, 42, 3336.
[3] C. T. Yim and D. F. R. Gilson, Can. J. Chem. 1969, 47, 1057.
[4] For similar set-ups see A. Charles, J. Sci. Instr. 1968, Series 2, 1, 64, and H. Dreeskamp, Z. Naturf. 1968, 23a, 940.
[5] See, e.g., W. B. Moniz and E. Lustig, J. Chem. Phys. 1969, 50, 1905 and references therein.
[6] R. Freeman and N. S. Bhacca, J. Chem. Phys. 1963, 38, 293.

Best wishes and regards.

Sincerely,

E. Lustig
BF-115

E. A. Hansen

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
800 BUCHANAN STREET
ALBANY, CALIFORNIA 94710

December 2, 1970

AIRMAIL--SPECIAL DELIVERY

Professor Barry Shapiro
1101 Merry Oaks
College Station, Texas 77840

Subject: 12th ENC to be held at University of Florida, Gainesville,
          from February 18 to 20, 1971

Dear Barry:

I hope this announcement will serve to reinstate my delinquent sub-
scription to the NMR Newsletter.

The 12th Experimental NMR Conference will be held on the campus of the
University of Florida, Gainesville, from Thursday, February 18, through
Saturday noon, February 20, 1971. This conference is devoted to new
developments in instrumentation and experimental techniques. It is not
intended as a vehicle for the presentation of results obtained by routine
NMR methods.

Sessions will consist almost entirely of invited papers, but a limited
number of contributed papers can be accepted. Anyone wishing to present
a paper in one of the currently scheduled sessions should communicate
directly with the chairman of the appropriate session. Session chairmen
will assign the lengths of all presentations.

The following sessions are currently being planned by the indicated
chairmen:

   User experiences with new generation high resolution spectrometers
      P. Bender
   Department of Chemistry
   University of Wisconsin
   Madison, Wisconsin   53706

   Structure coding and pattern recognition of NMR spectra
      T. Lusebrink
   IBM Research K04-025
   Monterey and Cottle Roads
   San Jose, California 95114

2

Fourier transform techniques
A. Allerhand
Department of Chemistry
Indiana University
Bloomington, Indiana 47401

Applications of paramagnetic shift reagents in high resolution NMR
P. Demarco
Lilly Research Laboratories
Eli Lilly and Company
Indianapolis, Indiana 46206

Developments in ^{13}C NMR
J. Stothers
Department of Chemistry
University of W. Ontario
London, Ontario, Canada
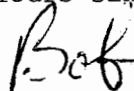
Progress in superconducting high resolution spectrometers
A. Bothner-By
Department of Chemistry
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Topics other than those listed here may be included, with both invited
and contributed papers. Anyone wishing to suggest additional topics or
to present a paper unrelated to the scheduled sessions should communi-
cate with the conference chairman as soon as possible. The chairman will
assign the lengths of these papers.

Additional information and an application to attend may be obtained from
the ENC Secretary: Professor Jay Martin Anderson, Department of Chemistry,
Bryn Mawr College, Bryn Mawr, Pennsylvania 19010.

Yours sincerely,

R. E. Lundin
Chairman, 12th ENC

THE OHIO STATE UNIVERSITY
DEPARTMENT OF CHEMISTRY
140 WEST 18TH AVENUE
COLUMBUS, OHIO 43210

November 30, 1970

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

Dear Barry:

Recently Mrs. Ying-Hseh Chen has been preparing a number of substituted benzyllithiums by addition of $\underline{t}$-butyblithium with tetramethylethylenediamine (1:1) to the appropriate α-methylstyrene in isooctane.

The benzyllithiums have proton shifts, see below, very similar to benzyllithium itself from which we conclude that the species look like conjugated anions, I.
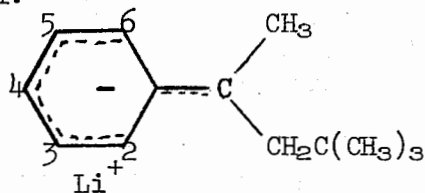
At 0° all the ring hydrogens are magnetically non-equivalent indicating slow rotation about the C_{ring} - C_{benzyl} bond. The nmr parameters for the unsubstituted system are: Shifts, tau scale, H_2, 3.03; H_3, 3.91; H_4, 2.27; H_5, 4.01; H_6, 3.37. Coupling constants, Hz: 2,3 9.2; 2,4 -1.31; 2,5 -0.1; 2,6 -2.83; 3,4 6.48; 3,5 -2.33; 3,6 -0.28; 4,5 6.51; 4,6 -1.22; 5,6 9.02. We are quite certain about the relative signs but not sure what they mean.

Above 0° the spectrum undergoes line-broadening and averaging and changes with increasing temperature from ABCDE to ABB'CC'. The complexity of a five spin system allows the rates responsible for this exchange process to be fitted with good accuracy using Binsch's program DNMR. The resulting activation parameters are Ea 19.4, $\Delta H^{\ddagger}$ 18.6, ±0.4 kcal respectively and $\Delta S^{\ddagger}$ is 0.3±1 eu. The kinetic order in contained reagent is 1 ±0.05.

The process responsible for these exchanges clearly involves rotation about the ring benzyl bond. Whether we have measured the barrier to rotation in the anion or whether rotation is chemically assisted by the lithium is a matter which has to be cleared up with more experiments now in progress.

With best regards.

Sincerely yours,

Gideon Fraenkel
Professor of Chemistry

GF/aa

ORGANISCH CHEMISCH LABORATORIUM
DER RIJKSUNIVERSITEIT TE UTRECHT
CROESESTRAAT 79
POSTGIRO 65985-TEL. 82311

UTRECHT, December 1, 1970
(NEDERLAND)

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

Long range coupling in alkylvinyl ethers and -thioethers.

Dear Professor Shapiro,

In June we acquired a Varian XL 100/15 nmr-spectrometer.
It soon turned out that the resolving power of this instrument,
in the internal ^{1}H lock mode, was very good indeed. We obtained
for instance in the centerlines of the o-dichlorobenzene multi-
plet (Varian sample 943346-26) a line-width at half height of
0.06 Hz. Since it was known (1,2) that in vinylethers and
vinylthioethers some coupling occurs over the heteroatom and we
had a large number of these compounds at hand, we decided to try
to obtain more accurate values of these coupling constants
with the XL 100.

The nmr-parameters of the methyl- and ethylvinyl ethers
and thioethers (20 % v/v in CCl_4, degassed) are given in the
table. The vinyl-parts of the spectra were analysed as ABX-
systems, treating the long range coupling constants as first-
order perturbations. As it is very easy, though of discutable
practical utility, to obtain accurate chemical shifts with the
XL 100 spectrometer, which operates in a digital frequency-swept
mode, most of the reported chemical shifts are accurate within
0.003 ppm.

From these data and from the data on a number of other
systems we studied also, we found that $^4J_{ad}$ is very sensitive
to the nature of the alkyl-substituent. It could be that the orien
tation of the alkyl-group with respect to the double bond is the
determining factor for this coupling.

Furthermore, we found $\left|{}^5J_{cd}\right| > \left|{}^5J_{bd}\right|$ in all cases studied sofar. This observation could be of use in determining the configuration around the double bond. Finally we would like to draw attention to the coupling of the protons in the methyl group in the ethylderivatives with the ethylenic pro-tons. This coupling is illustrated in figure 2, which shows on an expanded scale one of the four lines of proton a in ethyl-vinyl thioether. Figure 1 gives the observed spectrum of the methoxylprotons in methyl-vinylether.

A detailed account of this work on a larger number of compounds will be published.

Table 1
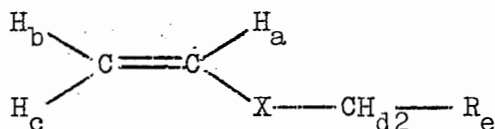
chemical shifts in ppm relative to TMS internal ; J in Hz

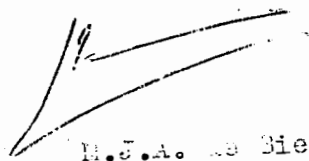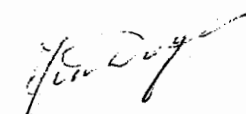| X =	O	O	S	S
R =	H	CH_3	H	CH_3
H_a	6.430	6.342	6.363	6.273
H_b	3.902	3.861	5.120	5.117
H_c	4.060	4.035	4.870	5.002
H_d	3.471	3.675	2.189	2.67 ± 0.01
H_e	–	1.256	–	1.30 ± 0.01
${}^3J_{ab}$	+6.85 ± 0.03	+ 6.90 ± 0.03	+10.06 ± 0.03	+10.10 ± 0.05
${}^3J_{ac}$	+14.26 ± 0.03	+14.37 ± 0.03	+16.52 ± 0.03	+16.70 ± 0.05
${}^4J_{ad}$	0.40 ± 0.02	0.53 ± 0.02	0.00 ± 0.02	0.18 ± 0.02
${}^5J_{ae}$	–	0.19 ± 0.02	–	0.18 ± 0.02
${}^2J_{bc}$	−2.13 ± 0.02	− 1.85 ± 0.02	0.17 ± 0.02	Not resolved $r_{b,c\frac{1}{2}} < 0.35$
${}^5J_{bd}$	0.20 ± 0.02	0.17 ± 0.02	0.19 ± 0.02	
${}^6J_{be}$	–	0.17 ± 0.02	–	
${}^5J_{cd}$	0.31 ± 0.02	0.34 ± 0.03	0.37 ± 0.02	0.28 ± 0.05
${}^6J_{ce}$	–	0.12 ± 0.02	–	N.r.
${}^3J_{de}$	–	7.0 + 0.1	–	7.3 + 0.1

-3-
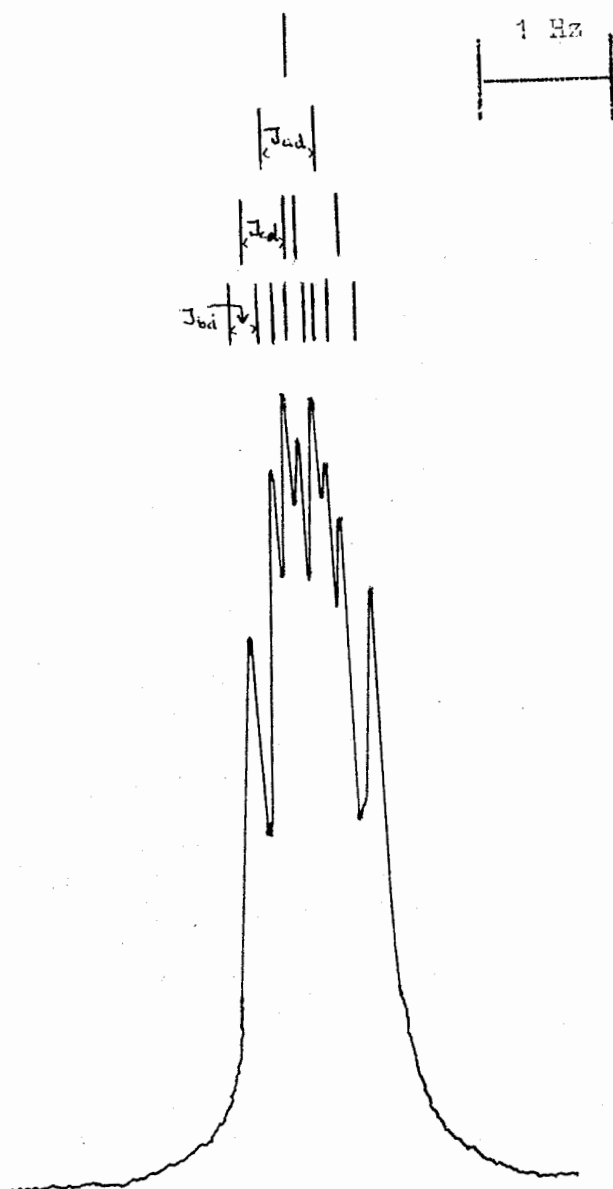
Figure 1

Figure 2

With best regards,

Yours sincerely,

H.J.A. de Bie

J.P.C.M. van Dongen

(1) J. Feeney and L.H. Sutcliffe, Spectrochim. Acta 24,1135 (1968).

(2) R.T. Hobgood, G.S. Reddy and J.H. Goldstein, J.Phys.Chem. 67, 110 (1963)

N.V. **PHILIPS-DUPHAR**

P O S T B U S   2   -   W E E S P   -   N E D E R L A N D

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

Uw ref./Your ref.	Onze ref./Our ref.	Afd./Dept.	Datum/Date
	FvD/BZ/211	56630	November 23, 1970

The assignment of the lines in an ABX system.

Dear Dr. Shapiro,

The assignment of the lines of an ABX system to A, B, X, and combined
transitions, given by Pople[1], is incomplete insofar as it is valid
only for the case in which $\nu_A - \nu_B > \frac{1}{2}(J_{AX} - J_{BX})$*. With this condition,
cos $2\emptyset_-$ is positive and cos $\emptyset_- >$ sin $\emptyset_-$. Consequently the basic wave
function $5(\alpha\beta\beta)$ predominates in the mixed wave function $5'[\cos \emptyset_- (\alpha\beta\beta)$
+ sin $\emptyset_- (\beta\alpha\beta)]$, and so does the basic wave function 6 $(\beta\alpha\beta)$ in the mixed
wave function 6' $[-\sin \emptyset_- (\alpha\beta\beta) + \cos \emptyset_- (\beta\alpha\beta)]$. Therefore the transitions
8 $(\beta\beta\beta) \rightarrow 5'$ ($'\alpha\beta\beta'$) and 6' ($'\beta\alpha\beta'$) $\rightarrow 2$ $(\alpha\alpha\beta)$ may be regarded as being
A-lines, the transitions 8 $(\beta\beta\beta) \rightarrow 6'$ ($'\beta\alpha\beta'$) and 5' ($'\alpha\beta\beta'$) $\rightarrow 2$ $(\alpha\alpha\beta)$ as
B-lines, the transitions 5' ($'\alpha\beta\beta'$) $\rightarrow 3'$ ($'\alpha\beta\alpha'$) and 6' ($'\beta\alpha\beta'$) $\rightarrow 4'$
($'\beta\alpha\alpha'$) as X-lines, and the transitions 5' ($'\alpha\beta\beta'$) $\rightarrow 4'$ ($'\beta\alpha\alpha'$) and 6'
($'\beta\alpha\beta'$) $\rightarrow 3'$ ($'\alpha\beta\alpha'$) as combination lines.
However, if $\nu_A - \nu_B < \frac{1}{2}(J_{AX} - J_{BX})$, which is the condition for the other
ABX solution with the same line positions, cos $2\emptyset_-$ is negative, hence cos
$\emptyset_- <$ sin $\emptyset_-$, and then the basic wave function 6 predominates in the mixed
wave function 5' and so does the basic wave function 5 in the mixed wave
function 6'. Therefore the assignment of all the transitions connected to
the levels of the mixed wave functions 5' and 6' must be interchanged, i.e.
the above-mentioned A-lines must be interchanged with the B-lines, and the
X-lines must be interchanged with the combination lines.
Based upon these considerations two different assignments ought to be taken
into account in a list of transitions for an ABX system (Table 1).

---

* The same notation and the same assumptions as those of Pople are used, i.e.
$\nu_A > \nu_B$ and $D_+ > D_-$ (viz. $J_{AX} > J_{BX}$).

The correctness of the two assignments may be verified easily :
for A- and B-lines, if we consider the two possible combinations of the
effective Larmor frequencies of the two sub-AB systems leading to the
two solutions; for the X- and combination lines, if we consider the
intensities in the X part at a steadily increasing value of $\nu_A - \nu_B$:
the relative intensities of X-lines will increase to unity, while the
intensities of the combination lines will decrease to zero.

Yours sincerely,

N.V. PHILIPS-DUPHAR   N.V. PHILIPS
Research Laboratories   Research Laboratories
Dept. 30

F. v. Deurse   *Bakker*

F.W. van Deursen   J. Bakker

1) J.A. Pople, W.G. Schneider, H.J. Bernstein,
   High-Resolution Nuclear Magnetic Resonance,
   McGraw-Hill Book Company, Inc. 1959, pp. 132-135.

TABLE 1   TRANSITION ENERGIES AND RELATIVE INTENSITIES FOR THREE NUCLEI ABX

Transition	Origin I	Origin II	Energy	Relative intensity
1. $8 \to 6'$	B	A	$\nu_{AB} + \tfrac{1}{4}(-2J_{AB}-J_{AX}-J_{BX})-D_-$	$1 - \sin 2\emptyset_-$
2. $7 \to 4'$	B	B	$\nu_{AB} + \tfrac{1}{4}(-2J_{AB}+J_{AX}+J_{BX})-D_+$	$1 - \sin 2\emptyset_+$
3. $5' \to 2$	B	A	$\nu_{AB} + \tfrac{1}{4}(2J_{AB}-J_{AX}-J_{AB})-D_-$	$1 + \sin 2\emptyset_-$
4. $3' \to 1$	B	B	$\nu_{AB} + \tfrac{1}{4}(2J_{AB}+J_{AX}+J_{AB})-D_+$	$1 + \sin 2\emptyset_+$
5. $8 \to 5'$	A	B	$\nu_{AB} + \tfrac{1}{4}(-2J_{AB}-J_{AX}-J_{BX})+D_-$	$1 + \sin 2\emptyset_-$
6. $7 \to 3'$	A	A	$\nu_{AB} + \tfrac{1}{4}(-2J_{AB}+J_{AX}+J_{BX})+D_+$	$1 + \sin 2\emptyset_+$
7. $6' \to 2$	A	B	$\nu_{AB} + \tfrac{1}{4}(2J_{AB}-J_{AX}-J_{BX})+D_-$	$1 - \sin 2\emptyset_-$
8. $4' \to 1$	A	A	$\nu_{AB} + \tfrac{1}{4}(2J_{AB}+J_{AX}+J_{BX})+D_+$	$1 - \sin 2\emptyset_+$
9. $8 \to 7$	X	X	$\nu_X - \tfrac{1}{2}(J_{AX}+J_{BX})$	1
10. $5' \to 3'$	X	Comb.	$\nu_X + D_+ - D_-$	$\cos^2 (\emptyset_+ - \emptyset_-)$
11. $6' \to 4'$	X	Comb.	$\nu_X - D_+ + D_-$	$\cos^2 (\emptyset_+ - \emptyset_-)$
12. $2 \to 1$	X	X	$\nu_X + \tfrac{1}{2}(J_{AX}+J_{BX})$	1
13. $7 \to 2$	Comb.	Comb.	$2\nu_{AB} - \nu_X$	0
14. $5' \to 4'$	Comb.	X	$\nu_X - D_+ - D_-$	$\sin^2 (\emptyset_+ - \emptyset_-)$
15. $6' \to 3'$	Comb.	X	$\nu_X + D_+ + D_-$	$\sin^2 (\emptyset_+ - \emptyset_-)$

I   for $\nu_A - \nu_B > \tfrac{1}{2}(J_{AX} - J_{BX})$

II for $\nu_A - \nu_B < \tfrac{1}{2}(J_{AX} - J_{BX})$

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE

NATIONAL INSTITUTES OF HEALTH

BETHESDA, MARYLAND 20014

Building 2, Room B2-26A   December 2, 1970

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

Short Title: ^{13}C T_1 and T_2 of Carbon Disulfide.

Dear Barry:

I have long wondered what your blue letters actually look like--and now
I know. I hope to avoid learning about the pink ones with this contri-
bution which may interest people involved in ^{13}C work.

Fourteen years ago, McConnell and Holm (1) stated that the ^{13}C spin-
lattice relaxation time in $^{13}CS_2$ is short compared with T_1 in $^{13}CCl_4$,
since chemical shift anisotropy provided a relaxation mechanism in $^{13}CS_2$.
No results were quoted, but recent preliminary measurements in our labo-
ratory indicate that chemical shift anisotropy is indeed important in
$^{13}CS_2$.

The results obtained for degassed 60% enriched $^{13}CS_2$ at 25° C and 15.08
MHz were:

$$T_1 = 44 \text{ sec}$$
$$T_2 = 38 \text{ sec}$$

T_1 was obtained from a series of $90°-\tau-90°$ pulse sequences, and T_2 by
the usual Meiboom-Gill modified Carr-Purcell technique. We used the
pulse spectrometer at NBS.

The interesting thing about the T_1 and T_2 values is, of course, that

$$T_1/T_2 = 44/38 \simeq 7/6,$$

which is the value theoretically predicted from the expressions for
relaxation by chemical shift anisotropy. (2)

These results do not agree particularly well with T_1's quoted by Lippmaa
(3), who obtained by adiabatic rapid passage at 28° C: $T_1 = 30$ sec at
15 MHz and $T_1 = 42$ sec at 10 MHz. His conclusion was that chemical shift
anisotropy is important, but not dominant, whereas our ratio of $T_1/T_2 \sim$
7/6 indicates chemical shift anisotropy to be the only mechanism. The
explanation for this discrepancy is presumably that we used sample tubes
which were constricted with a 1-1/2" long capillary below the surface of

Dr. Bernard L. Shapiro
December 2, 1970
Page 2

the $^{13}CS_2$. This restricts interchange between the liquid and gas phases, and thereby reduces spin-rotation contributions to the relaxation rate from molecules in the gas phase.

Considering the experimental uncertainty (possibly $\pm$ 2 sec) I hesitate to make too firm conclusions on the basis of two numbers, but we are about to do relaxation time measurements as a function of temperature and field strength. Otherwise, we are at present very excited about ^{13}C T_2 measurements which are short due to scalar ^{13}CH couplings and we will have a report on that soon.

Sincerely yours,

Gitte

Regitze R. Shoup
Laboratory of Physical Biology
National Institute of Arthritis
and Metabolic Diseases

1. H. M. McConnell and C. H. Holm, J. Chem. Phys. 25, 1289 (1956).

2. A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, Oxford, 1961, p. 316.

3. A. Olivson, E. Lippmaa and J. Past, Eesti NSV Teaduste Akadeemia Toimetised 16, 390 (1967).

Professor B. L. Shapiro,   December 2nd 1970
Dept. of Chemistry,
Texas A and M University,
College Station, Texas 77843.

New assignment for Ethyl pyridine

Dear Barry,

One of the great strengths of your informal newsletter is
the opportunity it provides for friendly criticism; an attempt to make
the same point in the formal literature too often degenerates into
undesirable polemics.

Charlie Reilly (TAMUNMR 146, 31) has pointed out that our assignment
of the carbon resonances C3 and C5 of 2-ethyl pyridine on the basis of
spin-lattice relaxation times is contradicted by his recent selective
proton decoupling experiments.   We have confirmed Charlie's result
by studying the undecoupled Fourier transform carbon-13 spectrum, arguing
that the low field resonance must be from C3 since it shows an additional
multiplicity ascribed to coupling to the methylene protons (Figure 1).
Selective irradiation of the methylene protons restores the C3 resonance
to a doublet of doublets of doublets (with some incidental partial
coalescence).   We feel that this is perhaps a more direct method of
assignment, since Charlie's experiment relies on selective irradiation
within the rather complex carbon-13 satellite spectrum of the ring protons.

The new assigment would appear to make the relaxation results[1] even
more interesting.   Ring carbons C3, C4 and C6 have essentially equal
spin-lattice relaxation times (22 $\pm$ 1 sec) whereas C5 has a much shorter
relaxation time (15 sec).   Why is C5 singled out in this way ?   It is
tempting to ascribe this to stacking of pyridine rings parallel to one
another with their dipoles opposed:
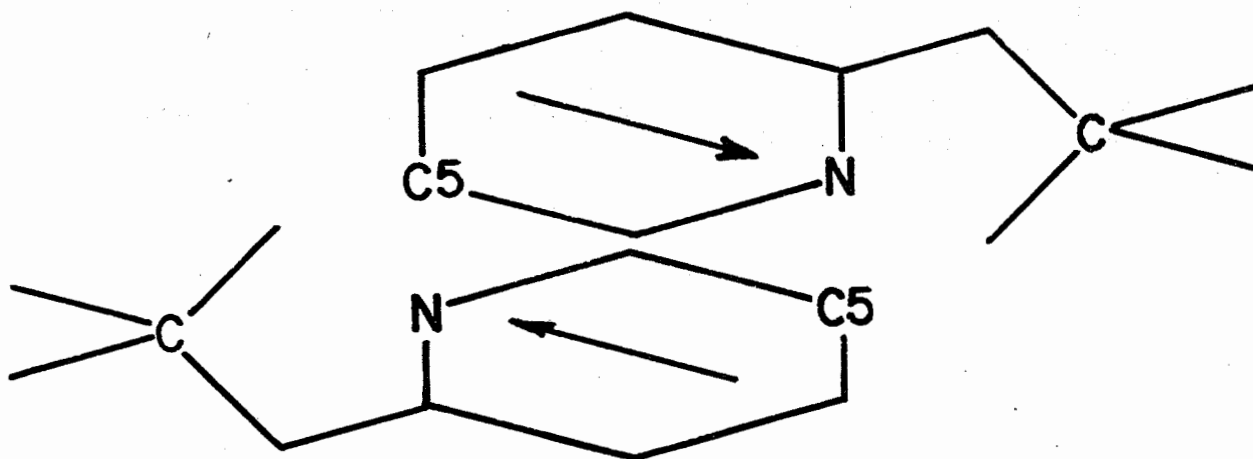
The methyl protons then approach the ring carbons C5 quite closely.
Similar considerations would apply if several rings were stacked together.
Preliminary experiments seem to indicate that when the methyl protons
are weakly irradiated there is a perceptible increase in the integrated

[1] J. Chem. Phys. 53, 4103 (1970).

147-51

varian

intensity of the C5 resonance, suggesting an intermolecular Overhauser effect. We are also planning to remeasure the spin-lattice relaxation times of a dilute sample, since if stacking is the correct explanation, the differences in T_1 should disappear at low concentrations.
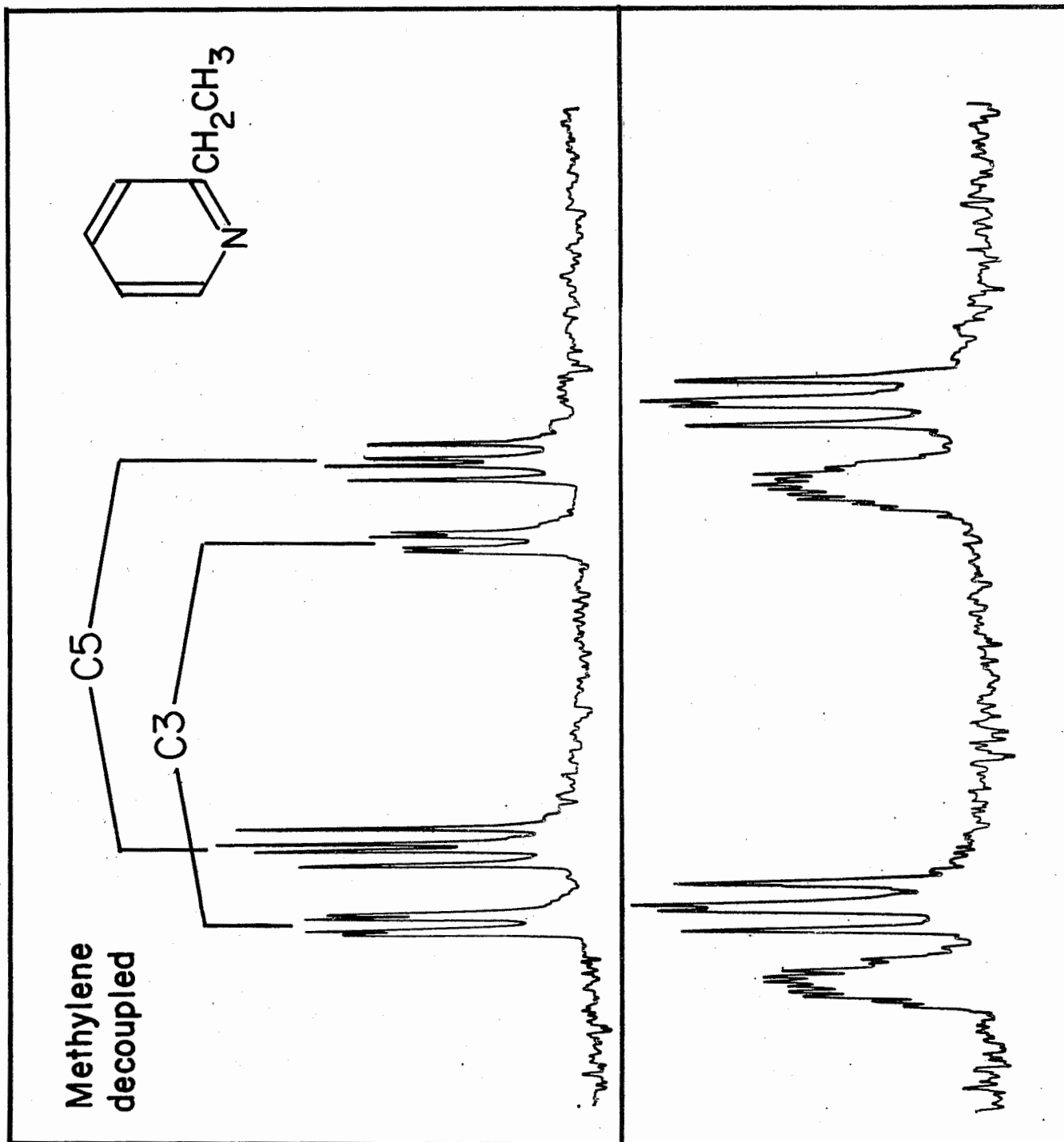
Best wishes,

Ray

Ray Freeman

Howard Hill

Howard Hill

As for you, Charlie,

BOSTON COLLEGE

A University of 12 Colleges and Schools

CHESTNUT HILL, MASSACHUSETTS · 02167

Department of Chemistry   December 3, 1970

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

Dear Barry:

The estimation of small splittings (especially those
which lie near or below the limits of resolution of most
spectrometers) has always been a problem. The elegant methods
developed by Freeman, Hoffman, Lusebrink, etc.al, are suffi-
ciently involved and tedious as to discourage all but the most
persistent spectroscopists. I'd like to describe a simple,
accurate method which can be used by anyone who has access
to a decoupler.

At slow sweep speeds, NMR lines are Lorentzian in shape,
so that it is possible to construct a shape function for any
multiplet, e.g., for a doublet,

$$\Gamma(\nu) = \frac{1}{b^2 + [(\delta\nu) - 1/2\,\Delta]^2} + \frac{1}{b^2 + [(\delta\nu) + 1/2\,\Delta]^2}$$

where 2b is the width at half-height of a simple line, Δ is the
line spacing, and $\delta\nu$ is the displacement from the center of
the pattern. When $\Delta = 0$, $\Gamma(\nu_0) = 2/b^2$, whereas $\Gamma(\nu_0) \rightarrow 0$ as
$\Delta \rightarrow \infty$. Hence one can construct a series of curves relating
Δ to percent maximum intensity at $(\delta\nu) = 0$ for various line-
widths. To read Δ directly from the curves, one needs to
know the intensity of the broadened absorption, the intensity
of the same absorption when $\Delta = 0$, and the linewidth of a
simple sharp peak. The latter two numbers can be obtained by
careful decoupling of the appropriate proton, the former by
direct measurement at identical instrument settings, but with
the decoupler set at an irrelevant frequency.

Ltr to: Prof. Bernard L. Shapiro
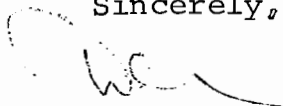December 3, 1970   pg.2.

        The method has been tested for a number of cases, of
which several are summarized below:

Compound	Our Method	Literature
3-methyl-2-butanone	0.35 ± 0.02	0.35
o-nitrobenzaldehyde	0.38 ± 0.02	0.40
methyl acetate	0.23 ± 0.02	0.22

and a manuscript is in preparation. I would particularly like
to test it on the 0.05 Hz coupling in 3-bromothiophen-2-alde-
hyde, but haven't been able to persuade any of my organic
friends to make some. If one of your readers could spare
40-100 mg, I'd greatly appreciate receiving it.

        Regards to all!

                                Sincerely,

                                D. J. Sardella
                                Assistant Professor

DJS/cp

Short title: Estimation of Unresolved Splittings

UNIVERSITY OF MARYLAND

COLLEGE PARK, MARYLAND 20742

DEPARTMENT OF CHEMISTRY

3 December 1970

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

Title: Booster amplifier for
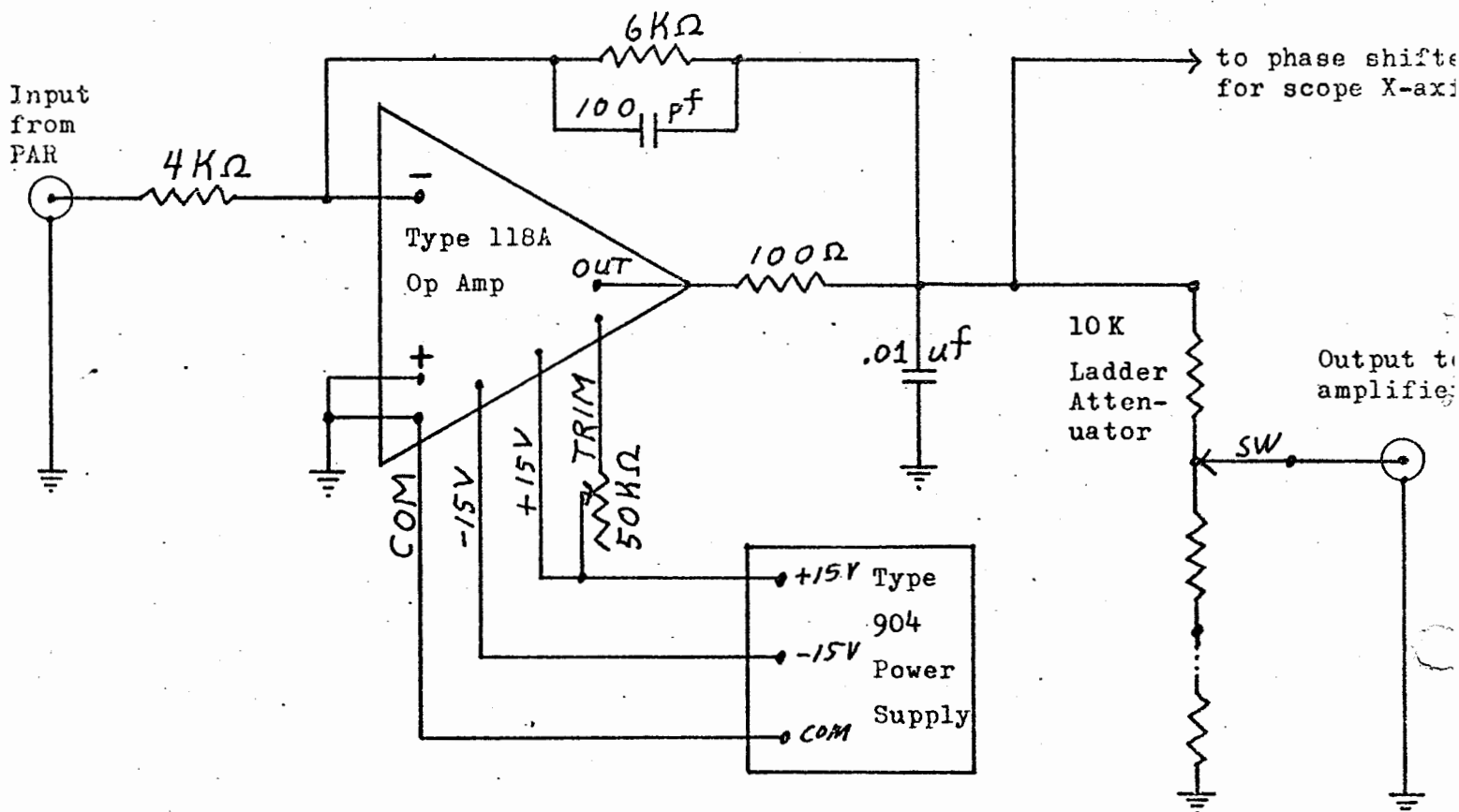driving Dyna Mark III amplifier

Dear Dr. Shapiro,

One problem with using a hi-fi audio amplifier such as the Dyna Mark III to drive modulation coils is that at very low modulation levels, the 60 cps hum from the amplifier may be noticeable. One way to circumvent the problem is to run the amplifier at higher power and use a fixed, high-power attenuator pad across the output of the amplifier to reduce both the hum and the desired signal. In order to boost the level of the reference frequency available from our PAR HR-8 to the 1.5V necessary, we are using the circuit shown below which uses one inexpensive operational amplifier (Analog Devices Model 118A).

The good news here is that we finally have a new magnet which works, a Varian 12", after three tries with a lower bidder; we hope to have some science instead of electronics for the next contribution.

Sincerely yours,

Gerald Ray Miller

C.F. Poranski

Author Index - TAMU NMR Newsletter No. 147

Sponsors:

Abbott Laboratories
American Cyanamid Company
Bruker Scientific, Inc.
Japan Electron Optics Laboratory Co. Ltd.
The Lilly Research Laboratories, Eli Lilly and Company
Monsanto Company
Nuclear Magnetic Resonance Specialties, Inc.
Unilever Research (U.K.)
Union Carbide Corporation
Varian, Analytical Instrument Division

Contributors:

The British Petroleum Company Limited (England)
Diaprep, Inc.
The Dow Chemical Company
Eastman Kodak Company
Farbenfabriken Bayer AG (Germany)
International Business Machines Corporation
Dr. R. Kosfeld, Abt. Kernresonanz, Inst. f. Phys. Chemie, TH Aachen (Germany)
The Perkin-Elmer Corporation
The Procter & Gamble Company, Miami Valley Laboratories
Shell Development Company
Siemens AG, (Germany)
Thompson-Packard, Inc.
University of Waterloo, Chemistry Department (Canada)