Texas
A &
M
University
N – M – R
Newsletter

No. 146
NOVEMBER, 1970

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                No. 148: 4 January 1971

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

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

THE UNIVERSITY OF NORTH CAROLINA
AT
CHAPEL HILL
27514

DEPARTMENT OF CHEMISTRY

October 28, 1970

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

ASTM Computer Program Survey

Dear Barry:

The survey of computer program usage which was initiated in the spring
of 1969 has now been completed. Questionnaires were distributed to conferees
at the recent Gordon Conference on Magnetic Resonance and to participants at
the ENC meeting of 1969. Also, a questionnaire was published in the TAMUNMRN.
This effort was supplemented by Dr. E. Lustig of the Food and Drug Administration
who made available the responses to an earlier questionnaire. A collection of
programs was also provided by Professor R. K. Harris.

A report has been prepared in which 44 programs are listed. The information
has been updated by the authors of the individual programs in the summer of 1970.
We conclude that at present the most satisfactory method of distributing these
programs is through the Quantum Chemistry Program Exchange (Q.C.P.E.) at Indiana
University. Many of these programs are presently listed by Q.C.P.E. and we have
included the appropriate catalog numbers.

The report has now been forwarded to Dr. T. C. Farrar, Chairman of ASTM
Sub-Committee E-13.7. Dr. Farrar plans to have copies of the report available
for distribution. Requests should be sent to:

Dr. T. C. Farrar
U. S. Department of Commerce
National Bureau of Standards
Washington, D. C.   20234

Sincerely yours,

C. S. Johnson, Jr.
Chairman of the Task Group on Computer
Applications of Sub-Committee E-13.7

CSJ:bs

FACULTÉ DES SCIENCES
DE MONTPELLIER

LABORATOIRE DE SYNTHÈSE ET D'ETUDE
PHYSICOCHIMIQUE D'HÉTÉROCYCLES AZOTÉS

R. JACQUIER
Professeur

Place Eugène Bataillon
Tél. : (67) 72.29.44 Poste 803

Montpellier, le   16 Octobre 1970

Professeur B. L. SHAPIRO

Department of Chemistry
Texas A and M University
College Station
TEXAS   (U.S.A.)

Titre :   ANALYSE A 60 ET A 100 MHZ D'UN SYSTEME AA'BB'

Cher Professeur Shapiro,

Dans le cadre d'un travail sur le comportement en RMN des pyrazolines-2, nous avons été amenés à analyser le système AA'BB' des protons 4 et 5 de ces composés.

Il est apparu alors que le passage de 60 à 100 MHz, en diminuant le rapport $J/\nu_o\delta$, conduit à la disparition de certaines transitions de faible intensité nécessaires à l'obtention de certains paramètres avec une précision correcte.
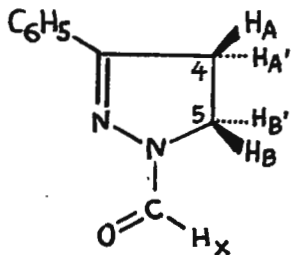
Ainsi, le spectre dans le deutérochloroforme à 100 MHz de la formyl-1 phényl-3 pyrazoline-2, I, ne présente (fig. 1a) aucune transition entre les deux demi-spectres. Analysé comme AA'BB'X au moyen de LAOCN 3 (1), nous obtenons les paramètres du Tableau Ia. On constate que les deux constantes de couplage géminales sont données avec une grande imprécision.

I

Le même échantillon, à 60 MHz, donne un spectre (fig. 1b) présentant trois petites transitions dans la partie centrale, le doublet appartenant aux protons B car $J(AX) \simeq 0$.

L'analyse conduit aux valeurs du Tableau Ib. Cette fois, toutes les constantes de couplage ont une précision comparable.

(1) S. CASTELLANO et A.A. BOTHNER-BY, J. chem. Phys., 1964, 41, 3863.

CDCl₃
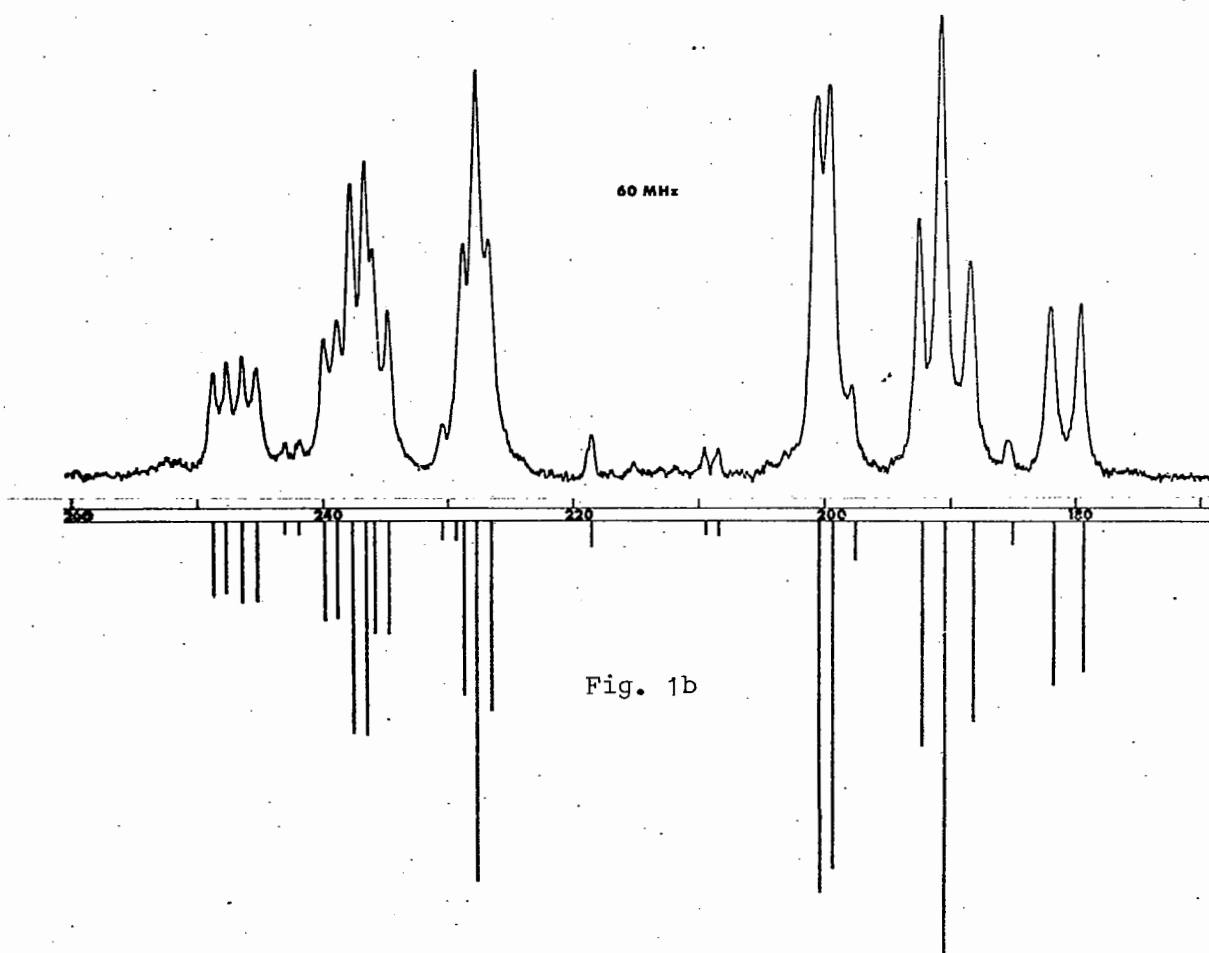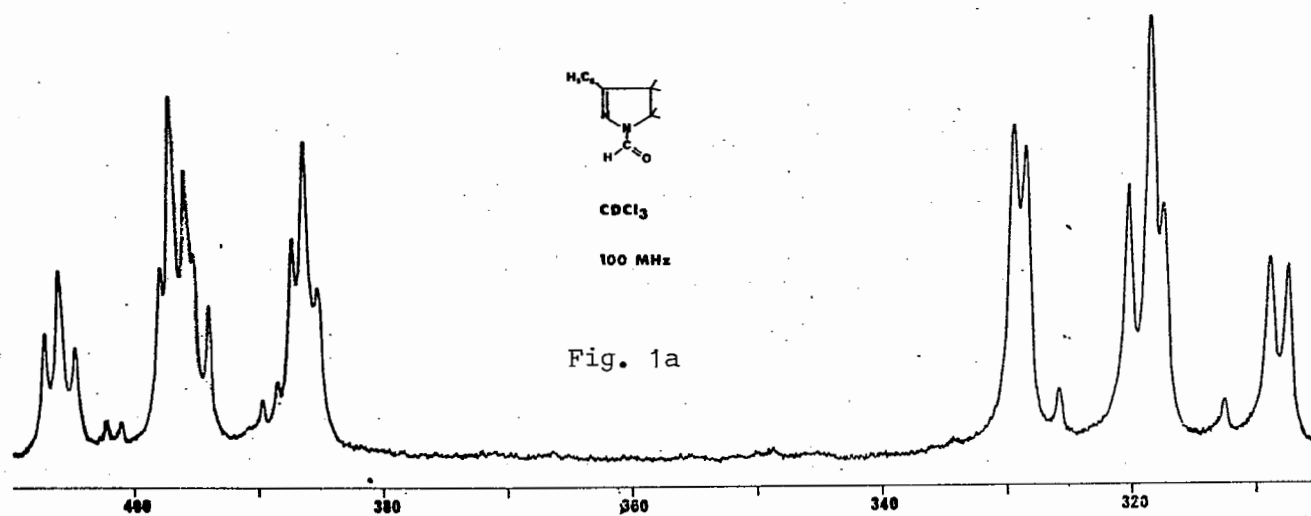
100 MHz

Fig. 1a

60 MHz

Fig. 1b

	Tableau I				Tableau II	
	Formyl-1 phényl-3 pyrazoline-2				Acétyl-1 phényl-3 pyrazoline-2	
	a) 100 MHz		b) 60 MHz		60 MHz	
	**	*	**	*	**	*
W (H_A)	318,902	0,012	191,509	0,011	190,455	0,005
W (H_B)	393,921	0,012	236,144	0,012	239,072	0,010
W (H_X)	884,0	***	530,5	***	150,0	***
J (AA')	-19,753	1,922	-17,381	0,018	-17,356	0,011
J (BB')	-14,212	1,925	-11,973	0,018	-11,823	0,011
J (AB)	12,353	0,032	12,351	0,026	12,397	0,015
J (AB')	7,725	0,029	7,650	0,024	7,678	0,013
J (BX)	1,153	0,024	1,103	0,022	0,42	***
RMS ERROR	0,070		0,065		0,019	

*   Erreur probable sur les paramètres donnée par LAOCN 3.
**   Déplacements chimiques et constantes de couplage en Hertz (Réf. TMS).
*** Ces déplacements chimiques n'ont pas été introduits dans l'itération.

Dans le cas de l'acétyl-1 phényl-3 pyrazoline-2, II, nous avons effectué l'analyse uniquement à 60 MHz, en négligeant l'interaction des protons B avec le groupe méthyle [J(AX) = 0, J(BX) = 0,42 Hz mesuré sur le méthyle]. Ceci nous a conduit à n'utiliser que les transitions de la partie AA' et seulement quelques unes de la partie BB', uniquement pour calculer ν(B). Le résultat obtenu est dans le Tableau II.
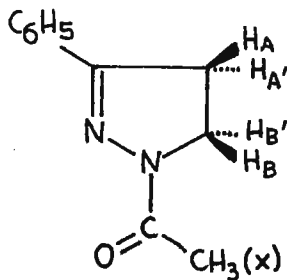
Veuillez croire, cher Professeur Shapiro, à l'assurance de nos sentiments les meilleurs.

II

J. ELGUERO   A. FRUCHIER

PS.   L'un d'entre nous (Alain Fruchier) souhaite aller la prochaine année scolaire (sept. 1971 - Jul. 1972) dans un laboratoire pour approfondir ses connaissances en RMN. Toute suggestion d'un laboratoire pouvant l'accueillir sera la bienvenue.

POLITECNICO DI MILANO

ISTITUTO DI CHIMICA

20133 - MILANO - P.za Leonardo da Vinci, 32

TELEFONO 292.109 - 292.110

Milano, September 10th, 1970

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

NMR Spectra of Δ^3- and Δ^4-pyrrolin-2-one

Dear Professor Shapiro,

        we have analysed the H spectra of Δ^3-
and Δ^4-pyrrolin-2-one [1] (inseparable mixture of I and II
2 : 1), including sign determination of all coupling constants,
made by tickling and triple resonance experiments.
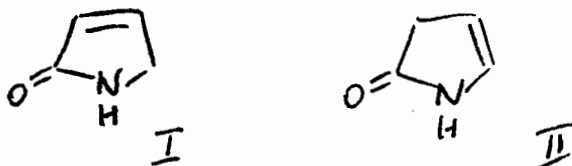
The spin systems are of type $A_2 XYZ$ and the results are reported
in fig. 1.

    The interest in these compounds is in part due to the presence
of the pyrrolic ring in many important natural substances, like
vitamin B_{12}, bile pigments, antibiotics. Moreover these small mo-
lecules show long-range couplings, which are interesting data for
testing the predictions of the current theory [2]. As a matter of
fact, there are still insufficient experimental data, particularly
concerning the small cyclic systems, and only few examples of posi-
tive J_{allyl} in non aromatic molecules [1,2,3].
    Moreover these compounds are very apt to show the potential
of sign determination for structural purpose, and are convincing
examples that the relatively small long-range couplings should
always be characterized by their signs, if one wants to use them
for structural determinations.

    In Δ^4-pyrrolin-2-one II, we have measured a positive
allylic type coupling of + 1.58 Hz, across the heteroatom, between
the NH and the vinylic hydrogen (J_{XZ}), both lying on the same
plane. This is in agreement with the theoretical formulation
of a σ electron mechanism for a transoid allylic coupling in a

planar ($\phi = \phi' = 180°$) conformation[2]. The two interacting protons are indeed in a " W " arrangement.

$^4J_{1,3}$ in pyrrole, involving proton on the nitrogen atom, is 2.45 (4) Hz, and the sign is reported[5] to be positive. The larger value of $^4J_{1,3}$ in pyrrole could be explained with the possibility of a " double path " of coupling, which lacks in Δ^4-pyrrolin--2-one.

The σ-electron mechanism for the 4-bond coupling J_{XZ} in Δ^4-pyrrolin-2-one II, can be in some way supported by the same value found for J_{YZ} (+ 1.50 Hz) in Δ^3-pyrrolin-2-one I. J_{YZ} in I involves the same fragments as J_{XZ} in II , with the same substituents and geometry; and the only difference is the lack of the double bond.

The other allylic transoid couplings are negative as expected by ϕ = 120°.

The substitution of $\diagdown NH \diagup$ group in molecule I with $-\overset{|}{\underset{|}{C}}-$ [2], $\diagdown S \diagup$ (6) or $\diagdown O \diagup$ (7) does not affect the allylic coupling J_{AX}.

sincerely yours

R. Mondelli

R. Mondelli

(1) The chemical part will be published in Tetrahedron.
(2) The full paper on NMR has been submitted to Organic Magnetic Resonance
(3) H. Gunther, Z. Naturforschg. <u>24</u>b, 680 (1969) and ref. quoted
(4) G. F. Katekar and A. G. Moritz, J. Austr. Chem. 1199 (1969)
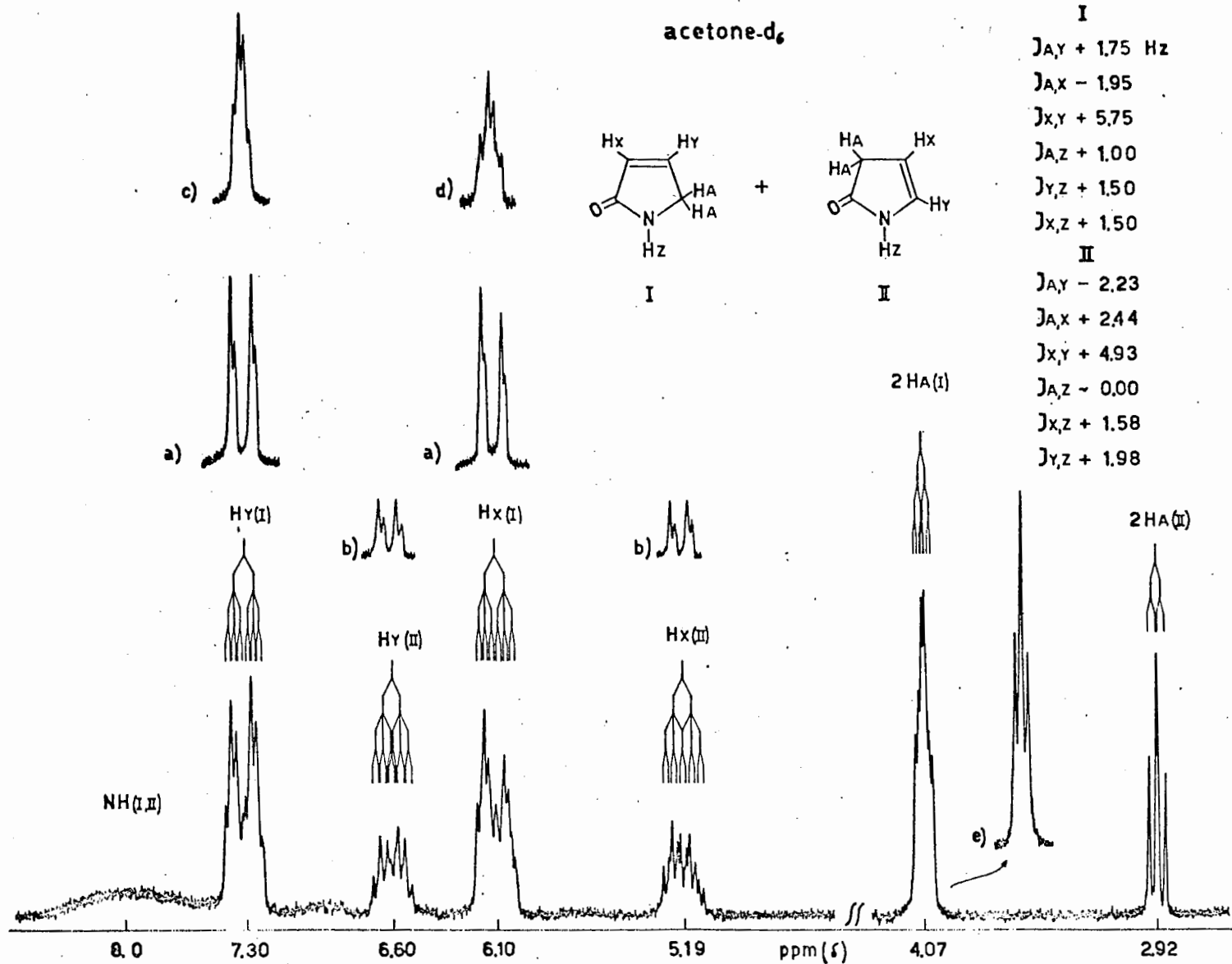(5) H. Fukui, S. Shimokawa, J. Sohma, Mol. Phys. <u>18</u>, 217 (1970)

fig. 1

Department of Chemistry

YORK
UNIVERSITY

FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW 463, ONTARIO

Dr. Bernard L. Shapiro,   October 7. 1970.
Department of Chemistry,
Texas A & M University,
College Station,
Texas 77843, U.S.A.

Dear Dr. Shapiro,   Ligand Exchange by NMR, a Double Rate Process.

We are currently setting up an NMR group at York, comprising
interested chemistry & biology faculty, and would like to start a subscription to
Newsletter with this opening communication.

Ligand exchange reactions of metal alkoxides are being
examined by NMR, in particular the process of self-alcoholysis which lends its-
elf to NMR because of its rate. Thus the exchange between <u>tert</u> -butyl alcohol
and titanium tert-butoxide can be studied via line shape measurements of the
alcohol group protons. The exchange can be expressed in an overall form as

$$M(OR)_4 + RO'H = M(OR)_3(OR') + ROH \quad .$$
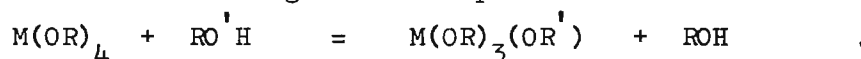
Line shapes are computer fitted, the programme designed for a Watfor compiler
(FortranIV). As a short cut to initial fitting the programme searches out line
widths at 1/4,1/2,and 3/4 height, shift difference between maxima and max/min
peak height ratios. Complete line shapes can be called for on a plot subroutine.

The choice of solvent is a particular problem. It must have
and adequate temperature range, must not contain ligating groups to compete with
the alcohol, and should have little or no specific solvent effect. Such solvents
are saturated hydrocarbons which unfortunately have resonances in the same region
as the <u>tert</u>-butyl group. A compromise is an aromatic ring with hydrocarbon sub-
stituents,or propylene carbonate. It is interesting to note that metal alkoxides
exhibit downfield shifts (relative to TMS) in aromatic solvents instead of the
more usual upfield solvent shift. Allowance has to be made for the temperature
variation of the shift by extrapolation from lower temperatures at which exchange
effects are negligible.

The exchange is observed to be catalysed by both acid and
base which can both be found as impurities in the system; acid coming from the

glass (washing with NaCl solution prior to distilled water seems to suppress this source); base being produced by partial hydrolysis of the alkoxide via trace amounts of water which are exceedingly difficult to remove. However, an unusual feature of the kinetics appears to be unfolding with reasonable consistency. The Arrhenius plot of rate against temperature shows two distinct portions, corresponding to two activation energies. The plots always show a low energy, low temperature portion of activation energy around 4kcals, and most show a high energy high temperature portion , activation energy around 18kcals, when appropriate temperatures can be reached. Owing to continuing difficulties with catalytic effects the order of reaction is not clear, except that the low energy route is probably at least bimolecular and the high energy route nearer unimolecular. this would fit the necessary change of activation entropy (given by the intercepts) which require a higher(negative)entropy for the low temperature process than for the high temperature one. We could thus be observing the change from an associative mechanism to a dissociative one. Arrhenius plots of this type are also observed in systems where tunnelling can occur, but are relatively rare for ligand exchange at metal atoms.

Arrhenius Plot. $Ti(OBu^t)_4$ + Bu^tOH exchange.

0.16M in alkoxide.
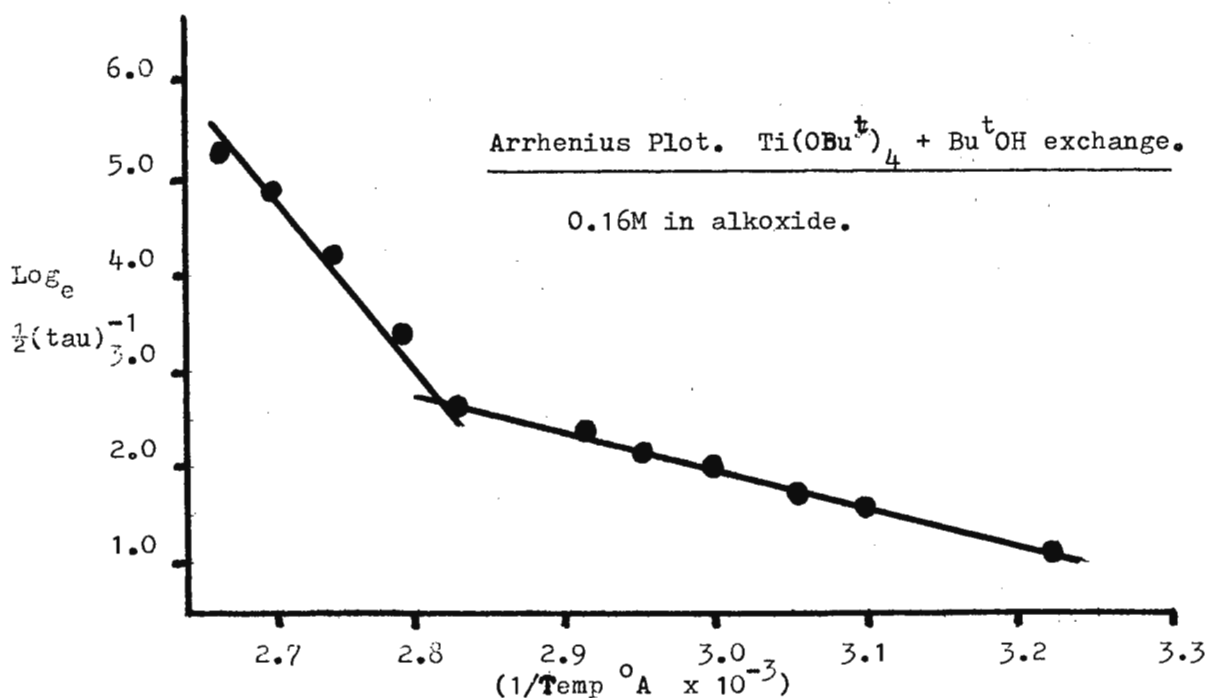
Yours sincerely,

C. E. Holloway

R. Ward.

MIAMI UNIVERSITY

OXFORD, OHIO   45056

DEPARTMENT OF CHEMISTRY

Telephone: 513, 529-3114

Address Reply to:

Miami University
c/o AFML/LPA
Wright-Patterson AFB
Ohio   45433

16 October 1970

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

PRECISION DC AMP FOR
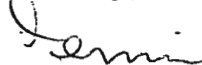KEITHLEY LOCK IN

Dear Barry:

Now that there is at last a worthy competitor (Keithley 800
series) for the PAR lock in amplifiers, I am certain that many
are already being applied in n.m.r. laboratories. One such appli-
cation is on the Varian HR 220 (presently with Dan Urry at UAB,
Birmingham) where we used the Keithley with success in locking the
spectrometer and also during frequency sweep experiments.

One characteristic deficiency, however, is lack of variable
DC amplification and very high output impedence. This means, of
course, that the 10v full scale dynamic range of the detector
cannot be fully utilized on the 1v Varian recorder, and that the
signal is distorted by impedence mismatch. The DC amplifier
integrator shown in the attached figure alleviates this problem
and also allows integration of the n.m.r. signal.

Amplifiers shown are Zeltex 148 and 148C Chopper stabilized
operational amplifiers and a Zeltex B-10 booster necessary for
full range drive into the 75 ohm 50 db (1 db/step) precision
attenuator.

Circuit operation is straightforward. The 148-B10 combination
is unity gain inverting while the 148C is in a gain of -5 config-
uration. Therefore, the attenuator would be set at 34 db for full
scale on the recorder with full scale out from the Keithley.
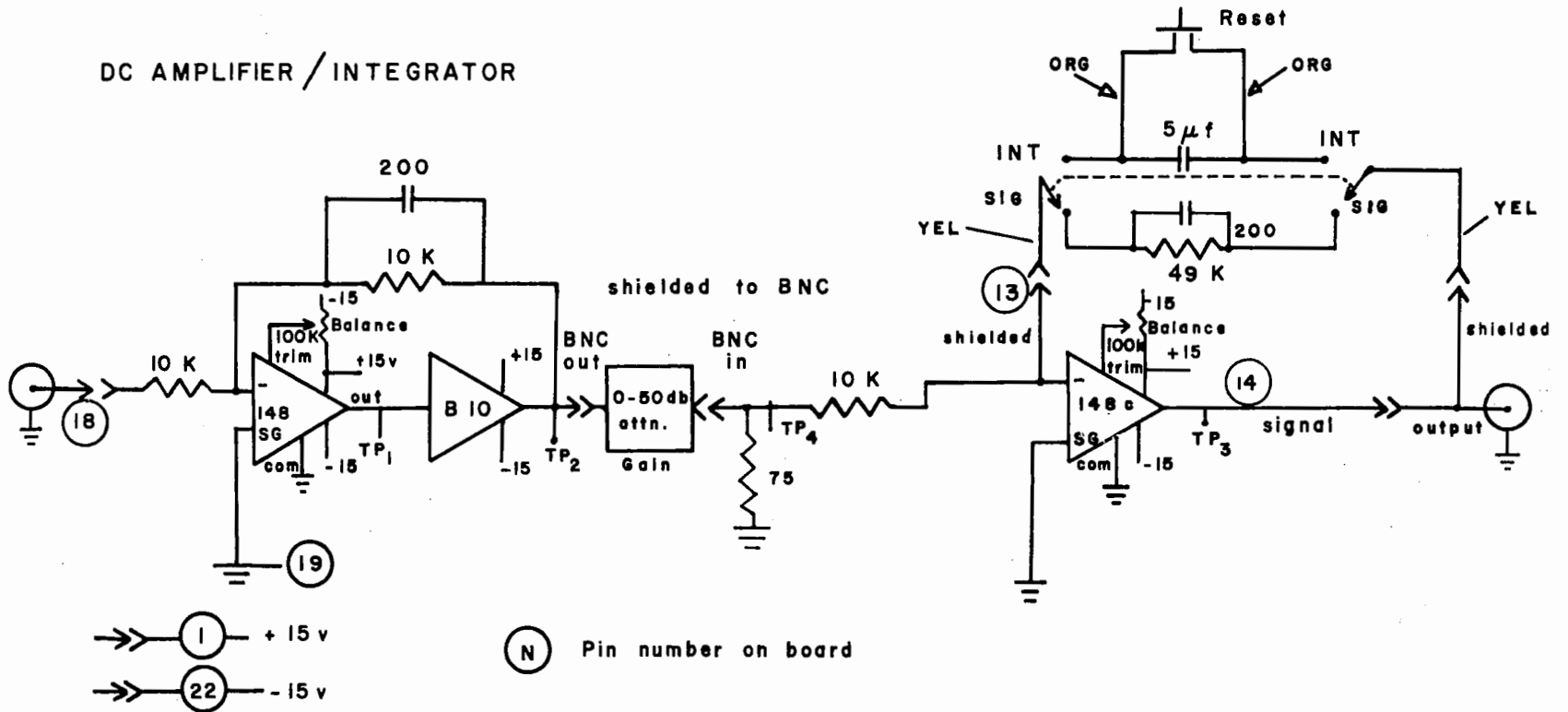
Sincerely,

DENNIS E. WISNOSKY

DEW/dlb

Enclosures

DC AMPLIFIER / INTEGRATOR

200

10 K

-15
Balance
100K trim
+15v
out
-
148
SG
com
-15
TP₁
B 10
+15
-15
TP₂

BNC out

shielded to BNC

0-50db attn.
Gain

BNC in

TP₄

10 K

75

Reset
ORG   ORG
5 μf
INT   INT
SIG
YEL
200
49 K
13
shielded
-15
Balance
100K trim
+15
-
148 a
SG
com
-15
TP₃
14
signal
SIG
YEL
shielded
output

10 K

18

19

1 + 15 v
22 - 15 v

N   Pin number on board

Trim pots 20 turn precision
All resistors 1% ¼ watt
5μf capacitor 5% polystyrene

D. E. Wisnosky 01970

146-11

THE UNIVERSITY OF NEW BRUNSWICK
FREDERICTON, N.B.

October 16, 1970

Dear Barry:

Having received your warnings about my impending excommunication,
I hasten to offer the following contribution:

COMMENTS CONCERNING REPLACEMENT OF 304TL TUBES WITH TRANSISTORS

The rising replacement cost of the set of 8 regulator tubes in the
V 2100 magnet power supply has led us to a consideration of alternatives.
Two methods have been reported in the Newsletter: Substitution of a single
watercooled 3CW 5000 TL tube (v. Parmakovich, TAMUNMR 128, 18) or construction
of a transistorized regulator section (W.H. Stegemann, TAMUNMR 131, 1).
We have chosen the second alternative and have copied Mr. Stegemann's
design fairly closely.

The problem with any transistor replacement for the 304 TL's is
the low breakdown voltage of transistors as compared with the voltage
drop required across the regulator section. This voltage drop must be
large enough to act as a buffer for line voltage variations and to eliminate
the ripple voltage from the 3 phase push-pull rectifier section. We have
found the 16 stages of Stegemann's circuit to be adequate as buffer for
line voltage variations, but we observed rather large 60 Hz and 120 Hz
ripple components (which must result from some unexplained asymmetry in
our rectifier or 3- phase line) and we have added an input choke to the 4
μf capacitor ripple filter at the rectifier output. After construction
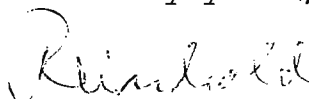of the transistorized regulator we first had high frequency oscillations

in the current regulation feedback loop. These could be suppressed by shaping the frequency response at the reference resistors. The circuit then showed good regulation and stability and seemed entirely satisfactory.

It had been in operation for 8 months when a catastrophic break-down of most of the 2N3055 power transistors occurred while the magnet was being operated at a 6% higher field for F^{19} spectrometry. Other components (except power line fuses) appear to be undamaged, the galvanometer in the Superstabilizer was protected with Si diodes (R.W. King, TAMUNMR 118, 54). We suspect that the breakdown may have been triggered by a line voltage transient caused perhaps by nearby construction work. We are now rebuild-ing the regulator with Zener diodes from the collector of the 2N3055 power transistors to the base of the driver transistor (BC 140) in each stage, in order to limit the voltage across each stage to a safe value.

We have also replaced the 872A mercury rectifier tubes with high voltage diodes (W.B. Monitz, 10th ENC 1969), and the 8 volt mercury reference batteries with a small power supply and IC regulator. No difficulties have been encountered with these modification.

With best regards,

Sincerely yours,

R. Kaiser, Professor

/cwp

UNIVERSITY OF LONDON KING'S COLLEGE
Strand, London, W.C.2R 2LS

Department of Chemistry

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

### Low temperature non-equivalence in a doubly asymmetric hydroxylamine

Recent interest in the slow interconversion of enantiomeric hydroxy-lamines[1,2,3] prompts us to report our results with a doubly asymmetric hydroxylamine, 0, N-dimethyl-N-1-phenylhydroxylamine (I).   At ambient in $CDCl_3$, the 100MHz spectrum of I showed the expected C-Me doublet at δ 1.40 (J H-CH$_3$ = 7.0 Hz), and N-Me and O-Me singlets at δ 2.44 and 3.43 p.p.m. respectively; the tertiary proton appeared as a quartet at 3.60 p.p.m.

At -40° the C-Me protons appeared as a quartet centred at δ 1.41 (δ Me$_A$ - δ Me$_B$ = 13.5 Hz), the N-Me protons as a doublet at 2.48 ($\Delta\delta$ = 25 Hz) and the O-Me protons as a doublet at 3.42 p.p.m. ($\Delta\delta$ = 32 Hz).   The coalescence temperature for all three groups of non-equivalent protons was ca -5°C (ca. -20 at 60 MHz).   We interpret these results as follows:
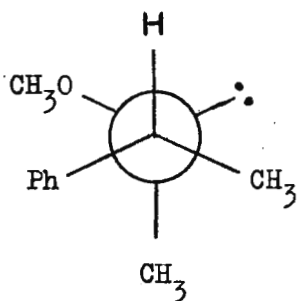
The doubly asymmetric hydroxylamine is a misture of two diastereomeric ("dl") pairs (1 - 4).
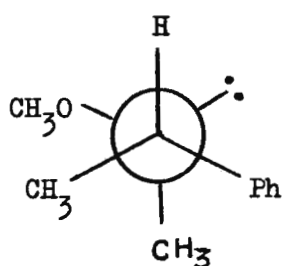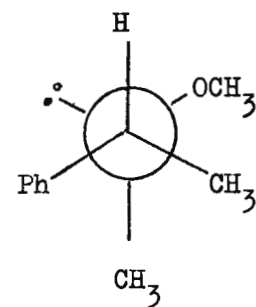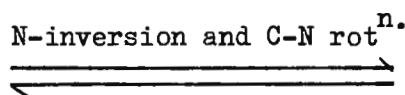
1.
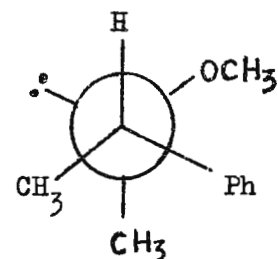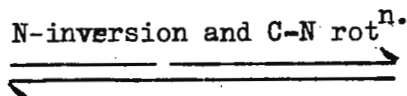
2.

3.

4.

1 and 2 diastereomers; 3 and 4 disastereomers; 1 and 4 enantiomers;
2 and 3 enantiomers.

Inversion of configuration at nitrogen (and rotation about the C-N
bond) converts a member of one diastereomeric pair into a member of the
other pair, (e.g. 1 → 2). Thus at 24° inversion is so rapid that the
separate methyl resonances assignable to the two diastereomers are not
observed, but at -40° the diastereomeric pairs are well defined in the
n.m.r. The above interpretation is oversimplified in that it takes no
account of rotation about the O-N bond. Strictly, in order for the
system to be totally degenerate three energy barriers must be surmounted,
viz:- N-inversion, rotation about the C-N bond and rotation about the

N-O bond.   These three processes would convert 1 into the enantiomer

of 3 and 3 (a diastereomer of 1) into the enantiomer of 1, i.e. lead

to complete degeneracy and hence the simple n.m.r.   The doubling of the

N-Me and O-Me resonance signals reported for 1, was not observed with

O,N-dimethylbenzylhydroxylamine[1], O-methyl-N-isopropylbenzylhydroxylamine[2,3]

or O-isopropyl-N-methylbenzylhydroxylamine[2,3].   This suggests that the

decreased rate of N- inversion is the principal factor involved in the

appearance of separate diastereomer resonances at low temperatures,

although the slowing down of rotation about the N-C and N-O bonds may help to

accentuate the chemical shift difference between the signals.

The original integrated spectrum at -40° indicated that the

diastereomeric pairs were present in approximately equal quantities.

Recent experiments with a freshly prepared sample of I however, definitely

showed unequal populations of the diastereomers (ratio 2 : 1) at -40°

for all three diastereotopic methyl groups.   Subsequent experiments on

the same sample failed to confirm this result and gave spectra very

similar to those obtained originally.   This unexplained anomaly is

currently under investigation and so far it appears that the effect is

connected with the age of the sample.

1.   D. L. Griffiths and J. D. Roberts, J.Amer.Chem.Soc., 87, 4089 (1965).

2.   M. Raban and G. W. J. Kenney Jr., Tetrahedron Letters, No.17, 1295 (1969).

3.   M. Raban, G. W. J. Kenney Jr. and F. B. Jones Jr., J.Amer.Chem.Soc., 91,
6677 (1969).

C. D. Hall.

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

Prof.Dr.P.Diehl
Dr.P.M. Henrichs
W. Niederberger

Basel, October 22, 1970

Prof. B. L. S h a p i r o
Chemistry Department
Texas A. & M. University
College Station

T e x a s — 77843

U.S.A.

Computer program SHAPE

Dear Barry,

   We have developed a computer program (SHAPE) for the
iterative calculation of geometry and degree of orientation
of a molecule from its direct couplings using a weighted-
least-squares method.

   The number of magnetic nuclei in the molecule should
not exceed eight. The direct coupling is defined according
to Saupe (Z.Naturforsch. 20A, 572 (1965): a pseudo-dipolar
part is not taken into account.

   Descriptions of the program and listings are available
upon request.

                              Sincerely yours,

        P. Diehl   P.M.Henrichs   W. Niederberger

School of Chemistry,
University of Bradford,
Bradford 7,
Yorkshire, England.

DWJ/CMW

21st September, 1970.

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

Dear Dr. Shapiro,

^{1}H Chemical Shifts in 9-Substituted Fluorenes

Recently, in collaboration with Dr. P. M. G. Bavin of SKF Laboratories Ltd.,
K.D.B. and D.W.J. have examined the p.m.r. spectra of over 40 9-substituted
fluorenes in CCl_4, acetone-d_6, and dimethylsulfoxide-d_6. In view of the correlations
often encountered between chemical shifts and substituent electronegativities, we
have taken the opportunity of combining the shifts, δ_9, (and also the shifts,
$\delta_{9,rel}$, relative to the parent) with those of other 9-fluorenes in the literature
in an attempt to assess their dependence on polarizability, dipole moment, Hammett
constants and related quantities.

While $\delta_{9,rel}$ tends to increase with mutually-consistent group electronegativity,
E [Wells, Prog.Phys.Org.Chem. 6, 111 (1968)] deshieldings for -CN,-C≡C- (cylindri-
cally symmetrical) and -CH=CH- are smaller, and those for -SH and -Ph somewhat larger,
than expected. Further, -Br and -Cl have much bigger shifts than for the average line,
-F is on the line, and -CF_3 has a much smaller shift; anisotropy of F appears to have
a surprisingly small effect. Deviations from linearity are less if δ_9 is plotted
against group electronegativity, E_p, determined by p.m.r.; the mean gradient is
1.2 p.p.m./E_p unit.

When δ_9 in 9-R-fluorenes is plotted against δ_{CH_3} in CH_3R (and much the
same is true for a graph against δ_{CH_2} in $PhCH_2R$), nearly all the points are below
the line of unit gradient drawn through R=H. Evidently substituents have less effect
on H-9 shifts in fluorenes than in methane and toluene. Electronegativity apart,
we detected no correlation between δ_9 and any of the following: Q (as used, for
example, by W. B. Smith et al., J.Phys.Chem. 74, 812 (1970)); Hammett constants σ_I,
σ_m, and σ_p; group dipole moment; and the substituent bulk (as given by cubes
of radii).
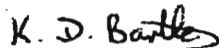
Of the aromatic chemical shifts, δ_4 tended to shift to higher fields with
"polar" Hammett constant, σ_I, and δ_1 to lower field with $-\Delta X$ and with
substituent size. Otherwise, δ_1 and δ_4 appeared independent of Q (see reference
above to W. B. Smith, et al), group E, dipole moment, and other Hammett constants.
The most divergent points in the graph of δ_4 against σ_I are for 9-fluorofluorene
(δ_4 = 0.45 ppm instead of 0.2) and 9-cyanofluorene (0.02 instead of 0.20 predicted
from the σ_I-value). Calculations with models of fluorene and its 9-F, 9-Cl, and
9-Br derivatives suggested that, in order for electric-field effects to make a
substantial contribution to H-4 shielding, constant B in the equation
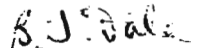
$$\sigma_E = -3BPId^{-6},$$

(where P is the C-R bond polarizability, I is the ionisation potential of R, and d is
the distance between R and the proton) would have to be of opposite sign and many
times larger than proton shieldings require.

K.D.B. is now at School of Chemistry, University of Leeds, England, and R.S.M.
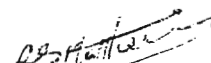is moving to Dept. of Chemistry, University of Durham, England.
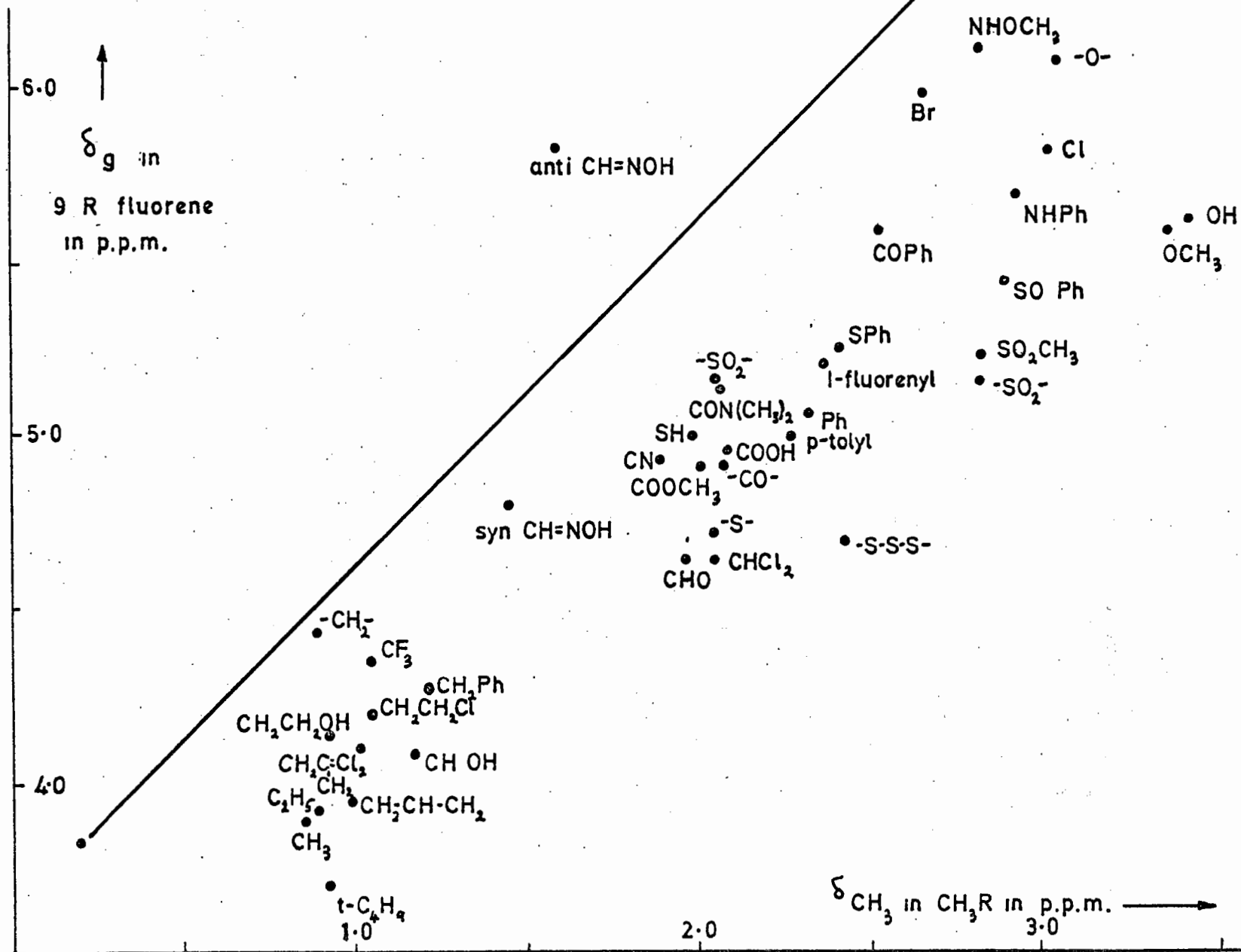
Yours sincerely,

K. D. Bartle   B. J. Dale   D. W. Jones   R. S. Matthews

Plot of δ_g in 9 R fluorene in p.p.m. (vertical axis) versus δ_{CH_3} in CH_3R in p.p.m. (horizontal axis).

Vertical axis labelled: δ_g in 9 R fluorene in p.p.m.

Horizontal axis labelled: δ_{CH_3} in CH_3R in p.p.m.

Data point labels: NHOCH$_3$, -O-, Br, Cl, anti CH=NOH, NHPh, OH, COPh, OCH$_3$, SO Ph, SPh, SO$_2$CH$_3$, -SO$_2$-, 1-fluorenyl, -SO$_2$-, CON(CH$_3$)$_2$, Ph, SH, p-tolyl, CN, COOH, COOCH$_3$, -CO-, syn CH=NOH, -S-, -S-S-S-, CHO, CHCl$_2$, -CH$_2$-, CF$_3$, CH$_2$Ph, CH$_2$CH$_2$Cl, CH$_2$CH$_2$OH, CH OH, CH$_2$C-Cl$_2$, C$_2$H$_5$, CH$_2$, CH$_2$CH-CH$_2$, CH$_3$, t-C$_4$H$_9$

NORTH TEXAS STATE UNIVERSITY

DENTON, TEXAS

DEPARTMENT OF CHEMISTRY

October 21, 1970

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

Dear Barry: The Conformation of 1,4-Dihydro-1-naphthoic Acid

There has just appeared convincing evidence that the 9-substituent
in 9,10-dihydroanthracenes is pseudo-axial [J. B. Stothers et al., J. Am.
Chem. Soc., 92, 5912 (1970)]. Presumably steric interaction of the
9-substituent with the aromatic peri protons is sufficient to force the
substituent out of the pseudo-equatorial position.

In view of these results, it would be of interest to ascertain the
effect of one aromatic ring, i.e., whether the peri proton of one ring
would be sufficient to force the substituent into the pseudo-axial position.
We have already collected data that can answer this question -- we have
investigated the nmr spectrum of 1,4-dihydro-1-naphthoic acid ($\underline{1}$) and have
discovered that indeed the carboxylate group is pseudo-axial.

Using a Jeolco PS-100 nmr spectrometer and the Laocoon III program,
the following parameters were obtained for 1,4-dihydro-1-naphthoic acid:

chemical shifts H_1-H_5 respectively τ 5.45, 3.93, 3.75, 6.53, 6.37.

coupling constants J_{AB}: J_{12} 4.59; J_{13} 1.22; J_{14} 3.93; J_{15} 3.93; J_{23} 9.62;
J_{24} 1.24; J_{25} 2.97; J_{34} 4.60; J_{35} 2.44; J_{45} 21.92.

The relative magnitudes of the vicinal [J_{12}, J_{34}, J_{35}] and allylic

[J_{13}, J_{24}, J_{25}] coupling constants are convincing evidence [M. Karplus,
J. Chem. Phys., 30, 11 (1959); M. Barfield, J. Chem. Phys., 41, 3825 (1964)]
that H_1 is pseudo-equatorial, and that the carboxylate group is therefore
pseudo-axial.

$\underline{1}$
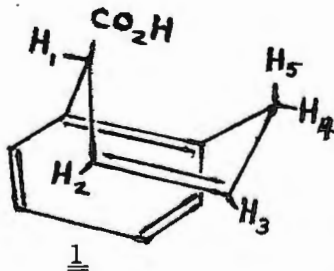
Sincerely,

James L. Marshall
Assistant Professor of Chemistry

NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

OTTAWA 7.

21st October 1970

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

ANALYSIS OF A 'DECEPTIVELY SIMPLE' ABX SPECTRUM USING SOLVENT PERTURBATIONS; DMSO BEWARE!

Dear Barry:

Thank you for commencing my subscription to the NMR newsletter. Our laboratory is primarily interested in applications of NMR to biological problems. We have a Varian XL-100-15, equipped to study ^1H, ^{19}F, ^{31}P, and ^{13}C, in continuous wave and Fourier transform modes. We are particularly interested in making contact with people who have written NMR or ESR programmes for the Varian 8K 620i computer.

Recently George Neville, Barry Blackburn, Roxanne Deslauriers, and I have been studying the conformations of amphetamine drugs such as amphetamine HCl.
We have been using the couplings between the methylene and methine hydrogens to monitor rotamer populations about the CH_2-CH bond. Usually the CH_2 and CH hydrogens constitute a normal ABX or ABC system which can be handled conventionally using LAOCOON III. In the case of amphetamine HCl, however, the CH_2 region of the spectrum consisted of only two lines - a 'deceptively simple' spectrum[1,2], which defied a proper analysis. By studying the spectra in various mixtures of DMSO-D_6 and D_2O, we were able to change the relative rotamer populations and obtain analyzeable spectra. Extrapolation of the coupling constants and chemical shifts from mixed solvents to pure D_2O looked as below. Spectral simulation

.....2

Professor B. Shapiro   − 2 −   21st October 1970
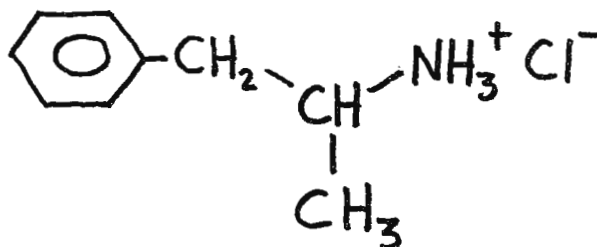
using the extrapolated parameters gave good agreement with the observed spectrum, and thus permitted analysis of the rotamer populations under the required solvent conditions.
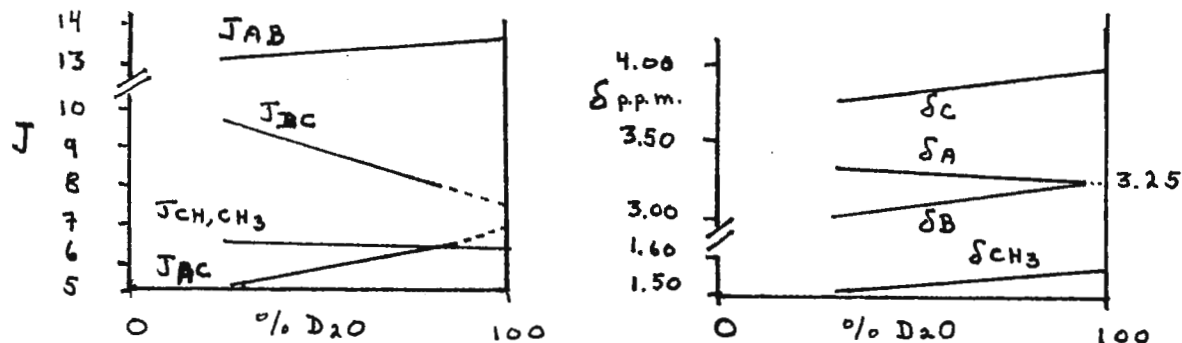
Finally, a word of caution regarding the use of DMSO–D$_6$ as a solvent for phenolic compounds. In recent studies of dipeptides containing tyrosine we have several examples of extraneous peaks developing with time in the aromatic hydrogen region, presumably due to reaction of DMSO–D$_6$ with the hydroxyl group of tyrosine.

Yours sincerely,

Ian

Ian C.P. Smith

ICPS:pg

[1] R. Abraham and H.J. Bernstein, Can. J. Chem. <u>39</u>, 216 (1961)

[2] G. Slomp, Applied Spectroscopy <u>2</u>, 263 (1969).

THE FOURTH INTERNATIONAL SYMPOSIUM ON MAGNETIC RESONANCE

25TH. ANNIVERSARY OF NUCLEAR MAGNETIC RESONANCE
ISRAEL, REHOVOT, AUGUST 23–27, 1971 — JERUSALEM, AUGUST 30–31, 1971

October 23, 1970.

ORGANIZING COMMITTEE
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J. S. Waugh, Cambridge (Mass.)

Corespondence Address:
Executive Committee
The Fourth International Symposium
on Magnetic Resonance
The Weizman Institute of Science
Rehovot, Israel.

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

Dear Professor Shapiro,

Would you please publish the following announcement in the NMR Newsletters:

Announcement

The Fourth International Symposium on Magnetic Resonance (25th anniversary of nuclear magnetic resonance) will take place at the Weizmann Institute of Science, Rehovot and the Hebrew University, Jerusalem, Israel, on August 23 - 31, 1971.

Among the invited speakers are:
F. Bloch & E.M. Purcell
W.A. Anderson (Palo Alto)
E.R. Andrew (Nottingham)
J.D. Baldeschwieler (Stanford)
E.D. Becker (Washington, D.C.)
G.J. Béné (Geneve)
H.J. Bernstein (Ottawa)
R. Blinc (Ljubljana)
A.D. Buckingham (Cambridge)
M. Cohn (Philadelphia)
P. Diehl (Basel)
S. Fujiwara (Tokyo)
R.M. Golding (Kensington)
H.S. Gutowsky (Urbana)
E.L. Hahn (Berkeley)
K. Hausser (Heidelberg)
G. Hertz (Karlsruhe)

D.J.E. Ingram (Keele)
J.J. Katz (Argonne)
D. Kivelson (Los Angeles)
M. Klein (Berkeley)
W.D. Knight (Berkeley)
G. Laukien (Karlsruhe)
C. MacLean (Amsterdam)
S. Meiboom (Murray Hill)
W.D. Phillips (Wilmington)
J.D. Roberts (Pasadena)
R.G. Shulman (Murray Hill)
C.P. Slichter (Urbana)
J.S. Waugh (Cambridge)

Prospective participants should address inquiries to the organizing committee. Participants interested in presenting papers at the symposium are invited to do so. Brief summaries should be submitted prior to April 1st, 1971.

The 1971 symposium will emphasize basic nuclear magnetic resonance and its applications. However, contributions in electron spin resonance, quadrupole resonance, cyclatron resonance, ferromagnetic resonance and acoustic magnetic resonance are invited.

All correspondence should be addressed to:

Executive Committee,
The Fourth International Symposium
    on Magnetic Resonance,
The Weizmann Institute of Science,
Rehovot, Israel.

Thank you in advance for your cooperation.

Yours sincerely,

Daniel Fiat

Daniel Fiat.

DF/mt

THE DOW CHEMICAL COMPANY

November 4, 1970

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

Dear Dr. Shapiro:-

AN INDIRECT NUCLEAR OVERHAUSER EFFECT VIA CHEMICAL EXCHANGE

An NMR investigation of 9-(2',4',6'-trimethylphenyl)xanthene, I, was recently completed in this laboratory.[1] At ambient temperature (+31°C.) the NMR of I exhibits three resonances at 1.60, 2.27 and 2.53δ due to the methyl substituents at positions 2', 4' and 6', respectively, and a singlet at 5.9δ due to H_9; the aromatic protons are centered near 6.88 δ. As shown in I, steric interactions force the 9-aryl ring to be approximately perpendicular to the
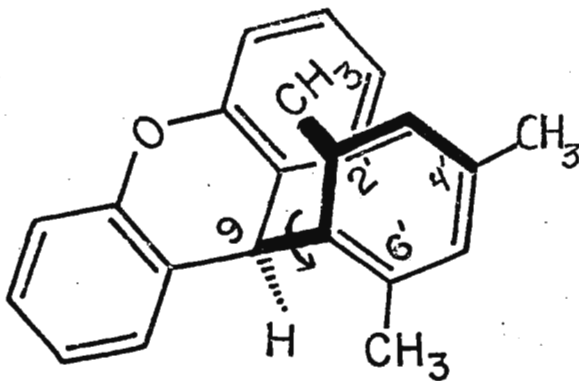
I

xanthyl moiety leading to a very different magnetic environment for the two ortho methyls. Upon raising the temperature the signals for these two methyl groups, Me-2' and Me-6', broaden and eventually coalesce at 95°C. The barrier to methyl magnetic equilibration was attributed to hindered rotation about the 9-aryl bond.

During the course of that study, nuclear Overhauser effect experiments were carried out to substantiate chemical shift arguments which assigned the low field Me-6' as being syn to H_9. These experiments were performed on a Varian HA-100 operating in frequency sweep mode using a thoroughly degassed $CDCl_3$ solution of I.

Dr. Bernard Shapiro   Page 2
Texas A & M University   November 4, 1970

Irradiation of the Me-6' signal resulted in a 23.0% enhancement in
the integral of H_9. Irradiation of the spatially more distant
high field Me-2' resulted in a 14.5% polarization of H_9. This
latter NOE can be attributed to a small but detectable chemical
exchange between Me-2' and Me-6' which transfers the partially
saturated Me-2' group at a rate fast compared to the methyl
relaxation time. The Me-4' resonance provided a convenient
standard and upon saturation yielded a -0.4% change in H_9.
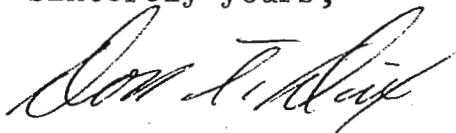
Solution of the appropriate coupled equations[2] under steady
state conditions yields the following expression for the indirect
N.O.E. effect (H_9/H_9^o) of Me-2':

$$\frac{H_9}{H_9^o} = 1 - \frac{\sigma}{\rho} \quad \frac{Me^o-6'}{H_9^o} \quad (S-1) \tag{1}$$
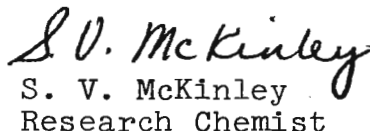
where $S = \dfrac{t_T}{T_{1,6'}} = \dfrac{Me-6'}{Me^o-6'}$ with $\dfrac{1}{t_T} = \dfrac{1}{T_{1,6'}} + \dfrac{1}{T_{exchange}}$

and σ and ρ represent the sum of various relaxation rates for
which the dominant contribution is due to the interaction of
H_9 and Me-6'. Upon irradiation of Me-2', the ratio, Me-6'/Me°-6',
was measured directly and found to be 0.259. Substitution of this
value into equation 1 predicts a positive polarization of 17%
for H_9 upon irradiation of Me-2', in reasonable agreement with
the observed value.

Sincerely yours,

Don T. Dix
Research Chemist

pat

S. V. McKinley
Research Chemist

1. S. V. McKinley, P. A. Grieco, A. E. Young and H. H. Freedman,
    J. Am. Chem. Soc., 92, 5900 (1970)

2. S. Forsen and R. Hoffman, J. Chem. Phys., 39, 2892 (1963)

DEPARTMENT OF ORGANIC CHEMISTRY

THE ROBERT ROBINSON LABORATORIES P.O. BOX 147 LIVERPOOL L69 3BX   TEL: 051 – 709 - 6022

The University of Liverpool

Professor B.L. Shapiro,
Chemistry Department,
Texas A and M University,
College Station,   26th October, 1970.
Texas 77843,
U.S.A.

HH, HF and FF Couplings in Fluoroethanes.

Dear Barry,

We have just finished an investigation on the solvent dependence of the N.M.R. spectrum of 1,2 difluoro and 1,1,2-trifluoro ethane and these results, with those of the 1,1,2,2 tetrafluoroethane (Mol. Phys. $\underline{19}$, 265 (1970)) give the $^3J_{HH}$, J_{HF} and $^3J_{FF}$ couplings of the discrete rotamers of all the simple fluoroethanes capable of exhibiting rotational isomerism.

However, a number of these couplings are averages over the two equivalent rotamers. We assume that the value of a given coupling in one rotamer is identical to the similarly oriented coupling in the other rotamer of the same compound. The couplings obtained in this way are shown in parentheses in the figures.

Some general trends may be noted.

Increasing fluorine substitution gives a progressive but very non-linear decrease in J_t^{HH} and J_t^{HF}, which is much larger when the fluorine is introduced at the CH end of the CH.CF fragment.

In difluoroethane J_g^{HH} varies from 0 to 6.2 Hz, depending on the orientation of the F nuclei, but increasing fluorine substitution evens out these effects to give $J_g^{HH} \sim$ 1.5 - 2.0 Hz.

J_t^{FF} is very dependent on fluorine substitution, varying from -30 to 0 Hz but in contrast J_g^{FF} shows no dependence at all and is relatively constant at -13 to -5 Hz.

Yours sincerely,

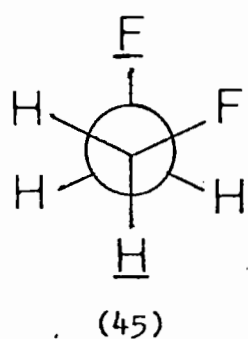Dr. R.J. Abraham.
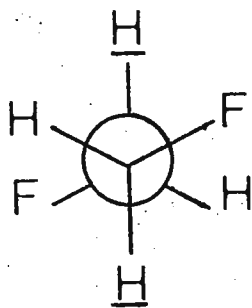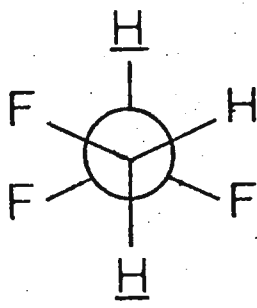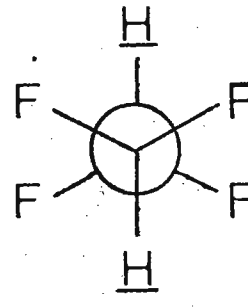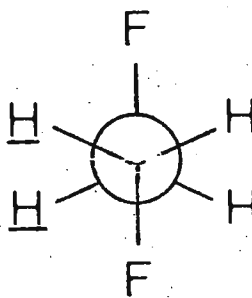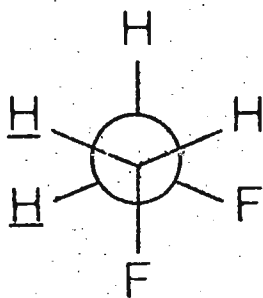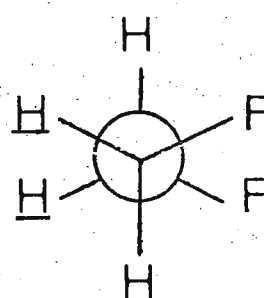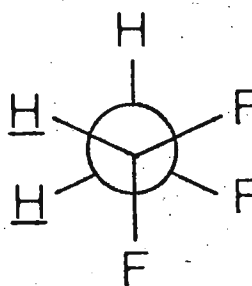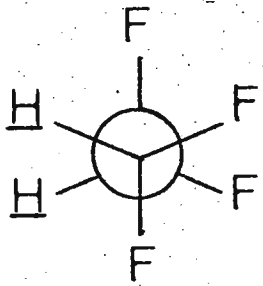
FIGURE 5, $^3J_{HH}$ COUPLINGS (Hz) IN FLUOROETHANES
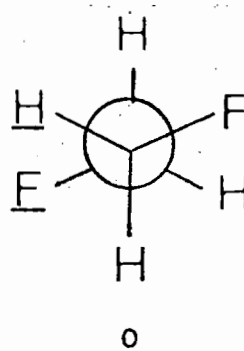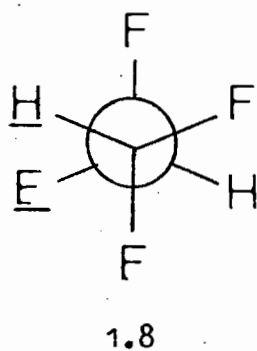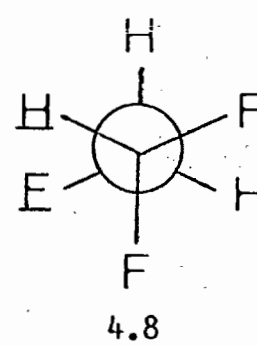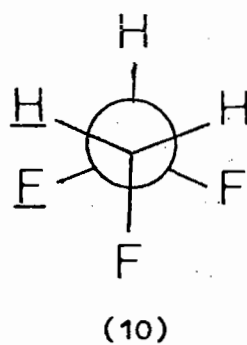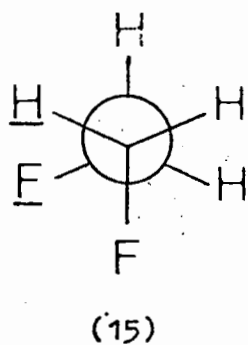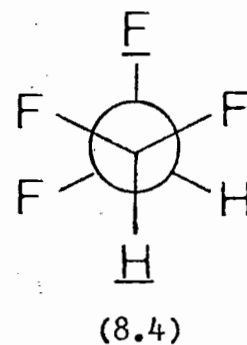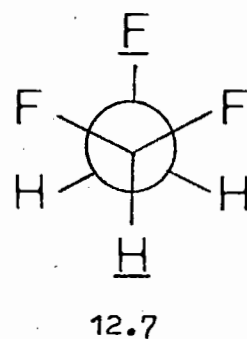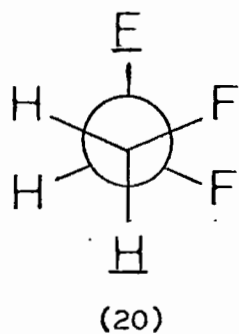
FIGURE 6, $^3J_{HF}$ COUPLINGS IN FLUOROETHANES
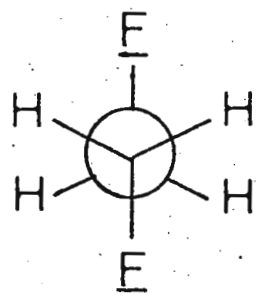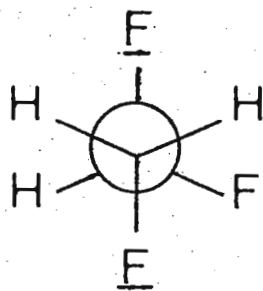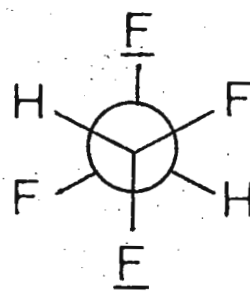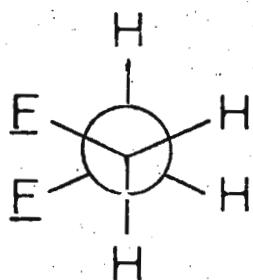
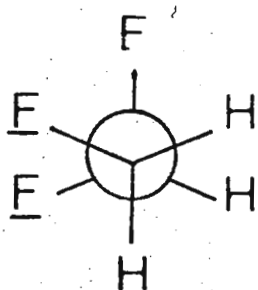FIGURE 7, $^3J_{FF}$ COUPLINGS IN FLUOROETHANES

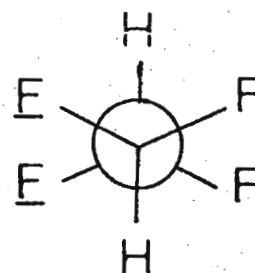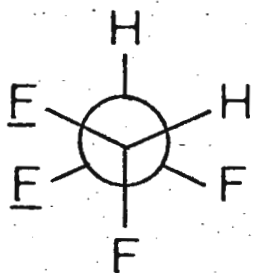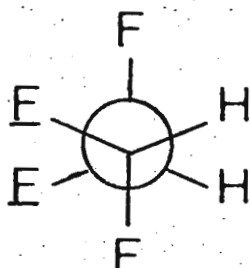# SHELL DEVELOPMENT COMPANY

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

MAILING ADDRESS
P.O. BOX 24225
OAKLAND, CALIF. 94623

November 3, 1970

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

^{13}C Spectra of Ethyl Pyridines

Dear Barry:

I was interested in Ray Freeman's recent letter (TAMU News-letter No. 143) in which he presented his pen-shaking Fourier Trans-form experiments with 2-ethyl pyridine. He assigned the C3 and C5 resonances on the basis of his ^{13}C relaxation time measurements.

I have checked Ray's assignment by the old-fashioned (but reliable) method of selective proton decoupling. First, the CH_2 decoupled spectrum of the 4 ring protons (Figure 1) at 100 MHz was analyzed by a standard iterative procedure to give the proton shifts (relative to internal HMDSX): HC5: 6.86 ppm; HC3: 6.94 ppm; HC4: 7.35 ppm; HC6: 8.40 ppm. The assignment of the proton resonance multiplets was readily made by comparison of the spectrum in Figure 1 with the ABX spectrum obtained (Figure 2) by irradiating HC6 in addition to the CH_2 protons. ^{13}C resonances at 22.63 MHz from C3 and C5 are shown in Figure 3 for four slightly different irradiating frequencies (reduced decoupling power) in the neighborhood of the proton resonances at 6.86 and 6.94 ppm. The calculated frequencies required to decouple the protons on C5 and C3 were -7912 and -7904 Hz (calculated from the mea-sured value of -8529 Hz required to decouple the protons in HMDSX). It is clear that the resonance on the left shows maximum sharpness at -7899 Hz whereas the one on the right shows maximum sharpness at -7910, i.e., the assignment must be as shown in the figure. These resonances are not as sharp as usually found in such selective decoupling experiments because at the low decoupling power necessary here, C5 is only partially decoupled from the proton on C6 to give a doublet whereas C3 is only partially decoupled from this proton as well as from the protons in the ethyl group. This latter observation is also consistent with the assignment shown in Figure 3. This assignment is opposite to that made by Ray on the basis of his T_1 measurements.

Dr. B. L. Shapiro — -2- — November 3, 1970

The ^{13}C resonances in 3-ethyl and 4-ethyl pyridines have also been assigned by selective proton decoupling. The chemical shifts are given below.

^{13}C Chemical Shifts

	CH₃ 2-0	CH₂	C2	C3	C4	C5	C6
	(ppm from TMS)						
HMDSX							
Pyridine	--	--	150.2	123.9	135.8	123.9	150.2
2-Et Pyridine	13.8	30.6	158.5	122.1	136.2	121.0	149.5
3-Et Pyridine	15.5	26.4	149.9	139.6	135.5	123.8	147.6
4-Et Pyridine	14.3	28.2	150.0	123.3	152.5	123.3	150.0

Sincerely yours,

C. A. Reilly

C. A. Reilly

240   180   120   60   0
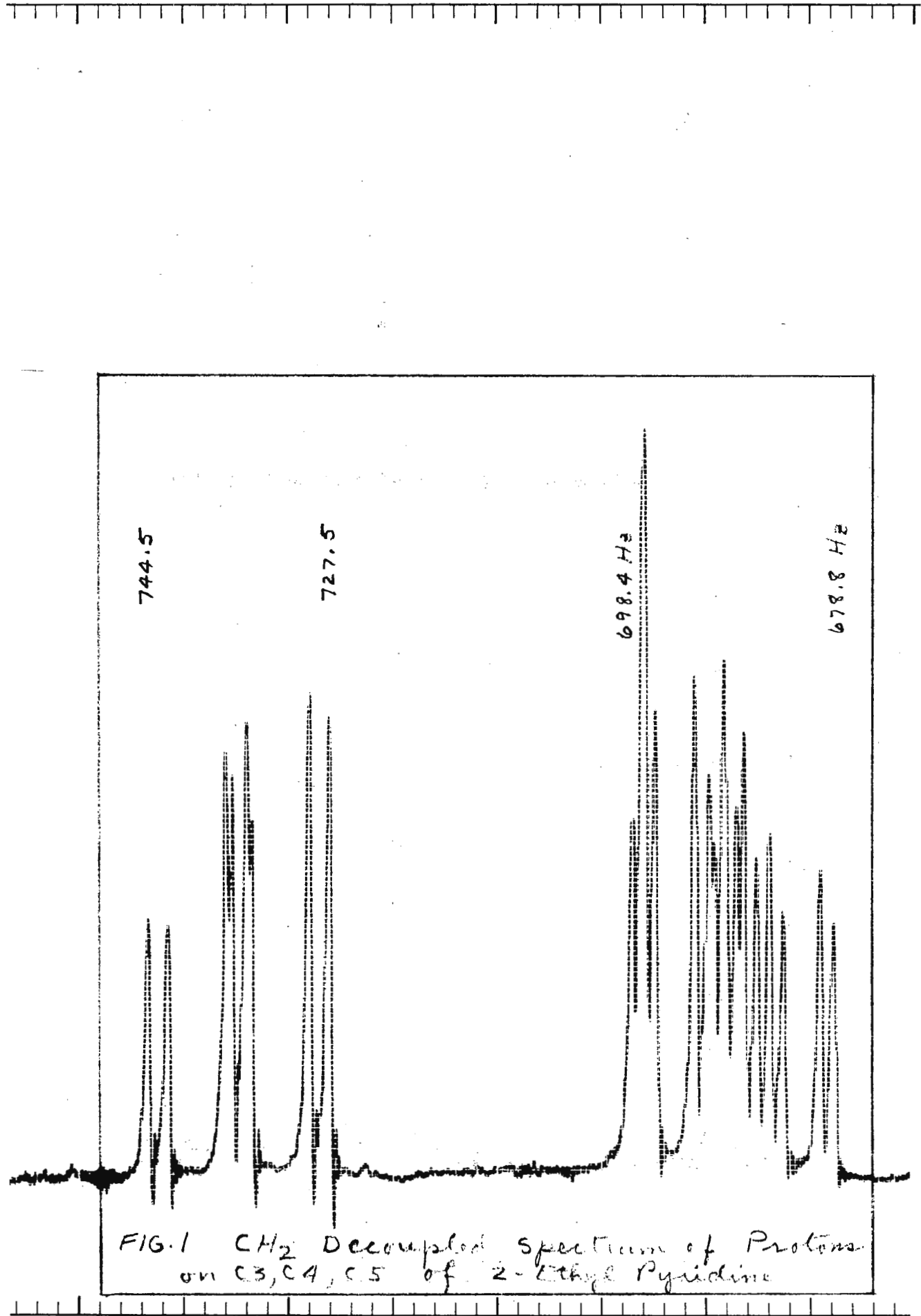400   300   200   100   0

744.5   727.5   698.4 Hz   678.8 Hz

FIG. 1   CH₂ Decoupled Spectrum of Protons
on C3, C4, C5 of 2-Ethyl Pyridine

FIG 2. C H₂ and HC6 Decoupled Spectrum of Protons on C3, C4 and C5

Fig 3

-7914

-7910

-7899

-7893

C3 C5
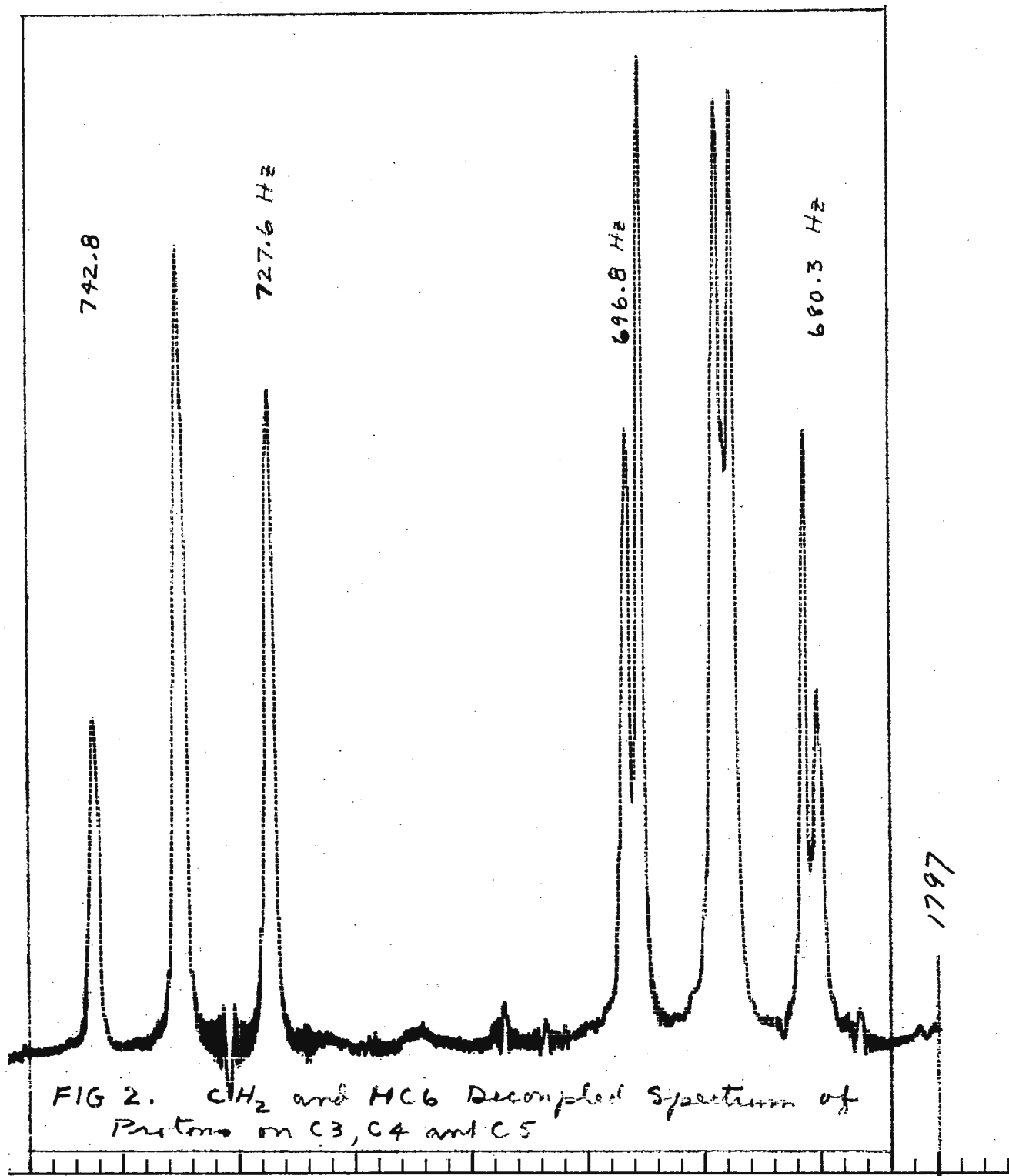
| SHELL DEVELOPMENT CO. | ^{13}C–NMR– |
| EMERYVILLE, CALIF. | 22.63 MHz |

SAMPLE

2-Ethyl Pyridine

SOURCE _____ EK P 7134

REFERENCE _____

SOLVENT _____ none

CONCENTRATION _____

TEMPERATURE, °C _____ 41 + Δ

INTERNAL STANDARD _____ HMDSX

STABILIZATION _____ C_6F_6 EXT CAP

BRUKER HFX-90 SPECTROMETER

SCAN WIDTH SETTING. . . . _20_ Hz/cm

SCAN TIME SETTING. . . . . _500_ sec

SCAN RATE . . . . _2.4_ Hz/sec

SCAN TIME. . . . . _____ sec

SCAN RANGE . . . _____ TO _____ Hz

NUMBER OF SCANS . . . . . _1_

RF UNITS: f_o . . . . _−54_ db

f_1 . φ 60 . . . . _−28_ db

f_2 . . . . _−36_ db

FREQUENCY OF f_2 . . As Noted Hz

DECOUPLING ☒ SELECTIVE
MODE: ☐ B B MOD _____

OPERATOR _C AR_ DATE 10/20/70
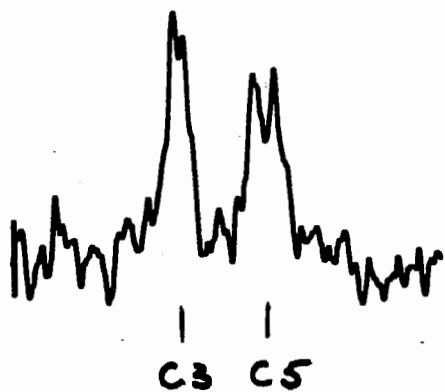
REMARKS
HmDSX at 4329 Hz
" Decouples at
−8529 Hz
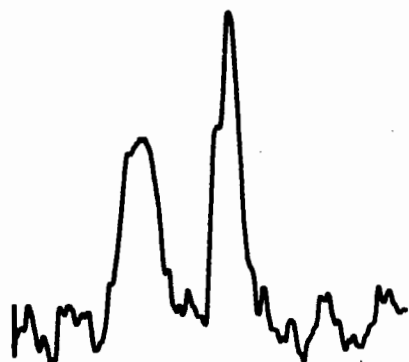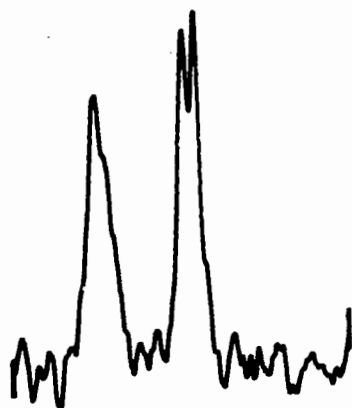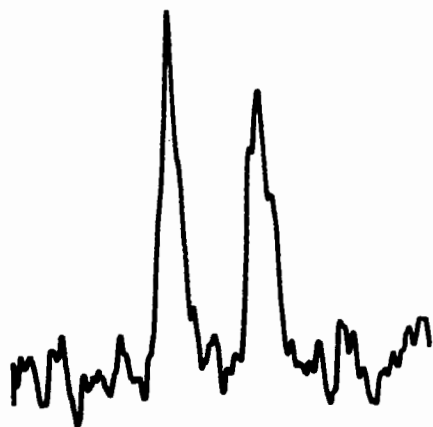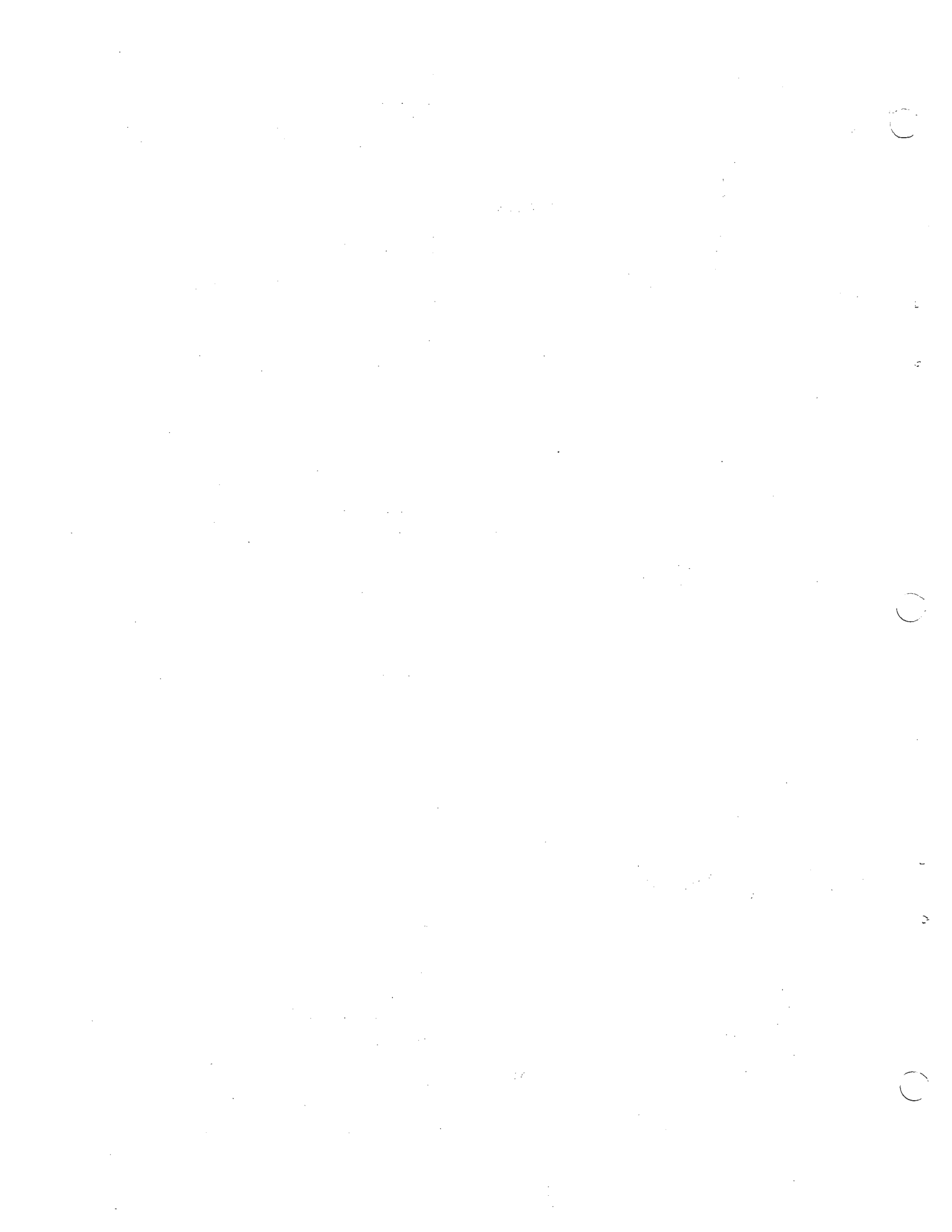
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