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Newsletter

No.123
DECEMBER, 1968

Deadline Dates: No. 124: 6 January 1969
                 No. 125: 3 February 1969

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

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

QUEEN MARY COLLEGE

(UNIVERSITY OF LONDON)
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TELEPHONE · ADVANCE · 4811
DEPARTMENT OF CHEMISTRY

Professor B.L. Shapiro.

31st October, 1968.

Dear Barry,

Nitrogen n.m.r.; multiple resonance; position available.

Your reminder came while I was away enjoying the NATO Summer School on N.M.R. at Coimbra, Portugal. I had several enquiries there, and elsewhere, about a review on 'Nitrogen n.m.r.' which Duncan Gillies and I wrote over a year ago, preprints of which were sent to about twenty interested groups. I can now report that after a quick updating, it will appear in the "Progress in N.M.R. Series". Duncan and I would be grateful for 'personal communications' or preprints of any relevant work for inclusion. I should perhaps emphasise that we are very close to our deadline.

Some of the suggestions in the first version of the review have been pursued in my Group. For example, Roger Price, who is now busy writing his thesis (and who is translating to Brucker in Karlsruhe next January), has investigated the N^{14} and N^{15} isotopomers of CH_3NC, and $|NH_nD_4-n|^+$ to see whether the nitrogen screening constants $^{14}\sigma$ and $^{15}\sigma$ differ for isotopomeric pairs. (If they do we may call the effect a "zero bond" isotope effect, by extrapolation of the term 1-bond isotope effect). We first became interested in this when Duncan Gillies (Ph.D. Thesis, 1965) found that his ^{15}N shifts for ^{15}N substituted amides matched the published ^{14}N shifts for ^{14}N amides despite literature reports of differences of about 200 ppm. (J.Chem.Phys., 1964, 40, 3440.)

For the pair of molecules NH_4^+ and MeNC, Roger obtained the results,

(i) $\dfrac{V_{15}}{V_{14}}$ for NH_4^+ $\qquad\qquad = 1.402, 757, 110 \pm 0.000, 000, 08$

(ii) $\dfrac{V_{15}}{V_{14}}$ for CH_3NC (42 mole % in TMS) $= 1.402, 757, 86 \pm 0.000, 000, 48$.

This yields a "zero bond" isotope effect of 0.54 ± 0.40 ppm. His other results are given in the table:

Isotopomer	Chemical Shift Relative to $^{15}NH_4^+$ in ppm.		Relative to $^{15}NH_3D^+$
	^1H	^{15}N	D
$^{15}NH_4^+$	0	0	–
$^{15}NH_3D^+$	– 0.017 ± 0.001	+ 0.29 ± 0.03	0
$^{15}NH_2D_2^+$	– 0.034 ± 0.002	+ 0.61 ± 0.03	– 0.02 ± 0.007
NHD_3^+	– 0.050 ± 0.002	+ 0.92 ± 0.04	– 0.04 ± 0.01

Queen Mary College.   31st October, 1968.

Professor B. Shapiro.

If these ^{15}N isotope shifts are compared with the corresponding ^{14}N isotope shifts obtained by W. McFarlane and R.R. Dean (J.C.S., 1968, 1535-8), ($^{14}NH_3D^+$ + 0.31 ppm., $^{14}NH_2D_2^+$ + 0.60 ppm., $^{14}NHD_3^+$ + 0.93 ppm.), it will be seen that there is no "zero bond" isotope effect in this series of molecules.

Malcolm Bramwell's results (Ph.D. Thesis, 1968) which were briefly mentioned in Newsletter No. 112, for J N^{15} - H in a number of substituted anilines, are shown in more detail in the figure. As Ted Becker reported for aniline itself (Newsletter N_o. 81), the coupling is dependent on the solvent. Malcolm has shown that the effect depends also on the substituent on the ring. Malcolm's (double resonance) ^{15}N shifts for these compounds, which were a result of a collaboration with Duncan Gillies using the 60 Mc/s machine at Royal Holloway College, are currently being checked on our HA.100, which has just gone operational for heteronuclear work, thanks to Roger Price. One reason for the check is that we are worrying about the ^{15}N shift in aniline. Our d.r. result (J.A.C.S., 1968, 90, 3167) for aniline-^{15}N impurity in $Me_3 Si$ ^{15}NH ϕ and $Me_3 Sn$ ^{15}NH ϕ differed by about 10 ppm from Jack Roberts' single resonance aniline-^{15}N (wet ?, neat) result, (Proc.Nat.Acad.Sci., 1964, 51, 735). Malcolm's d.r. result for aniline-^{15}N (dry; neat) agrees with Jack's, so we are worried about our silicon and tin work unless we can prove solvent shifts of about 10 ppm. Either way it is interesting.

On other fronts, we find we are being increasingly 'scooped' (presumably our originality is dropping off!). Part of Ron Emmanuel's work (Ph.D. Thesis, 1968) on methylene inequivalence in ethyl phosphines and methyl inequivalence in isopropylphosphines, has appeared elsewhere (see McFarlane, Chem.Comm., 1968, 229), as well as his work on substituted arene chromium tricarbonyls which I reported at the I.U.P.A.C. meeting in Munich during 1967 (see Sorensen and Price, Canad.J.Chem., 1968, 46, 515). The latest examples are Roger Price's studies on multiple "tickling" of the 'classical' molecule 2-3 dibromopropionic acid and also the more nearly AMX molecule vinyl acetate monomer. All Dr. V. Bystrov's results (Newsletter No. 118), including the observation of combination frequencies, have thus been confirmed quite independently.

These are all genuine overlaps. It is significant that we had not mentioned any of the above work in our previous contributions to the Newsletter, otherwise presumably we could have contracted out of those areas earlier.

Lastly, we shall probably have a postdoctoral vacancy in the group soon, for work on molecules containing ^{15}N. Anyone interested should write directly to me.

Best regards,

Ed

EDWARD W. RANDALL.

Hammett σ   vs J^{15}N-H

J^{15}NH c/s

a = p-nitroaniline

b = 2,4,6-tribromoaniline

c = 2,4-dibromoaniline

d = p-iodoaniline

e = p-bromoaniline

f = aniline

g = p-toluidine

h = m-nitroaniline

⊙ in acetone

+ in CDCl$_3$
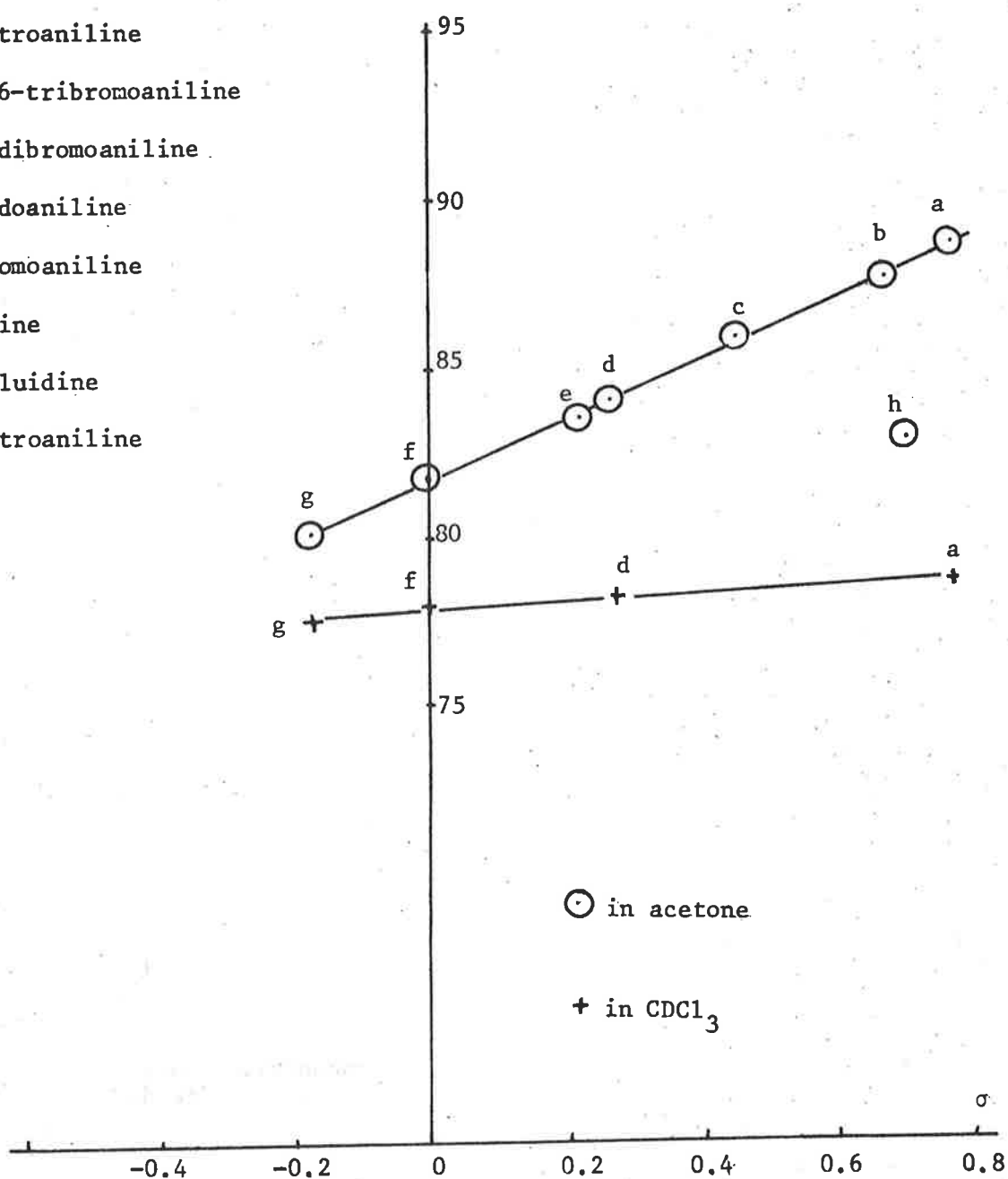
La Trobe University

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SCHOOL OF PHYSICAL SCIENCES

TELEPHONE: 478 2722

16th October, 1968.

Dr. B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
CHICAGO. ILLINOIS 60616, USA.

Dear Dr. Shapiro,

Subject: Calibration of time-averaged spectra

Since our new A60D has been commissioned a few months ago, we have started some work on directly bonded C^{13}-H coupling constants of aromatic compounds in dilute solutions. In this work we found that it is desirable to monitor the resolution of the instrument over the period of measurement and at the same time, calibrate the position of the satellite lines without introducing a relatively large Bloch-Siegert effect. For this, we use a Hewlett-Packard 3300A Function Generator, equipped with a 3302A Trigger-phase lock device. The frequency is controlled by an external DC source and output I is routed through the C-1024 providing the trigger signal. This is monitored by a frequency programmer which switches the function generator frequency to a preselected calibration frequency as soon as the trigger signal is switched off by the C-1024. This frequency is fed into the spectrometer Ext. Cal. Osc. input through an attenuator. This way, the function generator provides a calibrating signal comparable in intensity to the expected intensity of the satellite lines. The position of this peak serves as frequency calibration, while its width at half height indicates the extent of the deterioration of the resolution of the instrument. The stability of the device is such that drift is undetectable over a period of days. The device has been constructed by Mr. C. Ducza of our Physics Department.

Yours sincerely,

B. TERNAI

FREQUENCY PROGRAMMER
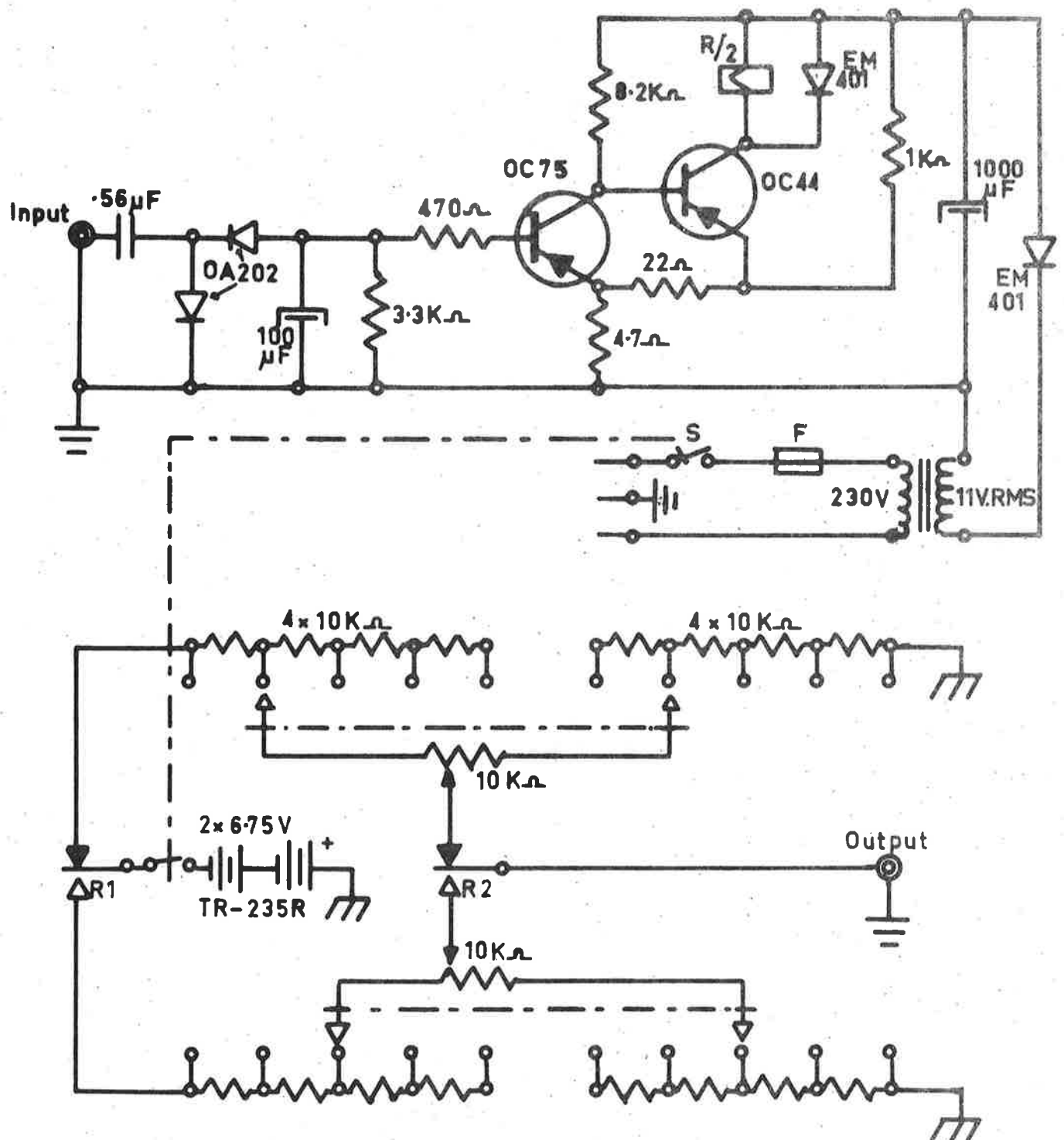
DeBarr Hall
620 Parrington Oval

THE UNIVERSITY OF OKLAHOMA

NORMAN, OKLAHOMA 73069

November 4, 1968

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

Dear Dr. Shapiro,

ON THE QUESTION OF ENDO,EXO PROTON ABSORPTIONS IN THE NMR SPECTRUM OF NORBORNANE

Somewhat peripherally to our interest in the bicyclo(2.2.1)heptyl system, we have prepared and examined the nmr spectra of a number of specifically-deuterated norbornanes. The 60 MHz spectra are shown in the accompanying figure.

It is well established that in norbornene, the anti-bridge proton absorbs at higher field than does the syn- bridge proton (1), and the 5,6-endo- protons absorb at higher field than do the 5,6-exo- protons (2). The latter question merits consideration in the saturated system, norbornane.

Comparison of the spectrum of norbornane (inset A) with that of exo,exo,exo,exo 2,3,5,6-tetradeuterionorbornane (inset D) and with that of 7-deuterionorbornane (inset F) reveals that the endo-protons absorb at about δ 1.1 ppm, roughly coincident with the bridge protons (width at half height = 2.5 Hz). Insets C and E, respectively, reveal the A A' A" A'" B B' B" B'" and A A' B B' endo-, exo- proton patterns. Clearly, the endo- protons absorb at higher field than do the exo- protons, congruent with the result cited above for norbornene.

The table below shos the approximate chemical shifts in ppm and the $\Delta\delta$'s in ppm for the endo- and exo- protons in norbornane and norbornene:

Compound	δ_{endo-} (Hz)	δ_{exo-} (Hz)	$\Delta\delta$ (Hz)
Norbornane	1.1	1.6	0.5
Norbornene	0.95	1.6	0.65

It is tempting to ascribe the small upfield shift of the endo- protons in norbornene relative to those in norbornane to an anisotropy effect of the norbornene 2,3- double bond.

Although the chemical purity of the octadeuterionorbornane is good, the isotopic purity leaves something to be desired (inset E).Nevertheless, a combination of spin-tickling experiments, the LAOCOON III computer program, and the patience of Job have permitted calculation of the A A' B B' spectrum. This work, carried out by Dr. Anna Laura Segre of the Istituto di Chimica Industriale del Politecnico in Milan, Italy, is near completion, and we hope to report the results of our collaboration in the near future.

Very truly yours,

Alan P. Marchand
Assistant Professor

Nancy Chia-cheng Wu

(1) JACS, 90, 3724 (1968).
(2) ibid.,p. 3721.

ISOTOPIC ANALYSIS
23.7% d_0
76.3% d_1
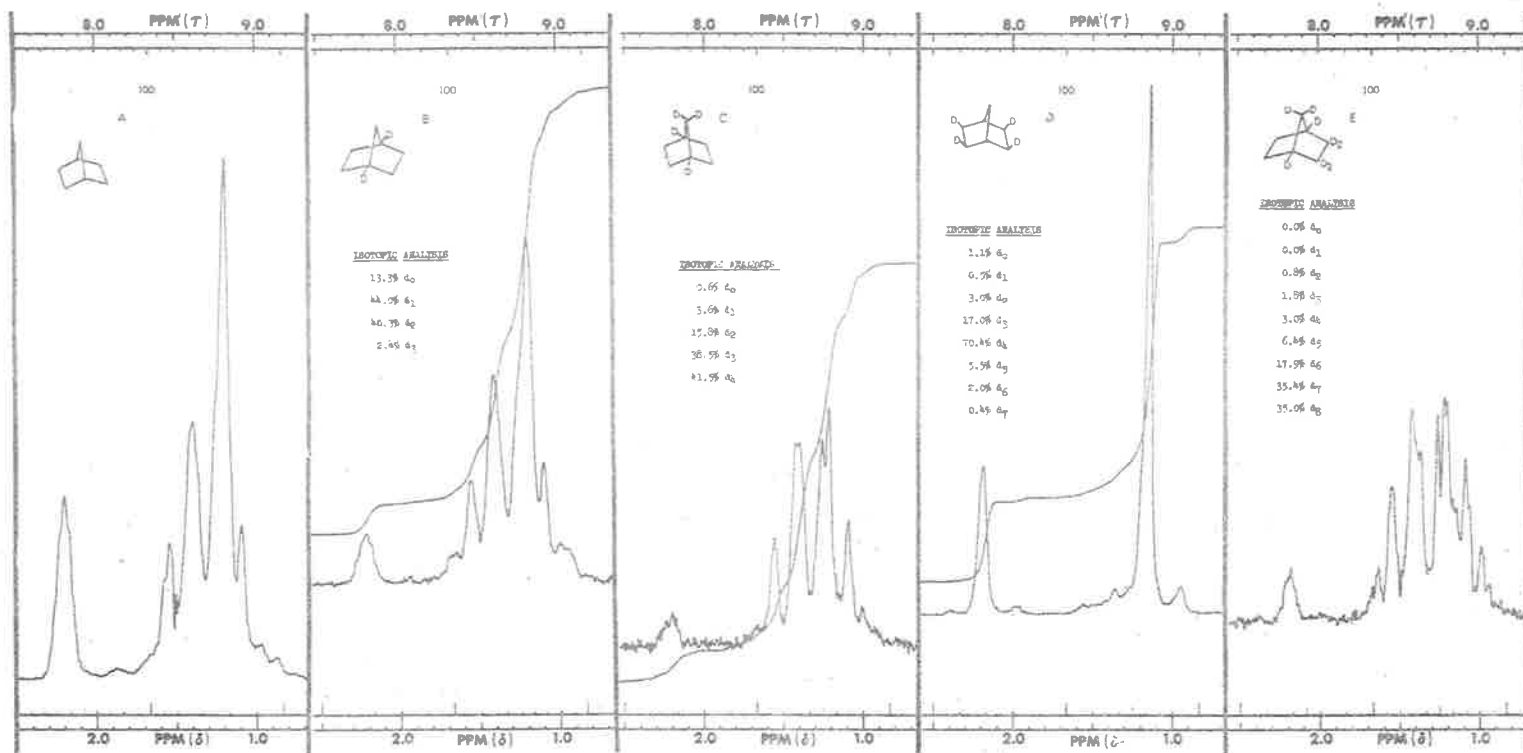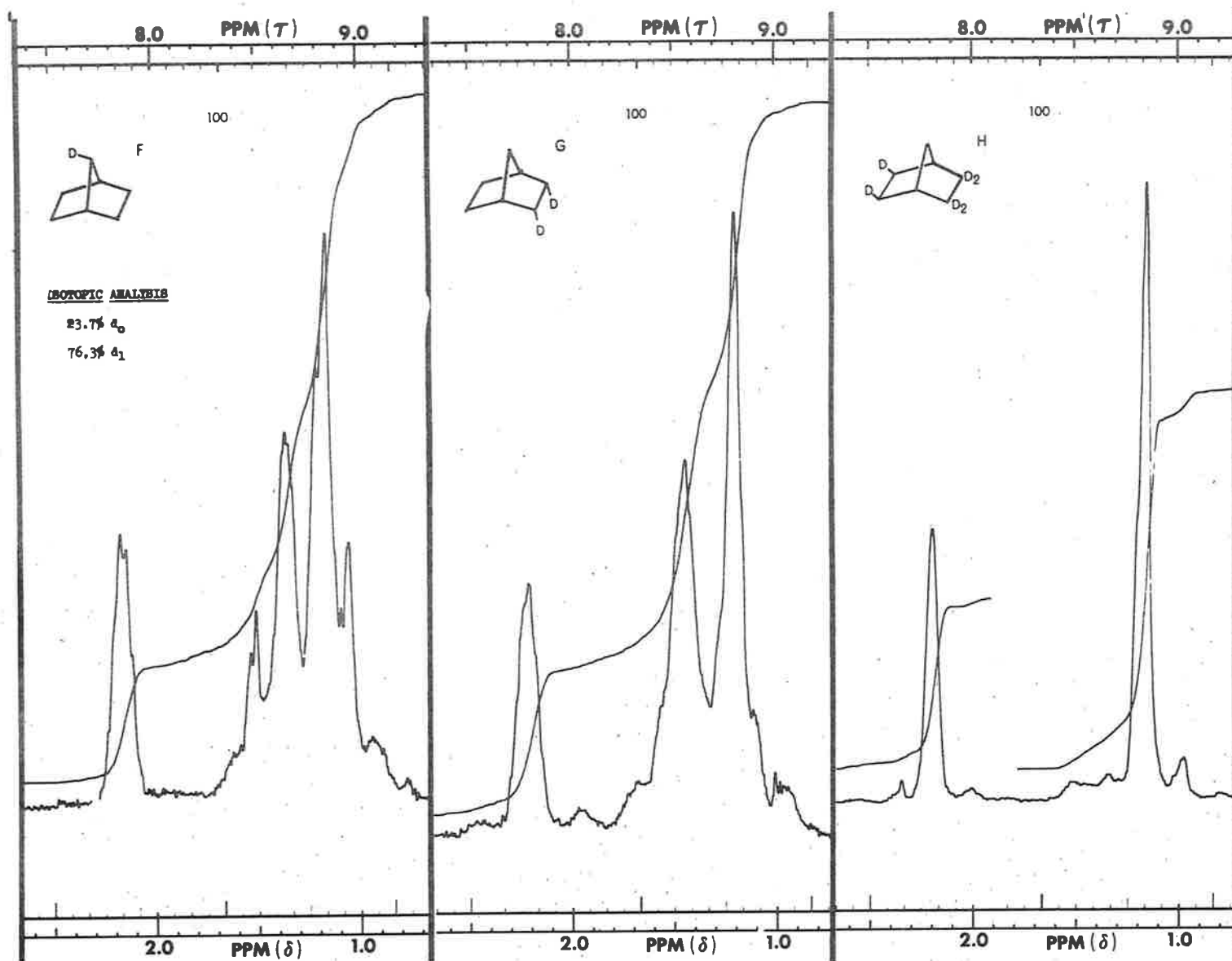
Monsanto

Monsanto Company
1700 South Second Street
St. Louis, Missouri 63177
(314) MAin 1-4000

October 28, 1968

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

Re: Alpha Branching

Dear Professor Shapiro:

We frequently need to determine hydrocarbon chain branching
at the carbon atom alpha to a substituent. With most pure
compounds this can be accomplished by measurement of the
area of the alpha carbon proton peak. This approach is
often unsatisfactory for isomeric mixtures however. With
many substituents, partial or extensive overlap of the
alpha methylene proton peak and the corresponding methine
proton peak, of the alpha branched isomer, occurs. We
have compiled chemical shift data for several substituents
to provide a guide for predicting whether such isomeric
components in mixtures can be identified and quantitatively
measured by NMR.

The attached table shows the compilation for twenty-one
common substituents. The data were obtained from the
literature as well as from our laboratory. The numbers in
parenthesis indicate the numbers of examples included.
Data were included only for non-cyclic compounds. Data
were excluded when the example contained a second substit-
uent less than two carbons removed from the indicated unit.
For many of the substituents listed, the data cover too wide
a chemical shift range to permit accurate prediction of
resolution. At 60 MHz, a chemical shift difference of at
least 0.4 ppm is usually necessary to avoid overlap because
of typical multiplet widths.

To more precisely determine the extent of resolution of
such components, we have examined isomeric compounds contain-
ing fifteen of the substituents listed. Seven of the
mixtures studied gave fully resolved peaks in CDCl$_3$ at 60
MHz permitting identification and quantitative analysis.
Somewhat surprisingly, no significant changes in relative
chemical shifts or degree of resolution were obtained when
benzene was used as the solvent. Mixtures of alcohols and

Professor Bernard L. Shapiro
October 28, 1968
Page 2

aldehydes which could not be analyzed using the alpha carbon
signal can be analyzed using the substituent signal. The
hydroxyl peaks of alcohols are resolved in specially prepared
DMSO. We observed that the aldehyde proton peaks of alpha
branched aldehydes are completely resolved from the corre-
sponding peak in the unbranched isomer.

This report provides a guide to better predict when NMR can
be used to determine alpha branching in isomeric mixtures.
It should be considered only a guide, however, since inter-
fering peaks which will preclude analysis may be present.
Peak overlap of the alpha carbon proton peaks caused by
either abnormally large multiplet widths or by relative
chemical shift changes due to other substituents may also
be encountered.

Martin W. Dietrich   L. Wayne Keiser[1]   Robert E. Keller

[1]Present address: Chemistry Department
                     University of Illinois
                     Urbana, Illinois

db
Attachment

Substituent	Spectral Resolution	RCH$_2$- δ(ppm)	RR^{1}CH- δ(ppm)
C=C		1.81-2.16(20)	2.18-2.63(5)
NR	A	2.09-2.76(32)	2.31-3.02(8)
CO$_2$H	A	2.18-2.70(21)	2.28-2.63(5)
C≡N		2.27-2.40(11)	2.72(1)
$\overset{O}{\overset{\|}{C}}$-R		2.28-2.47(26)	2.33-2.67(6)
$\overset{O}{\overset{\|}{C}}$-H	A,D	2.30-2.43(5)	2.05-2.32(3)
SH	A	2.37-2.52(9)	2.81-3.16(5)
Ar	A	2.38-2.77(21)	2.28-3.19(15)
$\overset{O}{\overset{\|}{C}}$-Cl	A	2.40-3.04(3)	2.91(1)
N-SO$_2$ Ar	A	2.93-3.60(6)	3.00-3.27(2)
N-Ar		2.97-3.89(14)	3.23-3.92(5)
OH	A,C	3.08-4.00(28)	3.20-3.70(24)
I	B	3.10-3.26(14)	4.17-4.34(3)
OR		3.20-3.60(12)	3.42-3.78(5)
Br	B	3.33-3.59(12)	3.99-4.04(9)
Cl	B	3.44-3.57(13)	3.90-4.13(4)
O$\overset{O}{\overset{\|}{C}}$-R	B	3.55-4.22(50)	4.83-5.13(5)
OP		3.78-4.40(27)	4.63-4.97(8)
OAr	B	3.83-3.90(11)	4.40(1)
O-$\overset{O}{\overset{\|}{C}}$-Ar	B	3.97-4.49(18)	4.90-5.30(6)
O-$\overset{O}{\overset{\|}{C}}$-O	B	3.98-4.33(5)	4.83(1)

A. Unresolved in CDCl$_3$ at 60 MHz.
B. Resolved in CDCl$_3$ at 60 MHz.
C. Resolvable in DMSO or by esterification.
D. Aldehyde proton signal resolved in CDCl$_3$ at 60 MHz.

UNIVERSITÉ DE LYON   FACULTÉ DES SCIENCES

PHYSIQUE PROPEDEUTIQUE

V Réf.:

N Réf.:   Villeurbanne, le   8 Octobre 1968.

Docteur Bernard L. SHAPIRO
Département of Chemistry
Texas A and M University
College station
Texas 77843
U.S.A.

Cher Professeur Shapiro,

Interconversion de tétrahydropyrannes.

La barrière de potentiel étant donnée, pour observer séparément 2 conformères, il faut que $\Delta\nu_{e-a}$ soit suffisant.

Tétrahydropyranne : On peut prévoir un déplacement important pour les protons en 2 ; l'expérience le vérifie puisqu'à - 100 °C, les protons axiaux et équatoriaux sont séparés de 0,55 ppm (1).

D'autre part on peut estimer à priori la différenciation à attendre pour les protons en 5 à partir de résultats portant sur le cyclohexane et le dioxanne 1,3 :
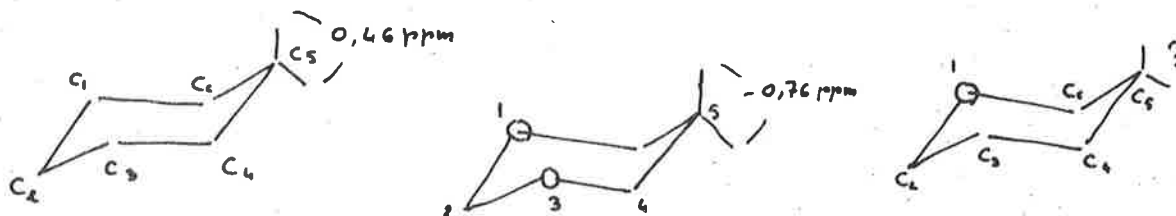
l'enchainement (C_2 C_3 C_4 C_5) du cyclohexanne donne lieu à une différenciation de 0,46 / 2 ppm tandis que celui du dioxanne (C_2 O_1 C_6 C_5) donne - 0,76/2 ppm.

En admettant l'additivité de ces effets le proton axial devrait être vers les champs faibles à -0,15 ppm de l'équatorial. De ce résultat nous ne retiendrons que l'aspect qualitatif. Cette proximité des résonances de H_{2e} et H_{2a} explique qu'à - 100 °C il soit encore possible d'irradier simultanément les protons en 3 afin d'observer la figure AB donnée par les protons en 2. (1).

Docteur Bernard L. SHAPIRO   Page n° 2.

Métoxy 2 - Tétrahydropyranne.

A température ordinaire on peut doser le taux des conformères.
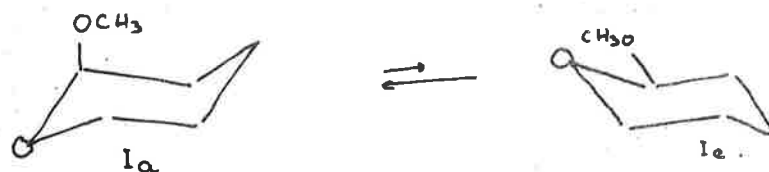
- Le dosage effectué sur la largeur de raie de H_2 conduit à 72 % de I_a (2)
- De notre côté nous avons trouvé 71,5 % à partir du déplacement chimique moyen en retenant δ_{2a} = 4,15 et δ_{2e} = 4,57 (3).

La forme I_a est stabilisée par effet anomère (4).

Il nous a semblé intéressant de chercher la confirmation de ces résultats par refroidissement : Etant donné le déplacement important que l'on peut attendre pour H_2 dans les 2 conformères on pensait voir apparaître distinctement à 200 °K les 84 % de forme I_a et les 16 % de forme I_e. Or l'expérience s'est soldée par un échec.

C'est donc que la barrière d'interconversion est notablement plus faible que celle du tétrahydropyranne. Cette différence de comportement est due au groupement métoxy : Effectivement si l'on "suit" l'évolution de l'énergie d'interaction entre dipôles électriques lors du passage d'un conformère à l'autre, on s'aperçoit que cette interaction a bien pour effet d'abaisser sensiblement la barrière de potentiel.

Recevez, cher Monsieur, nos sentiments les meilleurs.

                                    DUPLAN   DELMAU

(1). G. GATTI, A.L. SEGRE, C. MORANDI J. Chem. Soc. 1203 (1967).
(2). C. PIERSON, O.A. RUNQUIST J. Org. Chem. 33, 2572, (1968).
(3). C.B. ANDERSON D.T. SEPP Tetrahedron 24, 1707, (1967).
(4). E.L. ELIEL, N.J. ALLINGER. S.J. ANGYEL and G.A. MORRISON
     Conformational Analysis p. 408 Wiley New York (1965).

THE UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
RIVER CAMPUS STATION
ROCHESTER, NEW YORK   14627

DEPARTMENT OF CHEMISTRY

November 12, 1968

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

Dear Barry:

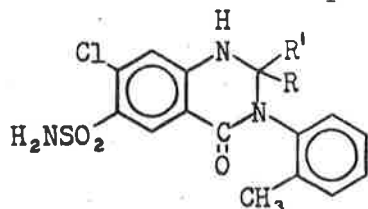### Hindered Rotation in Aryl Substituted Quinazolinones

One of our projects under way at present is the study of hindered rotation in a series of aryl substituted quinazolinones, of which the following three compounds are typical examples. Spectra are run at 100 MHz on a 4H-100 spectrometer, usually on DMSO-d_6 solutions.

I, R = R' = H

II, R = H, R' = CH_3

III, R = R' = CH_3

The environments of R and R' in these molecules are dependent on the conformations of the tolyl substituent about the C-N bond. Restricted rotation of this group results in the n.m.r. spectrum being sensitive to these environmental differences. When R=R' the rotational isomers (corresponding to the tolyl methyl group being above or below the plane of the rest of the molecule) are enantiomers, and are present in equal concentration. In I, the R and R' protons give rise to an AB quartet (δ_{AB} = 0.32 p.p.m., J_{AB} = 9.8 Hz) at low temperatures. This collapses to a singlet at higher temperatures when the environments are averaged by fast rotation of the tolyl group. In III, the R and R' methyl groups give rise to two peaks separated by 0.42 p.p.m.

When R≠R' the rotational isomers are diastereomers and are present in unequal concentration. At low temperatures the spectra of the diastereomeric forms (present in a ratio of 1.2:1.0) of II are easily recognized. Spin-spin interaction gives rise to a doublet (J=5.8 Hz) from the methyl group (R') and a quartet from the hydrogen atom (R) of each diastereomer, the intensities corresponding to the relative populations. The chemical shift differences between diastereomers are 0.17 p.p.m. for the methyl protons (R') and 0.37 p.p.m. for the isolated protons (R). When the sample is heated the composite spectrum from the mixture of diastereomers collapses to a single, time averaged spectrum. In particular, the two doublets arising from the methyl groups (R') collapse to a single doublet.

By complete line shape analysis of the collapsing AB system of I, and of the R' methyl spectrum of II over a range of temperatures,
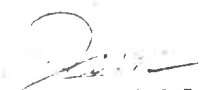
we have found $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$, and $\Delta S^{\ddagger}$ for the interconversion of the rotational isomers. Two sets of values of these parameters are obtained for II, corresponding to promotion from the two ground states to the common transition state. We are now using an improved non-linear regression program for computer fitting experimental and calculated spectra (see IITNMR February, 1968 for a discussion of our earlier version). This program works very well and will converge from highly inaccurate initial guesses, so we do not have to calculate any trial spectra. Spectra taken over the temperature range 9 to 49° C for I, and 24 to 80° C for II, were used in these calculations. The curves were fitted at about 60 to 90 points, the number of points used depending on the width of the region of interest.

Values of the kinetic parameters for I (at 298° K) are as follows: $\Delta H^{\ddagger} = 9.3 \pm 0.8$ kcal/mole, $\Delta G^{\ddagger} = 15.5 \pm 0.2$ kcal/mole, $\Delta S^{\ddagger} = 21.0 \pm 2.6$ e.u.

Changing R' from H in I to CH_3 in II has little effect on $\Delta H^{\ddagger}$ but causes a significant change in $\Delta S^{\ddagger}$, which takes on a large negative value (about -30 e.u.). It appears that the hetero ring is non-planar and flexible, but in the transition state for rotation in II this ring if restricted to a conformation with the methyl group forced away from the tolyl group. The steric requirements of the transition state of II with the hetero ring in such a conformation are similar to those of I, so $\Delta H^{\ddagger}$ is similar for both compounds, but the considerable loss of conformational mobility in the transition state is reflected in $\Delta S^{\ddagger}$.

In the case of III, steric interaction between the gem dimethyl group and the tolyl group cannot be relieved by conformational changes in the hetero ring, since one of the methyl groups must always be in such a position as to hinder rotation. In consequence, the barrier to rotation in III is so high that rotation is slow on the n.m.r. time scale, even at 200° C (diphenyl sulfoxide solution). The doublet arising from the gem dimethyl group shows almost no sign of collapse at this temperature.

Further compounds of this type with different substitution patterns are being studied. This work is being carried out in co-operation with the Strasenburgh Laboratories.

Yours sincerely,

J. R. Fehlner

L. D. Colebrook

UNILEVER RESEARCH LABORATORY

THE FRYTHE, WELWYN, HERTS.

TELEPHONE : WELWYN 5121

Your Ref.

Our Ref. EF/BLM   13th November, 1968.

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

T_1's by progressive saturation

Dear Professor Shapiro,

I should like to open an account with the Newsletter
by describing briefly some work I did a few months ago with
Dr. Robin Harris, at the University of East Anglia, Norwich.

The many techniques for measuring T_1 directly fall
into two classes : those using conventional high-resolution NMR
spectrometers, and those based on pulse methods, such as spin-echo
experiments. Both these techniques have their disadvantages - the
former in that auxiliary equipment such as a fast-response recorder
is required, and the latter in that normally only an overall T_1 is
obtained for all the transitions of a given nuclear species. We have
now worked out what we think is a new method, using a high-resolution
spectrometer with no ancillary equipment, and giving individual
relaxation times for each transition. This method is based on the
following equation for peak intensity at frequency   (this may be derived
fairly readily):

$$V_{ij} = BH_1 g(\gamma) \, Q_{ij} / \left[1 + \gamma^2 H_1^2 g(\gamma) \, Q_{ij} \, T_1^{ij}/2 \right].$$

In this equation $g(\gamma)$ is the lineshape function, which we do not need
to specify in this treatment; B is a constant containing instrumental
factors and proportional to the number of nuclei/ml. of sample; Q_{ij} is
the square of the matrix element of I_+ (the shift operator) between
between i and j; and T_1^{ij} is the relaxation time specific to the
transition ij (this relaxation time may depend on several relaxation
probabilities in the spin system). By putting $\gamma = 0$ we obtain the
peak height $V(0)$, and the resulting equation may be rearranged to give

$$H_1/V_{ij}(0) = \gamma^2 H_1^2 T_1^{ij}/(2B) + 1/\left[BQ_{ij} g(0) \right].$$

Thus by measuring peak heights for increasing values of
H_1 (going through saturation of the line) and plotting a graph of
$H_1/V_{ij}(0)$ vs. H_1^2, a straight line is obtained with slope proportional

- 2 -

to T_1. Absolute values of T_1 may be produced if a calibration of the instrument is carried out with a sample of known T_1; thus there is no need to know the absolute value of H_1 - only measurement of a quantity proportional to H_1 is required. Most spectrometers already provide some sort of calibration of their H_1 control, although we found it necessary to recalibrate the control on our HA-100 by measuring the voltage produced across the potentiometer of the audiofrequency oscillator supplying H_1.

We found that this method gave extremely good and reproducible straight lines. We used it to obtain relative values of T_1 for inner and outer lines of AB systems, and this told us something about the relaxation mechanisms involved. The only obvious disadvantage of the method is that it cannot be used where lines overlap, and of course lines tend to overlap more at high H_1's because the onset of saturation gives the peaks broad wings.

I hope the above qualifies me to receive the Newsletter from now on - I miss it sorely now that I can no longer read Robin's copy!

Yours sincerely,

Elliot G. Finer

ELLIOT FINER.

BOSTON COLLEGE

A University of 12 Colleges and Schools

CHESTNUT HILL, MASSACHUSETTS · 02167

Phone 332-3200
Area Code 617

Department of Chemistry

November 18, 1968

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

Dear Barry:

Barfield's truncated matrix sum method [1,2] has provided predictions of the magnitudes and signs of a large number of long-range HH coupling constants, and we have been trying to fill in some gaps in the experimental data in order to test some of his predictions. A few of our results are summarized below:-
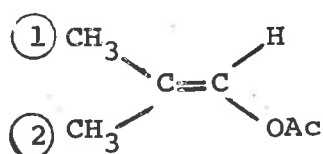
$^4J_{12}(exp) = -0.49$ *

$^4J_{12}{}^\tau(theo) = -1.16$
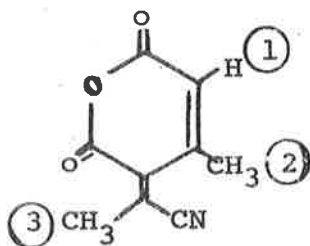
	J (exp)	J (theo)	no. bonds
J_{12}	-1.39	-1.65	4
J_{23}	-0.77	-0.71	6
J_{23}	-0.37	-0.43	6

References:

1. M. Barfield, J. Chem. Phys., **48**, 4458 (1968)

2. M. Barfield, J. Chem. Phys., **48**, 4463 (1968).

* However, $J(exp) = J^\sigma + J^\pi$, and we estimate J^σ at ~ +0.4 Hz, so $J^\pi(est) \sim -0.9$, in good agreement with theory!

Ltr to: Prof. B. L. Shapiro
November 18, 1968   pg. 2.
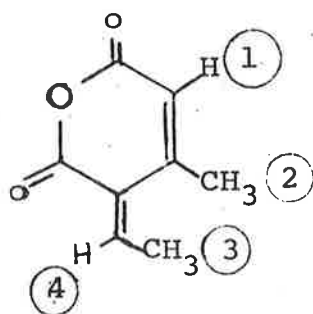
	J(exp)	J(theo)	no. bonds
J_{12}	| 1.29 |	−1.65	4
J_{13}	| 0.6 |	−0.71	6
J_{14}	| 0.88 |	+0.95	5
J_{23}	| 0.2(?) |	−0.43	6
J_{24}	| 0.0 |	+0.59	5
J_{34}	| 7.6 |	--	3

Although we haven't yet determined the signs of the couplings
in the second anhydride, the agreement between theory and
experiment is gratifying. Both anhydrides are a gift of
Dr. George Vogel of this department.

Now a request. We have been trying to convert
LAOCN-3 for use on our 360-40, but so far have only been
able to get Part I working. If any of your readers have
managed to effect the transformation, I'd appreciate hearing
from them about whatever changes were required.

Sincerely,

Dennis J. Sardella
Assistant Professor

DJS/cp

Short title: Long-range couplings and a request.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA   93106

November 18, 1968

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

Dear Barry: Spin Coupling in Isoindolines

Some time ago we reported that various N-acylisoindolines (I) showed
fine-structure on the resonances of the benzylic protons[1] These two
groups of nuclei are rendered magnetically non-equivalent by slow
rotation of the acyl group and we suggested that this fine structure
was the result of appreciable cross-ring spin-coupling interactions.
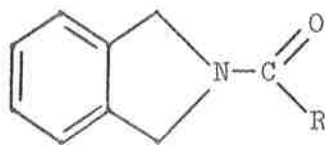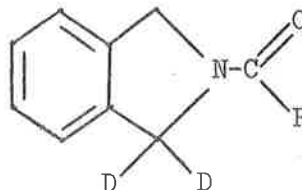
I   II

a, R = OCH_3

b, R = CH_3

c, R = C_6H_6

d, R = CF_3

In order to confirm this interpretation, we have synthesized the speci-
fically deuterated derivative, II. In Figure I are shown the resulting
p.m.r. spectra. For each series, the first trace is the experimental
spectrum of the undeuterated compound, the second trace is the theoretical
spectrum that is calculated using the parameters given in Table I and
the third trace is the experimental spectrum of the deuterated sample.
As can be seen, deuterium substitution considerably simplifies the spec-
trum, a result consistent with our original interpretation. It might
be noted that the coupling constant, $J_{AB'}$, can be smoothly correlated

-6-

with the Q parameters of Swain and Lupton,[2] suggesting that the conjugative ability of the substituent, R, is of primary importance in determining the magnitude of this coupling constant.

Table I
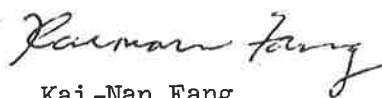
N.M.R. Parameters for N-Acylisoindolines

Substituent	δ_{AB}, p.p.m.	$J_{AA''}$, Hz	$J_{BB''}$, Hz	J_{AB}, Hz	$J_{AB''}$, Hz
OCH_3	0.071	-12.0	-12.0	0.9	2.6
CH_3	0.203	-13.0	-13.0	1.1	1.7
C_6H_6	0.252	--	--	~ 1.0	~ 1.2
CF_3	0.115	--	--	~ 0.6	~ 0.8

References

1. J. T. Gerig, Tetrahedron Lett., 4625 (1967).

2. C. G. Swain and E. C. Lupton, Jr., J. Am. Chem. Soc., 90, 4328 (1968).

Sincerely yours,

Kai-Nan Fang

J. T. Gerig

JTG:jas

R - OCH₃

R - CH₃

R - C₆H₆

R - CF₃

Figure I.

UNIVERSITY OF CALIFORNIA, IRVINE

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DEPARTMENT OF CHEMISTRY   IRVINE, CALIFORNIA   92664

November 15, 1968

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

Dear Barry: Double Resonance Without Trying

We have some sad operating experiences to report which we though might be of interest to others, if only to avoid a similar situation.

At Irvine, we have two spectrometers, an A56-60A and a HA-60. The HA-60 operates mostly at 56.4 MHz and is used in conjunction with a SD-60 hetero- nuclear spin decoupler. When our A56-60A was installed, it was placed about 30 feet from the HA-60 and around a corner so that any direct line-of-sight between the two instruments was blocked. However, the A56-60A operated poorly and unpredictably. It was almost impossible to use the adjust mode, except at very high rf field setting and, on the operate mode, the signal to noise ratio was variable and well below specifications. When an oscilliscope was placed at J701 of the field modular unit of the A56-60A to monitor the 21 KHz reference signal, we also observed a 10 KHz signal whose amplitud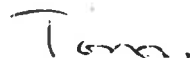e varied inversely with the rf field setting. This 10 KHz noise (which at times was as much as 10 v) on the 0.1 v 21KHz reference obviously caused the unsatisfactory performance of the A56-60A.

Eventually the source of this radiation was traced to the SD-60. Since all wires connected to the SD-60, as well as the SD-60 itself, emitted this radia- tion, all attempts to isolate the SD-60 by screening or grounding were unsuc- cessful. Similar problems with spurious radiation have been observed when operating the HA-60 at 60 MHz with the SD-60 on but disconnected from the probe. Lacking any better solution, we had to move the A56-60A to another location, four floors away!

Sincerely yours,
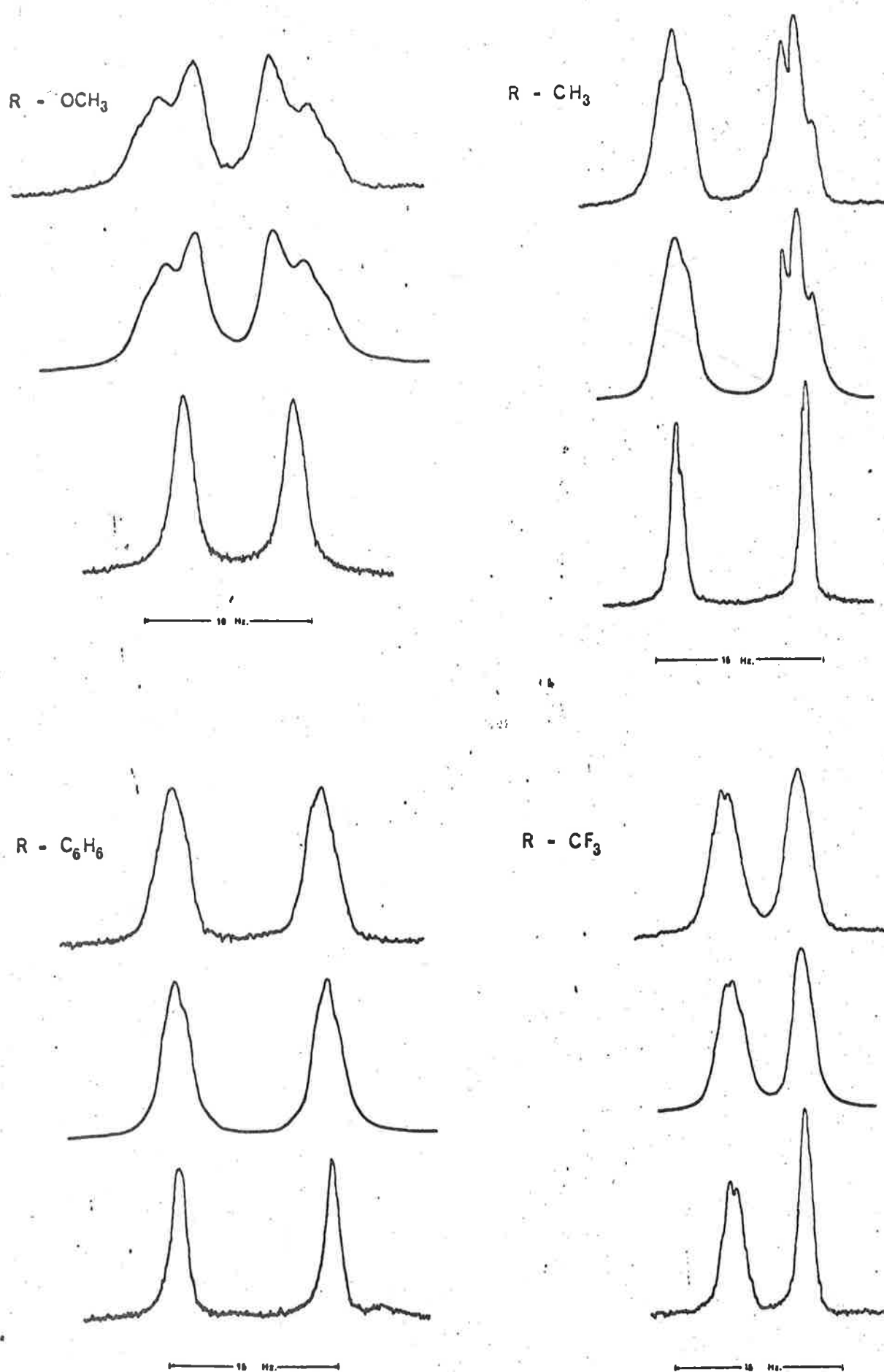
Stephen H. Smallcombe
Department of Chemistry

SHS/mp

UNIVERSITY OF CALIFORNIA, RIVERSIDE

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DEPARTMENT OF CHEMISTRY   RIVERSIDE, CALIFORNIA 92502

November 19, 1968

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

Title: The "Problem of Restricted Rotation
         in Amides and Thioamides".

Dear Barry:

In a recent issue of TAMUNMR, a "new" approach to the
determination of activation parameters for internal rotation
in a thioamide and amide was discussed and the justification
for this non-n.m.r. approach was based on the "difficulties
and pitfalls of the n.m.r. method".[1] The often quoted range
of 7-27 kcal/mole for the energy barrier in DMF was presented
as supporting evidence of these difficulties.

I feel that this presentation is quite misleading concern-
ing the present "state-of-the-art" of such n.m.r. studies.
Workers such as Gutowsky, Anet and Roberts have clearly demon-
strated the validity and usefulness of total lineshape and
spin-echo methods for obtaining kinetic data for fast rota-
tional and conformational changes in many types of systems.
We and others have concentrated our efforts on amides and re-
lated systems and have achieved good success.[2] A quite respect-
able list of such parameters for amides can now be obtained
from the recent literature.[2,3]

Some amide-type systems clearly exist (such as I and II
in reference 1) which cannot be easily studied by n.m.r. methods
due to the inherent complexity of their spectra. However the
simplest systems, which are potentially the most useful for
detailed understanding of substituent and medium effects, can
only be studied by n.m.r. methods. Such studies are continuing
in many laboratories and should, within the next few years,

Professor B. Shapiro
Page Two

provide a basis for a definitive discussion of the factors influencing the rotational reaction about the C-N bond.

Sincerely,

Bob

Robert C. Neuman, Jr.
Associate Professor of Chemistry

RCN/prm

References

1.) G. Helmchen, TAUMNNR, 122, 15 (1968)

2.) For leading references see R.C. Neuman, Jr. and V. Jonas, J. Am. Chem. Soc., 90, 1970 (1968)

3.) For a recent reliable study of DMF see A. Pines and M. Rabinovitz, Tetrahedron Letters, 3529 (1968)

Date 18th November, 1968.

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

Your Ref

Our Ref Res/RTJ/JLM.

Dear Professor Shapiro,

Evidence for (p-d)π overlap in Si-N bond

We have recently been looking at the [1]H N.M.R. spectra of the following compounds[1].

$$\text{I} \qquad \text{II} \qquad \text{III}$$
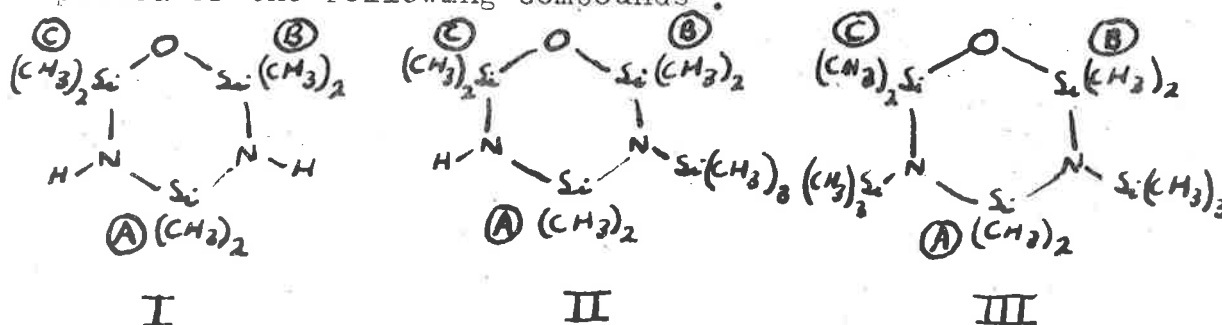
The chemical shift of the $SiMe_2$ group (A) shifts successively to low field as the N-Si$(CH_3)_3$ is substituted for $>$N-H. A similar shift is observed with the $SiMe_2$ groups B and C as shown in the following table.

Conc^n	Group	Shift (δ)	Group	Shift (δ)	Group	Shift (δ)
20% in CCl_4	IA	0.07 PPM	IIA	0.17 PPM	IIIA	0.32 PPM
	IB	0.07 PPM	IIB	0.17 PPM	IIIB	0.17 PPM
	IC	0.07 PPM	IIC	0.07 PPM	IIIC	0.17 PPM
20% in C_6H_6	IA	0.09 PPM	IIA	0.32 PPM	IIIA	0.44 PPM
	IB	0.15 PPM	IIB	0.24 PPM	IIIB	0.29 PPM
	IC	0.15 PPM	IIC	0.15 PPM	IIIC	0.29 PPM

As the steric hindrance of approach of solvent molecules is increased, the shifts are to low field in CCl_4, and to lower field in C_6H_6, rather than to high fields in CCl_4 and to low field in C_6H_6.[2] This suggests that the steric hindrance

effect as the cause of the shifts can be ruled out.

We think that the shift is due to a decrease in the electron density on the silicon atoms A, B and C, brought about by the additional Si-N (p-d) π overlap of the trimethyl silyl substituent. We would like to be able to use $-C(CH_3)_3$ as a substituent instead of $-Si(CH_3)_3$, but these compounds are extremely difficult to prepare.

Best Wishes,

Yours sincerely,

Roger

Roger T. Jones.

1. We wish to thank Dr. R.P. Bush, Midland Silicones Ltd., Barry, Glam., for making these compounds available to us.

2. D.H. Williams, J. Ronayne, and R.G. Wilson, Chem. Comm. 1039, (1967).

UNIVERSITY OF EXETER

Dr. K. G. Orrell
Department of Chemistry

Tel. 77911

Stocker Road,
Exeter

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

18th November 1968.

Dear Professor Shapiro,

We have been continuing our investigations of the isotropic shifts of heterocyclic ligand protons in complexes with Co(II), Ni(II) and Cu(II) trifluoroacetates. When the ligand (L) is 4-ethylpridine two series of complexes can be isolated, $M(CF_3CO_2)_2L_4$ and $M(CF_3CO_2)_2L_2$. The chemical shifts of the pure complexes are listed in the Table. These shifts were obtained by extrapolation of the shifts for known concentrations of complex in the co-ordinating ligand. For the Co complexes the large low field shifts of the ring protons can be explained in terms of β-spin delocalisation from ligand $\rightarrow$ metal and α-spin back-donation from metal $\rightarrow$ ligand. These mechanisms, however, predict that the α-H shift will be larger than the β-H shift. This, however, is not the case for the Ni complex. The high field shifts of substituent protons (Figure 1) are interpreted in terms of a hyperconjugation interaction involving the $-C-CH_2-CH_3$ fragment and the $p\pi$ orbital of the carbon at ring position 4 and also perhaps 3 and 5. The high field shifts indicate that the spin density at the 4-position carbon $p\pi$ orbital is negative and the hyperfine interaction constants for the α- and β-alkyl protons are also negative. This is in accordance with the results of the De Boer and Colpa for p-xylene and p-diethyl benzene anions but in contrast to 1-isopropyl-4-methyl benzene and 1-t-butyl-4-methylbenzene anions. In the case of the Ni and Cu complexes, however, the n.m.r. results indicate a small low field shift of the CH_3 protons associated with a negative hyperfine interaction constant.

Yours sincerely,

K. G. Orrell.

P.S. Short Title: Isotropic shifts of 4-ethylpridine complexes of
Co(II), Ni(II) and Cu(II).

TABLE

Chemical Shifts of 4-ethylpyridine Complexes

Metal	Complex	α-H/ppm	β-H/ppm	-CH$_2$-/ppm	-CH$_3$/ppm
Co	L4	-317	-79.5	+39.2	+18.1
	L2	-292	-84.9	+31.7	+12.1
Ni	L4	-62.8	-85.9	+30.0	(b)
	L2	(a)	-84.4	+20.6	-2.3(c)
Cu	L4	(a)	-177	+26.7	(b)
	L2	(a)	(a)	+15(d)	-2.9

(a) Bands too broad for detection.

(b) No variation in shift in the concentration range studied and thus no extrapolated value available.

(c) The magnitude, but not the sign, of this value is rather doubtful as there was a non-linear dependence of shift with concentration of complex in the range 0.95 → 1.0 mole fraction of ligand.

(d) This value is approximate since the -CH$_2$- band merged with the CH$_3$- band in the concentration range studied.

Spectra of (4-ethylpyr)$_2$Ni(TFA)$_2$

0.954 mole fraction of
free ligand

—CH$_3$ band

TMS

—CH$_2$—band

8·7   10 τ

0.865 mole fraction
of free ligand

—CH$_3$band

TMS

—CH$_2$—band

8·63   10 τ
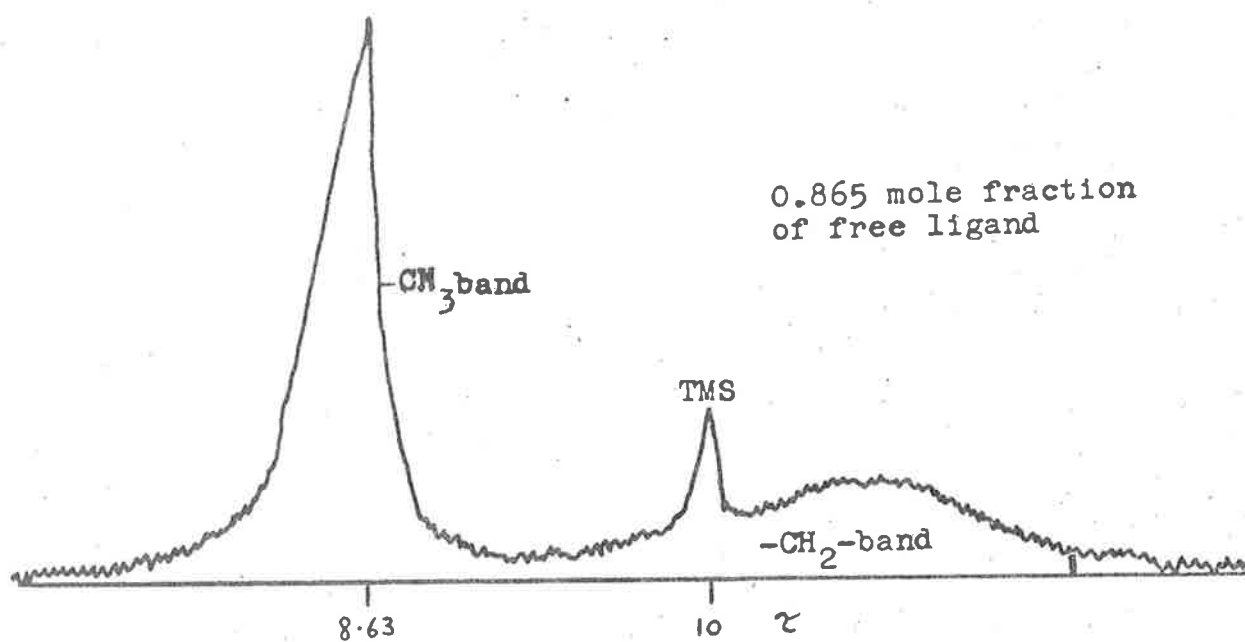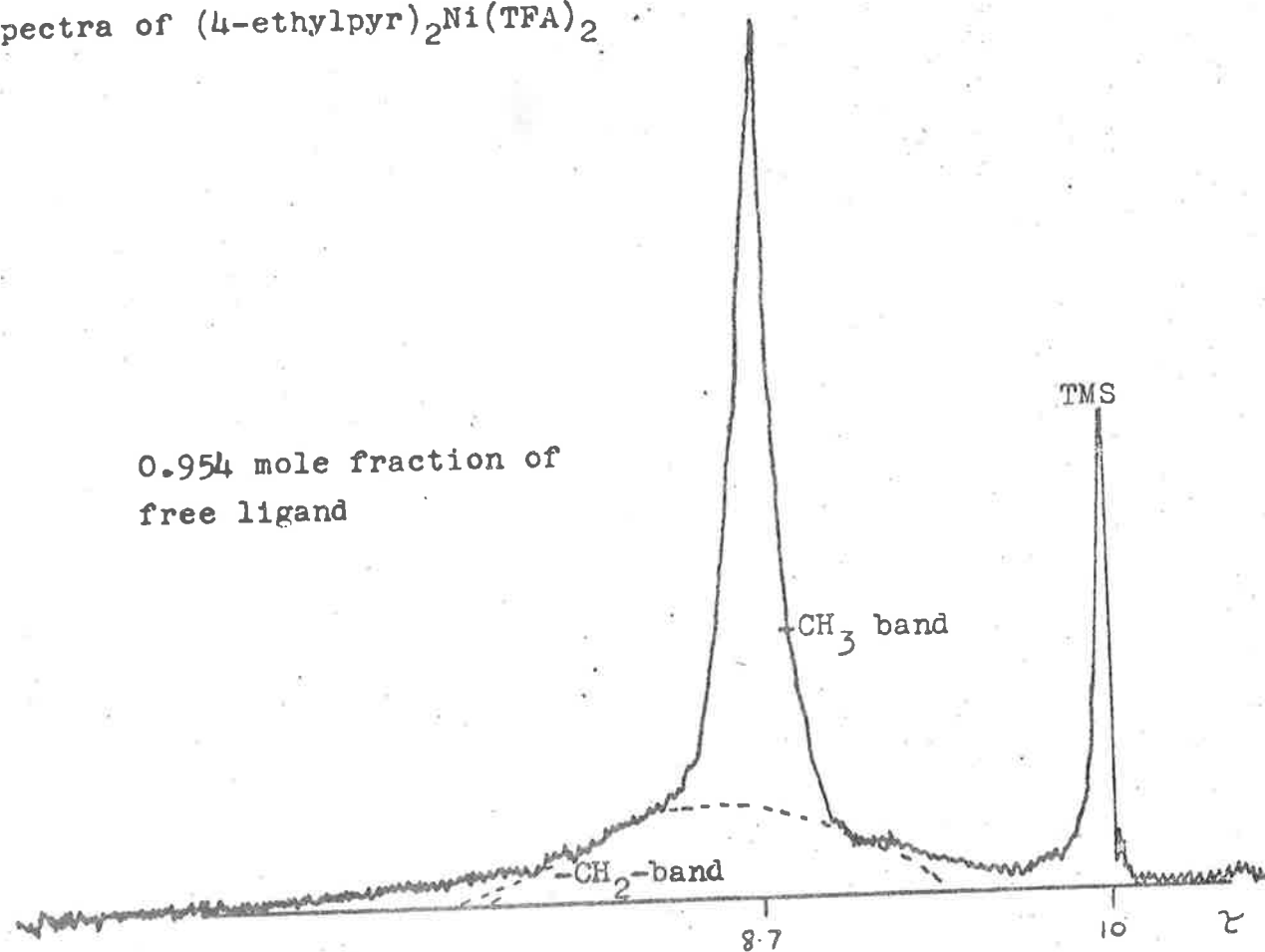
THE UNIVERSITY OF LIVERPOOL

DEPARTMENT OF ORGANIC CHEMISTRY

TELEPHONE: ROYAL 6022

THE ROBERT ROBINSON LABORATORIES,
OXFORD STREET,
LIVERPOOL 7.

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

14th November, 1968.

<u>Solvent Dependence of the Coupling Constants in
Meso-2,3-dibromobutane; Postdoctoral Position Available.</u>

Dear Barry,

My apologies as usual for having to be reminded to send in my contribution. We have just completed some work on the solvent dependence of the coupling constants in meso-2,3-dibromobutane[1].

We were interested in extending our solvent theory[2,3] to molecules of unknown ΔE^V in which the solvent dependence of the couplings now becomes a three parameter fit in ΔE^V, J_A and J_B, the couplings in the interconverting isomers A and B. Our previous results[2,3] had all been with molecules of known ΔE^V in which a much less critical two parameter fit is required.

This investigation was undertaken originally by Dr. K.K. Deb at Liverpool. Unfortunately he published these results surreptitiously during my year at Mellon Institute[4]. Even more unfortunate the experimental results therein are inaccurate and the theoretical parameters used incorrect.

We have repeated all these results and the solvent dependence of the vicinal CH.CH couplings in 1,1,2-trichloroethane (I) and meso-2,3-dibromobutane (II) are shown in the figure.

It can be demonstrated both theoretically and experimentally that our original theory will break down for very polar solvents. Essentially the energy difference between the isomers increases faster than predicted as the solvent dielectric constant gets very large. This results in the mathematical best fit of the solvent curve in the case of three unknown parameters giving unreal values of the three parameters. (In contrast the two parameter fit, being much less critical gives reasonable values). We suggest that in high dielectric media a "solvation shell" of oriented solvent dipoles begins to be formed around each solute molecule. A calculation of the average energy of the dipole-dipole interactions for an octahedral arrangement of solvent molecules around the solute was performed, and this gave this average energy $\langle w \rangle$ in terms of,

.....（ /

amongst other parameters, an "effective solvent-solute distance"
r. Rather than try to estimate r accurately ($\langle w \rangle$ is
proportional to r^{-3}), we determined this parameter experimentally
from the measurements of the 1,1,2-trichloroethane (I in the figure)
for which ΔE^v is known.

When to the original equations is added this new term the
mathematical best fit of the solvent curve II gave for meso-
2,3-dibromobutane, ΔE^v 2.0 ($\pm$ 0.1) and ΔE^1 0.90 ($\pm$ 0.1) kcals/
mole, J_t 10.3 ($\pm$ 0.1) and J_g 2.9 ($\pm$0.4) H_z . The long range
$J(CH.C.CH_3)$ can also be obtained. The trans and gauche oriented
couplings are + 0.5 ($\pm$ 0.2) and -0.3 ($\pm$ 0.1) H_z.

All these are very reasonable values (the J's are very close
to the values used by Anet[5] and Bothner-By[6] in their original
investigations on this compound). However it would be nice to
have the values of ΔE checked by some other technique.

Finally changing the subject completely, I am inviting
applications for a post-doctoral position here from next October.

I am looking in particular for someone to do some more
theoretical work in N.M.R.

With best wishes to you in your new position.

Yours sincerely,

R.J. Abraham.

1. R.J. Abraham, J.Phys.Chem. (in press).
2. R.J. Abraham and M.A. Cooper, J.Chem.Soc.(B), 202 (1967).
3. R.J. Abraham, L.Cavalli and K.G.R.Pachler, Mol.Phys. II 471
(1966)
4. K.K.Deb, J.Phys.Chem. 71, 3095 (1967).
5. F.A.L.Anet, J.A.C.S. 84, 747 (1962).
6. A.A. Bothner-By and C.Naar Colin, J.A.C.S. 84, 743 (1962).

$$(\epsilon-1)/(2\epsilon+1)$$

0.5

0.4

0.3

0.2

0.1

I

II

f (c.p.s.)

0.5

0.6

0.7

0.8

0.9

1.0

5.0

5.5

6.0

6.5

UNIVERSITY OF BRADFORD
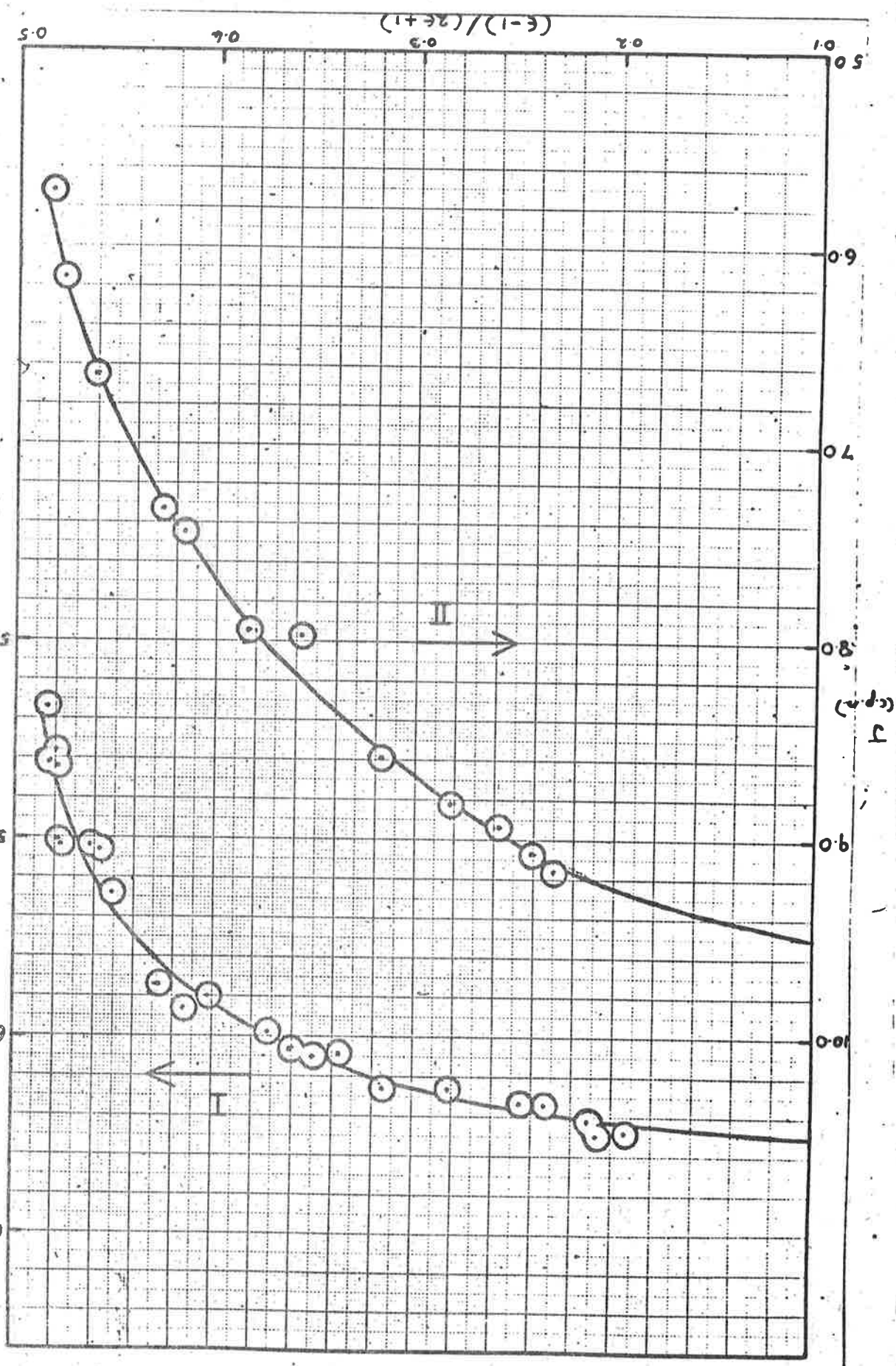
School of Chemistry,

Bradford 7 Telephone 29567/33466
England.

Vice-Chancellor and Principal
E G Edwards PhD FRIC

Please quote ref 21st October, 1968.

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

Dear Dr Shapiro,

Title: PROTON SHIFTS AND REACTIVITY INDICES IN POLYCYCLICS

P.M.R. can be used to study reactivity in aromatic systems directly, through identification of substitution products, as, for example, in the reactions of phenanthrene[1] and dibenz [b,f]oxepin[2]. Recently, comparisons of reactivity in aromatic substitution reactions have been made with P.M.R. chemical shifts[3] and also with E.S.R. hyperfine coupling constants.[4] We (K.D.B. and D.W.J.) have investigated apparently significant correlations between 107 P.M.R. chemical shifts in 29 polycyclic hydrocarbons and corresponding values of a number of Hückel LCAO indices for chemical reactivity in substitution reactions.

As Greenwood and McWeeny have pointed out[5], most of the several reactivity indices which have been proposed make similar predictions mainly because of the analytical properties of the equations from which they are derived. Broadly, indices may be classified as those arising from (i) isolated molecule methods; and (ii) localization methods. Of these, we have concentrated on the fairly readily calculable free valence index, F_r, a type (i) index specifying the residual ability of a carbon atom to form π- bonds, since chemical shifts in polycyclic hydrocarbons seem to be dominated by the π- electron distribution. For many relevant molecules, values of F_r are available in the literature[6]. Aromatic proton shifts, δ, qualified for inclusion only if they were singlets or derived from complete analyses, and if they had been measured in dilute solution in a supposedly inert solvent.

Comparison of F_r and δ values revealed an apparently significant statistical correlation for aromatic protons in alternant hydrocarbons. Further examination showed, however, that such correlations are merely a consequence of molecular geometry. Thus the C-C bonds in a parent polynuclear can be classified as NN, NJ, or JJ according to whether neither, one, or both C atoms are at ring junctions. Because of the larger HMO orders for NN than NJ bonds, the C atoms, which can in turn be classified into

    (a) non-peri (flanked by NN and NN);

    (b) peri (flanked by NN and NJ); and

    (c) peri-peri (flanked by NJ and NJ), will have F_r

increasing in this sequence (for non-hindered positions in alternants).
In the absence of steric hindrance, shielding of the aromatic protons
in the alternants will be dominated by proximity to ring currents. Since
(c) hydrogens are closer to more ring centres than (b) hydrogens and
these more than (a), chemical shifts will be expected to be in the sequence
$\delta_c > \delta_b > \delta_a$. Deviations from the consequent correlation between δ and F_r, i.e.
cases where the experimental deshieldings are greater than expected,
support this argument. Thus in the flat compact hydrocarbons coronene,
pyrene H(2), and benz[e]pyrene H(2), ring current contributions, which
give good approximations to the experimental shifts, are larger than in
more open alternants, whereas F_r values reflect only the immediate
surroundings of the C position $\underline{r}$ typical of (a) or (b) positions.

Analogous correlations between δ and F_r for sterically hindered positions
in alternants can also be shown to be fortuitous. A more detailed account
of these correlations in alternants and non-alternants has been submitted
to J. Phys. Chem.

The address of Dr K.D. Bartle is now Institute of Analytical Chemistry,
University of Stockholm, Roslagsvägen 90, Stockholm 50, Sweden.

Yours sincerely

K.D. Bartle,   D. W. Jones,   R. L'Amie,   R.S. Matthews.

References.

1. P.M.G. Bavin, K.D. Bartle and J.A.S. Smith, Tetrahedron, 21, 1087 (1965).

2. P.M.G. Bavin, K.D. Bartle and D.W. Jones, J. Heterocyclic Chem., 5, 327
    (1968).

3. J. Kuthan, Coll. Czech. Chem. Comm., 33, 1220 (1968).

4. C.P. Poole, Jnr., and O.F. Griffith, J. Phys. Chem., 71, 3672 (1967).

5. H.H. Greenwood and R. McWeeny, Adv. in Physical Org. Chem., 4, 73 (1966).

6. C.A. Coulson and A. Streitwieser, ''Dictionary of π-electron calculations''
    (Pergamon, London, 1965.)

LABORATORY OF PHYSICAL CHEMISTRY

THE UNIVERSITY

BLOEMSINGEL 10, GRONINGEN

THE NETHERLANDS

Groningen, November 14, 1968
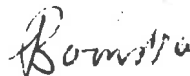
Analysis of Line Shapes with Mixed Gaussian-Lorentzian Broadening

Dear Dr. Shapiro:

Very often NMR line shapes are a result of the simultaneous presence of a Gaussian and a Lorentzian broadening process. For example, when studying a temperature dependent Lorentzian line width, a constant Gaussian broadening may be present due to field inhomogeneity or spread in sample alignment in oriented samples. The Gaussian width can be determined separately in those cases. Since the two widths do not add according to a simple relation, we calculated the widths of convolutions of a gaussian and lorentzian line, for various ratios of the widths. On the following page the results have been plotted on a log-log scale. The widths are expressed as the peak-to-peak distance of a derivative curve. When an experimental line width has been determined and its Gaussian contribution is known, the Lorentzian width can be read from this graph.

Sincerely,

(S.Boonstra)

(C.Migchelsen)

Experimental width
_____
Gaussian width

Lorentzian width
_____
Gaussian width

Peak-to-peak width of the derivative of a convolution of a Lorentzian and a Gaussian curve, to be used for determining the Lorentz line width from the experimental line width and the Gaussian contribution to the line width.

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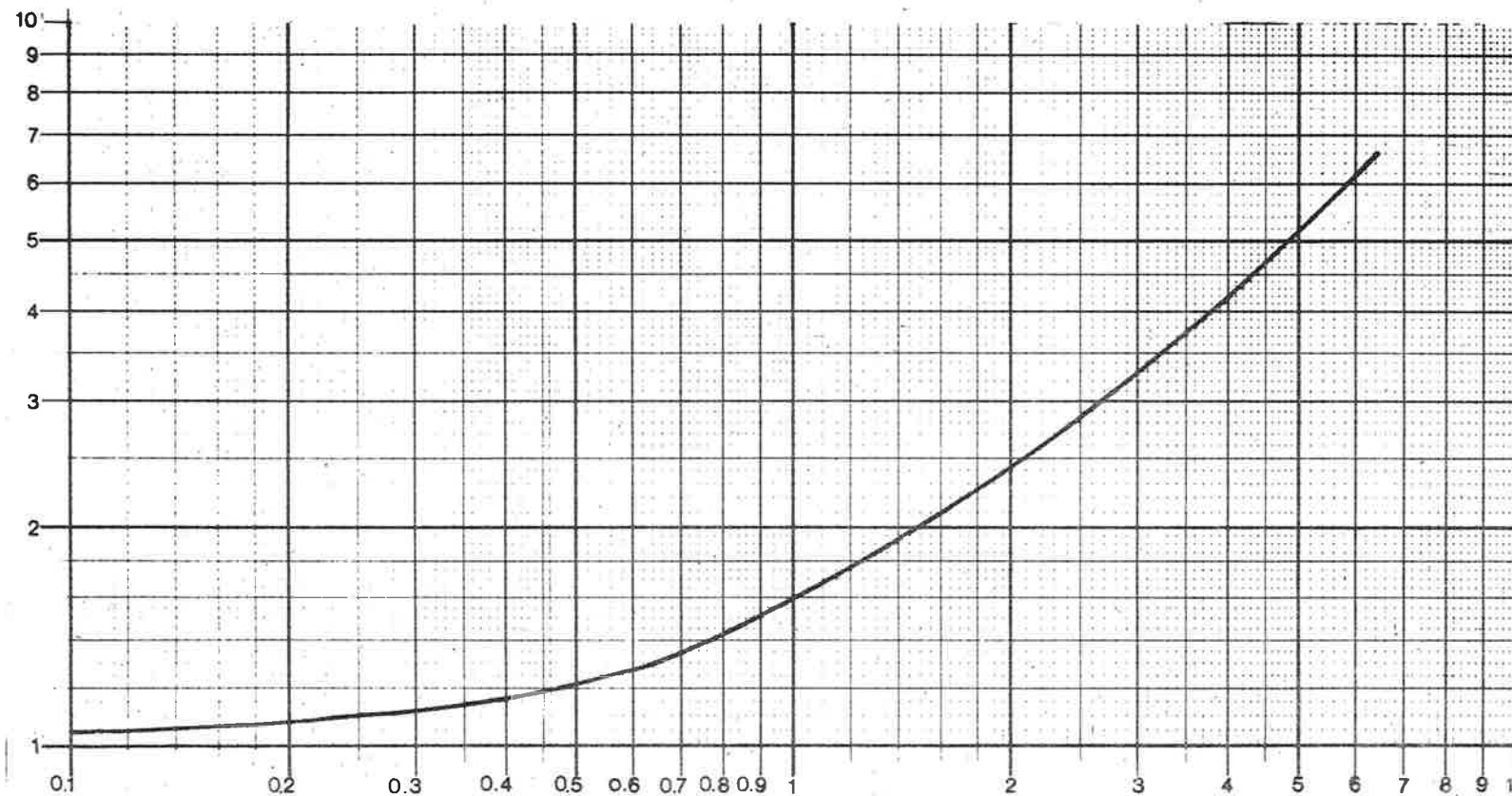
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213
[412] 621-1100

November 15, 1968

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

Dear Professor Shapiro:

SUBJECT: Sinister, Sinister, Rectus NMR

During a recent project we came across an unusual type of magnetic non-equivalence. It may be of interest to the pedagogues on your mailing list and we wish to report it in this way since we have no immediate plans for publication.

Bromination of methanetriacetyl trichloride in phosphorus oxychloride followed by quenching with methanol gave a good yield of a crude trimethyl methanetri-(2-bromoacetate):

$$HC(CH_2COCl)_3 + 3Br_2 \rightarrow HC(CHBrCOCl)_3 \rightarrow HC(CHBrCO_2CH_3)_3$$

Reactions in this series had been reported some time ago by Thorpe; however, our compounds do not correspond to what he reported. Recrystallization from methylcyclohexane readily resolved the product into two stereoisomers, m.p. 94-95° and m.p. 110-112°. Structural assignments followed from their nmr spectra (60 mh.), pertinent portions of which are reproduced on the accompanying page.

Yours truly,

William L. Mock

WLM:jaf

Enclosure

William L. Mock
Assistant Professor
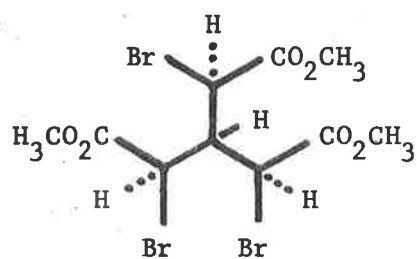 of Chemistry
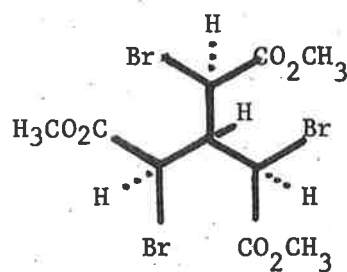
300　　　　　　　300　　　　　　4

600　　　　　　　600　　　　　4

300　　　　　　　300　　　　　2

150　　　　　　　　　　　　　　1

60　　　　　　　　　　　　　　4

30　　　　　　　　　　　　　　2

m.p. 110-112°

m.p. 94-95°

5　　　　　　　6　　　　　5　　　　　　6

Imperial Chemical Industries Limited

PHARMACEUTICALS DIVISION

Mereside, Alderley Park, Macclesfield, Cheshire

Telephone : ALDERLEY EDGE **2828**   Cables : AVLONTEX, MACCLESFIELD

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

Your Ref:

Our Ref: DG/FWB/DP

19th November, 1968.

Dear Professor Shapiro,

Modification to the Continuous Lock Signal Indication on a Varian HA 100

    We have constructed the Continuous Lock Signal Indication System of
F. W. van Deursen (IITNMR 111-1) and found that on our Varian HA 100
instrument we were unable to obtain the results in the aforementioned letter.
We have thus made the following modification to the circuit.
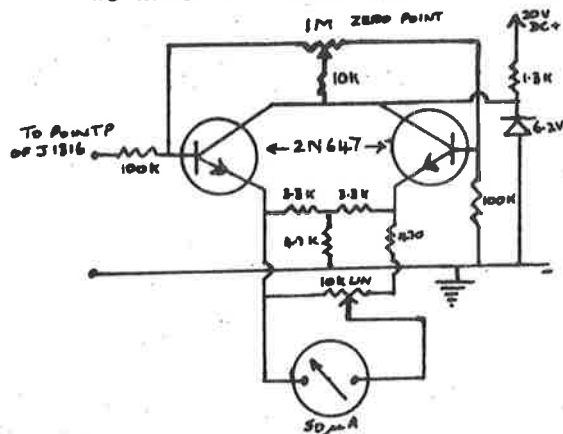
1. The PNP type transistors BCZ 11 were changed
   for an NPN type 2N647.

2. The + 6V supply for these transistors was
   obtained from the + 20V DC supply of the
   Internal Reference NMR Stabilized Controller
   V4354 and was controlled by a 6.2V Zener
   diode.

3. A sensitivity control was fitted to the meter
   to allow lock signals greater than 1V p-p
   to be used in certain circumstances.

    These modifications are incorporated in the diagram. We hope that if other
readers have experienced difficulties with van Deursen's circuit then they may
be interested in our modification. We find that it is a very useful way of
monitoring the lock signal and hence leads to easier training in the operation
of Varian HA 100 instruments. Please credit this letter as the contribution of
Dr. G. R. Bedford of these laboratories.

Yours sincerely,

D. GREATBANKS   F. W. BARCLAY
Chemical Research Department

123-41

8 MÜNCHEN 2, den   20.11.1968

Arcisstraße 21
Ruf-Nr. (0811) 5592/330/331/332
Telex Nr. 05/22854

Herrn
Prof.Dr.B.L. S h a p i r o
Texas A u. M University
College of Science,
Dept. of Chemistry,

College Station, Texas 77843
        U. S. A.

^{1}H-N.M.R.Spectra of Paramagnetic Co(II)-Complexes.

Sehr geehrter Herr Professor Shapiro !

In letzter Zeit haben wir uns mit der Untersuchung paramagnetischer
Übergangsmetallkomplexe des Typs $M(C_5H_5)_2$ mit Hilfe der kernmagne-
tischen Resonanz beschäftigt. Als besonders bemerkenswert stellte
sich bei diesen Untersuchungen heraus, daß der bislang angenommene
Mechanismus der Spinübertragung des ungepaarten Elektrons auf den
Liganden entlang chemischer Bindungen für keinen der 6 π-Aromaten-
Übergangsmetallkomplexe mit "Sandwich-Struktur" die experimentell
erhaltenen Spektren befriedigend erklärt. Die KMR-Spektren dieser
Verbindungsklasse können jedoch bei Annahme einer direkten Wechsel-
wirkung von ungepaarten Elektronen in teilweise besetzten d-Funk-
tionen des jeweiligen Zentralmetallions mit s-Bahnfunktionen
sterisch günstig angeordneter Wasserstoffatome der Ringliganden
zwanglos gedeutet werden.
Weiterhin konnten wir zeigen, daß bei diesem Komplextyp die Elek-
tronenrelaxation durch Symmetrieerniedrigung durch Substitution
wesentlich verlangsamt werden kann. So zeigt der Komplex Bis-
(cyclopentadienyl)-kobalt(II) bei Raumtemperatur kein EPR-Spektrum,
jedoch ein KMR-Spektrum mit der aus der Tabelle ersichtlichen
Linienbreite.

Verbindung	Linienbreite des Fünfringpro-tonensignals
Bis(cyclopentadienyl)kobalt(II)	185 Hz
Bis(methylcyclopentadienyl)kobalt(II)	280 Hz bzw. 235 Hz
Bis(indenyl)kobalt(II)	1800 Hz

Der entsprechende methylsubstituierte Komplex weist bereits we-
sentlich größere Linienbreiten im Kernresonanzspektrum auf, außer-
dem spaltet das Signal der Ringprotonen, - durch die erniedrigte
Symmetrie des Komplexes bedingt -, auf. Bis(indenyl)-kobalt(II)
schließlich, also eine Verbindung bei der ein Benzolring in 1,2-
Stellung an den Cyclopentadienylring annelliert ist, zeigt bei
Raumtemperatur ein EPR-Signal bei g = 2,036. Das Signal ist in
acht Linien aufgespalten (Hfs-Konstante = 60,9 Gauß).Das ^{1}H-KMR-Spek-
trum dieser Verbindung weist für die Protonen des Cyclopentadienyl-
ringes ein Signal mit der Halbwertsbreite von 1800 Hz auf; eine
Auflösung des Signals der drei Ringprotonen war daher nicht mehr
möglich.

                    Mit besten Grüßen

                        Ihre

November 22, 1968

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

Dear Barry:

Off-Resonance Heteronuclear CW Decoupling

For some time now we have been obtaining 25.1 MHz ^{13}C spectra using
an HA-100 with homonuclear lock on ^{13}C enriched samples. Our spectra have
been greatly simplified and enhanced in signal-to-noise by simultaneously
using proton noise decoupling following the technique of Ernst. [1] Nat-
urally, we sometimes wish to be able to assign peaks in the ^{13}C spectra to
CH doublets, CH_2 triplets and CH_3 quartets. We can, of course, run an un-
decoupled spectrum, but the time required to obtain adequate signal-to-noise
increases and the multiplets overlap so badly in many cases that we hesitate
to do this. We have found that assignment information can be more easily
obtained from a spectrum taken with Off-Resonance CW Decoupling (ORCWD). For
this we switch the V3512-1 Heteronuclear Noise Decoupler from noise (incoherent)
mode to CW (coherent) mode and offset the frequency from the previously set
optimum value to about 500 Hz away, either to higher or lower frequency.

The benefits of this technique are illustrated in fig. 1 which shows
the ^{13}C spectrum of 3-methylpentane (8 mm tube in a 12 inch magnet) run with
noise decoupling, ORCWD, and undecoupled. With ORCWD we, in effect, have
control over the magnitude of $J_{C,H}$ and can change the amount of H_2 frequency
offset to compress or expand the splitting of the multiplets. We lose infor-
mation on $J_{C,C,H}$ and $J_{C,C,C,H}$ which _might_ have been detected in the undecoupled
spectrum, but we usually don't regret this since both couplings are often
around 5-7 Hz making assignments difficult, anyway.

Professor B.L. Shapiro
November 22, 1968
Page two

We have also used ORCWD to calibrate the strength of H_2. We do the following: (1) lock to the single peak from CW decoupled ^{13}C enriched CH_3I (5 mm tube) using a 2500 Hz sideband, (2) change the lock sideband frequency to 2550 Hz and sweep upfield to relock to the second peak of the quartet (it's now a quartet because we changed H_0 without correspondingly changing the decoupler frequency), and (3) record the quartet on the 100 Hz sweep width (this means scanning through the lock). The residual splitting is Jr and from this $\gamma H_2 \sim (200-2Jr)J/Jr$. [2] A sample measurement is shown in fig. 2. If ever needed, it is possible to measure γH_2 this way to an accuracy of about $\pm 1\%$. This technique could be extended to other combinations of nuclei, e.g. $^{31}P - \{H\}$. Here one could lock to P_4O_6 and look at $P(OMe)_3$ with ORCWD.

With best regards,

Sincerely,

Roy

LeRoy F. Johnson

LFJ:jc

Enclosures

(1) R.R. Ernst, J. Phys. Chem. 45, 3845 (1966)
(2) see reference (1), page 3854

$$\overleftarrow{\text{—— 17.0 Hz ——}} \quad \overleftrightarrow{\text{—— 17.0 Hz ——}}$$

$$\delta H_2 \sim \frac{\Delta \omega \cdot J}{Jr}$$

$$\delta H_2 \sim \frac{(200 - 2Jr) J}{Jr}$$

$$\delta H_2 \sim \frac{166 \cdot 151}{17} \; Hz$$

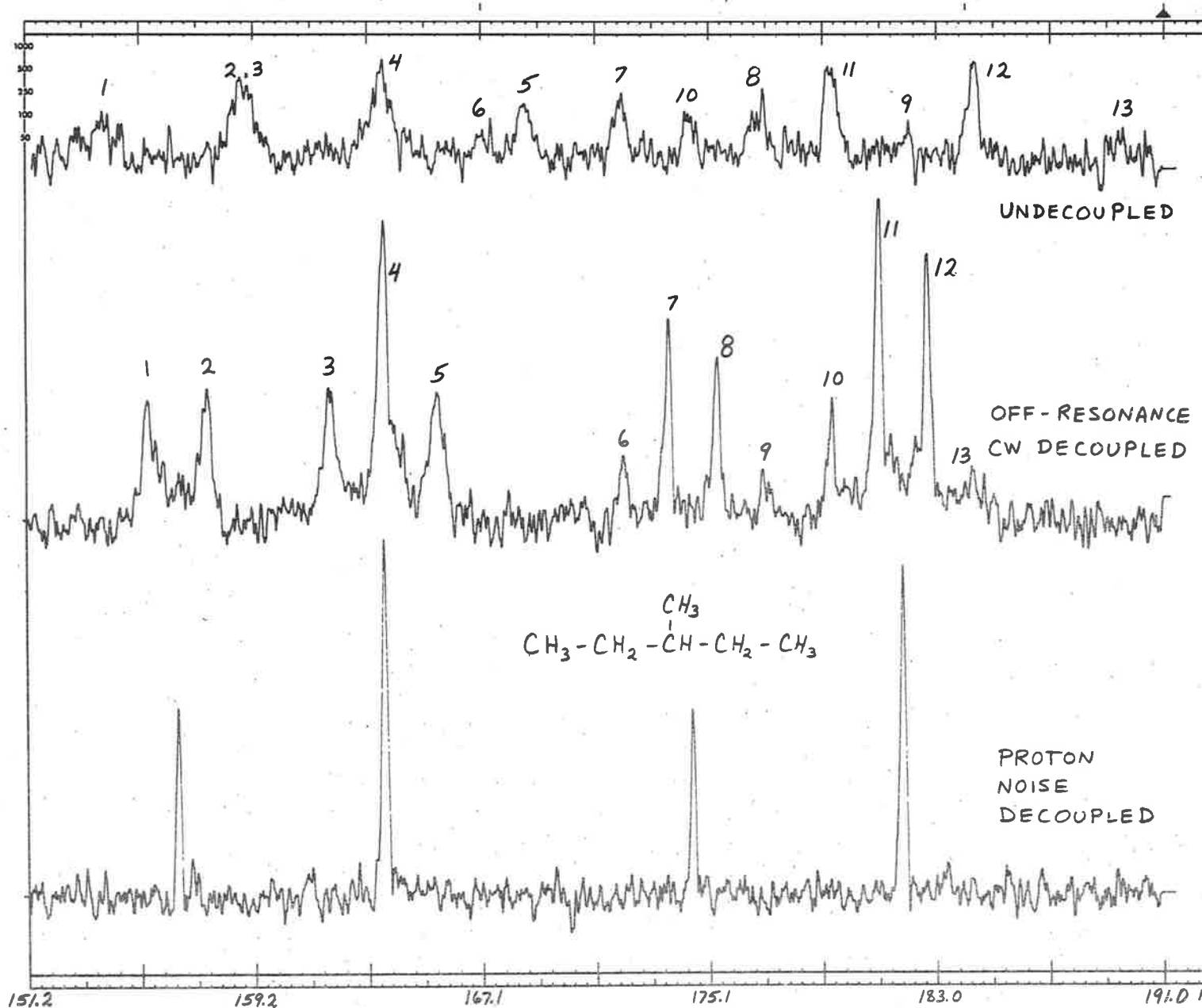$$\delta H_2 \sim 1500 \; Hz$$

$$H_2 \sim 350 \; milligauss$$

for second line lock

$$\Delta \omega = \frac{\gamma_{H'}}{\gamma_{C^{13}}} \left(\Delta \omega_{C^{13} lock} - \frac{Jr}{2} \right)$$

$^{13}CH_3 I$
quartet
(first 3 lines)

$25.15 \, MHz$

Fig. 2.
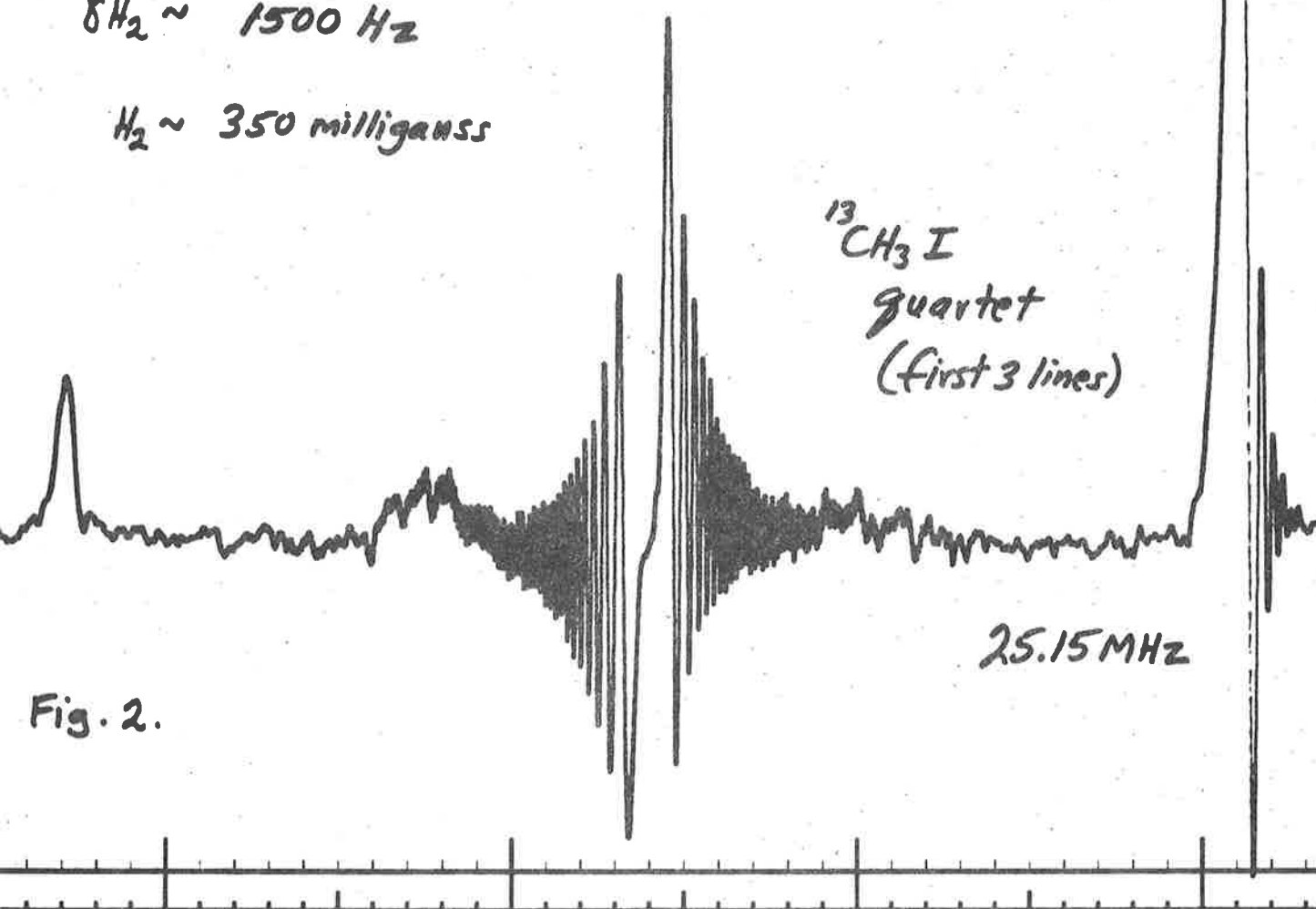
HA-100 SPECTRUM

25.15
100 MHz NMR
SPECTRUM NO.
OPERATOR: LFJ DATE 11-68
SAMPLE 3-METHYL
PENTANE
8mm TUBE

UNDECOUPLED

OFF-RESONANCE
CW DECOUPLED

20 SCANS EACH

$CH_3 - CH_2 - \overset{\overset{\textstyle CH_3}{|}}{CH} - CH_2 - CH_3$

PROTON
NOISE
DECOUPLED

SINGLE SCAN

SOLVENT	NONE	
TEMPERATURE	40	°C
FREQ. RESPONSE	5	Hz
R.F. ATTENUATOR	13	db
SWEEP TIME	50	sec
SWEEP WIDTH	1000	Hz
SWEEP OFFSET		Hz
SPECTRUM AMP.	3-6K-X.4	
LOCK SIGNAL	13 CS₂ cap.	
FIELD MILLIGAUSS (MAN. OSC. FREQ.)	.06	m. gauss
FIELD MILLIGAUSS (SWEEP FREQ.)	.6	4051 Hz
FIELD SWEEP ☐	RF FREQ. SWEEP ☒	

SOLVENT	NONE	
TEMPERATURE	40	°C
FREQ. RESPONSE	5	Hz
R.F. ATTENUATOR	13	db
SWEEP TIME	50	sec
SWEEP WIDTH	1000	Hz
SWEEP OFFSET		Hz
SPECTRUM AMP.		
LOCK SIGNAL	13 CS₂ capillary	
FIELD MILLIGAUSS (MAN. OSC. FREQ.)	.07	m. gauss
FIELD MILLIGAUSS (SWEEP FREQ.)	.6	Hz m. gauss
FIELD SWEEP ☐	RF FREQ. SWEEP ☒	

VARIAN associates   CHART S-100A
PRINTED IN U.S.A.

151.2   159.2   167.1   175.1   183.0   191.0 PPM FROM CS₂ (EXT.)

123-45

Battelle Memorial Institute · COLUMBUS LABORATORIES

505 KING AVENUE COLUMBUS, OHIO 43201 · AREA CODE 614, TELEPHONE 299-3151 · CABLE ADDRESS: BATMIN

November 22, 1968

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

Dear Barry:

A reply to an Editorial Comment in Newsletter No. 122.

Your editorial comments in Newsletter No. 122 are, I believe, well taken except for one point, i.e., "contributions dealing with the likes of how to clean spectrometer cooling coils, etc. should not be considered adequate".

I have received all issues of the Newsletter and I am convinced that experimental-type contributions are of far greater value than theoretical or data-reporting type contributions regardless of how mundane they appear to be in their final statement. Theoretical and data-type contributions are helpful; but for one doing exploratory work to read theoretical or data-type Newsletter reports directly applicable to his research is unlikely.

To me, Newsletter contributions contributing to improved laboratory operation procedures show much more ingenuity than presentation of such things as sum rule equations which could be derived by almost anyone by known methods. In fact, development of experimental and troubleshooting techniques often requires much more time and thought than cranking out the analysis of a spectrum.

Most theory and data presented in the Newsletter are eventually published. To my knowledge no current journal accepts simple accounts of prospective cures for frustrating problems which could be classified as "handy dandy hints to practicing NMR spectroscopists" with no more documentation than the author's conscience succeeded by his signature. The Newsletter has done a beautiful job of communicating such accounts.

Ruling as "unacceptable", experimental techniques which are very useful but lack the glamour of computer association would severely detract from the Newsletter's value. I believe, such contributions like the doling of Ph D theses' fragments also must be left to the contributor's conscience.

Very truly yours,

Tom

Thomas F. Page, Jr.
Senior Research Chemist
Organic & Polymer Characterization

TFP:kr

TEXAS A&M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

2 December 1968

Dr. Thomas F. Page, Jr.
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201

A Reply to "A Reply to An Editorial Comment in Newsletter No. 122"

Dear Tom:

Thank you very much for your thoughtful letter of November 22. I am sorry
that my phrasing of the editorial comment to which you objected was not sufficiently
precise - in fact, you took a somewhat different meaning from that which was intended.
I hope the following will help clarify this both for yourself and for others who
may have the same impression.

My negative nudging concerning the cleaning of spectrometer cooling coils was
intended primarily as a particularly clear example of a somewhat minor experimental
matter about which I feel more than enough has already appeared in the Newsletter
pages. There are other such items, as well, in my opinion. While it is true that
there are several ways that a man can maintain his Newsletter subscription with
minimum effort and communication, I felt that a mild step toward experimental trivia
could be taken. It is less clear what to do about non-experimental trivia without
promulgating a full-blown editorial function, which as you know I am reluctant to
do. In the vast majority of cases, leaving such matters to the contributor's con-
science has worked very well, and I see no reason to rock the boat.

Let me make one thing absolutely clear (you see - he's not even inaugurated
yet, and I am already using one of his phrases!); the objectionable editorial comment
was not intended to suppress the appearance of experimental matters of any kind in
the Newsletter. I agree with you very much that this is one of the unique functions
which this medium of communication can provide. The current issues of the Newsletter
in fact contain several such items, I hope this will always be the case. I was
merely trying to get across the idea that there are some things which have been said
both in the more formal literature and in the Newsletter several times now for many
years, and it is time that something a little more substantial - or at least
different - be used as Newsletter subscription material.

Let me hasten to add, however, that such perhaps repetitive experimental matters
might be added at the end of a contribution dealing with other, more timely or
substantive matters. This same device has been used effectively by several News-
letter contributors to announce positions available, hardware for sale, etc.

Sincerely,

Barry

Bernard L. Shapiro
Professor

BLS/jc

UNIVERSITY OF CALIFORNIA

LAWRENCE RADIATION LABORATORY
BERKELEY 4, CALIFORNIA

November 25, 1968

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

Title: Deuterium Quadrupole Coupling
Constant in CD_2Cl_2.

Dear Barry:

While working on the NMR of protons, deuterons and chlorines in the liquid crystal phase of solutions of poly-γ-benzyl-L-glutamate in CH_2Cl_2-CD_2Cl_2 we required the quadrupole coupling constant of the deuterons to establish the orientation parameter applicable to the C-D bond direction. A cursory search of the literature failed to reveal the value; in fact there appears to have been no measurement of this quantity in any methane-like molecule.

From the ^{35}Cl and proton splittings we were able to deduce

$$\frac{e^2qQ}{h} (D) = 160 \text{ kHz}$$

It is well known that the thermal relaxation of a quadrupolar nucleus is dominated by random modulation of the quadrupole interaction.

From Abragam's book, pages 314 and 347, we find

$$\frac{1}{T_1} = 4 \pi^2 K \left(\frac{e^2qQ}{h}\right)^2 \tau_c.$$

where K depends on nuclear spin and τ_c is the correlation time. For a simple molecule such as methylene chloride there is only a single correlation time. Since the quadrupole coupling constant for ^{35}Cl is known, a measurement of the chlorine-T_1 serves to determine τ_c. It follows immediately that a measurement of the deuterium-T_1 provides all the remaining information necessary to determine the deuterium quadrupole coupling constant.

Employing this procedure we obtained a value of

$$\frac{e^2qQ}{h} = 150 \text{ kHz}.$$

The two values are in excellent agreement considering the different assumptions of the two methods and the complete neglect of asymmetry parameters, if any.

Sincerely,

D. Gill & Mel Klein

DG:glw

SECOND INTERNATIONAL SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

São Paulo (Brasil), 8-11 July 1968

F. F. C. L.,
UNIVERSITY OF SAO PAULO,
CAIXA POSTAL 8105
SAO PAULO, BRASIL.

WORKING COMMITTEE
E. GIESBRECHT.
S. MATHIAS.
L. W. REEVES.

November 26, 1968.

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

Announcement of "3rd or 4th International Symposium on Nuclear Magnetic Resonance. Israel 1971; 25 Years of NMR."

Dear Barry:

During the 'Second International Symposium on Nuclear Magnetic Resonance' in Sao Paulo July 8th to 11th, 1968, the question of a further meeting was discussed for 1971. Professor Fujiwara and I monitored, by the consent of that meeting, proposals for the location of the 1971 symposium. We submitted these to 25 world authorities in the field and on a straight majority decision the proposal of Dr. Daniel Fiat of the Weizmann Institute won. Dr. Fiat is anxious to proceed with his arrangements and so I can announce either the "Third" or "Fourth International Symposium on Nuclear Magnetic Resonance" to take place in Israel in 1971.

The ambiguity of the numbering arises because Dr. Fiat will contact Dr. Coogan in Australia and they will decide whether the Melbourne meeting recently announced by Professor Gutowsky in this newsletter shall be in the series.

I might point out that 1971 marks the 25th anniversary of the experiments of Bloch and Purcell. I wish Dr. Fiat all the success in his symposium.

Yours sincerely,

Len Reeves

L.W. Reeves,
Professor.
(Mailing Address:
Department of Chemistry
University of British Columbia
Vancouver 8
B.C. Canada)

LWR:ef.

c.c. Dr. Daniel Fiat, Israel
Dr. Coogan, Australia
Professor Fujiwara, Tokyo.

November 29, 1968

List of Computer Programs for NMR

There is a need for an up-to-date reference or review on the use of computers in NMR spectroscopy. It is to be hoped that someone is just writing one (I am not). As a practical step in that direction, I propose to compile an annotated list of all NMR-related computer programs, accompanied by a directory of users who are willing to share information on the programs.

Not only those already using programs will benefit from knowing what else is available on the subject. But I think that in particular persons wanting to start using programs would like to have an idea with whom they could consult, in their geographical area, or having a similar type of computer. At any rate, a lot of duplication of effort could be avoided in the writing, extending and adapting of programs.

All types of programs should be considered: simulation of common high-resolution spectra, iteration, multiple resonance, free induction decay, Fourier transform, broad-line, spectra of oriented molecules, rate processes etc. etc. It does not matter whether a program is original, or whether it has already been cited in the literature.

The proposed list would include anyone who uses programs applicable to NMR and, at the same time, is willing to cooperate with others.

For this list I need the following information:

1. Name and purpose of the program
2. Modification(s) made on the program
    (if original program was written by someone else)
3. Language and version of the program
4. Details of plot routine (if applicable)
5. Details on computer used, such as: type, size, memory,
    system, time-sharing possibilities, running time

Should there be a sufficient and rapid response, a provisional list based on the above will be available at the next ENC.

> Ernest Lustig, Chairman
> Session on "Computers in the
> Analysis of NMR Spectra," 10th ENC

PS. If you wish, use the format of the blank (next page).

Please use one sheet for each program.

1. Name and purpose of program

2. Modification(s) made on the program

3. Language and version of the program

4. Details on plot routine

5. Details on computer used, such as: type, size, memory, system, time-sharing possibilities, running time

6. Person or organization to be contacted on the above

Please mail to: Dr. Ernest Lustig, SC-410
                 Chairman, Session on "Computers in the
                     Analysis of NMR Spectra, 10th ENC
                 Food and Drug Administration
                 Washington, D. C. 20204
                 USA

STANFORD UNIVERSITY
STANFORD, CALIFORNIA

DEPARTMENT OF CHEMISTRY   November 27, 1968

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

Dear Barry,

                                    Re: Copier for NMR Spectra,
                                          New Books of Interest,
                                          Post Doctoral Position.

        Thanks for the reminder. I've been meaning to send
this in for some time and that gave me the impetus to get
with it.

Copier for NMR Spectra:

        In our laboratory we frequently have need for two or
more copies of our spectra. An obvious solution to this
problem is to use a slave recorder. But this requires
that the second copy be made only at the time the original
is run and that there be an auxiliary recorder for each
instrument in use. Several methods of producing copies
which we investigated were rejected on the basis of high
cost, poor quality copies or the necessity of piecing
together two or three sheets to give one spectrum.

        A copier which not only meets our needs but which has
proven to be more versatile than a slave recorder for us
is the A. B. Dick Model 650. This machine accepts originals
up to 11 inches wide and cuts the copy to the same size as
the original. It is sensitive to nearly all colors, in-
cluding the blue grid of nmr spectra so the copies have
the calibration built in. The convenience of being able to
mark up a copy with tentative assignments without destroy-
ing the original has obvious advantages. Others in our
department find it useful for copying infrared ord and
plotted mass spectra as well.

Page #2   November 27, 1968

Recent Books:

Two reference books which we find useful for finding model compounds are:

Bovey, F. A., "NMR Data Tables for Organic Compounds", Interscience, 1967. Organized by empirical formula, after Chem. Abstracts, the book is essentially one long table showing structural formula, solvent, concentration, chemical shift, coupling assignments and literature references. Data are compiled from 26 journals and three catalogs over the period 1959-62.

Brügel, W., "Nuclear Magnetic Resonance Spectra and Chemical Structure", Academic Press, 1967. This book approaches the data from the structural features and tabulates the chemical shift and coupling data within structural groups or ring systems. Data are tabulated for numerous derivatives showing the effects of different substituents.

Since the two books approach the data from totally different aspects, we find they nicely complement each other as a quick entry into the literature when searching for nmr data of model compounds.

Post Doctoral Position:

We expect to have an opening at the postdoctoral level in our NMR laboratory about August, 1969. Persons interested in acquiring experience in a wide variety of NMR applications should write to me for further details.

Sincerely yours,

LOIS J. DURHAM

LJD:cmk

TEXAS A&M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

2 December 1968

Copier for NMR Spectra

NMR laboratories may wish to consider another recorder for NMR spectra. For about one month now we have had a Royfax 12 Copier and are very pleased with it. It is basically the same as the A. B. Dick 650 with all of the advantages to which Lois Durham refers on page 52. In addition, however, it is considerably more economical to operate (rental plans which include supplies and paper are available), and our limited experience so far indicates that the Royfax has a somewhat lesser tendency to mangle or tear long originals inserted slightly off line.

B. L. Shapiro

NORTHERN ILLINOIS UNIVERSITY

DEKALB, ILLINOIS 60115

THE MICHAEL FARADAY LABORATORIES

DEPARTMENT OF CHEMISTRY

November 27, 1968

Area Code 815

Telephone 753-1181

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

THE ENERGY BARRIER IN N,N-DIMETHYLTRIMETHYLACETAMIDE

Dear Barry:

Recent measurements of the energy barriers for internal rotation in dimethyl amides by NMR techniques have led to a linear correlation of the standard free energies of activation with the inductive and steric characteristics of the substituent groups [R. C. Neuman and V. Jonas, J. Am. Chem. Soc., 90, 1970 (1968)].

In the course of some general work on highly substituted amides, we found the thermodynamic parameters for a 10 mole % solution of N,N-dimethyltrimethyl-acetamide (TMA) in CH_2Cl_2: E_a = 11.5 ± 0.3 Kcal/mole, log A = 12.3 ± 0.3, $\Delta F^*_{298.2}$ = 12.2 Kcal/mole.

These activation parameters may be compared with those of pure dimethyl-acetamide-d_3 (DMA) [Neuman and Jonas]: E_a = 19.6 ± 0.3 Kcal/mole, log A = 13.8 ± 0.2, $\Delta F^*_{298.2}$ = 18.2 Kcal/mole. The lower barrier in TMA may be attributed to (1) the steric size of the t-butyl substituent and (2) its electron-donating ability, as compared with the methyl substituent in DMA.

Applying the correlation found by Neuman to TMA, one predicts a value of $\Delta F^*_{298.2}$ = 13.6 Kcal/mole. That our result is 1.4 Kcal/mole lower may be due to the fact that the free energy values used by Neuman were obtained from studies of pure amides. Our studies were necessarily done in solution because of the low coalescence temperature of pure TMA (-38° C) which is also the approximate freezing point. Further studies in dilute   solution certainly appear worthwhile in order to assess the solvent effect upon activation parameters.

We are indebted to William Tung of Michigan State University for making available a computer program for calculating lifetimes by the method of total line shape analysis.

Sincerely yours,

Lori

Laurine L. Graham

Carnegie-Mellon University

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

11 November 1968

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

Title: The design of a twin-T bridge for NMR probe with
high sensitivity

Dear Barry:

First I would like to ask you to accept my apologies
for the delay in submitting my contribution to the Newsletter.

During my stay at Mellon Institute I have derived a few
useful formulae for those, who even in the days of so many available
powerful NMR spectrometers are forced to design their own probe.
This may be the case when certain improvements are necessary
(external lock for example) or when special experiments are planned.

The formulae are concerned with the well known twin-T
bridge described first by Anderson (1) Almost always the signal to
noise ratio at the output of the bridge is important and it was
shown in (2) that in a properly designed bridge this ratio can be
held close enough to the signal to noise ratio of a crossed coil
probe. For the high overall S/N ratio of course the noise matching
to the preamplifier is a must (3) and so the output impedance of the
bridge becomes important.

Without going into detailed derivation of the formulae,
here are the necessary steps for designing the elements of the bridge
with predetermined noise figure. (Fig. 1).

1. First we design the receiver coil according to our
specific problem taking into account the general rules as outlined
for example in (3) and we measure the parallel resonant resistance
R_p of this coil at the operating frequency.

2. Second, we find the optimum resistance R_{opt} of the
generator giving the minimum noise figures F_a with the used
preamplifier including the connecting cable between the bridge and
preamplifier. This may be done by measurement, calculation or simply
taken from specification of the preamplifier. Very often it will be
the value of the characteristic impedance of the used cable i.e. 50 Ω
or 75 Ω

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     3. Third, we choose the noise factor of the bridge F_b which expresses the loss in signal to noise ratio as compared with crossed coil probe. A practical value of F_b will be between 1.05 (0,21dB) and 1,2(0,79dB).

Then, the following formulae will give with very good approximation the wanted elements of the bridge:

$$C_2 = \frac{1}{\omega \sqrt{F_b R_p R_{opt}}}$$

$$C_1 = \frac{C_2}{2}\left(F_b - 1\right)$$

$$C_a \geq 10\, C_1 \sqrt{\frac{R_p}{F_b R_{opt}}}$$

$$C_{cmax} \simeq 2\, C_a$$

$$R_b = \frac{1}{2 R_p \omega^2 C_1 C_2}$$

$$C_{3max} \simeq \frac{2}{\omega^2 L}$$

The output and input admittances of the bridge at balance will be

$$Y_o \simeq \frac{1}{R_{opt}} + j\omega C_2\left(1 + \frac{R_p}{F_b R_{opt}} \frac{C_1}{C_a}\right) \simeq \frac{1}{R_{opt}}$$

$$Y_i \simeq j\omega \frac{C_a}{2}$$

and the overall noise factor of the bridge and preamplifier F

$$F = F_a F_b$$

We can neglect the effect of the output susceptance of the bridge if it is at least four times smaller than the output conductance.

If C_1 becomes too small to be practically realizable by a single capacitor then it may be advantageous to use a simple T network instead. (Fig. 2). The effective coupling capacity is then

$$C_{1ef} = \frac{C_6}{1 + \frac{C_5 + C_6}{C_4}}$$

If we can to a small extent sacrifice the independence of phase and amplitude balance (which in practice is true only at low frequencies where stray capacitancies and inductancies may be neglected) we can simplify the last bridge by removing C_a and C_c and by using for amplitude balance a variable capacitor C_5 (Fig.3).

Then, the following formulae have to be used:

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$$C_2 = \frac{1}{\omega \sqrt{F_b R_p R_{opt}}}$$

$$C_{1ef} = C_2(F_b - 1)$$

$$R_b = \frac{1}{R_p \omega^2 C_2 C_{1ef}}$$

$$C_{5max} \simeq (10 \div 50) C_6$$

$$C_4 = \frac{C_{5max}}{2\left(\frac{C_6}{C_{1ef}} - 1\right)}$$

$$Y_0 = \frac{1}{R_{opt}} + j\omega C_2 \simeq \frac{1}{R_{opt}}$$

$$Y_i = \frac{1}{R_b} + j\omega \frac{C_4 C_5}{C_4 + C_5}$$

To get the balance of the bridge according to given formulae we have to keep stray couplings as small as possible. These couplings may be due to stray capacitancies or common ground leads and we have to be careful especially on higher frequencies.

With all best regards,

J. Dadok

1. H. L. Anderson, Phys. Rev. 76, 1460 (1949).

2. D. Gheorghiu, A. Valeriu, Nuc. Instr. and Methods 16, 313 (1962).

3. J. Dadok, 6th ENC, Mellon Institute, Pittsburgh, February 1965.

Fig. 1

Fig. 2

Fig.3
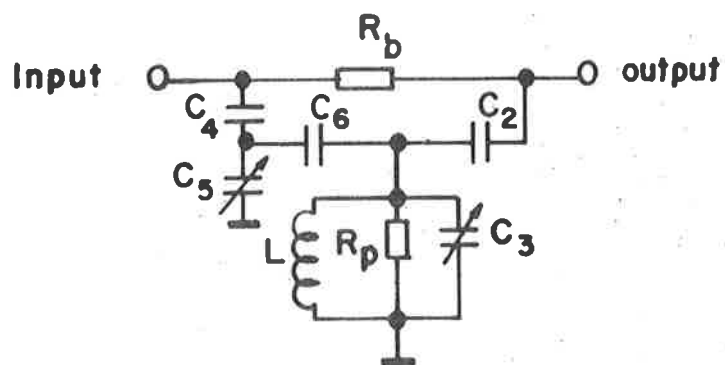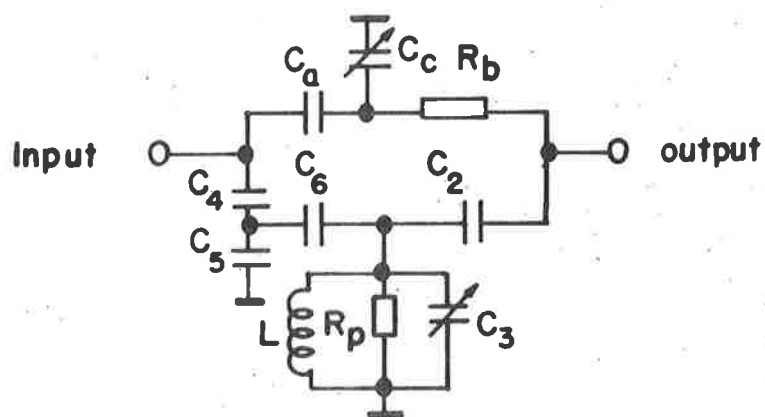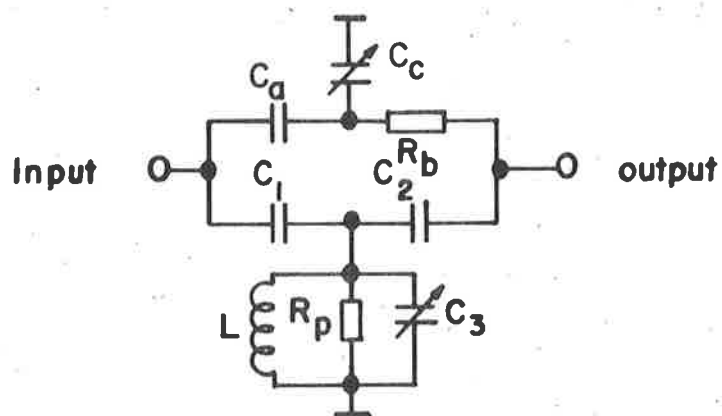
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PASADENA, CALIFORNIA 91109

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

November 27, 1968

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas   77943

Dear Dr. Shapiro:

AB-Exchange Program

The theoretical spectra of the exchanging AB-systems, which were reported by Johnson in a recent TAMU-NMR,[1] seemed incorrect in two, but perhaps minor, details. First, because the two coupling constants J_{AB} are equal, the separation between the two signals of the A-part is expected to remain constant. However, in the spectra shown, this coupling appears to be at least 1 Hz greater in spectrum 4 than in spectrum 1.

Second, below the coalescence point for the B-part, which is approximately reached in spectrum 3, two B-parts with two lines each should be visible. The two peaks in the region of +20 Hz belong to I-B. On the other hand, at least one line of II-B should be observable, the other line is probably hidden under line 2.

As a check, we made calculations for the same system with Gerig's exchange program,[2] assuming a population of 0.5 for each conformation (see the figure). At first glance, Johnson's and our spectra look identical, but with respect to the details about which we were concerned, the results are different: the lines corresponding to J_{AB} have a constant spacing, and the missing peak is observable in spectrum 4. The differences in our and Johnson's spectra might correspond in fact to minor errors in the program or, possibly, poor reproduction of the spectra, and may only be important if an exact fit is desired.
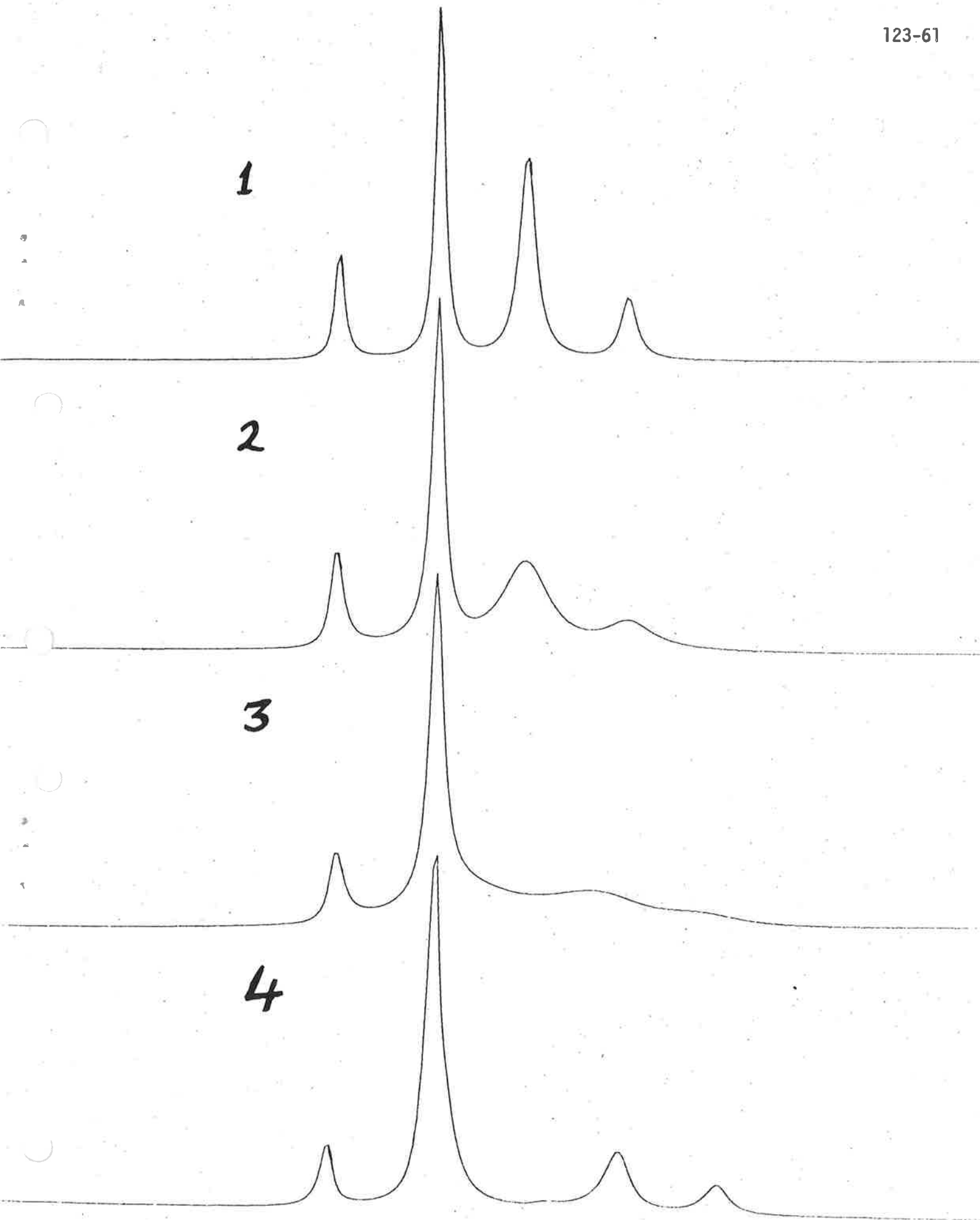
Sincerely yours,

Wolfgang Bremser

John D. Roberts

1) C.S. Johnson, TAMU-NMR, 122, 26 (1968).
2) J.T. Gerig and J.D. Roberts, J. Am. Chem. Soc., 88, 2791 (1966).

TATA INSTITUTE OF FUNDAMENTAL RESEARCH

National Centre of the Government of India for Nuclear Science and Mathematics

Telegrams : ZETESIS　　　HOMI BHABHA ROAD, BOMBAY 5　　　Telephone : 213141

November 26, 1968

Dear Dr. Shapiro,

Solid State NMR at the Tata Institute.

Nuclear Magnetic Resonance spectrum of ^{115}In in the intermetallic compound InBi was recorded in the temperature range $77^{\circ}$to 390°K. It has been found that the Knight Shift is positive at higher temperatures and decreases with decreasing temperature. It changes sign at about 230°K whereas the quadrupole coupling constant which is also a function of temperature passes through zero at about 170°K. The results have been interpreted in the light of the crystal structure of the compound.

A second-order quadrupole shifted NMR line of ^{87}Rb was observed in the paraelectric phase of Rb H_2PO_4. The quadrupole coupling constant (Q.C.C.) obtained was 9.964 Mc/s. At the curie point ($T_c = -126^{\circ}$C), the signal disappeared and could not be traced in the ferroelectric phase due to stains in the crystal.

Yours sincerely,

D.L.R. Setty,　　R. Vijayaraghavan

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

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