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No. 77  
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Bacon, Birchall, Gillespie, Vekris Se <sup>77</sup> High-Resolution Spectra	1
Anderson, J. E. Substituent Effects on Ring Inversion	4
Gagnaire, Vottero C <sup>13</sup> Satellites for AA'BB' Systems Where $J_{AB} = -J_{AB'}$ ; Long-Range Spin-Spin Coupling	6
Martin, J. S. Frequency-Sweep Decoupling With the R.S.I.; NMRIT Modification	9
Halasa, Smith, G. E. P., Jr. NMR Analysis of the Reaction Product of Oxalyl Chloride with N,N-Diethylthiourea	12
Abraham Postdoctoral Position Available	13
Roberts Analysis of the Cyclobutene Proton NMR Spectrum	14
Gronowitz, Hoffman, Gestblom Thiophene Thiols and Signs of Unresolved Couplings	16
Harris NMR Spectrum and Conformation of Myrcene; Appeal for Computer Program	18
Chapman P <sub>4</sub> O <sub>6</sub> as Phosphorus NMR Standard; New Preamplifier for RS2 Spectrometer	20
Lauterbur Carbon Spectra of Five-Membered Heterocycles	22
Fulmor, Morton Adaptation of the Varian Code to Termatrex Cards	24
Haigh, Palmer, Semple Haloquinolines: Concentration-Dependent Effects	25
Jonás Program for Conformation Assignment	28
Noth, Vahrenkamp Note on the Spin-Spin-Coupling of Boron to <sup>11</sup> B, <sup>31</sup> P and <sup>117</sup> , <sup>119</sup> Sn	30
Kullnig Structure of 1,2-Dihydro-2-methyl-1-(o-nitrobenzyl)isoquinoline	32
Reeves, Wells An Oversimplified Complex Spectrum-Perfluoromethylcyclohexane	36
Cavalli Syn-Anti Assignments to Oximes from Solvent Effects	40



Deadline dates: No. 78: 19 March 1965  
No. 79: 19 April 1965

A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication".

### Se<sup>77</sup> High-resolution Spectra

The low isotopic abundance (8.1%), long relaxation times and low n.m.r. sensitivity of the Se<sup>77</sup> nucleus have made absorption mode selenium magnetic resonance of selenium containing compounds extremely difficult. No reports of high resolution spectra appear in the literature; only two very limited broad line studies have been done, that by Dharmatti and Weaver (1) and that by Walchi (2). We have found it possible to extend the side-band technique previously reported for C<sup>13</sup> (3) and P<sup>31</sup> (4) to Se<sup>77</sup>.

Modulation techniques are vital for selenium spectroscopy since base-line stabilization must be effected if the weak selenium resonance signal is not to be swamped by noise. However, centre-band operation of the Varian V-3521 Integrator is impossible for selenium resonance, since the modulation index  $\beta$ , defined as

$$\beta = \frac{\gamma H_m}{2\pi \nu_m}$$

where  $\gamma$  = magnetogyric ratio of nucleus,  $H_m$  = modulating field, and  $\nu_m$  = frequency of modulating field, must have a value of 1.8 for maximum signal to noise ratio in this mode, which is impossible for selenium owing to its low magnetogyric ratio. It has been shown (5), that base-line stabilized operation can be effected for small modulation indices ( $\beta \ll 1$ ) by observing the first side-band signals by introducing 90° phase shifts (relative to those for centre-band operation) in both the r.f. and the audio modulation. The 90° shift in audio phase is obtained by insertion of a capacitor between the modulation output and the sweep coils. The capacitor also reduces the intensity of the modulating field somewhat, and therefore the modulation index. The value of the capacitance must be chosen, therefore, to give a suitable value of  $\beta$ , smaller capacitances giving smaller modulation indices. For this work a 2 $\mu$ F capacitor was used, which gave a selenium modulation index of  $\beta = 0.24$ . An r.f. phase shift of 90° followed by careful fine adjustments of both audio phase and r.f. phase permits the elimination of the centre-band signal and observation of the upper and lower first side-bands separated by twice the modulation frequency of 2034 c/s.

Anderson (5) has given the theory for side-band operation of a modulation system. His theory shows that the first side-band resonance under the above conditions is given by

$$m_1 = \gamma \left( \frac{1}{2} \beta H_1 \right) M_0 T_2 \frac{1}{1 + (\Delta\omega + \omega_m)^2 T_2^2 + \gamma^2 \left( \frac{1}{2} \beta H_1 \right)^2 T_1 T_2}$$

Comparison of this expression with that for an unmodulated absorption mode resonance

$$m_1 = \gamma H_1 M_0 T_2 \frac{1}{1 + (\Delta\omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2}$$

shows the side-band resonance to be a resonance centred on the modulation

frequency and of the same form as the simple absorption mode resonance except that the effect of the r.f. field on signal intensity and saturation is reduced by the factor  $\frac{1}{2}\beta$ . In other words, side-band operation at a modulation index  $\beta$  is equivalent to an attenuation of  $20 \log \frac{1}{2}\beta$ . For  $\beta = 0.24$ ,  $20 \log \frac{1}{2}\beta = 18$  db. Increase of the r.f. power by this amount, therefore, should give a side-band signal with a signal to noise ratio comparable to that which would be obtained by the simple absorption mode method, while eliminating long term noise. Saturation does not occur, despite the high power level, since the saturation factor is reduced to  $\gamma^2 (\frac{1}{2}\beta H_1)^2 T_1 T_2$ .

We have found that satisfactory high resolution selenium resonance signals on samples in 15 mm. o.d. tubes can be obtained by sweeping the field at 1 gauss per minute, using an r.f. field of approximately 5 milligauss (power  $\approx 30$  db below  $\frac{1}{2}$  watt). Very weak signals can be observed using adiabatic rapid passage by increasing the r.f. field to approximately 70 milligauss (power  $\approx 5$  db below  $\frac{1}{2}$  watt). When using adiabatic rapid passage, side-band operation is still used in order to retain the advantages of base-line stabilization. It should be noted that the r.f. field and power levels quoted above are the total levels. The effective r.f. field and power levels are of course 18 db below this, as discussed above.

Tables I and II give chemical shifts and coupling constants obtained at an oscillator frequency  $\nu_0 = 10.276$  Mc/s.

Full details of this work will be published in the Canadian Journal of Chemistry.

1. S. S. Dharmatti and H. E. Weaver. Phys. Rev. 86, 259 (1952).
2. H. E. Walchli. Phys. Rev. 90, 331 (1953).
3. J. N. Shoolery. MELLONMR No. 42
4. T. J. Flautt. MELLONMR No. 45
5. W. A. Anderson in N.M.R. and E.P.R. Spectroscopy. Pergamon Press, New York, 1960. p. 180.

J. Bacon  
T. Birchall  
R. J. Gillespie  
S. L. Vekris

Department of Chemistry,  
McMaster University,  
Hamilton, Ontario, Canada.

Table I  
Chemical Shifts

	Physical State	$\delta$ (p.p.m. from $\text{SeOCl}_2$ )
$\text{SeOBr}_2$	liquid	-80.3
$\text{SeOCl}_2$	liquid	0
$\text{SeOFCl}$	$\text{SeOF}_2/\text{SeOCl}_2$ mixture	0.4
$\text{H}_2\text{SeCl}_6$	aqueous sol'n	28.0
$\text{SeOF}_2$	liquid	100.8
$\text{H}_2\text{SeO}_3$	sat. sol'n in water	196.6
$\text{Se}_2\text{Cl}_2$	liquid	204.5
$\text{Na}_2\text{SeO}_3$	sat. sol'n in water	226.1
$\text{Se}_2\text{Br}_2$	liquid	304.9
$\text{SeCl}_4$	sat. sol'n in DMF	325.2
$\text{SeF}_4 \cdot \text{BF}_3$	liquid (m.p. $46^\circ$ )	356.8
$\text{SeF}_4$	liquid	386.8
$\text{SeF}_4 \cdot \text{SO}_3$	liquid (m.p. $70^\circ$ )	421.8
$\text{K}_2\text{SeO}_4$	sat. sol'n in water	454.8
$\text{HSeO}_3\text{Cl}$	sol'n in $\text{SO}_2$	475.8
$\text{H}_2\text{SeO}_4$	slightly aqueous	478.1
$\text{HSeO}_3\text{F}$	impure liquid containing $\text{H}_2\text{SeO}_4$	487.0
$\text{SeO}_3$	sat. sol'n in $\text{POCl}_3$	521.8
$\text{SeO}_2\text{F}_2$	liquid	531.2
$\text{SeO}_3$	liquid (m.p. $120^\circ$ )	535.3
$(\text{CF}_3)_2\text{Se}$	liquid	784.6
$\text{SeF}_6$	liquid	868.7
$(\text{CF}_3\text{Se})_2$	liquid	950.9
$(\text{CF}_3\text{Se})_2\text{Hg}$	sol'n in methanol	1145.2
$\text{CF}_3\text{SeHgCl}$	sol'n in methanol	1246.
$\text{H}_2\text{Se}$	liquid	1704.5

Table II  
Coupling Constants

	$J$ (c/s)	
	a	b
$\text{SeOF}_2$	$837 \pm 2$	$837.1 \pm 0.6$
$\text{SeOF}_2$ (mixture with $\text{SeOCl}_2$ )	$826 \pm 15$	$828.0 \pm 1.0$
$\text{SeOF}_2$ (mixture with $\text{SeOBr}_2$ )	$818 \pm 10$	-
$\text{SeOFCl}$	646	$647.5 \pm 2.0$
$\text{SeO}_2\text{F}_2$	$1577 \pm 20$	$1583.9 \pm 0.6$
$\text{SeF}_6$	$1432 \pm 25$	$1420.9 \pm 0.5$
$\text{HSeO}_3\text{F}$	$1445 \pm 2.5$	$1453.6 \pm 0.7$
$\text{H}_2\text{Se}$	$62 \pm 1.5$	$63.4 \pm 0.5$
$(\text{CF}_3)_2\text{Se}$	-	$11.1 \pm 0.2$
$(\text{CF}_3\text{Se})_2$	-	$6.4 \pm 0.2$
$(\text{CF}_3\text{Se})_2\text{Hg}$	$39.2 \pm 1.0$	$39.5 \pm 0.6$
$\text{CF}_3\text{SeHgCl}$	-	$35.8 \pm 0.5$

a from selenium spectrum

b from fluorine or hydrogen spectrum

UNIVERSITÉ DE STRASBOURG  
Faculté des Sciences

INSTITUT DE CHIMIE

Téléphone 35.43.00

Boîte postale 296

Dr J.E.Anderson,  
Labo. Ourisson.

Strasbourg, le 30 janvier, 1965.  
2, rue Goethe

Professor B.L.Shapiro,  
Chemistry Department,  
Illinois Institute of Technology,  
CHICAGO, Illinois, 60616.

Dear Dr Shapiro,


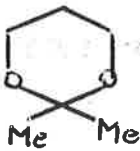
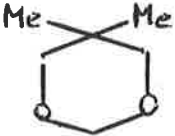
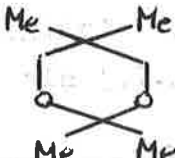
Substituent Effects on Ring Inversion

While investigating substituent effects on ring inversion, it appeared worthwhile to extend the studies of Haier et al. (Tet. Lett., (1962), 16, 683) in the 1,3-dioxane series, which is ideal in many ways, since the two-position is free of coupling with other positions, and in substituted dioxanes, there may be several signals suitable for treatment.

The work was carried out at Glasgow with Dr J.C.D.Brand, on an A.E.I. RS2 spectrometer operating at 60Mc. The results obtained are summarised in the Table.

Yours sincerely,

J. Edgar Anderson

	Coalescence Temperature	$\Delta A^\ddagger$ kcal/mole	$\Delta S^\ddagger$ e.u.	$\Delta G^\ddagger$ kcal/mole at 200°K.
	2-H      -85°C	10.2 ± 1.0	+6.2 ± 5.2	9.0 ± 0.2
	2-Me      -126°C	5.6 ± 0.6	-12.4 ± 3.5	8.1 ± 0.2
	2-H      -58°C 4,6-H      -62°C 5-Me      -58°C	12.4 ± 0.8	+9.5 ± 3.5	10.5 ± 0.2
	2-Me      -108°C 4,6-H      -100°C 5-Me      -100°C	9.1 ± 0.9	+3.8 ± 4.8	8.3 ± 0.2

Kinetic Data obtained by Slow, Intermediate and Fast Exchange treatments

RÉPUBLIQUE FRANÇAISE  
PREMIER MINISTRE  
COMMISSARIAT A L'ÉNERGIE ATOMIQUE  
CENTRE D'ÉTUDES NUCLÉAIRES DE GRENOBLE  
CHEMIN DES MARTYRS - GRENOBLE (ISÈRE)

ADRESSER LA CORRESPONDANCE :  
BOITE POSTALE 269 - GRENOBLE

TÉL. 87-59-11

Laboratoire de CHIMIE  
ORGANIQUE PHYSIQUE

PV/FR

Professor B.L. SHAPIRO  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center

CHICAGO, Illinois 60 616  
U. S. A.

RÉFÉRENCE A RAPPELER :

a/ COP. 1/65-53

VOTRE RÉF. :

VOTRE LETTRE DU

MEL 5

GRENOBLE. LE 27 janvier 1965

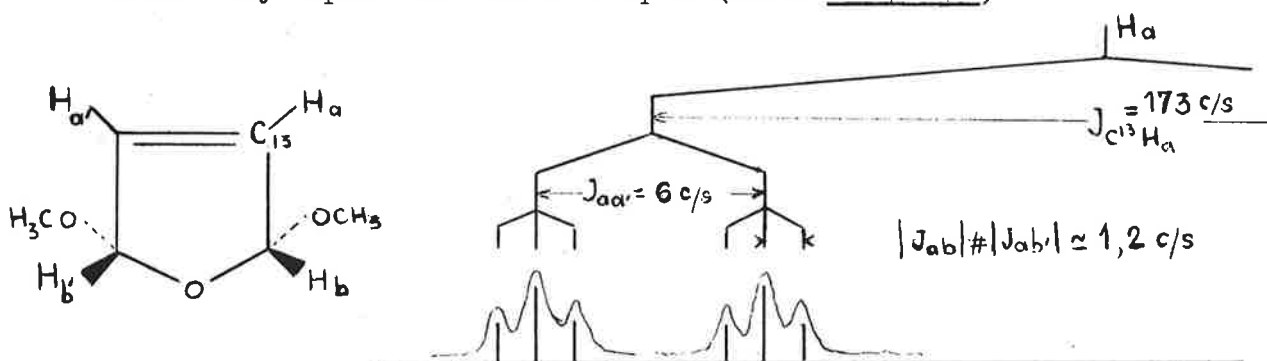
$C^{13}$  Satellites for AA'BB' systems where  $J_{AB} = -J_{AB'}$  ;  
long-range spin-spin coupling.

Cher Docteur SHAPIRO,

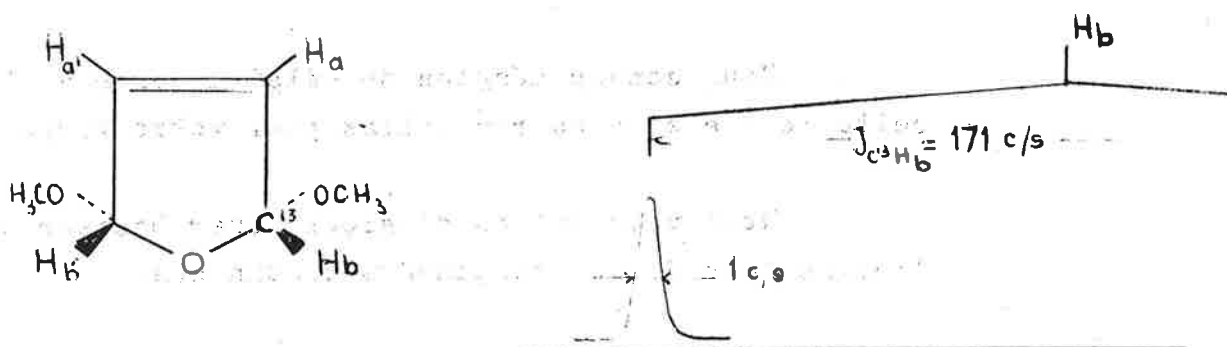
Nous avons depuis quelque temps un système d'intégration par un analyseur multicanaux (analogue au C.A.T.) mis au point par INTERTECHNIQUE.

Voici les résultats obtenus dans un exemple : les "satellites"  $C^{13}$  des dimethoxy-2,5 dihydro-2,5 furannes cis et trans.

1°/ Dérivés cis : le satellite correspondant aux protons vinyliques est très simple (deux triplets)

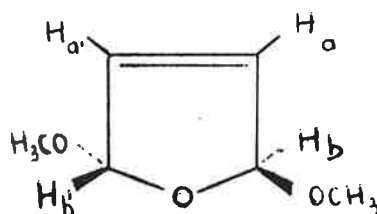


Le "mystère" est que le satellite des hydrogènes b et b' est un singulet un peu élargi (largeur à mi-hauteur  $\approx 1$  c/s) :



La réponse est due à ce que  $J_{bb'} \approx 0$  et  $J_{ab} = -J_{a'b}$  ; les protons a et a' ayant un rapport  $J/\delta \gg 1$ , le proton b ne "voit" que  $|J_{ab} + J_{a'b}|$  soit environ zéro.

2°/ Dérivés trans :



Les satellites C<sup>13</sup> et le spectre sont conformes aux valeurs suivantes de couplages :

$$J_{C^{13}Ha} = 186 \text{ c/s}$$

$$J_{C^{13}Hb} = 176 \text{ c/s}$$

$$|J_{ab} + J_{ab'}| \text{ faible}$$

$$|J_{aa'}| = 6 \text{ c/s}$$

$$|J_{bb'}| = 4 \text{ c/s}$$

L'existence d'un couplage à longue distance  $J_{bb'}$ , fort dans le dérivé trans et nul dans le dérivé cis montre

.../.



l'importance de la géométrie dans la valeur de ce couplage.

Nous sommes désolés du délai apporté à l'envoi de cette lettre et vous remercions pour votre rappel à ce sujet.

Nous vous prions d'agréer, cher Docteur SHAPIRO, l'expression de nos sentiments distingués.

D. GAGNAIRE

Ph. VOTTERO

Laboratoire de Chimie Organique Physique.



DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA  
CANADA

February 5, 1965.

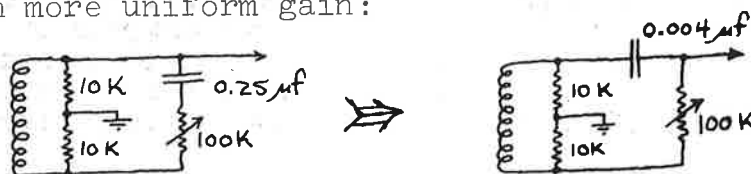
Professor B. L. Shapiro,  
Department of Chemistry,  
Illinois Institute of Technology,  
Technology Centre,  
Chicago, Illinois, 60616,  
U. S. A.

Dear Dr. Shapiro:

Last week, Dr. Lemieux mentioned to me that he'd received your reminder that our contribution was sadly overdue. Please accept my apologies for the delay. I hope that you can send us the issues of the newsletter we've missed. Our subscription should be sent to Dr. Lemieux, who passes it on to Dr. Masamune and myself.

We have been extending the facilities connected with our HR100 spectrometer by adding the variable-temperature probe, and have built a frequency-sweep decoupler, based on the Research Systems, Inc. Homonuclear Spin Decoupler. Your readers may be interested in our experience with it.

The R.S.I., as received, would not stay locked while irradiating with  $H_2$  great enough to do more than "tickle". We have modified the unit to improve its stability. ("We", in this case, means primarily Glen Bigam and Rudy Kadlec.) In particular, the audio phase-shift circuits were rebuilt as shown, to give a greater phase-shift range with more uniform gain:



We now use the R.S.I. unit for field-frequency lock only, and have modified a V3521 integrator for variable frequency detection, by widening the detector amplifier bandpass to 800-3500 cps., and rebuilding the "phase box" to allow a  $90^\circ$  shift in phase with no change in gain.

.....

-2-

The swept frequency,  $\nu_1$ , is obtained by placing two ganged 10K helipot in the two halves of the phase-shift circuit of a Hewlett-Packard 200 AB oscillator. These are servo-driven, in anticipation of a CAT with a ramp-voltage output.  $\nu_1$  is injected into the V3521 via a switched input between C208 and the cathode of V202.

A nice thing about the new V4332 and V4333 probes is the provision of two independent sets of modulation coils. This allows one to minimize interaction between signal generators, impedance mismatch, etc. We inject the decoupling signal,  $\nu_2$  and the 2 kilocycle locking signal,  $\nu_3$  into the "D.C. modulation" coils via the linear sweep. It is necessary to switch off the B<sup>+</sup> to the linear sweep, as the "off" position on this unit does not turn off the 50 kilocycle oscillator.

Our system will now decouple isolated groups of nuclei with J's up to about 10 c.p.s. The enclosed spectra of 1,2-dichloroethyl ethyl ether show how this can be used to elucidate the superimposed spectra of the two methylene groups. Strong irradiation of the methyl group reveals a classic AB spectrum, with  $J_{gem} = 9.5$  c.p.s., arising from the  $-CH_2-$  protons in the ethyl group. Their non-equivalence arises in the asymmetry of the chlorinated carbon two bonds away. The remaining three lines belong to the nearly equivalent  $-CH_2Cl$  protons in the dichloroethyl group.

We find that keeping the lock-in stable at high levels of irradiation is as much art as science. We have devised some empirical methods for minimizing overload of amplifiers, spinner noise, heterodyne signals, etc., and would welcome correspondence with others who may be contending with these problems.

The core of our new IBM 7040-1401 computer is somewhat overstocked with monitors, so that the new version of NMRT\* overruns the memory capacity by about 1000 words. Al Heyworth of the Computing Centre and Dr. Werner Poesche have modified the program to fit the available storage by removing the title card and reducing the dimensions a bit. The only casualty seems to be the ten-spin (4,4,2) case, which I suspect will never be missed.

Details of the frequency-swept decoupler and FORTRAN listings of the modified NMRT program will be sent to any interested parties.

Yours sincerely,

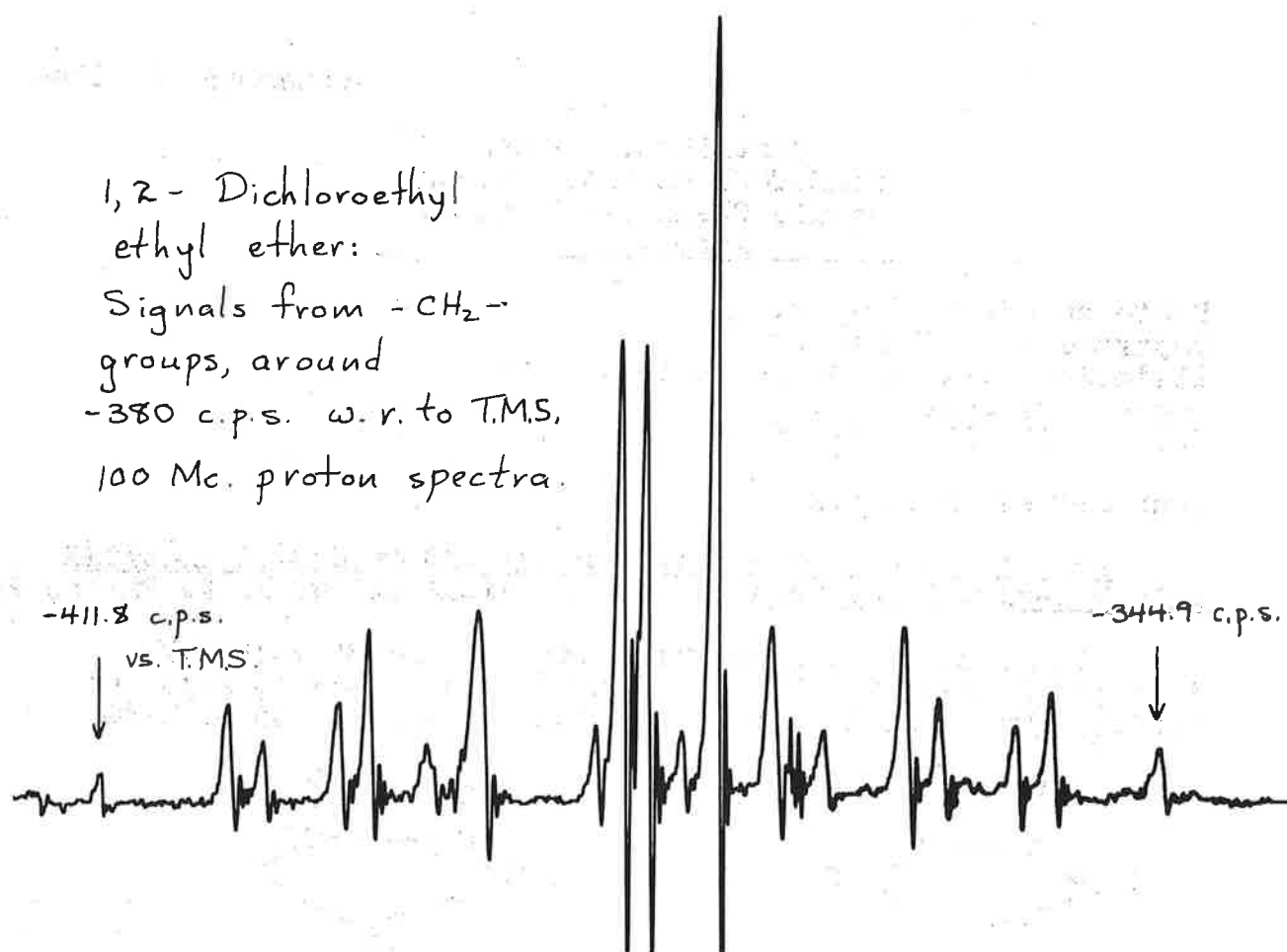
*John S. Martin*  
John S. Martin.

\* Reference: Ferguson and Marquardt,  
J. Chem. Phys. 41, 2087 (1964)

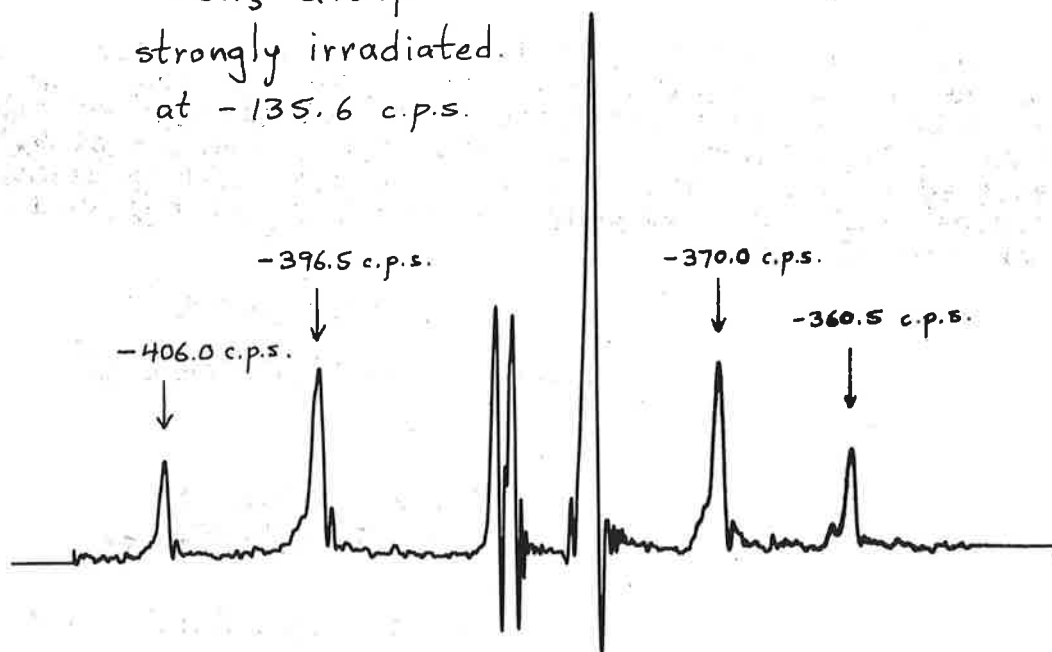
Enclosure.

1,2-Dichloroethyl  
ethyl ether:

Signals from  $-\text{CH}_2-$   
groups, around  
-380 c.p.s. w. r. to T.M.S.,  
100 Mc. proton spectra.



$-\text{CH}_3$  Group  
strongly irradiated  
at -135.6 c.p.s.



September 11, 1964

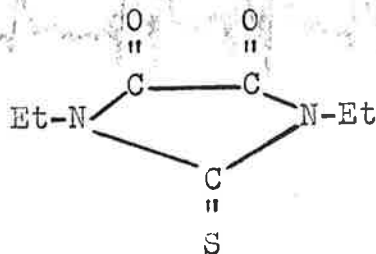
Contribution From  
 FIRESTONE CENTRAL RESEARCH  
 Organic Chemicals Division  
 Akron, Ohio

Professor B. L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Technology Center  
 Chicago 16, Illinois 60616

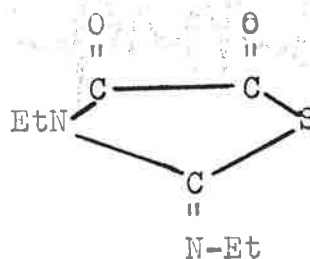
Dear Professor Shapiro:

NMR analysis of the reaction product of oxalyl chloride with N,N-diethylthiourea, by A. F. Halasa and G. E. P. Smith, Jr.

When oxalyl chloride was allowed to react with N,N-diethylthiourea, a solid product (I) was isolated, m.p. 101 - 102°C. Two possible structures can be assigned to Compound I.



IA



IB

Structure IA has equivalent ethyl groups, while in Structure IB, they are not equivalent. The NMR of Compound I, as determined on the DP-60 (Varian Associates), showed one type of ethyl group, only, with the usual splitting: a quartet at 4.1 ppm, assigned to the methylene groups, with relative peak area of 4 protons, while at 1.40 ppm, the methyl groups appeared with relative peak area of 6 protons.

Very truly yours,

CENTRAL RESEARCH LABORATORIES

Dr. A. F. Halasa

*A. F. Halasa*

Dr. G. E. P. Smith, Jr.

*G. E. P. Smith, Jr.*

AFH/GEPS:bm

THE UNIVERSITY OF LIVERPOOL  
DEPARTMENT OF ORGANIC CHEMISTRY

TELEPHONE: ROYAL 6022



THE ROBERT ROBINSON LABORATORIES,  
OXFORD STREET,  
LIVERPOOL 7.

Dr. B.L. Shapiro,  
Department of Chemistry,  
Illinois Institute of Technology,  
Chicago,  
Illinois, 60616,  
U.S.A.

8th February, 1965.

Dear Dr. Shapiro,

I wonder if I may follow your example and enquire about the availability of Postdoctoral fellows through I.I.T.N.M.R.?

I am looking for someone to work on various problems in high resolution Proton Magnetic Resonance. These require some practical and also considerable theoretical knowledge. Thus, either experience in N.M.R. or an interest in theoretical work would be desirable. In particular, computer experience would be an asset. The commencing date would be arranged mutually. Salary in accord with the usual stipends for University Post-doctoral Fellows.

Many thanks,

Best wishes,

*Ray Abraham*

R.J. Abraham.

## CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

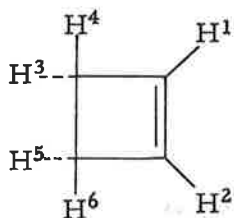
February 8, 1965

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

Dear Barry:

Our discovery some years ago that cyclobutene gave two quite sharp proton resonance lines was made a bit before the limits on "deceptively simple" spectra were very well understood and led to some erroneous speculations about why the coupling constants should be negligibly small.

Dr. S. Borčić has done a very nice job on the complete analysis of the couplings in cyclobutene with the aid of deuterium substitution and the  $^{13}\text{C}$  satellite spectra (enhanced with the CAT).



$$\delta_1 = 5.95 \text{ ppm.}$$

$$J_{^{13}\text{C}-\text{H}^1} = 170 \text{ cps.}$$

$$\delta_3 = 2.57 \text{ ppm.}$$

$$J_{^{13}\text{C}-\text{H}^3} = 140 \text{ cps.}$$

$$J_{12} = (-?) 2.70 \text{ cps.}$$

$$J_{34} = -12.00 \text{ cps.}$$

$$J_{13} = -0.80 \text{ cps.}$$

$$J_{35} = +1.65 \text{ cps.}$$

$$J_{15} = +1.55 \text{ cps.}$$

$$J_{36} = +4.35 \text{ cps.}$$

The spectra are insensitive to the magnitude and sign of  $J_{34}$  which was taken to have a value similar to that found by Ken Servis for 2,2-dibromocyclobutenone.

Dr. Bernard L. Shapiro

2

February 8, 1965

An interesting question in the analysis is the sign of  $J_{12}$ . We get a faintly better fit to the  $^{13}\text{C}$ -satellite spectrum of the vinyl protons with  $J_{12}$  negative than positive. The trend of  $J_{12}$  with ring size is from 11.8 cps. for cyclooctatetraene to 9.6 cps. for cyclohexene to 5.4 cps. for cyclopentene. Perhaps thence to negative values for cyclobutene and cyclopropene? It might be interesting for the theorists to predict this one before the definite experimental evidence has been obtained.

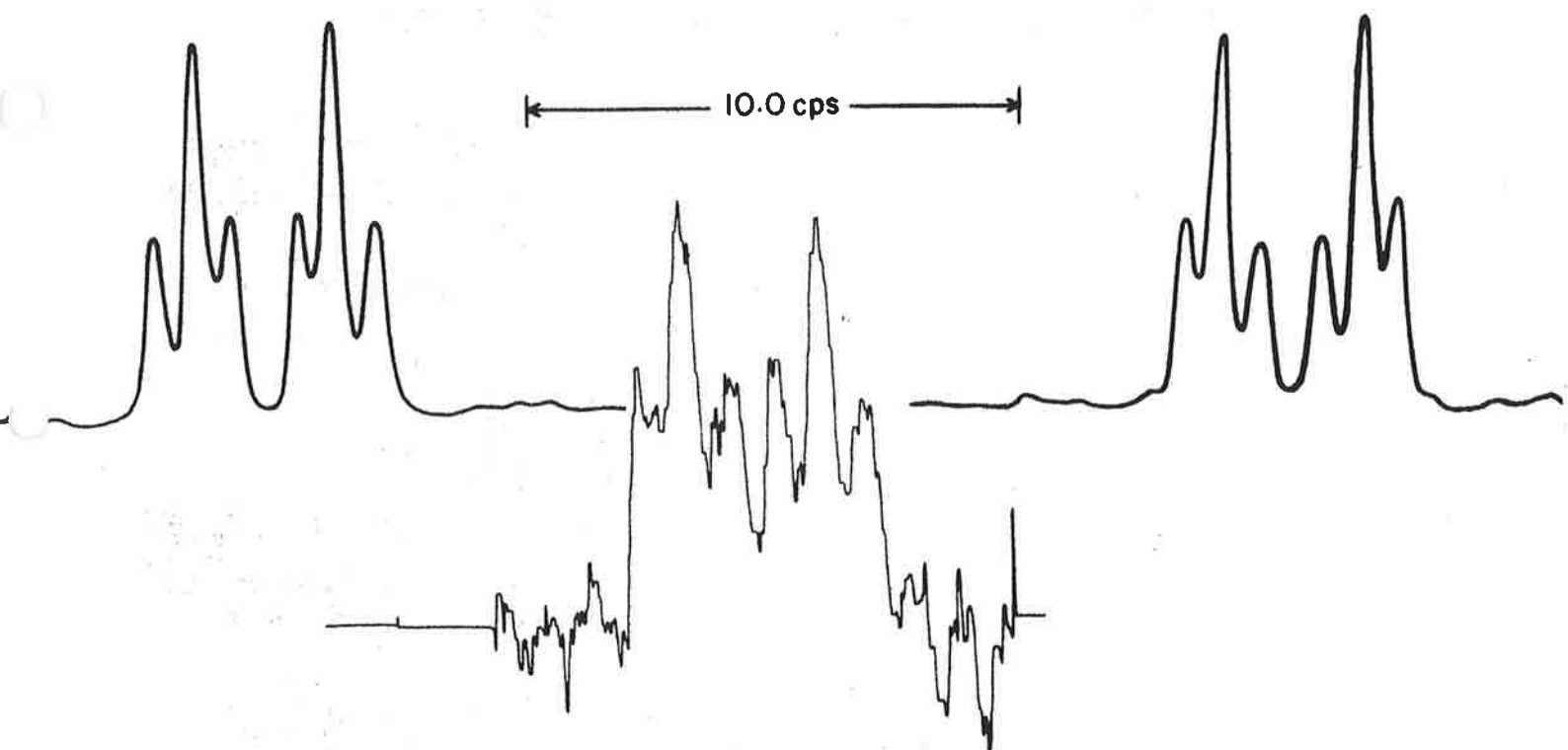
With all good wishes,

Very truly yours,

*Jack*

John D. Roberts

JDR:bi



Proton n.m.r. spectrum of cyclobutene showing  $^{13}\text{C}$  satellites of vinyl hydrogens. Observed spectrum, middle, and computed spectra with  $J_{12} = +2.70$  cps. (left) and  $J_{12} = -2.70$  cps. (right).





*Fysiska Institutionen, Uppsala, 9th February, 1965*

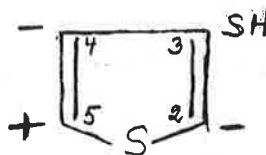
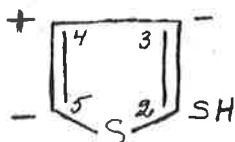
Dr B. L Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago 16, Illinois  
U.S.A.

Thiophene thiols and signs of unresolved couplings.

Dear Professor Shapiro,

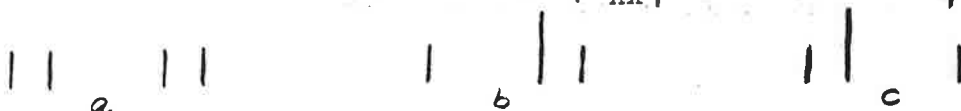
We have recently completed an extensive investigation of signs of side-chain spin couplings in thiophene thiols and methyl substituted thiophene thiols by selective decoupling experiments.

The signs of the thiol proton couplings to the various ring hydrogens are indicated below,



i. e. a nicely alternating pattern. Replacement of any of the ring hydrogens by a methyl group produces no reduction in magnitude of the corresponding coupling but a reversal in sign as predicted for a  $\pi$ -electron coupling.

In connection with this work we found that it is possible to determine the signs of couplings which are too small to permit resolutions of the corresponding splittings. That this is possible may be seen from the figure below, illustrating the appearance of a band X in an AMX spectrum. We assume  $|J_{AX}| = 0.4$  c/s and  $|J_{MX}| = 0.1$  c/s.



a illustrates the single resonance spectrum and b and c the patterns obtained on decoupling of  $J_{AX}$ . It is evident from these patterns that

the resolution required to obtain the sign of  $J_{MX}$  is determined by the splitting 0.3 c/s which is very much larger than  $J_{MX}$  itself. This work has been submitted for publication in Arkiv Kemi.

In addition we have determined the signs of long-range couplings in methylsubstituted thiophenes (Acta Chem.Scand 18, 1905 (1964) and Arkiv Kemi, In press) and furans (Acta Chem.Scand, In press) The signs of the methyl couplings show the same alternating pattern as that displayed by the thiol couplings.

Yours sincerely

*Salo Gronowicz*

Salo Gronowicz

*Ragnar A. Hoffman*

Ragnar A Hoffman

*Bo Gestblom*

Bo Gestblom

## University of East Anglia

From Dr. R. K. Harris.

School of Chemical Sciences  
 Wilberforce Road, Norwich NOR 77H  
 Telephone Norwich 52651  
 ENGLAND

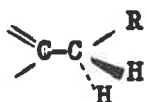
10th February, 1965.

NMR SPECTRUM AND CONFORMATION OF MYRCENE; APPEAL FOR COMPUTER PROGRAM

Dear Barry,

Your prodding "reminder" has done its usual work, and here is my current "subscription" to I.I.T.N.M.R. We are still in the period of "settling in" in this new University, and at the moment we only have a 40Mc/s. instrument (the first Perkin-Elmer product, secondhand from Cambridge!), but this situation should change soon. Meanwhile the Perkin-Elmer performs very well, but has few accessories.

Mr. A. V. Cunliffe and I have been analysing the spectrum of myrcene, a substituted 1,3-butadiene (see below). The series of lines at lowest field are due to  $H_3$  and form a remarkably simple pattern (approximately four triplets) when compared to the resonances due to the analogous proton of isoprene (2-methyl-1,3-butadiene). The complexity of the isoprene spectrum is presumed to be due to coupling between  $H_3$  and the methyl protons. The simplicity of the myrcene spectrum indicates that coupling between  $H_3$  and  $H_5$  or  $H_5$  is negligible. Such a contrast between isoprene and myrcene can probably be traced to the conformation of myrcene. The coupling in isoprene presumably occurs only when the methyl proton in question is in the same plane as the diene chain - the zig-zag condition for spin-spin coupling through four bonds (see, for example, Banwell and Sheppard, Disc. Faraday Soc., No. 34, 115 (1962)) is then fulfilled. The observed coupling for isoprene is, of course, the average for the three equivalent conformations given by hindered internal rotation of the methyl group. If the conformation of myrcene is as shown, with  $C_A$  in the diene plane, negligible 3,5-coupling is to be expected. Such a conformation follows the usual rule that bulky substituents (in this case the  $CH_2CH = CMe_2$  group) tend to eclipse double and not single bonds in compounds of the type



A full analysis of the butadiene part of the myrcene

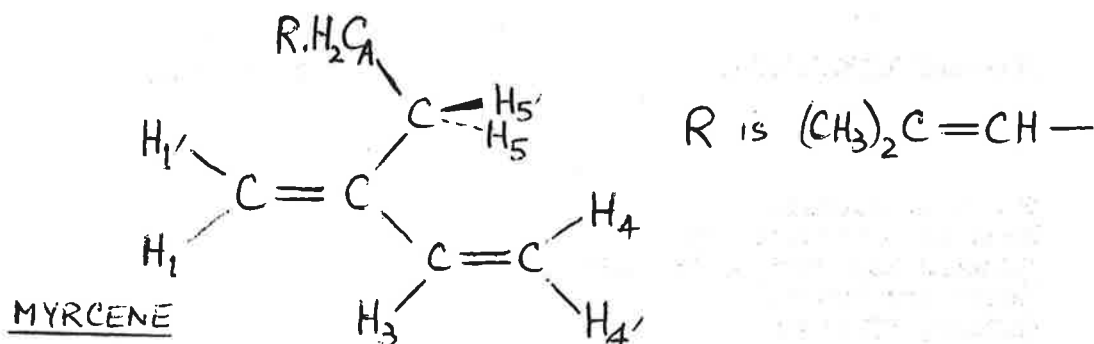
spectrum has now been made. The coupling constants and chemical shifts (which

Dr. B. L. Shapiro.

- 2 -

10th February, 1965.

are available to anyone interested) are comparable to those for other 1,3-butadienes (Hobgood and Goldstein, J. Mol. Spect., 12, 76 (1964) and also Bothner-By and Harris, unpublished work). I should add that the myrcene work was started in collaboration with Aksel Bothner-By while I was at the Mellon Institute, Pittsburgh.



Another topic I am investigating here with Mr. R. A. Spragg is the spectra of N,N'-dinitrosopiperazines. Work on the parent compound is in press in J. Mol. Spect. Finally, much of Mr. Cunliffe's time has been spent on modifying the LAOCOON 2 program for use on locally-available computers. This is now nearly completed, but it has been a trying job. I am now thinking, with Mr. C. M. Woodman of developing a program for a six-spin (or maybe less) system capable of handling nuclei of spin  $> \frac{1}{2}$ . If anyone has such a computer program, I would be grateful if they would get in touch with me and let me have a copy of the program listing.

Best wishes,

(Dr. R. K. Harris).

Dr. B. L. Shapiro,  
Illinois Institute of Technology,  
Technology Center,  
Chicago 60616,  
U.S.A.

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DATE

Res/G.2050(B)/ACC/JB.

11th February, 1965.

Dr. B. L. Shapiro,  
Department of Chemistry,  
Illinois Institute of Technology,  
Technology Centre,  
Chicago, Illinois,  
U.S.A.

Dear Dr. Shapiro,

Quite a number of laboratories expressed an interest in  $P_4O_6$  after our last communication (IITNN No. 68) describing the use of this material as a standard for phosphorus NMR. The marketing of  $P_4O_6$  has been held up by production difficulties, but things are now moving again, and we will be sending out data sheets and price details to interested laboratories during the next few weeks.

A note on this subject has been submitted to Chemical Communications; preprints are available on request. Some spectra illustrating the usefulness of  $P_4O_6$  are attached.

We have built for our RS2 spectrometer a new 60 Mc/s pre-amplifier incorporating an ECC 2000 valve, to a design supplied by AEI. This is a great success, increasing the signal/noise by a factor of about 2½ (slightly more than the AEI built version!), and we can recommend the design to other RS2 users.

Yours sincerely,

A. C. ChapmanD. J. Mowthorpe.

HEAD SALES OFFICE: 1 KNIGHTSBRIDGE GREEN LONDON SW1

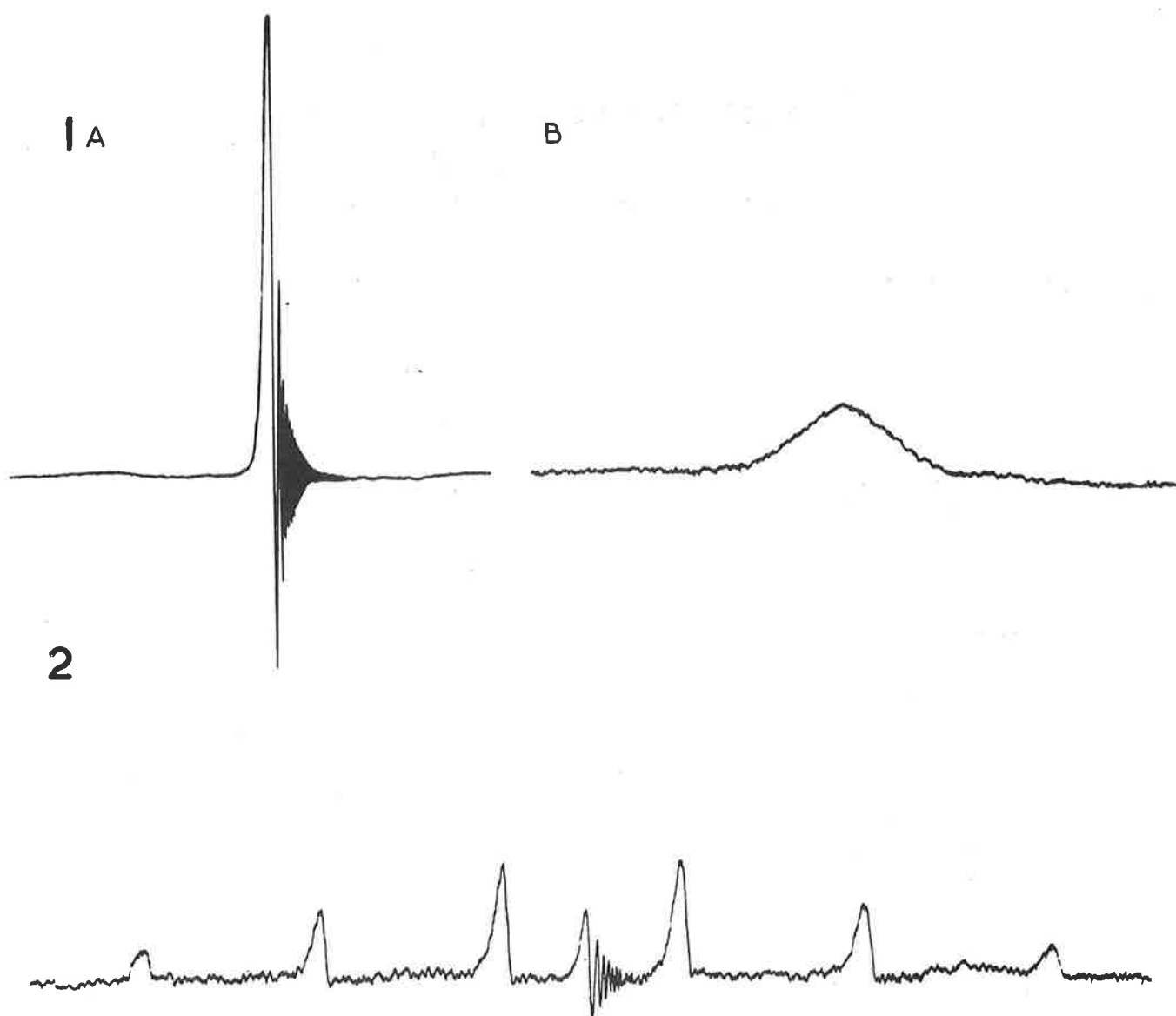


Fig. 1. a) The spectrum of  $P_4O_6$  recorded at 25 Mc/s. The line width is about 0.3 c/s.  
 b) 85% phosphoric acid recorded under the same conditions as (a), except that the gain is increased by four times.

Fig. 2. The spectrum of trimethyl phosphite and a sideband from a capillary of  $P_4O_6$ , showing the narrower line from the latter compound.

## STATE UNIVERSITY OF NEW YORK

AT STONY BROOK

STONY BROOK, LONG ISLAND, NEW YORK

Zip Code 11790

DEPARTMENT OF CHEMISTRY

February 16, 1965

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

Dear Barry:

We have done some work on the  $C^{13}$  spectra of five-membered heterocycles, in addition to that on the azines reported here last month. The interpretation of the results is somewhat sketchier because of the greater difficulty of making good calculations on the five-membered ring compounds and because fewer have been studied. Data for furan, pyrrole, thiophene and, for comparison, vinyl acetate, are given in the table below. The latter are close to those reported by Maciel in IITNMRN number 75.

Compound	Position	$\delta_c$ (ppm)
furan	CH-2,5	51
	CH-3,4	84
pyrrole	CH-2,5	74
	CH-3,4	85
thiophene	CH-2,5	67
	CH-3,4	66
vinyl acetate	C=O	26
	=CH	51
	=CH <sub>2</sub>	96
	-CH <sub>3</sub>	172

You will note that all of the carbon shieldings in the

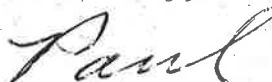
Dr. Shapiro

-2-

February 16, 1965

heterocycles are greater than that in benzene ( $\delta_c = 65$  ppm) with the exception of the 2,5 positions in furan, and that in thiophene the shieldings are almost the same as those in benzene or those of non-terminal olefinic carbons. Also, the vinyl carbon shieldings in vinyl acetate and vinyl ethers are very similar to the shieldings in furan (allowing for the difference between  $=CH$  and  $=CH_2$  groups). In interpreting these results, we have abandoned the use of local charge densities in favor of the effective nuclear charges from calculations such as those of Pujol and Julg [Theoret. chem. Acta, 2, 125 (1964)]. Although reasonable agreement with experiment seems to be possible if both pi and sigma contributions are calculated with the aid of the general Karplus and Pople theory, detailed comparisons do not seem to be possible yet. We also have a few scattered data on substituted heterocyclics, but I will refrain from giving the rather uninteresting results now.

Yours truly,



Paul C. Lauterbur  
Associate Professor

PCL/ms



## LEDERLE LABORATORIES



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February 15, 1965

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

Dear Dr. Shapiro:

In view of the interest being shown in the storage and retrieval of proton n.m.r. data, we thought it worthwhile to describe a system we are working on:  
Adaptation of the Varian Code to Termatrex Cards

1. Our system is an adaptation of the Varian p.m.r. code to the Termatrex optical coincidence system. It is a simplification in that there are the same three categories for proton environment: Main groups, sub groups and sub-sub groups. However, sub groups and sub-sub groups are entered as a composite code. Thus, for Varian #368 we code 2 Bb not 2 BbBb or for Varian #29 we code 2 Beg not 2 BeBg. We designate the protons of interest as the main group, the Varian sub group as  $\alpha$  (Alpha) and the sub-sub groups as  $\beta$  (Beta). The deck is thus, comprised of twenty-three cards for the main groups, thirty-seven cards each for the groups Alpha and Beta. Actually, we do not use the Alpha-numerical code at all, instead we have the proton types depicted on the head of the card. This removes the "indirect" language problem. Proton types within a structure are numbered in sequence; this numerical sequence is continued on through the following structures ad infinitum, i.e.,

	1	2		3	4	5	
Structure #1	$\text{H}_3\text{C}$	- OH	Structure #2	$\text{CH}_3$	$\text{CH}_2$	- OH	--- etc., etc.

The number given the proton type is entered as an address since we are coding and filing types, not compounds or even necessarily, complete structures.

The advantage to the system is speed, compactness and the fact that after the library contains enough of a particular type of proton no more need be entered. Eventually we will code and file only very unique protons. A disadvantage is the necessity of maintaining an index which shows what number was given to a particular type of proton within a structure or spectrum. We are experimenting using chemical shift cards with a one half  $\delta$  (delta) unit span, we may narrow or increase this range depending on how things work out.

Sincerely yours,

W. Fulmor

George O. Morton  
Organic Chemical Research Section

WF:mph

Department of Chemistry,  
Edinburgh University,  
West Mains Road,  
Edinburgh 9,  
Scotland.

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

12 February 1965

Dear Dr. Shapiro,

As a first contribution from the Edinburgh group, who are using a 60 Mc/s Perkin-Elmer instrument, here is an abstract of a paper being submitted to J.C.S.

Preparation and Nuclear Magnetic Resonance Spectra  
of some Haloquinolines. Nearly Degenerate ABX Spectra.

By C. F. Haigh, M. H. Palmer and B. Semple

The preparation of three new 7-halo-2-methylquinolines is described. The proton magnetic resonance spectra of eleven quinolines containing 5- or 7-halogen substituents are presented. The influence of the halogens on the chemical shifts parallels that found in substituted benzenes; the contributory causes are dissected: the small effect on protons *peri* to the halogen seems anomalous. The several protons are affected differently by changes of concentration in carbon disulphide: this phenomenon has been studied in some detail. The easily confused protons 4 and 8 can be distinguished by their different dependence on concentration. Diehl's additive substituent theory of solvent effects is extended, and used to interpret both these concentration effects and also solvent effects on quinoline spectra.

Four of these compounds exhibit partially degenerate ABX spectra. The appearance of such spectra is qualitatively described, and classified by a series of inequalities: these (together with  $^{13}\text{C}$  satellites in concentrated solution) are used as aids in the complete analyses.

We illustrate two points. Fig. 1 shows the upfield  $^{13}\text{C}$  satellites (in natural abundance) of H-5 and H-6 in 7-bromoquinoline, at concentrations of (a) 36 and (b) 53 mole % in  $\text{CS}_2$ , and (c) as the neat liquid. In the main  $^{12}\text{C}$  proton spectrum, these protons are A and B of an ABX system (X is H-8, and  $J_{AX}$  and  $J_{BX}$  are comparatively small); and second-order analysis of the partially-degenerate spectra gave  $J_{AB} = 8.9$  c/s, and  $\nu_5 - \nu_6 = (a) + 1.2$ , (b)  $- 2.2$  and (c)  $- 5.5$  c/s at 60 Mc/s. This marked concentration-dependence is neatly confirmed by the satellite spectra ( $J_{\text{CH}(5)} = 163$ ,  $J_{\text{CH}(6)} = 168$  c/s).

-2-

Secondly, fig. 2 shows the concentration-dependence of the proton resonances in 7-fluoroquinoline, plotted relative to internal T.M.S. Relative to an external reference, the absorptions in the case of the neat liquid should be about 59 c/s upfield of those given in the figure. As mentioned in the abstract, marked relative concentration-dependence of different protons in the same molecule is quite general in those quinolines we have studied.

Sincerely yours,

C. W. Haigh\*  
M. H. Palmer  
B. Semple

\*Present address: University College, Swansea.

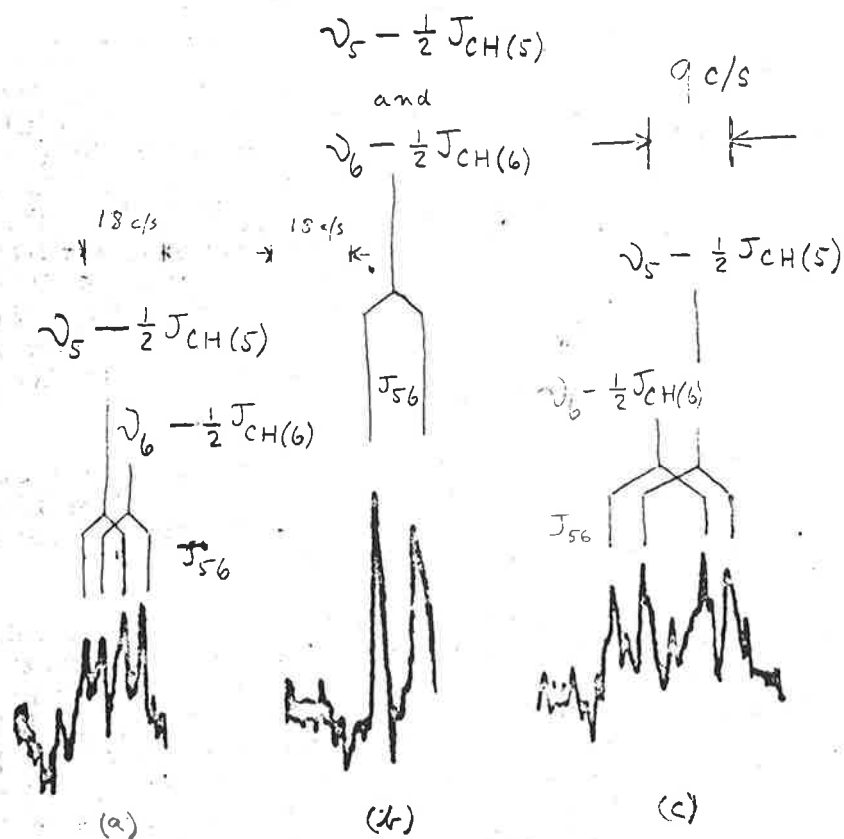
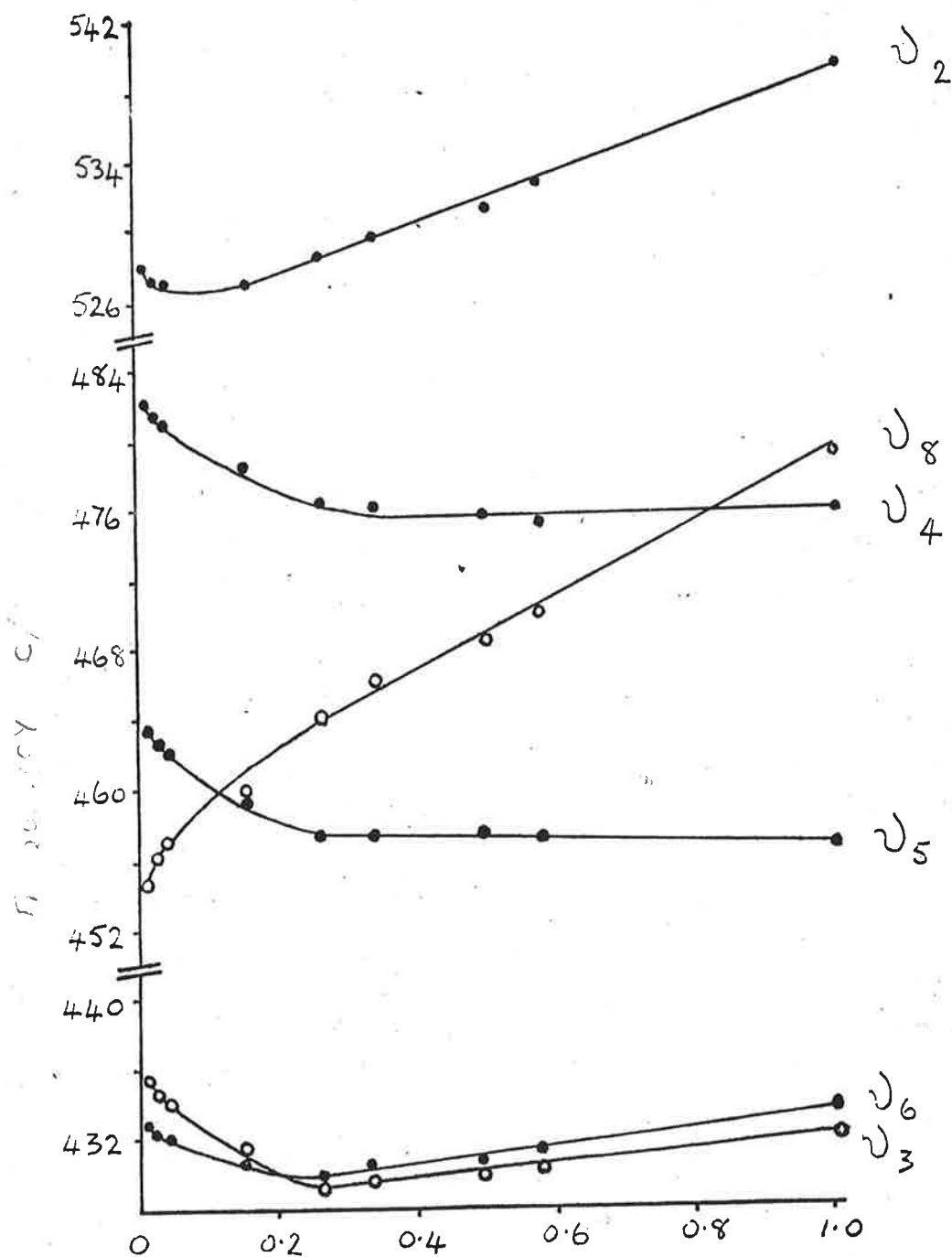


FIG. 1

Fig. 2  
7-Fluoroquinoline in Carbon Disulphide



Mole Fraction of 7-Fluoroquinoline

CZECHOSLOVAK ACADEMY OF SCIENCE  
INSTITUTE OF ORGANIC CHEMISTRY AND BIOCHEMISTRY,

NA CVIČIŠTI 2,

PRAHA 6

Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
CHICAGO, Illinois 60616  
U. S. A.

February 12th, 1965

Dear Barry,

Thank you very much for your reminder. The delay is due to my catching up with local chores.

At present our instrumental situation has improved as in addition to our 40Mc/s prototype instrument a new 80Mc/s instrument (designed by Dr. J. Dadok) is working quite well. Most of the time we spend working on structures of natural products and considerably less time we devote to our own projects.

Among other things we have recently measured a number of nucleosides containing ribose and we tried to analyse their NMR spectra. For evaluation of the data, i.e. for assignment of conformation, we employ a simple computer program which I wrote at the time when I was enjoying my stay in the laboratory of Professor H. S. Gutowsky.

This is a very simple program which uses as input data the measured coupling constants between ribose ring hydrogens and the final result is the assigned conformation, dihedral angles and amount of buckle of the corresponding mode.

The program works in the following way:

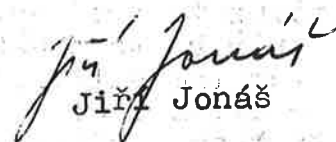
A preliminary calculation was performed to obtain a set of dihedral angles  $T_{12}$ ,  $T_{23}$ ,  $T_{34}$ ,  $T_{45}$ ,  $T_{51}$  as a function of the amount of buckle  $D$  (in Å) of the ring for  $C_S$  and  $C_2$  modes. These  $T_{ij}$  theoretical values were used as constants in the program for comparison with experimental values.

First, the input  $J_{12}$ ,  $J_{23}$ ,  $J_{34}$  coupling constants are read in and the corresponding experimental dihedral angles  $E_{ij}$  are calculated from the Karplus equation. These experimental dihedral angles  $E_{ij}$  are compared with theoretical angles  $T_{ij}$ ; the sum of squares of deviations between these values is calculated for all combinations of three consecutive theoretical angles for individual D. The minimum sum of the squares of deviations for a particular set of theoretical angles is found for the  $C_S$  mode and also for the  $C_2$  mode and on the basis of these two values the conformation is assigned. The assigned conformation, the theoretical angles  $T_{ij}$ , D are given as printed output.

We have tested the applicability of this program for a number of our compounds and some literature data and so far it works quite satisfactorily. We suppose that this procedure has some advantages when following the effect of substituents on conformation in a series of closely related compounds. It is quite interesting to observe the magnitude of the difference between the minimum sum of squares of deviations for  $C_2$  mode with that for the  $C_S$  mode. In some cases in spite of the fact that the assignment was correct this difference was nearly within the limit of accuracy of the experimental data thus providing additional evidence that the Karplus equation should not be employed to calculate the dihedral angles to within  $1^\circ$ .

With best personal regards,

Sincerely yours,

  
Jiří Jonáš

## INSTITUT FÜR ANORGANISCHE CHEMIE

DER

## UNIVERSITÄT MÜNCHEN

Priv. Doz. Dr. H. Nöth

8 MÜNCHEN 2,

MEISERSTR. 1

FERNSPRECHER 55 79 76

15.2.65

Associate Professor Bernard L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Technology Center  
 Chicago, Illinois 60616

Dear Professor Shapiro,

We have just started nmr-work, primarily in the field of boron-chemistry. Since we are aware of the value of the IIT-letters, we would be grateful if you would include our name in your mailing list and send us copies of the IIT-letters from the beginning of 1965, if available. We would, of course, subject ourselves to the regulations regarding the IIT-letters.

As our starting contribution we wish to present some data concerning trigonal planar or tetrahedrally coordinated boron bonded directly to other nuclei with magnetic moments in order to examine whether or not spin-spin-coupling can be observed.  $^{11}\text{B}$  with  $^1\text{H}$  is always present, and with  $^{19}\text{F}$  apart from few exceptions as well. As becomes evident from the table, this is not necessarily the case when boron is bonded to another  $^{11}\text{B}$  or to  $^{31}\text{P}$ . On investigation of the unsymmetrically substituted diboron compounds, neither the expected boron-boron-coupling nor a separation of the nmr-signals could be observed. As the chemical shift of these compounds relative to tetrakis-dimethylamino-diboron is small (about 1 ppm) the coupling constant and hence the  $I/\delta$ -ratio might be too great as to give a visible AB-spectrum.

In the boron-phosphorus series coupling and non-coupling occurs. (The data on  $\text{Me}_2\text{P}(\text{BH}_3)_2$  are from J. N. Shoolery, Discussions Faraday Soc. 19, 3 215 (1955) ) Since the described diphosphinoborane also contains an amino-group bonded to boron, the observed  $^{11}\text{B}$ -resonance shows a broad signal as most of the aminoboranes do. The absence or non-observability of spin-spin-coupling in monomeric aminoboranes may therefore be due to the quadrupole-relaxation effect exerted by both boron and nitrogen. Contrary to these findings, boron-tin coupling, as measured from the satellite pattern of the main  $^{11}\text{B}$ -nmr-signal, is extensive.

Further studies shall clarify the observed discrepancies.

grouping	compound	chemical shift relative to BF <sub>3</sub> -ethyl etherate $\delta$ [ppm]	coupling constant I [cps]
<sup>11</sup> B- <sup>1</sup> H	B <sub>2</sub> (NMe <sub>2</sub> ) <sub>3</sub> Cl	-37,4	--
	B <sub>2</sub> (NMe <sub>2</sub> ) <sub>3</sub> Ome	-35,4	--
<sup>11</sup> B- <sup>31</sup> P	Me <sub>2</sub> PH·BH <sub>3</sub>	+37,4	50
	(MeO) <sub>2</sub> P·BH <sub>3</sub>	+45,1	99
	Bu <sub>3</sub> P·BH <sub>3</sub>	+40,5	--
	Et <sub>2</sub> N-B(PEt <sub>2</sub> ) <sub>2</sub>	-51,0	--
<sup>11</sup> B- <sup>117</sup> , <sup>119</sup> Sn	(Me <sub>2</sub> N) <sub>2</sub> B-SnMe <sub>3</sub>	-38,7	940

All measurements were made in a VARIAN HR 100 A nmr-spectrometer system operating at 32,1 Mc for boron and were established by the phosphorus-nmr recorded at 40,5 Mc.

Sincerely yours

H. Nöth

H. Nöth

H. Vahrenkamp

H. Vahrenkamp



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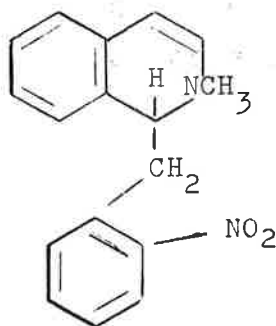
RENSSELAER, NEW YORK

Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois

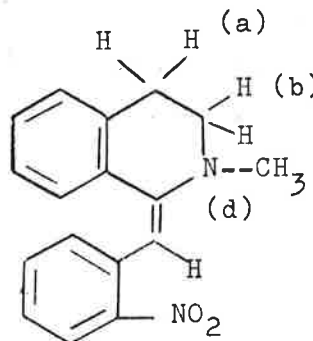
RE: Structure of 1,2-Dihydro-2-methyl-1-(o-nitrobenzyl)isoquinoline.

Dear Prof. Shapiro:

The base catalyzed condensation of o-nitrotoluene and 2-methylisoquinolinium iodide leads to a product to which J. Gadamer et al. [Arch. Pharm., 263, 81(1925)] assigned structure I. J. A. Weisbach and co-workers [J. Med. Chem., 6, 91(1963)].



I



II

challenged this structure and assigned structure II on grounds of UV- and NMR- spectral data (N.M.R. spectrum and interpretation from Dr. G. O. Dudek).

We have repeated the synthesis and obtained the same compound (by m.p. and UV- criteria) but cannot agree with the interpretation of the NMR- spectrum.

"Pair of triplets (at  $\delta$  3.20; 4.82) from the methylene groups a and b (see structure II). Triplets are expected as each methylene group is coupled to the protons of the other....."

It is readily discernible from fig. 1 that the signal at  $\delta$  = 3.2 ppm has twice the intensity of the signal at  $\delta$  = 4.62 ppm. This fact alone eliminates the possibility of having structure II and supports structure I. The structure of the signal at  $\delta$  = 3.2 ppm indicates the nonequivalence

Professor B. L. Shapiro  
Illinois Institute of Tech.

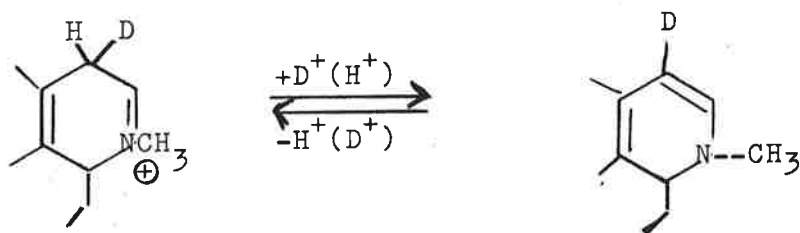
- 2 -

February 12, 1965

of the methylene protons of the 1-benzyl group. The bar-diagram which is inserted into fig. 1 shows the calculated line positions and relative intensities ( $J_{AB} = -12$  cps.;  $J_{AX} = +8.2$  cps.;  $J_{BX} = 4.8$  cps.;  $\gamma_A - \gamma_B = 14.3$  cps.). The numbers below the bars correspond to numbers of the transitions in table 6-15 of Pople, Schneider and Bernstein; "High-resolution Nuclear Magnetic Resonance" McGraw-Hill Book Co., Inc. p. 134.

The signal at 5.63 (5.33 in fig. 1) was interpreted: "It is the vinyl hydrogen, split into a doublet by inter- and non- interaction with the nitro group due to rotation of the nitrophenyl ring around bond d."

It is the vinyl proton on carbon-4 and couples with the proton on carbon -3 ( $\delta = 6.03$  ppm). The signal at 5.33 ppm disappears when  $D_2O$  is added to the solution ( $\sim 50\%$  reduction in fig. 2). This exchange also affects the signal at 6.03 ppm. The quartet structure is replaced by a doublet (center). The ease of this exchange is understandable since I is an ene-amine.



Sincerely,

R. K. Kullnig  
R. K. Kullnig

RKK/hr

Fig. 1

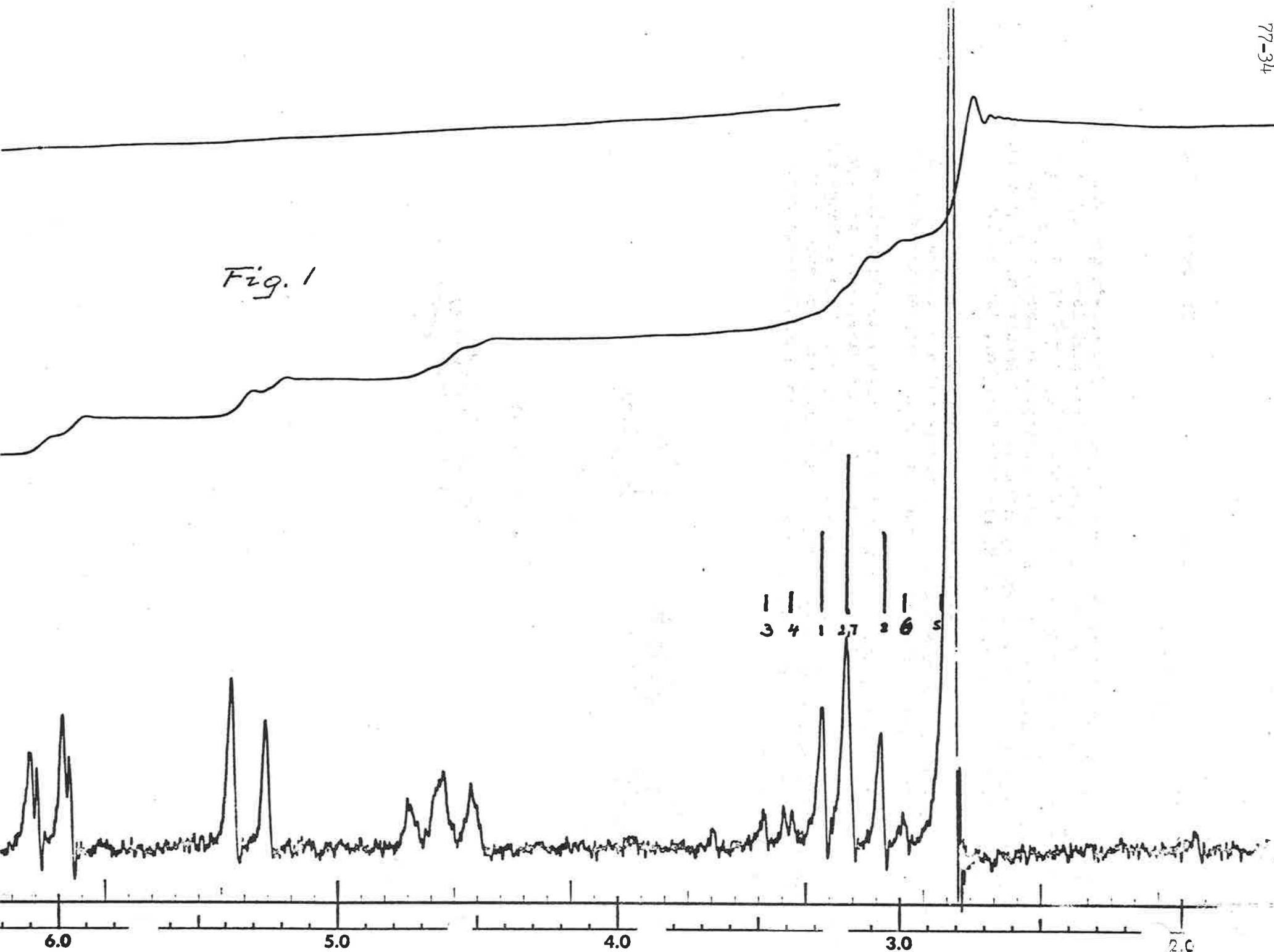
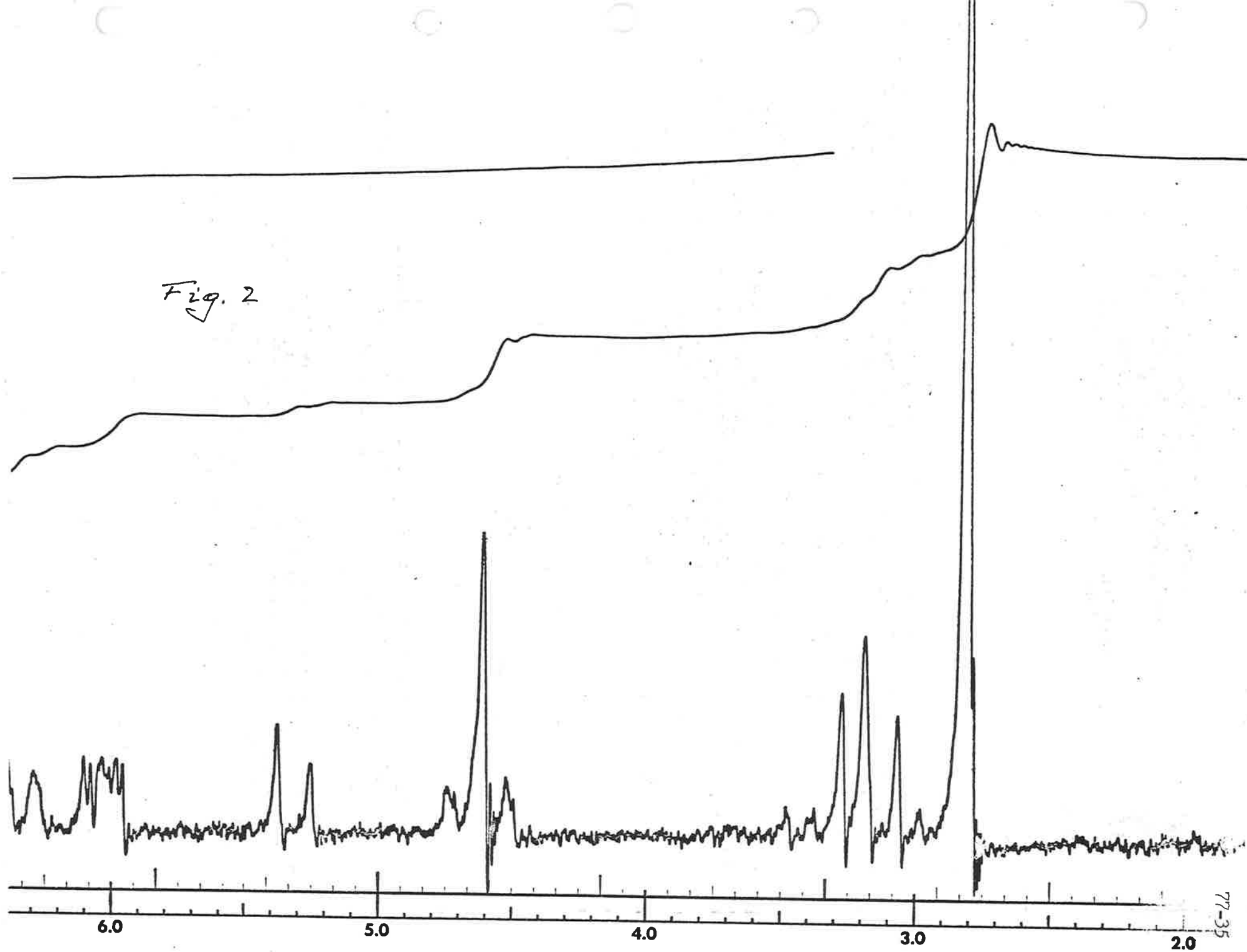


Fig. 2



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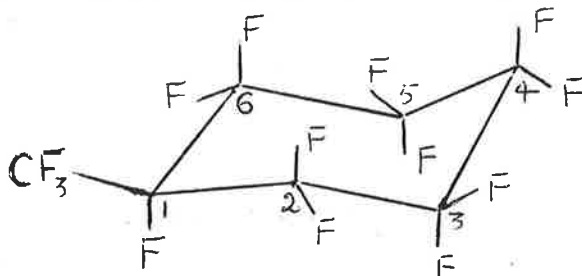
BASIC PHYSICS DIVISION

12th February 1965

Dear Barry,

Following Feeney, Suttcliffe and Walker's letter I.I.T. N.M.R.N. 75 6 I thought it appropriate to add a few points since we have had the spectrum of perfluoromethyl cyclohexane tucked away in our drawers for about two years with our own spectral assignments. We have spectra at 40, 56.4 and 94 Mc with some decoupled (partly) spectra at 94 Mc. My own laziness has dogged the job of writing this up but I am hoping to do this during my sabbatical year.

Spectra show magnetic equivalence for the axial and equatorial fluorines at carbon 2 and 6 and the long range couplings suggested by Suttcliffe. The work is a combined 'Canadian Effort'. Ted Schaeffer ran the 56.4 Mc spectra for us while we still laboured ourselves at 40 Mc and Bill Patterson who was then at Alberta ran the 94 Mc spectra with decoupling. Ted Wells who was with me at the time played a major part in our efforts at Vancouver. Without extensive explanations I could not begin to discuss this whole problem in your excellent newsletter. In order however to inject a little space into your columns I will first disagree with the Liverpool assignments in the methyl groups. A diagram will help:-



The  $\phi$ methyl group spectrum is shown as figure 1. You will see the basic first order (pseudo) splittings are; quintette 13.85 cps doublet 5.95 cps and quintette 0.85 cps. The splittings are close to those of Suttcliffe but we do resolve a quintette rather than triplet for the 0.85 cps splitting.

The obvious explanation, though who knows if it is the right one, is a 5.95 cps coupling to the lone fluorine on C1, 13.85 cps coupling to the fluorines on carbons 2 and 6 which should not be equivalent because the molecule is locked ( $\text{CF}_3$  equatorial) and a long range splitting to fluorine atoms on C3 and C5 again with  $\text{CF}_3$  apparent magnetic equivalence. We would say therefore that the 0.85 cps splitting is not necessarily a coupling constant but some virtual equivalence of fluorines on C3 and C5. Coupling to the fluorines on C4 is eliminated.

/For

B. L. Shapiro,  
Associate Professor,  
Chemistry Department,  
Illinois Institute of Technology,  
Chicago,  
Illinois,  
U.S.A.



For some amusement you might examine figure 2 taken at 56.4 Mc of the lone fluorine on C1. Our assignments are certainly reasonable and suggest pseudo first order splittings of 17.2 cps (quintette) 8.6 cps (quintette) and 5.75 cps (quartette). The 5.75 and 5.95 cps appears to be fair agreement for the  $\text{CF}_3$ -CF coupling. We interpret again the quintettes in terms of apparent magnetic equivalence assigning the larger value to the coupling C1 to C3 and the smaller value to the coupling C1 to C2.

I have probably used up enough space to warrant a warning so I will close with the hope that my meeting with Les Suttcliffe will not come to blows in a few weeks.

Best wishes,

*Len Reeves*

L. REEVES

FIG. 1

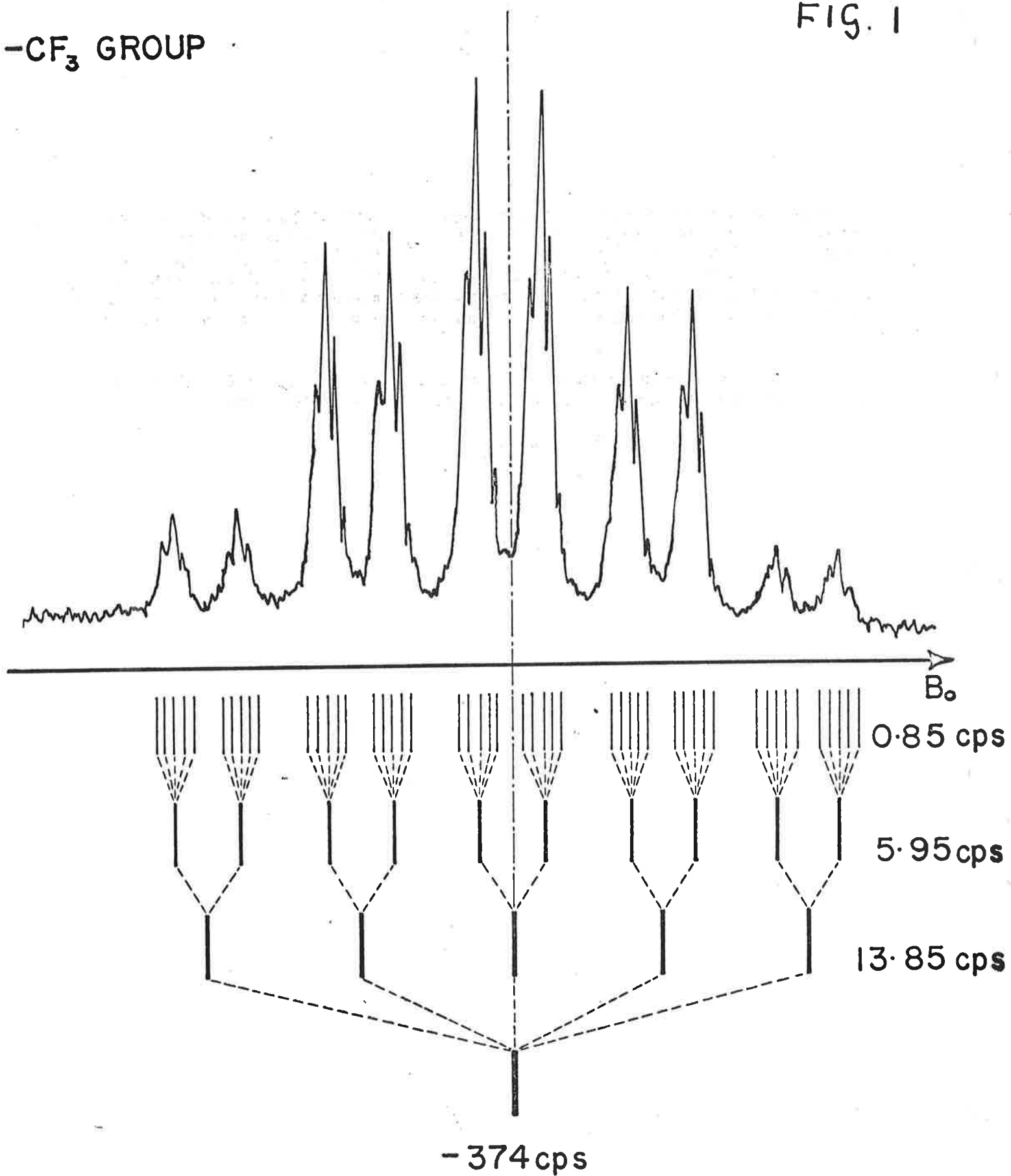
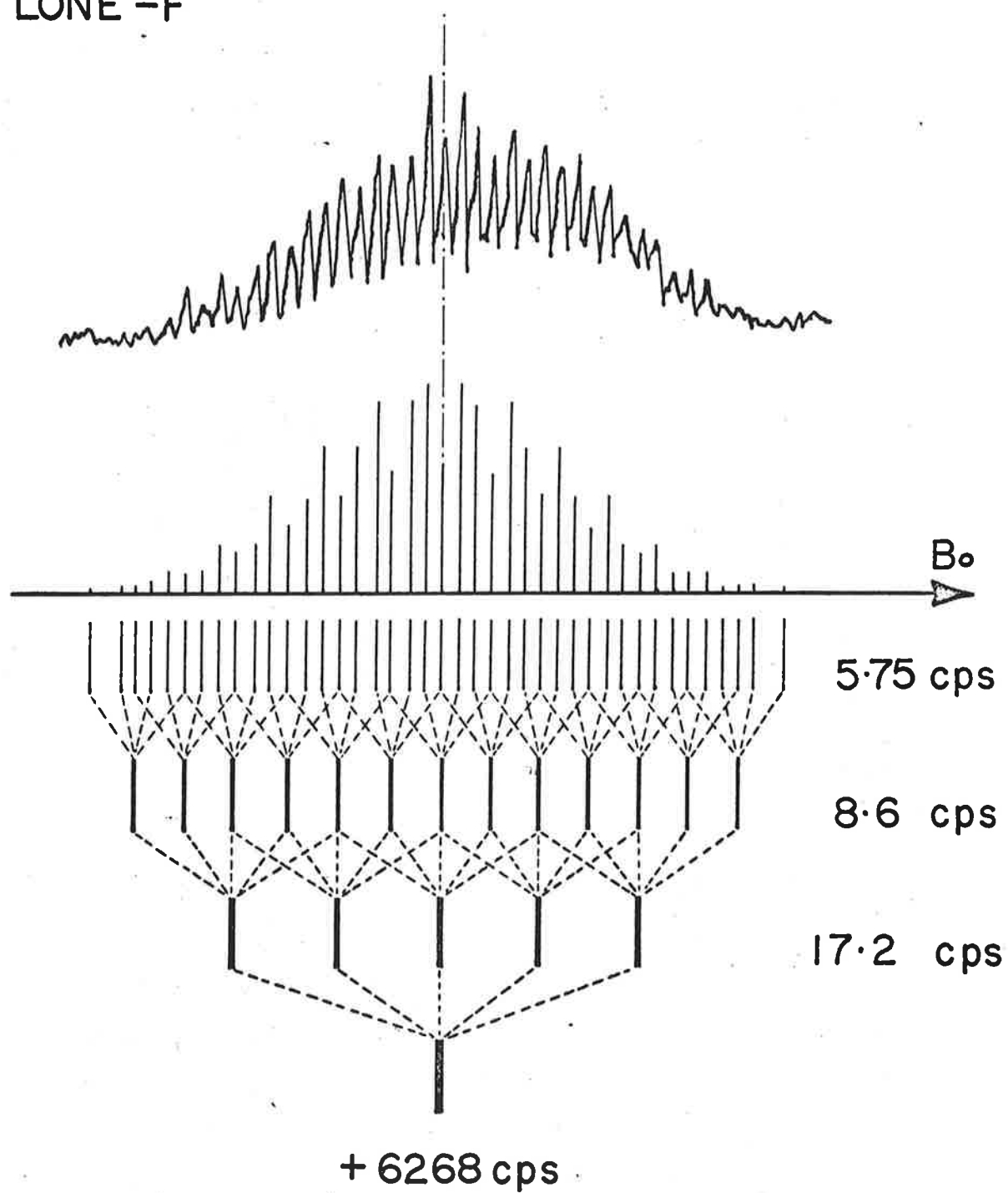
 $-\text{CF}_3$  GROUP

FIG. 2.

LONE - F





## SOCIETÀ EDISON

SOCIETÀ PER AZIONI CON SEDE IN MILANO  
CAPITALE SOCIALE L. 375.000.000.000 - INTERAMENTE VERSATO

LABORATORIO RICERCHE DI BOLLATE

AZIENDA CHIMICA

BOLLATE February 15, 1965

Località Traversagna - Telefoni 2910 - 2919  
Casella Postale N. 15

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

Nella risposta citare il N° 3104/LCav/ca

Subject: syn-anti Assignments  
to oximes from solvent  
effects.

Dear Professor Shapiro,

we have started a programme of study of  
a few oximes and would like to report some preliminary results.

It has been recently<sup>(1)</sup> presented a  
method for assigning from solvent effects syn and anti structures  
to several compounds of the type:  $R_1R_2C = N \setminus Z$ . It has been shown  
that both cis and trans hydrogen in  $\alpha$  and  $\beta$  position to  $C = N \setminus Z$   
groups resonate at higher fields in aromatic solvents than in  
aliphatic ones, and that the degree of up-field shift of cis hydro-  
gens is different from that of corresponding trans. This inequali-  
ty was proposed as a convenient method for assigning syn and anti  
structures to oxime isomers. As far as oximes are concerned the  
 $\Delta V$  values ( $\Delta V = \nu$  in aliphatic solvent -  $\nu$  aromatic solvent) are  
larger for trans hydrogens than for cis hydrogens:  $\Delta V(\text{trans}) > \Delta V(\text{cis})$ .

So far we have looked through a few simple  
aliphatic oximes, either aldehydoximes or ketoximes (see table 1  
hereby enclosed), in several solvents and we have observed, in ad-  
dition to the aromatic solvent effect put forward by Karabatsos  
and coworkers, another solvent effect using pyridine. Contrary to  
the behavior of aromatic solvents as benzene, it has been observed  
that the cis and trans hydrogens to oxime group resonate at lower  
fields in pyridine than they do in aliphatic solvents.

In addition the down-field shift is larger  
for cis hydrogens than for trans hydrogens, that is to say  $\Delta V(\text{cis}) > \Delta V(\text{trans})$ . Even if it is premature to generalize because of the  
small number of oximes observed so far, the use of pyridine as a  
solvent seems to provide a method as convenient as the one using  
benzene for assigning syn and anti structures to oxime compounds.

This finding can be probably ascribed to an association complex between oximes and pyridine. Since the down-field shifts of the cis-hydrogens are always larger, it is likely that the pyridine has to prefer a certain site for coordination. If the shifts are due, as it is likely, to the anisotropy associated with the ring current effect of pyridine, it is rather interesting to note that they could simply be rationalized in terms of an hydrogen bond involving the hydroxyl of the oxime groups and the lone pair of electrons on the heteroatom of pyridine. Such an arrangement, considering the directional properties of the unshared electrons of pyridine would determine predominantly down-field shifts of cis-hydrogens, as observed.

Work is in progress looking into the O. methylethers of the corresponding oximes. We hope this can throw more light on the nature of the interaction between oximes and pyridine.

Yours sincerely,

Luciano Cavalli



(1) G.J. Karabatsos, R.A. Taller, F.M. Vane, J.A.C.S. 85, 2326, 1963

Encl.: No. 1

Table No. 1

$R_1 R_2 C = NOH$		$\Delta \nu = \nu_{\text{aliphatic solvent}} - \nu_{\text{benzene}}$						$\Delta \nu = \nu_{\text{aliphatic solvent}} - \nu_{\text{pyridine}}$					
$R_1$	$R_2$	$\Delta \nu(H_1)$		$\Delta \nu(*CH_3)$		$\Delta \nu(*CH_2)$		$\Delta \nu(H_1)$		$\Delta \nu(*CH_3)$		$\Delta \nu(*CH_2)$	
		cis	trans	cis	trans	cis	trans	cis	trans	cis	trans	cis	trans
H	CH <sub>3</sub>	6	15	15	24			(a)	(a)	-6	+2		
H	CH <sub>2</sub> CH <sub>3</sub>	1	10			6	18	(a)	(a)			-12	-1
CH <sub>3</sub>	CH <sub>3</sub>			10	16					-6	0		
CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>			4	10	1	11			-10	-5	-13	-5
CH <sub>3</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub>					1	11					-13	-6

values are in c.p.s. All solutions were at 10% mole fraction. All NMR spectra were determined at 60 Mc. on a A-60 at the temperature of the probe ( $\sim 38^\circ C$ ). Assignments of hydrogens as cis and trans were based on arguments already given by other authors (see: W.D. Phillips, Ann. N.Y. Acad. Sci. 70, 817, 1958; E. Lustig, J. Phys. Chem. 65, 491, 1961; ref. (1)). CCl<sub>4</sub>, CDCl<sub>3</sub> and CS<sub>2</sub> were used as aliphatic solvents.

(a) signals overlapped by the solvent.

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