

*Remar*

Mailed:  
30 October 1963

Monthly  
Ecumenical  
Letters from  
Laboratories  
Of  
N - M - R

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DEADLINE FOR NEXT ISSUE  
November 22, 1963

Miesięczny zbiornik nieoficjalnych prywatnych Listów z Laboratorji badających magnetyczny rezonans jądrowy. Informacje zawarte w tym zbiorze są tylko dla użytku czytelnika. Nie wolno cytować z wyjątkiem bezpośredniego zezwolenia autora poszczególnego listu. W tym wypadku materiał cytowany powinien być opisany jako "informacja prywatna".

ÉCOLE NATIONALE SUPÉRIEURE  
DE CHIMIE8, RUE DE L'ÉCOLE-NORMALE  
TÉLÉPHONE 72.49.19Prof. Max Mousseron,  
Director.

September, 1963

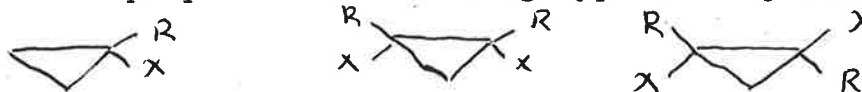
Dr. A.A. Bothner-By,  
Mellon Institute,  
4400, Fifth Avenue,  
Pittsburgh, 13.  
Penn.  
USA

Dear Dr. Bothner-By,

I am afraid this contribution is very much overdue, but I hope it may interest your readers.

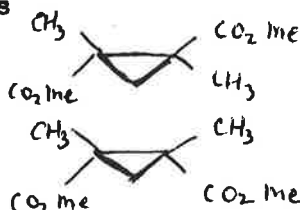
With André Pavia we have been investigating the chemical shift and coupling constants of a certain number of cyclopropane derivatives with particular reference to the effect of the substituents on these parameters.

We have prepared the following type of compounds



R = Me, -CN, -CO<sub>2</sub>Me,  $\emptyset$   
X = -CO<sub>2</sub>Me, -CN

The tetrasubstituted compounds, which give either single line (for the trans) or simple AB (for the cis) spectra have given the following values



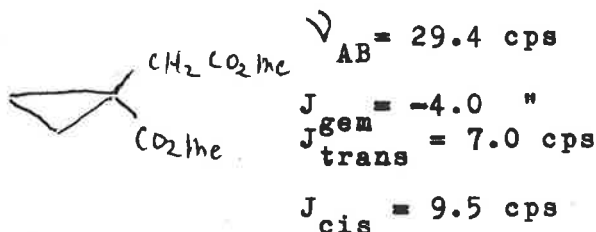
$\tau = 8,58$  (cyclopropane protons, single line)

$\tau_1 = 8,09$   
 $\tau_2 = 9,37$   $J_{gem} = 4,5$  cps.

For the 1-1 substituted compounds, having chosen an approximate fit for A<sub>2</sub>B<sub>2</sub> spectra from Prof. Wiberg's book we used the usual analysis and have found a very satisfactory fit for the following parameters:



$\nu_{AB} = 32.0$  cps  
 $J_{gem} = -3.5$  "  
 $J_{cis} = 9.5$  "  
 $J_{trans} = 6.5$  "



This compound was prepared by Messrs Soulier and Elghandhour; we thank them for their cooperation.

The two figures enclosed show the spectrum obtained for one of these compounds together with a comparison of the calculated and the experimental values.

It may seem surprising that the geminal coupling constant is lower than in cyclopropane carboxylic acid itself and in the tetrasubstituted compound, cis-1-2-dimethylcyclopropane-1-2-carboxylic ester, but a fit was not possible for the 1-1 substituted derivatives using values of  $J_{\text{gem}}$  of the order of 4 to 5 cps.

These calculations have been rather tedious to carry out, inspite of the fact that we have at our disposal at the Faculté des Sciences an IBM 1620 which enables us to calculate the eigenvalues and eigenvectors of the matrices.

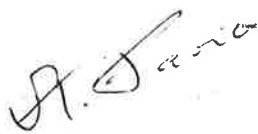
Before attempting to program the operations we have carried out, i.e. different trial values of the parameters, I should very much appreciate if you or one of your readers could tell me how to program an  $A_2B_2$  spectrum.

We have spectra of a whole series of cyclopropane derivatives and intend to carry out the analysis both from the point of view of chemical shift and its relation to long range shielding by carbonyl, nitrile or phenyl on adjacent protons in the rigid cyclopropane structure and the spin-spin coupling constant as a function of angle in substituted cyclopropanes.


This work will be the subject of a Ph.D thesis by one of us (A.P.) and the results will be published in the Bulletin de la Société Chimique de France.

We are pleased to acknowledge our gratitude to Professor Falguerettes and M. Filiatre of the Dept. of Mathematics for their invaluable help in the calculations on the IBM 1620.

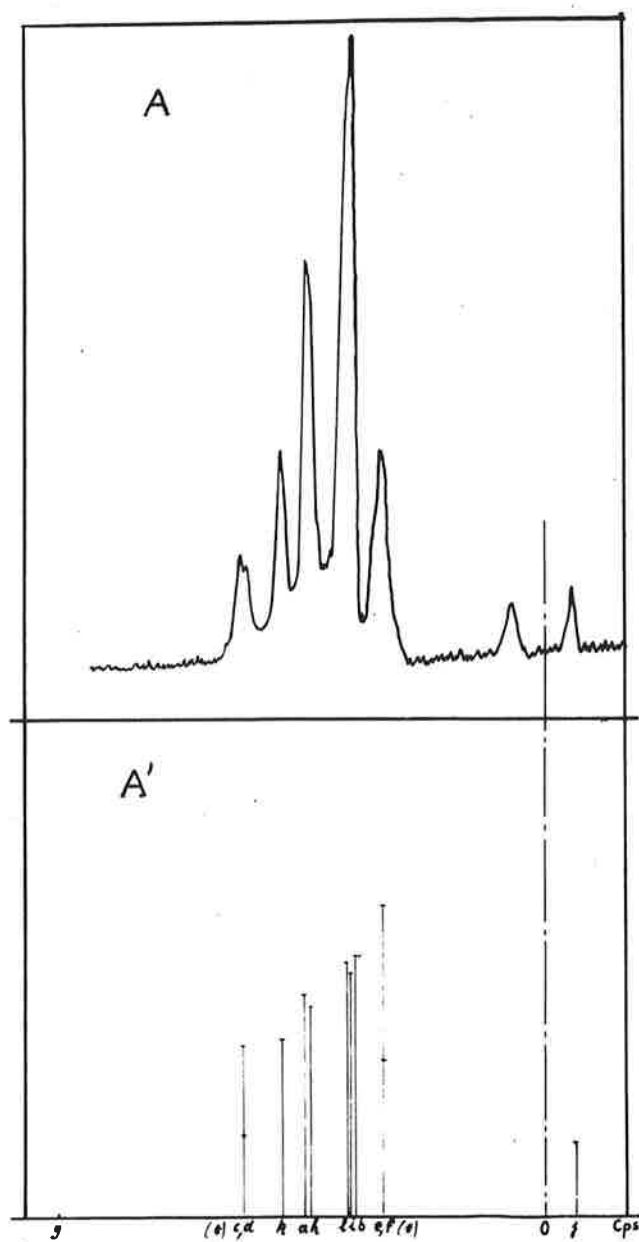
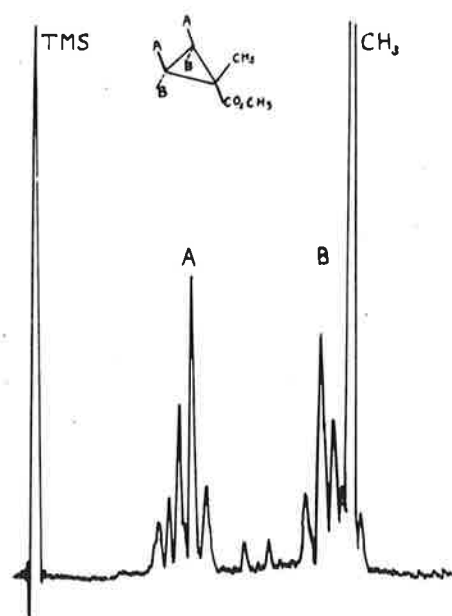
Yours sincerely,



André Pavia  
 Assistant à la Faculté  
 des Sciences



James WYLDE  
 Chargé de Recherches,  
 C.N.R.S.





COMMONWEALTH

OF AUSTRALIA

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION

## DIVISION OF COAL RESEARCH

TELEGRAMS: FUELRES, SYDNEY  
TELEPHONE: WW 0261

The Laboratory is situated  
in Delhi Road, North Ryde.

P.O. BOX 175,

CHATSWOOD, N.S.W.

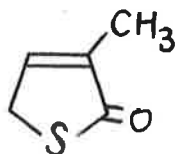
September 23d, 1963

Long-range coupling via sigma-pi contact interactions.  
Absolute magnitudes of allylic and homoallylic coupling  
constants; effect of pi-electron density; some results  
on indoles.

Dear Dr. Shapiro,

Long-range coupling ( $H^1-H^1$ ) in allylic, homoallylic<sup>1</sup>, allenic and acetylenic systems can be satisfactorily rationalised in terms of a mechanism involving sigma-pi configuration interactions<sup>2-7</sup>. Scrutiny of available data and some further results reveal additional features of interest:

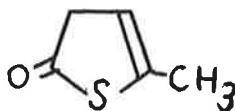
a) The absolute magnitudes of the five-bond homoallylic coupling constants can be larger than those of the four-bond allylic coupling constants. E.g. in the following structures the homoallylic coupling constants are larger in each case, although they must involve an additional  $\cos^2\theta$  factor<sup>1</sup> (admittedly for a more favourable angle) which must be smaller than unity:



$$J_{CH_3, CH_2} : 1.9c/s$$

$$J_{CH_3, CH} : 1.5c/s$$

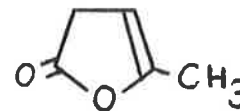
Reference: 8



$$J_{CH_3, CH_2} : 2.5c/s$$

$$J_{CH_3, CH} : 1.5c/s$$

Reference: 9



$$J_{CH_3, CH_2} : 2.7c/s$$

$$J_{CH_3, CH} : 1.6c/s$$

Reference: 10

The very large homoallylic coupling constants in the eleutherins<sup>11</sup> and futronolide<sup>12</sup> provide additional evidence. The phenomenon may be explained by considering a small<sup>2</sup> additional spin-spin interaction via the sigma framework, which would be expected to be positive in

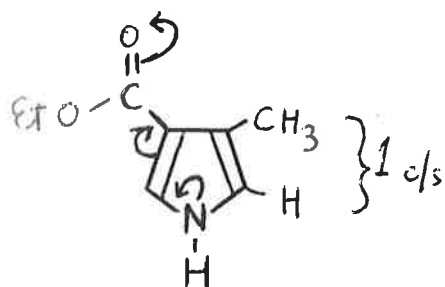
sign, and which would thus add to the magnitude of the positive homoallylic coupling constants and subtract from the magnitude of the negative allylic coupling constants.

61-5

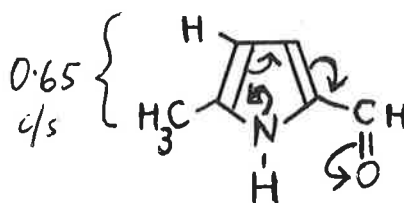
Similarly, it is known<sup>13-17</sup> that for comparable allylic and homoallylic systems there is a tendency for a reversal in the relative magnitudes of the cisoid and transoid interactions. Here one could invoke a residual "all sigma" coupling which is positive in sign and larger for the trans than for the cis case, in analogy with coupling across three bonds in simple unsaturated systems.

Simple calculation (making allowances for the crucial  $\cos^2\theta$  dependence) allows us to estimate the magnitude of the residual sigma interaction to be about 0.5 c/s, a not unreasonable value.

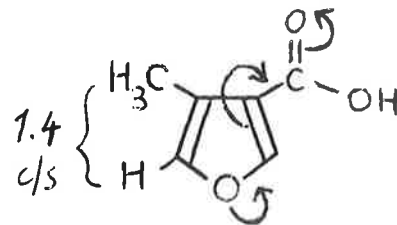
b) Common sense suggests that allylic and homoallylic spin-spin interactions should depend on the pi-electron density, or bond order, of the double bond involved. The magnitudes of the side-chain ( $\text{CH}_3\text{-C=CH-}$ ) coupling constants in benzenes<sup>18,19</sup> pyrroles<sup>20</sup> furans<sup>21</sup> thiophenes<sup>3,4</sup> and propenes<sup>13-15</sup> appear to be in accord with this view. We have also observed that the methyl group in 9-methyl phenanthrene gives rise to a fairly clean doublet ( $J$  approx. 1 c/s) which is far larger than the usual ring-methyl interaction in aromatic compounds and is in accord with the localized nature of the 9-10 bond in phenanthrenes. The correlation of allylic coupling constants with bond-order could give a new experimental method for determining the latter, in particular as regards the effect of substituents on the ground state of molecules. From results on some substituted heterocyclic compounds (references above) it would appear that the electronic distribution is seriously affected (in the ground state) by the presence of certain substituents. Some examples, with rationalizations, are shown below:



Reference: 20



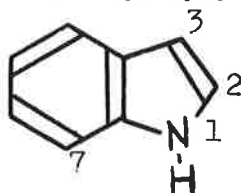
Reference: 20



Reference: 20

61-6 On the other hand, allylic coupling constants in conjugated ketones and esters (e.g. reference 16) and in  $\beta\beta$ -dimethyl styrenes (our unpublished data) are not very markedly different from those found in unconjugated systems (although the trend is towards lower values, as expected). This could have some implications regarding relative contributions of charged structures to the ground-states of such systems. Interestingly, there is a tendency for the cisoid and transoid coupling constants to be closer in conjugated than in unconjugated systems.

c) In connection with the above we have some preliminary first order data on indoles:



Compound	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{3,7}$	Side-chain
Indole	2.4	2.2	3.2	0.7	-
1-Me-indole	-	-	3.1	0.7	-
2-Me-indole	-	P	-	P	1.0
3-Me-indole	P	-	-	-	1.1
1,2-diMe-indole	-	-	-	P	0.95

P signifies that an interaction was present but could not be estimated at the resolution available. The long-range coupling of  $H_3$  to the ring was assigned to  $H_3, H_7$  by analogy with well known systems<sup>22</sup>. The N-H,  $H_3$  coupling cannot involve sigma-pi mechanism as the methyl signal in 3-methyl indole (skatole, ugh!!) is a clear doublet which remains unchanged on N-deuteration. The larger side-chain couplings than in pyrroles<sup>20</sup> are as expected on the bond-order hypothesis.

Best regards

*Sever Sternhell*

(S.Sternhell)

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7. Gronowitz and Hoffman , MELLON-M-R 51 12 (1963)
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15. Whipple, Goldstein and McClure , ibid 82 3811 (1960)
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17. Richards and Beach , J. Org. Chem. 26 623 (1961)
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20. Gronowitz, Hornfeldt, Gestblom and Hoffman , Arkiv Kemi 18 133 (1961)
21. Abraham and Bernstein , Canad. J. Chem. 37 1056 (1959)
22. Kokko and Goldstein , Spectrochim. Acta 19 1119 (1963) and refs. therein



UNIVERSITY OF ILLINOIS URBANA

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING

THE WILLIAM ALBERT NOYES LABORATORY

September 27, 1963

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh, Pennsylvania

Dear Dr. Shapiro

In a paper in press, I am publishing results concerning the N. M. R. spectra of phenylchlorosilanes and phenylchlorostannanes. It has been established, that the ring protons can be divided into two groups, down field from benzene. The areas of corresponding bands are in the ratio 2:3 and assigned to ortho protons (the bands at lower field) and to meta and para protons. The splitting between these two groups showed a surprising variation dependent upon the number of chlorine atoms attached to the central atom. To account for this variation, suppose that the most chlorinated of these compounds have an ionic or at least partially ionic structure, where the metal-carbon bond has a partial double bond character. To clarify this structure I decided to complete the analysis of the spectra of the most questionable of these compounds. Among these,  $(C_6H_5)_2SiCl_2$ , (I), has the best resolved spectrum and I began with it. Direct analysis was attempted without any success, so I prepared the para-deuterated derivative, (II), from para-deuterated bromobenzene and silicon tetrachloride. The spectra of (II) is an  $A_2B_2$  nearly an  $A_2X_2$ . Following the classical method, I used this fact to determine the K. L. M. and N. usual constants making the most reasonable assignment. Spectra were computed using the FREQUINT IV program, and agreement with the experiment obtained for the following values:

$$J_A = 3.50 \text{ cps. } J_B = 1.9 \text{ cps. } J = 8.25 \text{ cps. } J' = 0.05 \text{ cps.}$$

$$\nu_A - \nu_B = 29.8 \text{ cps.}$$

Notice that the value of the  $J'$  coupling constant is smaller than that generally found for protons para to each other, and the large difference in  $J_A$  and  $J_B$  which arise in both case from protons meta to each other.

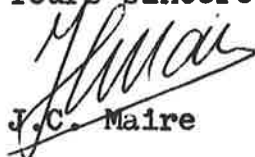
University of Illinois  
Page No. 2

Dr. Shapiro--

The next step is to return to (I). Two supplementary coupling constants and one chemical shift are required. These can be obtained by preparing derivatives deuterated in the meta or ortho position. An alternative way is to assign to these constants reasonable values and to fit the computed spectra with the experiments by stepwise approximation. These two procedures are presently under experimentation.

I wish to acknowledge my indebtedness to Professor Gutowsky, in whose laboratory I performed the most part of this work, and to Dr. Derbyshire for helpful discussions.

Yours sincerely,



J.C. Maire

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**M**onthly  
**E**cumenical  
**L**etters from  
**L**aboratories  
**O**f  
**N - M - R**

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".

## THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

3rd October, 1963.

Dr. Barry Shapiro  
Mellon Institute  
4400 5th Avenue  
Pittsburgh 13, Pa.

Dear Barry:

We read with interest a recent letter by A. Tzalmone of Varian A. G. in Mellon News No. 59, p. 10. This reports a Group IV element  $\text{Ge}^{73}$  coupling to protons in  $\text{Ge}(\text{CH}_3)_4$  a value which we had expected not to be available because of quadrupolar relaxation. In our recent letter, Mellon News No. 57, p. 30 we showed correlation of  $J_{\text{K-C-H}}$  where 'K' is a group IV element with atomic number  $Z_K$  in the form  $\sqrt{J/\mu} = A.Z_K + B$  where A and B are

constants. We indicated the limitation that  $\text{sp}^3$  hybridisation must obtain at the group IV atom.  $\text{Ge}^{73}\text{-C-H}$  satisfies our chemical conditions in  $\text{Ge}(\text{CH}_3)_4$  but in order to use the coupling constant reported we must correct J for both nuclear moment and spin of 9/2. The correction required is  $\left(\frac{9 \times J}{\mu}\right)^{1/2}$

which gives 30.2 cps per nuclear magneton, the sign being neglected. A value  $\sqrt{\frac{9 \times J}{\mu}}$  fits very well on our previous curve as shown on the

accompanying graph.

Regarding a recent letter by S. D. Kaez and N. Flitcroft, Mellon News 58, p. 53 on the  $\text{Sn}^{119}\text{-H}$  coupling in  $(\text{CH}_3)_2\text{SnH}_2$  we can say that this has been remeasured here both in solvents and in the pure substances and our original measurement of 1797.1 cps is one we still find to be correct. Remarks that they make on a value for  $J_{\text{Sn-H}}$  in  $(\text{CH}_3)_3\text{SnH}$  do not have any bearing on our number for  $(\text{CH}_3)_2\text{SnH}_2$ .

I enjoyed my recent but very rapid visit.

Yours sincerely,

*Len Reeves*

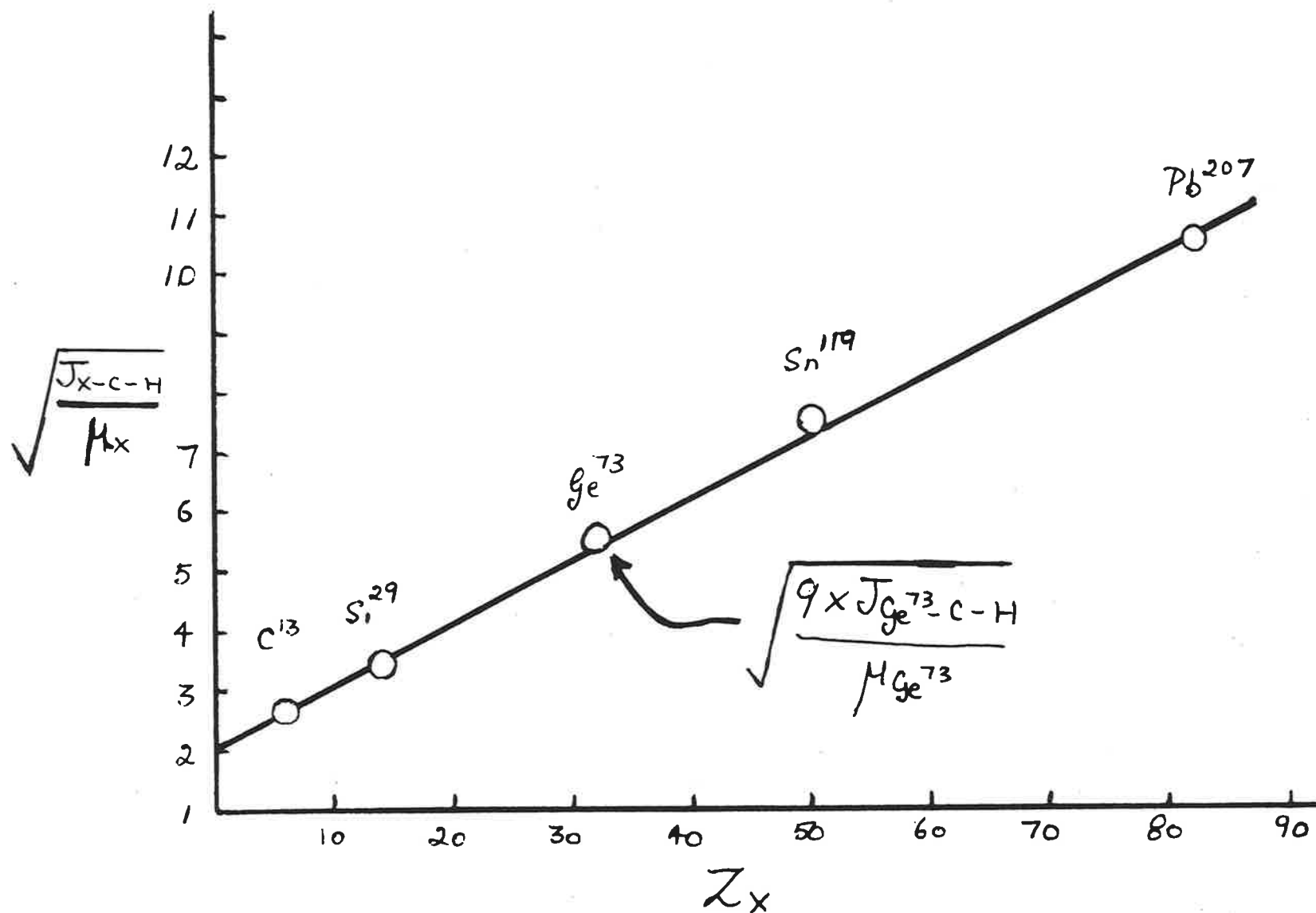
L. C. Reeves

*Ed Wells*

E. J. Wells

LRR/iam

# Coupling Constants of Group IV elements.



TELEPHONE  
549-8111

RESEARCH TRIANGLE PARK  
BOX 731, DURHAM, NORTH CAROLINA

**CHEMSTRAND**  
RESEARCH CENTER, INC.

October 8, 1963

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

We have undertaken a program to improve the overall system performance of our Varian DP-60 spectrometer. One phase of the program involved modification of the RF system to provide increased sensitivity, and was accomplished with the aid of personnel from Solid State Laboratory, Research Triangle Institute, who designed and constructed the electronic components. This modification consists of two units, (1) a nuvistor preamp (replacing the Varian preamp) followed by (2) a low-noise, high gain amplifier (LeI Model IF 3047). The preamp provides a few db gain while maintaining the lowest noise figure practical within the limitations of space and strong magnetic field. The amplifier provides sufficient gain so that the noise figure of the receiver will be secondary with respect to the noise figure of the system.

Significant improvements have been achieved in signal-to-noise ratio for both high resolution and wide line applications -- as shown by the accompanying figure (forward and backward traces of  $\text{CHCl}_3\text{-CCl}_4$  solutions). Further information is available for those interested.

Yours sincerely,

*Wallace C. Lawrence*  
Wallace C. Lawrence

FS/63-289/ds

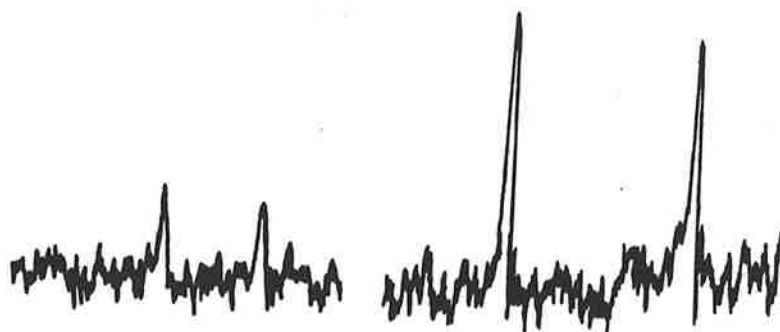
# DILUTE SOLUTION SENSITIVITY ( $\text{CHCl}_3$ in $\text{CCl}_4$ )

Molar Concentration  
of Hydrogen Nuclei

Varian  
System

Modified  
System

0.008 m/l



0.004 m/l



0.002 m/l



D E P A R T M E N T   O F   C H E M I S T R Y  
THE UNIVERSITY OF MICHIGAN • ANN ARBOR, MICHIGAN

October 9, 1963

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Barry:

A-60 Miscellanea

Our A-60 equipped with the V-6031 Variable Temperature Probe has been in operation for about six months. Some comments on our installation may be of general interest.

Anticipating less than optimum performance due to the hardware present in the V-6031 probe, we decided not to "over-control" environmental variables. As a result our installation is quite simple and yet effective in that we have had no difficulty exceeding performance specifications. The installation is housed in a ventilated but not air-conditioned room (14x12x12'), used solely for this purpose. We utilize a house compressed air source (10 - 15 psi) for sample spinning. Initially the air was filtered through a cotton-stuffed polyethylene bottle; however, due to annoying leakage and pressure drop we switched to the "Aqua-jet" and "Whirlflow" combination previously suggested.<sup>1</sup>

As a reservoir for our recirculating magnet cooling water we utilize a 30-gallon cylindrical polyethylene tank. This tank is a standard item carried by laboratory plasticware suppliers and in 3/16" wall thickness costs about \$45.00, including lid. The water level is easily seen through the translucent tank and evaporation loss is negligible. The distilled water supply is cooled by tap water via 30' of immersed copper coil (1/2" diameter). Tank water temperature is usually 20-22°C and is regulated by occasionally adjusting the tap water flow rate; during the hottest part of the summer (above 90°F) it does not exceed 28°. A 3" dial thermometer with 12" stem (Brooklyn Thermometer Co., #65200, \$14.00) inserted through the lid of the tank allows reading the tank water temperature from a distance. All hose connections to the tank are made to copper tubing inserted in the side and just below the lid.

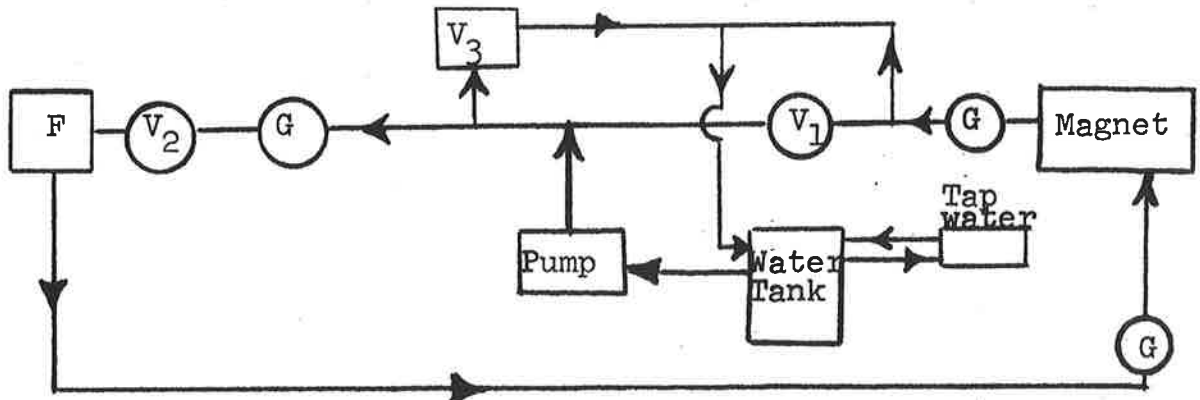
We originally installed an Eco pump<sup>2</sup> for water circulation but this soon failed. For the past few months we have utilized a Burks Super Turbine Pump<sup>3</sup> which has been flawless; it operates at low noise and vibration levels.

The remainder of our water system (sketched below) consists of 5/8" brass fittings and includes hand valves V<sub>1</sub> (normally closed) and V<sub>2</sub> (fully open), relief valve V<sub>3</sub>, pressure gauges G, and water filter F. The relief valve is set at 30 psi and operates as a

October 9, 1963

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by-pass valve allowing cool water to mix with warm water from the magnet. The entire water circulating system is quite compact and easily fits into the "dead" space between the console and magnet placed at right angles.



Sincerely yours,

*D. T. Longone*  
D. T. Longone

- (1) Koster, Lundergan, Poradek and Danti, MELLONMR, 47-2 (1962).
- (2) Beach, MELLONMR, 42-17 (1962).
- (3) Decatur Pump Co., Decatur, Ill., Catalog #10C17 with 1/4 HP, 1725 RPM, single phase motor, About \$119.



# THE UPJOHN COMPANY

FINE PHARMACEUTICALS SINCE 1886

KALAMAZOO, MICHIGAN

SCIENTIFIC ADMINISTRATION  
301 HENRIETTA STREET

September 25, 1963

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Barry:

We have been thinking some about the determination of signal-to-noise ratio since it is a useful measure of the performance of an NMR spectrometer and of the improvement possible by a CAT accessory.<sup>1</sup> Since no standard method could be found and several methods of determination were prevalent, we would be interested in hearing comments of the Mellon-NMR readers on the following statistical approach.

Noise in a spectrometer is defined as the random signal arising as the result of statistical fluctuations in any part of the circuit.<sup>2</sup> It is observed as a random variation of the chart in the absence of any signal and is measured from a record of the baseline. Absolute noise<sup>2a</sup> is defined as the maximum peak-to-peak displacement in the baseline measured by the separation of two parallel lines that will just enclose the record. The mean ( $\bar{y}$ ) of the baseline is thus zero and in a normal instrument is a line through the center of the record. Since the quantitation of noise is a statistic describing the precision of the baseline, it is better defined as RMS noise<sup>2b</sup> which is actually the standard deviation (s) of a series of measurements of the displacement of the observed trace from the mean baseline at various positions along the record.

$$s = \sqrt{\frac{\sum (\bar{y}-y)^2}{n-1}}$$

This is a tedious determination and an approximate method, based on the range, is much easier. For any sample of measurements of size 100 or more, the standard deviation is approximated<sup>3</sup> by the range divided by 5.02. Thus, if a sufficiently large sample of the baseline is taken, including more than 100 excursions, and lines are drawn parallel to the trace through the most intense positive and negative peaks<sup>a</sup> the peak-to-

---

<sup>a</sup> In the unusual case spikes whose excursions are larger than the rejection quotient (Q) may be neglected from consideration.

Dr. B. L. Shapiro

-2-

September 25, 1963

peak distance between these lines (absolute noise) will be a measure of the range and the standard deviation (s) is this distance divided by 5.02. Since most quantitative results are expressed at the 95% confidence level, the noise should be too. At the 95% confidence level, the RMS noise value would actually be  $\pm 1.982s$  and

$$\text{RMS}_{95} \text{ noise} = \pm \text{range} \times \frac{1.982}{5.02} \approx \pm \text{range} \times 0.4$$

This is the 95% confidence interval of a single reading of the baseline as might, for example, lie underneath a single sharp resonance peak. This is the statistic that is important in describing the capability of an instrument in quantitation by peak height measurements.

The 95% confidence level of the mean baseline is considerably smaller, i.e.,

$$\pm \text{RMS}_{95}/\sqrt{n} \text{ or } \pm \text{range} \times 0.04$$

thus this line seems to be a good place to start in the measurement of signal height. Signal height is measured from the peak of the signal to the mean baseline.<sup>b</sup> The signal can vary in intensity, depending on whether the baseline error is additive or subtractive at the moment. Hence, an average value should be used. This measurement should be based on 5 to 10 traces to improve the precision of the measurement.

Signal-to-noise ratio is then the signal height divided by the noise. A sample determination may be seen in Figure 1.

On a 1% (wt.) sample of ethyl benzene in carbon tetrachloride in a 4.28 mm., i.d. sample tube, the third line of the quartet should show a signal-to-noise ratio (S/N) of 7 to 9 when the instrument is performing well.

#### Acknowledgement

Grateful acknowledgement is made of the helpful discussions with Dr. O. S. Carpenter of the Statistical Section of The Upjohn Company and Mr. Robert Williams and Mr. Cappy Joller of Varian Associates.

#### References

1. a. See advertisement, P. 2a, 3a of September 5, 1963 issue of J.A.C.S.  
b. Allen, L. C. and L. F. Johnson, J.A.C.S., 85, 2668 (1963).

---

<sup>b</sup> Varian specifies to include the absolute noise in this measurement.

Dr. B. L. Shapiro

-3-

September 25, 1963

2. a. "Absorption Spectroscopy" by R. P. Bauman, John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 79, 149, 170.
- b. "The Encyclopedia of Spectroscopy," G. L. Clark, Editor, Reinhold Publishing Corp., New York, N. Y., 1960, p. 460.
3. "Reference Data for Radio Engineers," Fourth Edition, International Telephone and Telegraph Corp., New York 4, N. Y., 1956, p. 995; W. J. Dixon and F. J. Massey, Jr., "Introduction to Statistical Analysis," McGraw-Hill Book Co., Inc., New York, 1957, Table 8 (b) 1, p. 404.

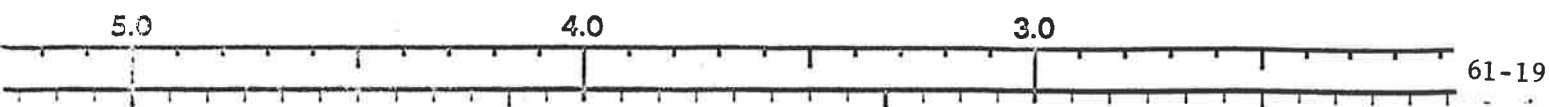
I hope this entitles me to a renewal of my expired subscription to Mellon NMR.

Very truly yours,



George Slomp  
Physical and  
Analytical Chemistry

alb



300

200

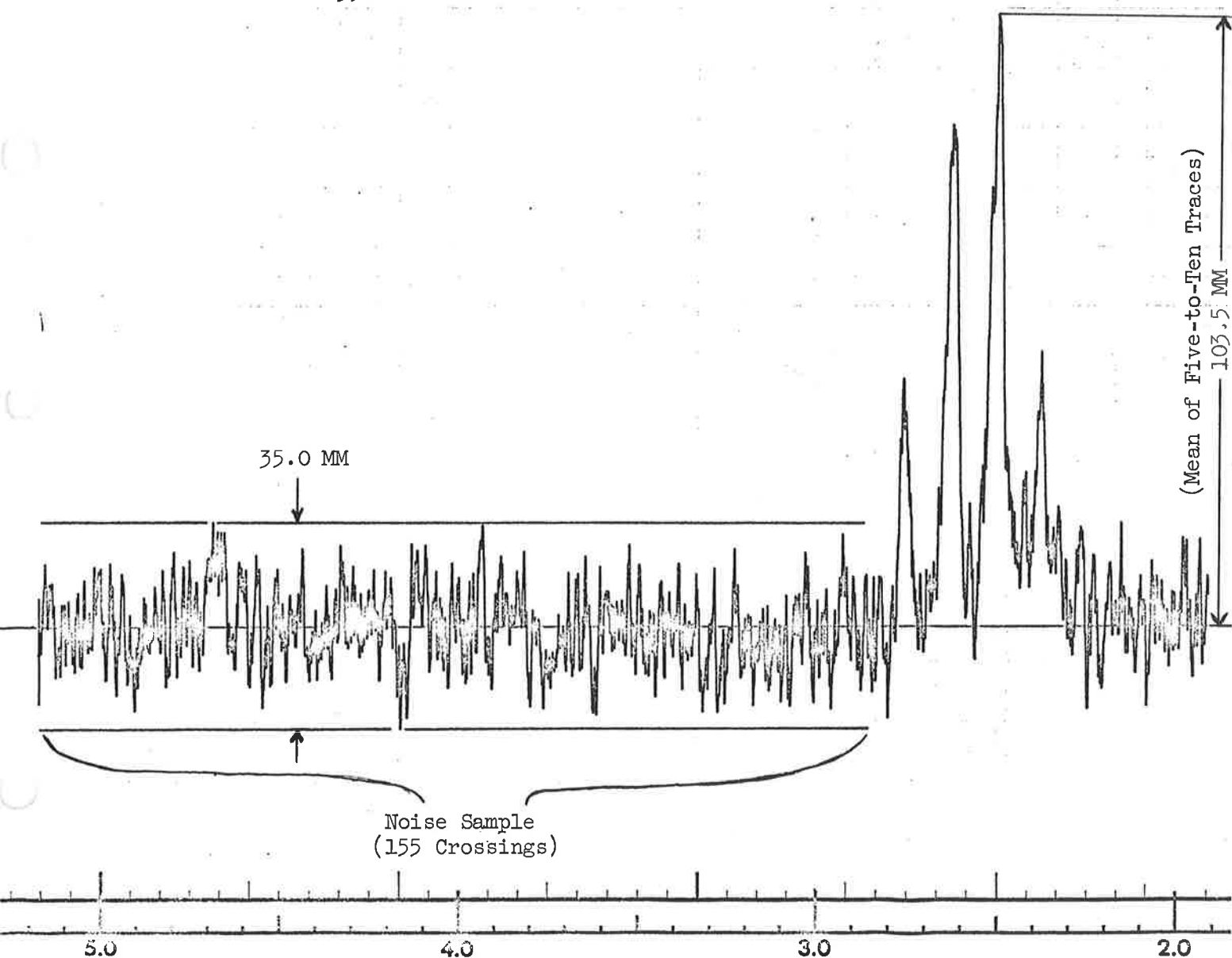
Figure 1

Example of Calculation of Signal-to-Noise Ratio

1% Ethyl Benzene in CCl<sub>4</sub> Solution in 4.28 mm., i.d. Cell

Filter Bandwidth	0.4 cps.
R.F. Field	0.16 mG.
Sweep Time	500 sec.
Sweep Width	500 cps.
Spectrum Amp.	500

$$\frac{S}{N} = \frac{103.5 \times 2.5}{35.0} = 7.4$$



Dr. C. von Planta



c/o F. HOFFMANN-LA ROCHE &amp; CO.

LIMITED COMPANY

ADDRESS: P.O. BOX 20700, BASLE 2, SWITZERLAND — TELEPHONE: 323820 — TELEGRAMS: ROCHE BASLE — TELEX: 62292

DEPARTMENT Phy.A. (= Physics department)  
Pa/to

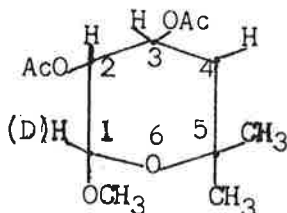
Basel, October 14, 1963

Dr. B.L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pa.

Dear Dr. Shapiro,

Here is my contribution to Mellon MR which I hope will not come too late.

"We have recently studied the conformation of the compound methyl-2-3-di-O-acetyl- $\alpha$ -noviosid which has the following structural formula:



By nuclear magnetic resonance spectroscopy it is possible to determine the conformation of the protons 2, 3 and 4 of the compound in question in  $\text{CDCl}_3$ -solution (10%). Spectrum no. 1 shows the signals of the protons 1, 2, 3 and 4. The spectrum should be treated as an ABCX spectrum with several vanishing coupling constants.

The corresponding compound deuterated in position 1 gives the spectrum no. 2. Now the spectrum is easily analysed as one of the ABX type revealing the following parameters:  $J_{24} = 0$ ,  $|J_{34}| = 10,1$  cps,  $\nu_4 = 203$  cps (to TMS).  $|J_{23}| = 3,4$  cps,  $\nu_3 = 321$  cps,  $\nu_2 = 314$  cps. On the spectrum no. 2 are also shown the lines calculated with the above parameters which fit rather nicely the experimental data.

From the values of the coupling constants we can deduce the conformation of the protons 2, 3 and 4: proton 2 equatorial, protons 3 and 4 axial.

-2-

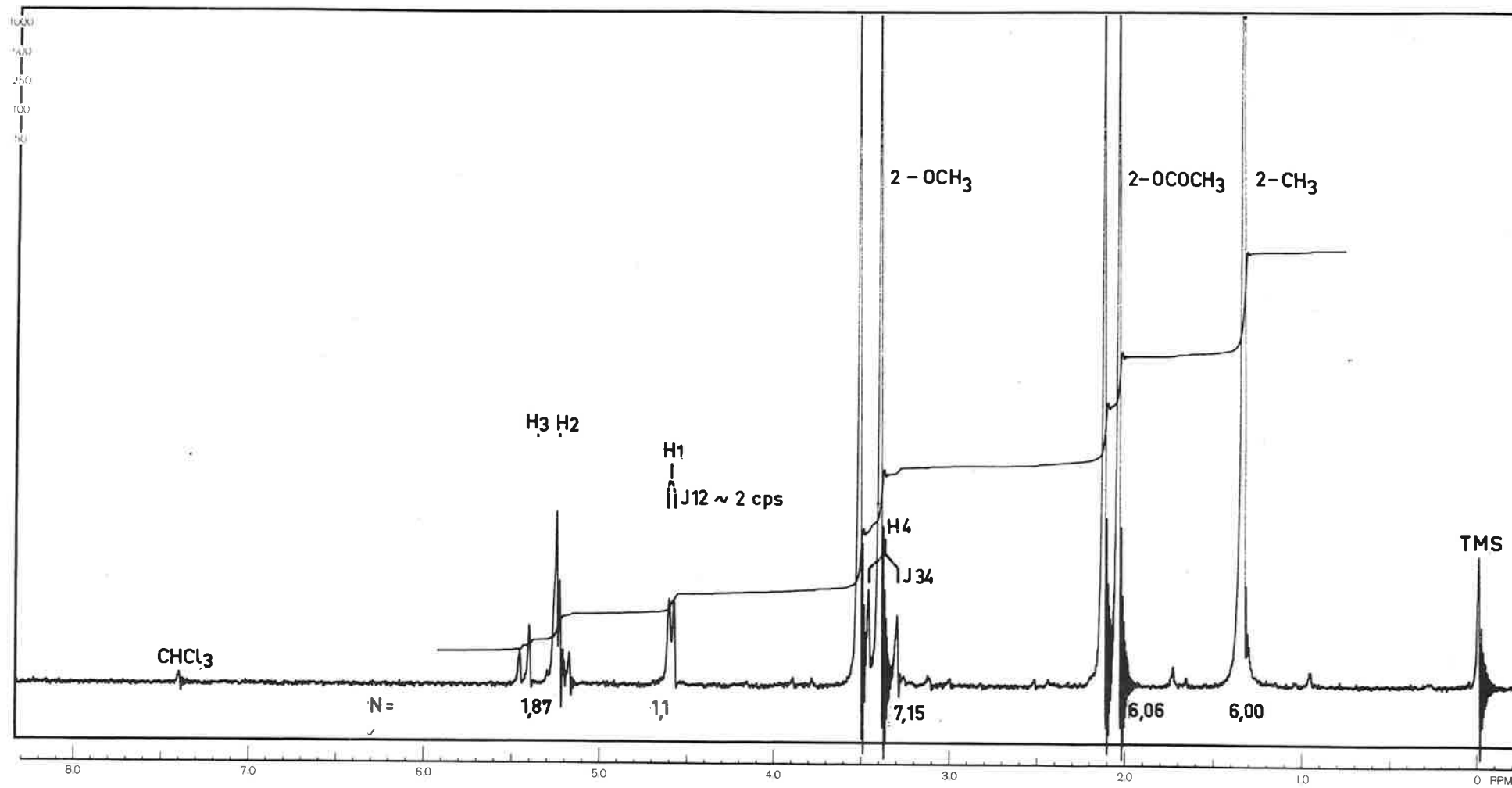
The compounds discussed here were prepared by Drs. Vater-  
laus and Furlenmeier of the chemical research department."

I thank you for sending us Mellon MR which is of great value.

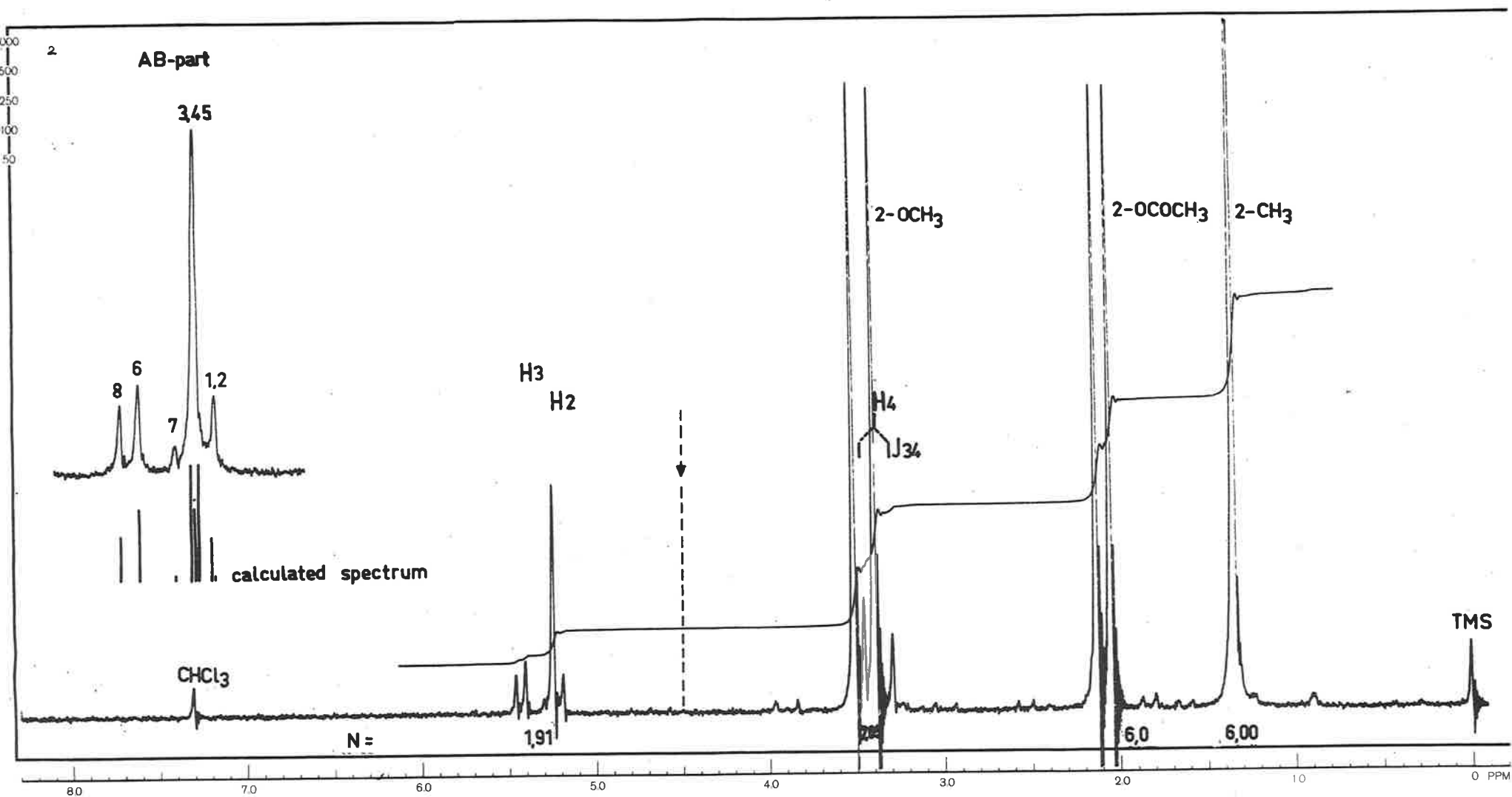
Sincerely yours,

*C. v. Plank.*

Spectrum no. 1



Spectrum no. 2





Herrn

Dr. B.L. Shapiro

Mellon Institute

4400 Fifth Avenue

Pittsburgh, Pa.

U.S.A.

Sehr geehrter Herr Dr. Shapiro!

Im Verlauf unserer Arbeiten über  $^{117,119}\text{Sn-H-}$  und  $^{207}\text{Pb-H-}$ Kopplungskonstanten fanden wir bei Methylcyclopentadienyl-Derivaten der genannten Isotope erstmalig eine Aufspaltung der Signale der olefinischen Protonen eines "Dien"-Cyclopentadienyl-Fünfringes. Diese Erscheinung ließ sich bisher für Verbindungen mit derartigen Liganden, wie etwa  $(\text{C}_5\text{H}_5)_2\text{Hg}$ ,  $\text{C}_5\text{H}_5\text{CuP}(\text{C}_2\text{H}_5)_3$  oder  $(\text{CH}_3)_3\text{SiC}_5\text{H}_5$ , niemals beobachten. Dabei zeigte sich, daß bei der Umsetzung des  $\text{SnCl}_4$  oder der Organobleihalogenide mit  $\text{Na-C}_5\text{H}_4\text{CH}_3$  die Metall-C-Bindung stets ausschließlich zu dem die Methylgruppe tragenden Kohlenstoffatom ausgebildet wird. Es wurden die in der Tabelle angeführten Verbindungen untersucht. Dabei ergab sich, daß die Aufspaltung der olefinischen Protonensignale des Fünfringes wesentlich von der Zahl und der Art der am Metall sitzenden Liganden abhängt.

Das  $^1\text{H-NMR}$ -Spektrum des  $(\text{CH}_3)_3\text{PbC}_5\text{H}_4\text{CH}_3$  zeigt noch für die olefinischen Protonen der Methylcyclopentadienyl-Gruppe nur ein von zwei Satelliten durch  $^{207}\text{Pb-H-}$ Spinkopplung begleitetes, scharfes Signal. Im Spektrum des  $(\text{C}_2\text{H}_5)_3\text{PbC}_5\text{H}_4\text{CH}_3$  jedoch findet sich für die olefinischen Protonen bereits ein  $\text{A}_2\text{B}_2$ -System mit verschiedenen Pb-H-Kopplungskonstanten für die relativ zur Methylgruppe  $\alpha$ - und  $\beta$ -ständigen Protonen. Die J-Werte für Pb-H( $\alpha$ ) sind jeweils größer als für Pb-( $\beta$ ). Im NMR-Spektrum des  $(\text{CH}_3)_2\text{Pb}(\text{C}_5\text{H}_4\text{CH}_3)_2$  findet sich gegenüber der Tri-äthyl-Verbindung ein Anwachsen der Pb-H( $\alpha$ ) und Pb-H( $\beta$ ) Kopplungskonstanten, wie auch der Kopplung zwischen Pb und Methylgruppe des  $\text{C}_5\text{H}_4\text{CH}_3$ . Interessanterweise wird für  $(\text{C}_5\text{H}_4\text{CH}_3)_4\text{Sn}$  keine Kopplung zwischen Zinn und den H( $\beta$ ) beobachtet.

Die Protonenresonanzspektren wurden mit einem Varian A60 Spektrometer aufgenommen. Die chemical shifts  $\delta$  [gegen intern.TMS positiv nach niedrigeren Feldstärken] und die Kopplungskonstanten sind alle in Hz angegeben.

Mit freundlichen Grüßen und herzlichem Dank für die MELLONMR Letters

Klaus P. Fritz

Gerd J. Knecht

Prof. Dr. Schwarzkopf

	(me) <sub>3</sub> Pb(mcp)	(ät) <sub>3</sub> Pb(mcp)	(me) <sub>2</sub> Pb(mcp) <sub>2</sub>	(mcp) <sub>4</sub> Sn
$\delta$ H( $\alpha$ )		344	338	289
$\delta$ H( $\beta$ )	344.5	355	350	349
$\delta$ CH <sub>3</sub> (C <sub>5</sub> H <sub>4</sub> CH <sub>3</sub> )	129	133	129	118
$\delta$ CH <sub>3</sub> (M-CH <sub>3</sub> )	37	-	28.5	-
$\delta$ C <sub>2</sub> H <sub>5</sub> (M-C <sub>2</sub> H <sub>5</sub> )	-	87	-	-
J <sub>M-CH<sub>3</sub></sub> (C <sub>5</sub> H <sub>4</sub> CH <sub>3</sub> )	17.5	15	25	21.5
J <sub>M-H(<math>\alpha</math>)</sub>	39.5	22	33	45.5
J <sub>M-H(<math>\beta</math>)</sub>		15	30	0
J <sub>M-CH<sub>3</sub></sub> (M-CH <sub>3</sub> )	58	-	51	-
J <sub>M-CH<sub>2</sub>-CH<sub>3</sub></sub>	-	36.5	-	-
J <sub>M-CH<sub>2</sub>-CH<sub>3</sub></sub>	-	149.5	-	-
Lösungsmittel	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>6</sub>	CS <sub>2</sub>
Konzentration[%]	10	50	10	10

me = -CH<sub>3</sub>, mcp = C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>. Die Vorzeichen der Kopplungskonstanten wurden nicht bestimmt. Die Satelliten für <sup>117</sup>Sn und <sup>119</sup>Sn wurden nicht einzeln festgelegt.

**U. S. INDUSTRIAL CHEMICALS CO.**

DIVISION OF NATIONAL DISTILLERS AND CHEMICAL CORPORATION

RESEARCH DEPARTMENT • 1275 SECTION ROAD • CINCINNATI 37, OHIO

October 10, 1963

Dr. Barry Shapiro  
Mellon Institute  
Pittsburgh 13, Pa.

Dear Dr. Shapiro:

In the course of developing an NMR quantitative method, we observed that the recorded integral of a NMR peak is slightly dependent on the sharpness of the peak. The difference in integrated area between a peak with maximum transient wiggles and the same peak without wiggles was found to be almost 10%. The peak with wiggles gave too high an integrated area.

The above observation was made on a Varian DP-60 Spectrometer with a V-3521 NMR Integrator and a Moseley 2D2 X-Y recorder. The pen speed of the recorder is 20 inch per second. The sweep rate of the magnetic field used was about 15 cps./second.

The cause of the mentioned variation is still not determined, and it could be fundamental or just instrumental. Since 10% variation in the integrated area could cause a serious error on most quantitative works such as hydrogen content determination, we feel we should present this information at the monthly "Mellon" letter for those who are working in the quantitative NMR field.

Very truly yours,

U. S. INDUSTRIAL CHEMICALS CO.

  
Hung Yu Chen

HYC/sbb

## LEDERLE LABORATORIES



A Division of AMERICAN CYANAMID COMPANY  
PEARL RIVER, NEW YORK (AREA CODE 914) 735-5000

October 14, 1963

Dr. Barry Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

For over a year we have used a sampling technique with our A-60 which might interest some of your readers.

A savings of 25-30% in sample size is achieved by using short lengths of glass rod in the bottom of the sample tubes. As a means of conserving scarce samples or obtaining a higher concentration for a small amount by decreasing the total volume, the method works quite well.

The maximum allowable length of glass rod is critical. For the ambient temperature probe, a rod 1/4" long is useable; for the variable temperature probe the glass rod is 5/16" long. The O.D. of the glass rod is an easy fit with the I.D. of the sample tubes.

Other advantages of this "semi-micro" technique are speed and convenience.

For comparison, we have included the spectrum of thymol (Spec. No. 270, Varian catalogue) in Varian thin wall and NMR Specialties medium wall sample tubes, with and without the glass plugs.

Sincerely yours,

*W. Fulmor*  
W. Fulmor  
*G. O. Morton*  
G. O. Morton

V. L. Canady  
Organic Chemical Research Section

*V. L. Canady*

WF:sao  
Enclosures (2)

Varian Thin Wall

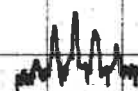
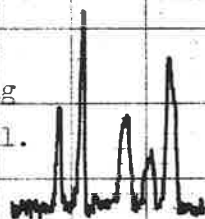
Spec. Amp. = 4.0

Sweep time = 500 sec.

Filter Bandwidth = 2 cps

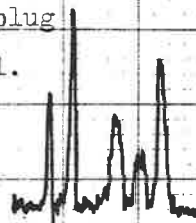
With glass plug

28 mg./0.28 ml.



Without glass plug

39 mg./0.39 ml.



NMR Specialties Medium Wall

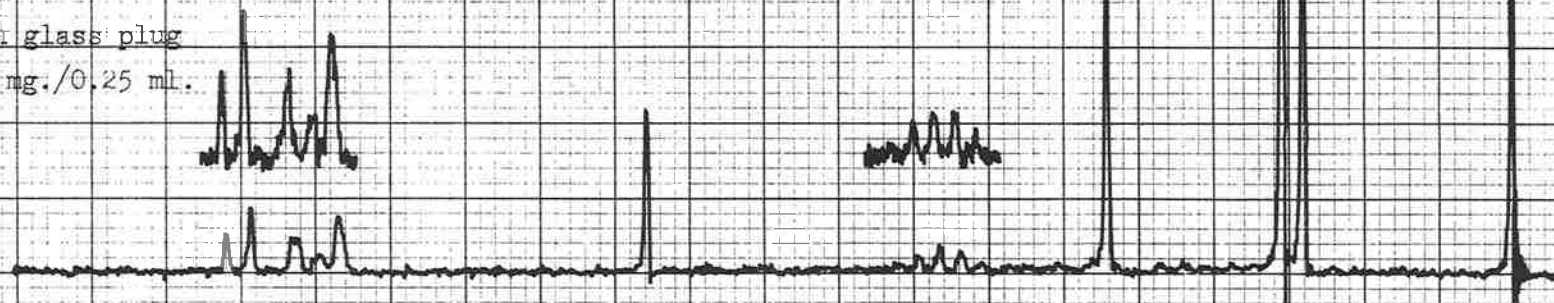
Spec. Amp. = 5.0

Sweep time = 500 sec.

Filter Bandwidth = 2 cps

With glass plug

25 mg./0.25 ml.



Without glass plug

18 mg./0.18 ml.



Oct. 16, 1963

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

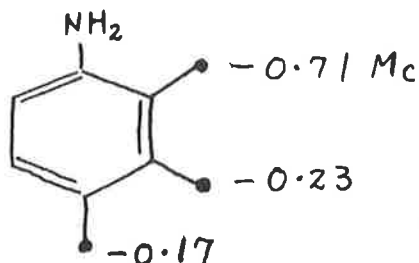
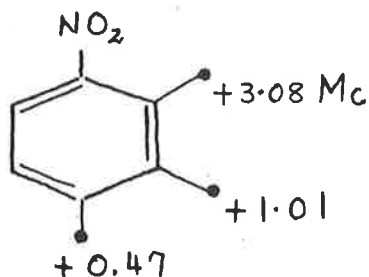
Effect of the Intramolecular Electric Fields  
on the Quadrupole Resonance Frequency

Dear Dr. Shapiro:

As you know the quadrupole frequency of the halogen nuclei in substituted benzenes depends on the position of the nuclei with respect to the functional group. The frequency shifts due to this position effect have been interpreted in terms of the inductive effect of the functional group, or of the charge density on the carbon atom. For example Hooper and Bray suggested that the frequency of  $\text{Cl}^{35}$  was expressed by the linear relationship with Hammett  $\sigma_1$  value:

$$\nu(\text{Cl}^{35}) = (34.826 + 1.024 \sum \sigma_1) \text{ Mc.}$$

However, our recent calculation shows that the effect of the intramolecular electric field due to the functional group on the  $\text{Cl}^{35}$  resonance is also significantly large. The field effect may often contribute more largely than the inductive effect at long-range distances from the functional group. The estimated shifts are briefly shown in the figure.



We have roughly estimated the frequency shift in the deuteron resonance.

Sincerely yours

清水 博

Hiroshi Shimizu

清水 恵子

Mitsuko Shimizu

Department of Chemistry  
College of Arts and Sciences  
Chiba University  
Chiba, Japan

# HARVARD UNIVERSITY

## DEPARTMENT OF CHEMISTRY

61-31

*12 Oxford Street*  
*Cambridge 38, Massachusetts, U.S.A.*  
October 23, 1963

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Barry:

Yesterday Charlie Krabek brought it to my attention that there might be other researchers interested in having a computer program capable of handling not only more than eight protons, but also capable of considering nuclei with spin greater than one-half.

In the course of my work here at Harvard I have written such a program for the I.B.M. 7090. This program can be used to calculate spectra for ten spins one-half, and it will handle nuclei up to spin three. The program computes the single resonance NMR spectrum for a set of coupling constants and chemical shifts which are given as input data. The program requires four scratch tape units.

I would be glad to send a listing of the Fortran deck with its subroutines to anyone interested. Unfortunately, the logistics of supplying duplicate decks seems overwhelming at present.

Very truly yours,

*Robert C. Hopkins*

Robert C. Hopkins

RCH:ms



## MICHIGAN STATE UNIVERSITY EAST LANSING

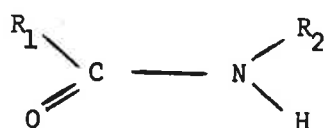
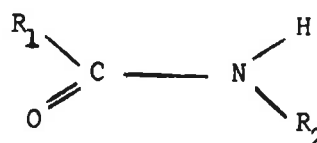
KEDZIE CHEMICAL LABORATORY • COLLEGE OF SCIENCE AND ARTS • DEPARTMENT OF CHEMISTRY

October 22, 1963

Dr. Bernard Shapiro  
 Mellons Institute  
 4400 Fifth Ave.  
 Pittsburgh, Pa.

Dear Barry:

Although some are already complaining about the amount of NMR work being done on amides, we continue to find them interesting and, to take the strain off DMF, DMA, etc., we have even made some new ones. There has been considerable discussion of configuration about the peptide bond in N-monosubstituted amides and, even recently, doubt has been expressed whether cis isomers are present. In four N-monosubstituted formamides

I cisII trans

(I or II with  $R_1 = H$  and  $R_2 = Me, Et, i-Pr, t-Bu$ ) cis isomers (I) have been found by NMR and the isomer ratio has been measured. At room temperatures in the pure liquids there is 8-18% cis isomer, with the percentage increasing as the size of group  $R_2$  increases.

The assignment of the more intense set of lines to the trans isomer could, of course, be made intuitively but it is supported by three more or less independent arguments outlined below.

- (1) The relative chemical shifts of the methyl resonances of the  $R_2$  group may be used to assign the peaks to the appropriate isomers (Hafton and Richards, Mol. Phys., 3, 253(1960) and 5, 139(1962); LaPlanche and Rogers, J. Am. Chem. Soc., 85, 0000(1963). The more abundant isomer has the methyl resonance at higher field ( $R_2 = Me, Et, i-Pr$ ) and so would be identified with the trans isomer by analogy with previous work on N, N-disubstituted amides.

- (2) In the proposed complexes with benzene noted in benzene solutions (see

above references) the ring is attracted to the amide nitrogen and tends to stay as far away from the carbonyl oxygen as possible. The upfield shift of the  $R_2$ -methyl peaks from the cis isomer would then be greater because of proximity to the benzene ring. It is indeed found that benzene dilution shifts the weaker set of  $R_2$ -methyl lines more rapidly to higher field so these would be assigned to the cis isomer.

- (3) The coupling constants between the formyl proton and the NH proton (in 1.0 M sulfuric acid solutions of the formamides) are larger for the isomer with the less intense set of lines, ( $R_2$  = Me, Et, i-Pr). The cis isomer has a trans arrangement of protons across the C-N bond, which is partially a double bond, and so should show the larger  $J_{\text{NH-CH}}$  value. Since this is observed we again would assign the weaker set of lines to the cis isomer.

It is gratifying that these diverse methods for assigning the lines agree so well. We conclude that in N-substituted formamides the trans form (II) predominates but there is always a measurable fraction of cis isomer(II) present. The interesting question of temperature dependence is being studied.

When the formyl proton is replaced by an alkyl group ( $R_1$  = Me, Et, i-Pr, t-Bu) only one set of lines is seen and the above criteria show that they are those from the trans isomer (II). Since the barrier is presumably too high for rapid rotational averaging, and accidental coincidence of the  $R_2$ -methyl group lines is unlikely by analogy with other compounds studied, the single set of lines indicates that less than about 2% of cis isomer is present. This is an expected result since steric interactions between  $R_1$  and  $R_2$  would make the cis isomer less stable as the size of  $R_2$  increases.

Coupling constants have been measured for the formamides in sulfuric acid solution. Protonation on oxygen in these solutions increases the fraction of cis isomer and again this is expected since the steric interaction between  $R_2$  and hydroxyl would be larger than in the unprotonated amide and the trans form relatively less favored.

As a separate matter I might mention that I will have post-doctoral appointments in NMR-EPR open for next year.

Yours sincerely,



Max T. Rogers  
Research Professor of Chemistry



Laurine LaPlanche

## UNIVERSITY OF ILLINOIS

Department of  
CHEMISTRY AND CHEMICAL ENGINEERING

URBANA

61803

The William Albert Noyes Laboratory

October 22, 1963

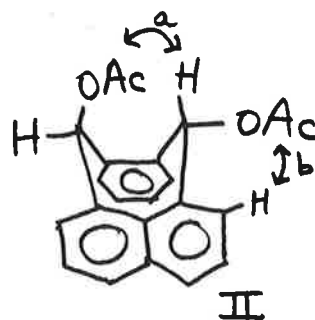
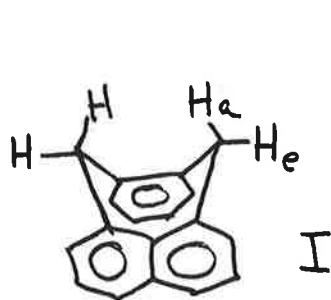
Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

As our initial contribution to Mellon-m-r, I would like to relate some preliminary results on conformational equilibria in the 7,12-dihydropleiadene system, which Mr. Joseph Bieron and I are investigating at the State University of New York at Buffalo and also here during my visiting lectureship.

We have studied the temperature dependence of the n.m.r. spectra ( $\text{CDCl}_3$ ) of 7,12-dihydropleiadene (I) and trans-7,12-diacetoxy-7,12-dihydropleiadene (II) on the A-60. The  $-\text{CH}_2-$  signal of I goes from a singlet at  $+30^\circ$  to an AB quartet ( $\delta_{\text{H}} = 73$  c.p.s.,  $J_{\text{ae}} = 15$  c.p.s.) at ca.  $-30$  to  $-35^\circ$ . In II, we follow the acetate methyl group which is a singlet (7.8 $\tau$ ) at room temp. and gives a doublet ( $\delta_{\text{H}} = 15$  c.p.s.) at  $-25^\circ$ . We have calculated activation parameters, using the Gutowsky-Holm eq. for relating  $k$  to  $T_c$  and Plette and Anderson's fast exchange approximation for line width measurements above  $T_c$ .

The data are summarized below:



$T_c$	$+7^\circ$	$+7$
$k(\text{at } T_c)$	$162 \text{ sec}^{-1}$	$33 \text{ sec}^{-1}$
$\Delta F^\ddagger$	13.6	14.5
$E_a$	12	10.8
$\Delta S^\ddagger$	-5.7 e.u.	-13.2 e.u.

Dr. B. L. Shapiro  
October 22, 1963  
Page 2

Inspection of models suggests that 7- and 12- substituents should raise ground state energies more than (planar) transition state energies, due to "bow-stern" and "peri-H" interactions (a and b in II, above) in the folded, boat-like ground state. In the case of II, however, the rotational barrier is higher than I, rather than lower, and we are inclined to attribute this to the large  $-\Delta S^\ddagger$  in II, which results from the partial freezing of rotation in the acetate groups necessary to permit passage over the transition state.

The values given are being checked by further measurements and related work in this ring system is in progress. We feel that these data, although still not on quantitative grounds, provide an interesting example of entropy effects in conformational changes.

Sincerely yours,



Peter T. Lansbury  
Associate Professor



U. S. NAVAL ORDNANCE TEST STATION  
CHINA LAKE, CALIFORNIA

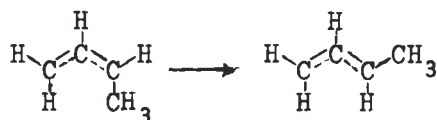
IN REPLY REFER TO:

5052/DWM:tp  
21 Oct 1963

Dr. Bernard L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Barry:

When our earlier NMR studies of 1-methyl- $\pi$ -allylcobalt tricarbonyl (and its homologs) showed that the complex could be synthesized as a mixture of *syn*- and *anti*- isomers, we decided to go ahead and see what thermodynamic information might be gleaned from a kinetic study of the *anti*  $\rightarrow$  *syn* isomerization reaction:



The experimental work consisted of several months of reaction rate measurements and equilibrium constant determinations at temperatures from 40° to 140°C. NMR provided the analytical means for estimating the isomer ratio, a value readily obtained from the relative heights of the *syn*- and *anti*-methyl doublets. No other analytical method could have provided such a straightforward measure of this variable.

What we found was an equilibrium constant varying from 20 to 30, favoring the *syn*- isomer. The lower stability of the *anti*- isomer is a consequence, we believe, of steric repulsion between the methyl and the 1- position proton. The homologous 1,3-dimethyl complex was found to exist only as the less hindered *syn*, *syn*- or *syn*, *trans*- forms, while the 1,1,3 trimethyl complex existed only in the less hindered form with only one *trans*- methyl. Efforts to synthesize a 1,1,3,3-tetramethyl complex failed, presumably because of the prohibitive steric repulsion between two *trans*- methyls.

From the temperature-dependence of the equilibrium constant we obtained an estimate of the heat of reaction of 1.85 kcal/mol, close to the average value of  $\Delta F = RT \ln K = 2.15$  kcal/mol.

The rate measurements yielded both forward and reverse rates and activation energies, since the previously measured equilibria provided the ratio of forward and reverse rates. The specific rate expressions are:

$$K_1 = 0.869 \times 10^{13} \exp (-29.0 \times 10^3/RT) \text{ sec}^{-1}$$

$$K_2 = 0.527 \times 10^{13} \exp (-30.8 \times 10^3/RT) \text{ sec}^{-1}$$

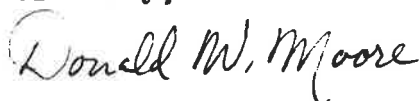
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21 Oct 1963

The activation energies are somewhat less than the values listed for normal cis-trans isomerizations (35-45 kcal/mol) and probably reflect the lowered bonding energy of the delocalized  $\pi$ -system.

We hope to present this work at the forthcoming Southwestern Regional ACS meeting in December.

Sincerely,

A handwritten signature in cursive script that reads "Donald W. Moore". The signature is written in dark ink and is positioned above the typed name.

DONALD W. MOORE

Code 5052

General Research Branch

# Battelle Memorial Institute

5 0 5   K I N G   A V E N U E   C O L U M B U S ,   O H I O   4 3 2 0 1

AREA CODE 614, TELEPHONE 299-3191

October 23, 1963

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh, Pennsylvania

Dear Barry:

We have been looking into the problem of end-group analysis and molecular weight determination of polyalkylene glycols and polyalkylene glycol esters and have submitted an abstract of our work for consideration by the Pittsburgh Conference Committee for presentation at the 1964 Conference. Possibly some of the MELLONMR readers will be interested in a few of our results.

We have noted that in solvents like pyridine it is possible to differentiate methylene and methine groups attached to a hydroxyl group from those attached to an ether oxygen. This effect is demonstrated quite nicely by the enclosed 60 Mc./sec. spectra of the  $-\text{CH}_2-$  resonances of triethylene glycol. In  $\text{CDCl}_3$  the outer components of the  $\text{A}_2\text{B}_2$  spectrum of the  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-$  groups are barely discernable - the central portion of the  $\text{A}_2\text{B}_2$  spectrum being hidden by the resonance of the four equivalent  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$  protons. In pyridine, however, one can clearly see and integrate the low field portion of the  $\text{A}_2\text{B}_2$  spectrum. This makes it possible to calculate number average molecular weights without using the  $-\text{OH}$  resonance area and thus circumvents the problem of obtaining low molecular weight values because of the presence of a small amount of water.

For example, the molecular weight of a sample designated as Carbowax 600 was calculated to be 422 using the hydroxyl and methylene resonances measured in  $\text{CDCl}_3$  solution. However, using pyridine and only data derived from the  $-\text{CH}_2-$  resonances we calculate a molecular weight of 592 for the same sample. By boiling point elevation of benzene the molecular weight was found to be 596. The difference between 422 and 592 corresponds to only 2 per cent by weight of  $\text{H}_2\text{O}$ .

## Battelle Memorial Institute

Dr. B. L. Shapiro

2

October 23, 1963

We have used this technique with polyethylene glycols to molecular weight 6000, with several polypropylene glycols and with some esters. However, we are presently awaiting the delivery of a new digital voltmeter and with it we should be in a much better position to define the limits of the technique.

We shall send you more data after we have received our voltmeter.

Best personal regards.

Yours truly,



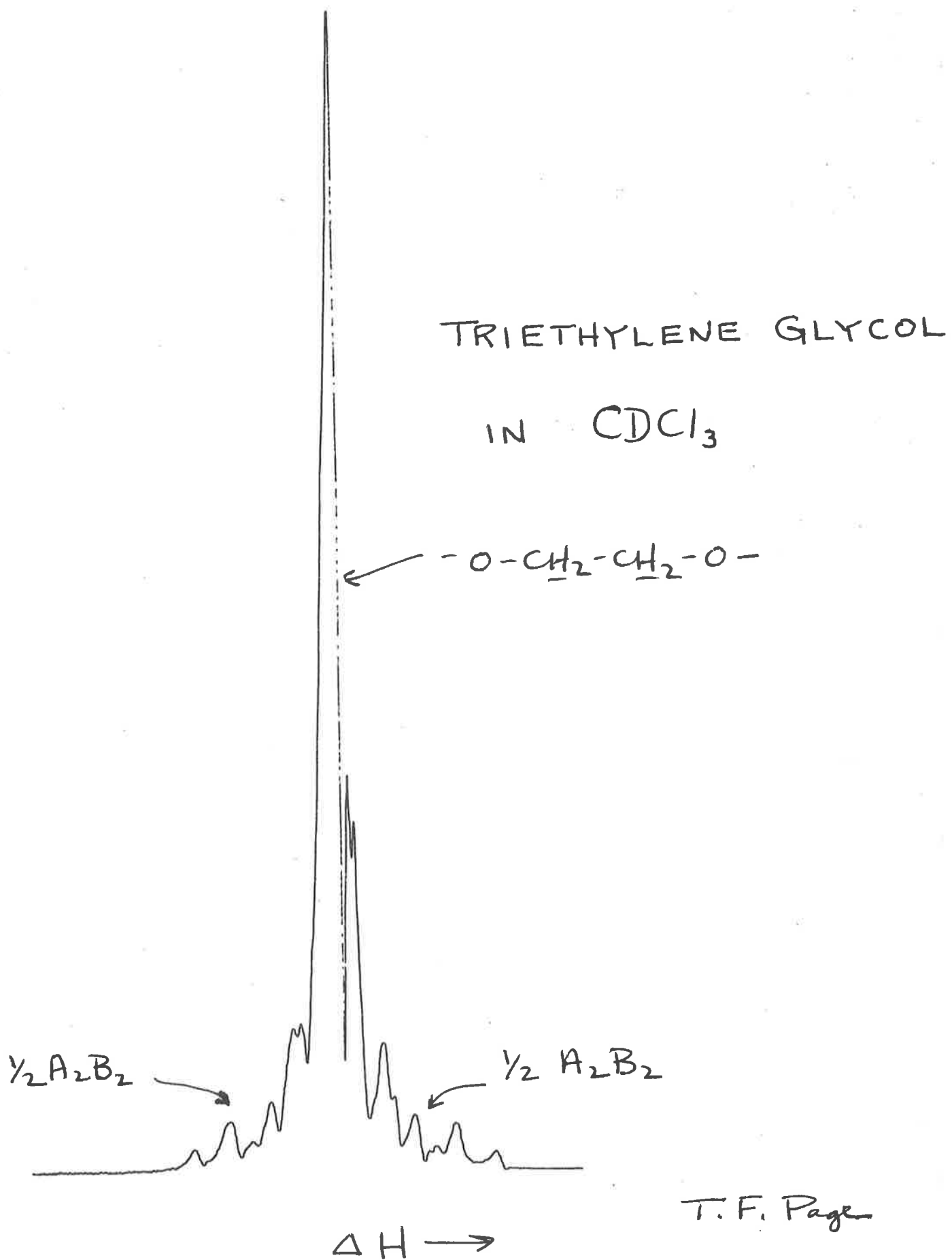
Thomas F. Page, Jr.



Warren E. Bresler  
Molecular Spectroscopy

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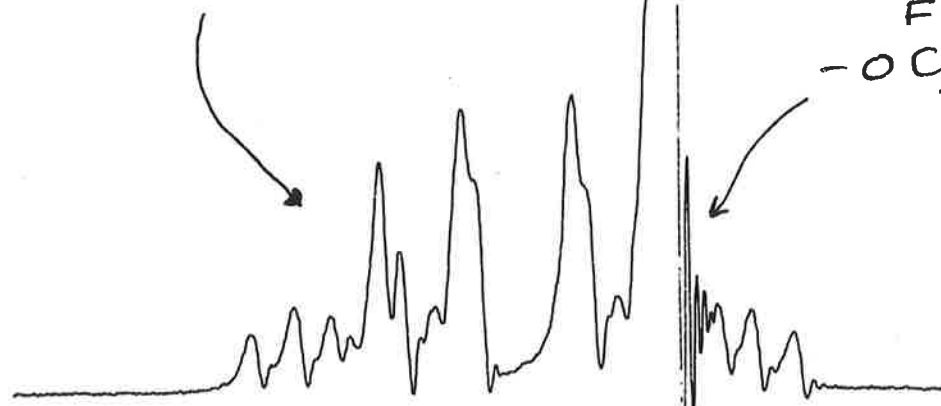


## TRIETHYLENE GLYCOL

IN PYRIDINE

 $\frac{1}{2} A_2 B_2$ 

FROM

 $-CH_2-\underline{CH_2}-OH$  $-O-CH_2CH_2-O-$  $\frac{1}{2} A_2 B_2$ 

FROM

 $-O\underline{CH_2}CH_2OH$  $\Delta H \rightarrow$ 

T. F. Page

## STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY

Department of  
Chemistry and Chemical Engineering

October 24, 1963

Dr. Bernard L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

We have recently developed a general molecular orbital treatment of spin-spin coupling of directly bonded nuclei and have applied it to  $C^{13}$ -H couplings in substituted methanes of the form CHXYZ. This formulation, which uses bonding orbitals, takes into account substituent effects and yields a square-root additivity rule, namely

$$\sqrt{J_{CH}} = \eta_x + \eta_y + \eta_z \quad (1)$$

where  $\eta_x$ ,  $\eta_y$  and  $\eta_z$  are parameters associated with the individual substituents.

The above theoretical expression is derived on the basis of the approximate second-order perturbation theory of Ramsey and on the assumption that the Fermi contact term is dominant. The ground-state wave function is constructed from equivalent orbitals which are orthonormal and which obviously possess values at the hydrogen nucleus as well as at the carbon nucleus.

If the four equivalent orbitals are designated  $\psi_1$ ,  $\psi_x$ ,  $\psi_y$  and  $\psi_z$ , then the completely antisymmetrized wave function for the bonding electrons of the molecule is

$$\Psi_0 = \frac{1}{(8!)^{1/2}} \sum_{\mathcal{P}} (-1)^{\mathcal{P}} \mathcal{P}^{\mathcal{P}} [\psi_1(1)\alpha(1) \psi_1(2)\beta(2) \psi_x(3)\alpha(3) \psi_x(4)\beta(4) \\ \times \psi_y(5)\alpha(5) \psi_y(6)\beta(6) \psi_z(7)\alpha(7) \psi_z(8)\beta(8)].$$

Symbols  $\alpha$  and  $\beta$  designate the two possible spin coordinates of an electron.  $\mathcal{P}^{\mathcal{P}}$  is the permutation operator exchanging the space and spin coordinates of the electrons. When this wave function is placed in the Fermi contact expression the following equation results:

$$J_{CH} = 6K (H_1C_1 + H_xC_x + H_yC_y + H_zC_z)^2. \quad (2)$$

Dr. Bernard L. Shapiro

-2-

October 24, 1963

In this equation

$$K = \frac{2}{12 h \Delta} \left( \frac{16 \pi \hbar}{3} \right)^2 \gamma_C \gamma_H ,$$

$H_1$  is the value of  $\psi_1$  at the hydrogen nucleus,  $C_x$  is the value of  $\psi_x$  at the carbon nucleus, etc.

In order to delve into the nature of the products  $H_1C_1$ ,  $H_xC_x$ ,  $H_yC_y$  and  $H_zC_z$ , it is necessary to specify wave functions  $\psi_1$ ,  $\psi_x$ ,  $\psi_y$  and  $\psi_z$  for a series of substituted methanes. Such information is not available at this time and the validity of Eq. (2) must await the determination of these functions.

Eq. (2) can be made to yield an additivity rule provided certain assumptions are made, some more plausible than others. Although the constant  $K$  contains the average of the electronic excitation energy,  $\Delta$ , we will assume that  $K$  is independent of substituent effects. In addition we will assume that the product  $H_1C_1$  is associated with the equivalent orbital of the C-H bond and remains constant for the substituted methanes. Furthermore products  $H_xC_x$ ,  $H_yC_y$  and  $H_zC_z$  are assumed to be predominantly dependent upon substituents X, Y and Z, respectively, and are assumed to vary independently. We can now define parameters  $\eta_x$ ,  $\eta_y$  and  $\eta_z$  as follows:

$$\begin{aligned} \eta_x &= (6K)^{\frac{1}{2}} (1/3 H_1C_1 + H_xC_x) , \\ \eta_y &= (6K)^{\frac{1}{2}} (1/3 H_1C_1 + H_yC_y) , \\ \text{and } \eta_z &= (6K)^{\frac{1}{2}} (1/3 H_1C_1 + H_zC_z) . \end{aligned}$$

Each  $\eta$  factor is associated with a substituent. Eq. (2) becomes Eq. (1), a square-root additivity rule.

Table I shows that Eq. (1) reasonably summarizes the data. The factors, shown in Table II, were obtained by fitting the data with a method of least squares.

A more detailed description of this work is being sent to the Journal of Chemical Physics for publication.

Sincerely yours,

*Edmund R. Malinowski*

Edmund R. Malinowski  
John P. Larmann  
L. Z. Pollara

Table I. A comparison of observed and calculated values of  $J_{CH}(CHXYZ)$ 

CHXYZ	$J_{CH}(\text{obs})$ (cps)	$J_{CH}(\text{calcd})$ (cps)	CHXYZ	$J_{CH}(\text{obs})$ (cps)	$J_{CH}(\text{calcd})$ (cps)
CH <sub>4</sub>	125 <sup>a</sup>	123	CH <sub>2</sub> Cl <sub>2</sub>	178 <sup>a</sup>	178
CH <sub>3</sub> F	149 <sup>a</sup>	151	CHCl <sub>2</sub> CN	189 <sup>b</sup>	191
CH <sub>3</sub> Cl	150 <sup>a</sup>	149	CHCl <sub>3</sub>	209 <sup>a</sup>	210
CH <sub>3</sub> Br	152 <sup>a</sup>	150	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> F	151 <sup>c</sup>	157
CH <sub>3</sub> I	151 <sup>a</sup>	148	CH <sub>2</sub> F <sub>2</sub>	185 <sup>c</sup>	192
CH <sub>3</sub> CN	136 <sup>a</sup>	133	CHF <sub>3</sub>	238 <sup>c</sup>	233
CH <sub>3</sub> COOH	130 <sup>a</sup>	127	CHFC1 <sub>2</sub>	220 <sup>c</sup>	217
CH <sub>3</sub> CH <sub>3</sub>	126 <sup>a</sup>	122	CHF <sub>2</sub> Cl	231 <sup>c</sup>	225
CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	126 <sup>a</sup>	124	CH <sub>2</sub> (COOH) <sub>2</sub>	132 <sup>c</sup>	132
CH <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	127 <sup>b</sup>	126	CH <sub>2</sub> ClCOOH	152 <sup>c</sup>	154
CH <sub>3</sub> CH <sub>2</sub> I	149 <sup>b</sup>	146	CHCl <sub>2</sub> COOH	181 <sup>c</sup>	183
CH <sub>3</sub> CH <sub>2</sub> Br	151 <sup>b</sup>	148	CH <sub>3</sub> OCH <sub>3</sub>	140 <sup>c</sup>	142
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	152 <sup>b</sup>	151	CH <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub>	162 <sup>c</sup>	163
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	153 <sup>b</sup>	151	CH(OCH <sub>3</sub> ) <sub>3</sub>	186 <sup>c</sup>	185
(CH <sub>3</sub> ) <sub>2</sub> CHBr	151 <sup>b</sup>	146	CHBr <sub>3</sub>	206 <sup>a</sup>	211
CH <sub>2</sub> ClCN	161 <sup>b</sup>	161	CH <sub>2</sub> FCN	166 <sup>d</sup>	168
CH <sub>2</sub> I <sub>2</sub>	173 <sup>a</sup>	176	CHF <sub>2</sub> CN	206 <sup>d</sup>	205
CH <sub>2</sub> Br <sub>2</sub>	178 <sup>b</sup>	179	CH <sub>2</sub> (CN) <sub>2</sub>	145 <sup>d</sup>	145

<sup>a</sup> N. Muller and P. E. Pritchard, J. Chem. Phys., 31, 768, 1471 (1959).

<sup>b</sup> Observed in this laboratory by Richard Magee, National Science Foundation Undergraduate Research Participant, 1961.

<sup>c</sup> N. Muller and P. I. Rose, J. Am. Chem. Soc., 84, 3973 (1962).

<sup>d</sup> G. P. van Kelen and Z. Eckhaut, J. Mol. Spec., 10, 141 (1963).

Table II. Substituent Factors,  $\eta$ , for Various Groups

Substituent	$\eta$ (cps <sup>1/2</sup> )	Substituent	$\eta$ (cps <sup>1/2</sup> )
-H	3.69	-OCH <sub>3</sub>	4.53
-F	5.08	-C <sub>6</sub> H <sub>5</sub>	3.77
-Cl	4.82	-CN	4.17
-Br	4.84	-COOH	3.89
-I	4.79	-CH <sub>3</sub>	3.60

## MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH 13, PA.

October 22, 1963

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pa.

Dear Barry:

I was very much interested in Peter Bladon's letter (MELLONMR #60 p. 16) on the chlorofluorobenzenes. We have been doing similar studies on these compounds as well as on the bromo-fluorobenzenes and several benzotrifluorides.

We have found two interesting features concerning these highly substituted compounds:

- (1) The additivity relationship of Gutowsky<sup>1</sup> et al., shows large deviations in a number of cases.
- (2) The meta fluorine-fluorine coupling constant varies widely while the ortho and para coupling are much less affected by substitution.

Concerning the first point, we predicted the F19 chemical shifts using the equation

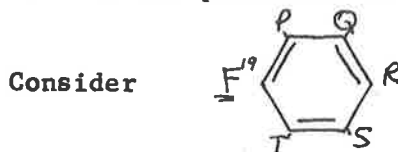
$$\phi^* \text{ (predicted)} = 113.23 + \Sigma F^{19} \text{ shielding parameters}$$

where 113.23 is the  $\phi^*$  value for fluorobenzene according to the Filipovich, Tiers definition<sup>2</sup>. The shielding parameters were taken from the data of Gutowsky<sup>1</sup> or Taft<sup>3</sup> and where necessary, converted into ppm with positive numbers corresponding to increased shielding relative to CFC13.

- 
1. H. S. Gutowsky, et al. J. Am. Chem. Soc., 74, 4809 (1952).
  2. G. Filipovich and G. V. D. Tiers, J. Phys. Chem. 63, 761 (1959).
  3. R. W. Taft, Jr., J. Phys. Chem., 64, 1805 (1960).

## 2.

These predicted shift values are shown in Table III. We applied a correction factor to the predicted shifts as follows:



If the predicted shift of  $F^{19}$  deviates from the observed shift, it is probably due to the perturbation of P by Q, T by S, etc. It was thought, therefore, that a measure of these effects might be obtainable empirically. The empirical relationship which we derived is as follows:

$$\phi^* (\text{corrected}) = \phi^* (\text{predicted}) - (P_o, Q_m) + (T_o, S_m)$$

where subscripts o and m indicate ortho and meta substituents to the  $F^{19}$  atom in question and in that respective order. The secondary effect of para substituents was ignored.

By looking at deviations of predicted and observed shifts we got the following table of correction factors.

Table I

$(P_o, Q_m)$	Correction Factor
(X, H) or (H, X) where X = H, F, Cl etc	0
(Br, F)	1
(F, Br)	4
(Cl, F)	1
(F, Cl)	3
(F, F)	4
(Cl, Cl)	7
(Br, Br)	7

The corrected  $F^{19}$  shift values are shown in Table III. The  $\Delta(C - O)$  values when compared to the  $\Delta(P - O)$  values are a measure of the worth of the correction in compounds studied. This correction is certainly not 100% valid but it considerably improves the predicted  $F^{19}$  shift values in most cases. Table II summarizes the  $J_{FF}$  data which we obtained from the compounds studied. The large variation of meta  $J_{FF}$  with substitution is interesting, but we have no explanation for it at present.

Table II  $J_{FF}(\text{cps})$ 

<u>ortho</u>	<u>meta</u>	<u>para</u>
20.5; 20.1	1.6; 1.7; 1.8	7.9; 8.0
20.0; 20.2	1.9; 2.2; 2.3	9.7; 9.8
20.2; 20.9	2.4; 4.3; 5.8	
20.6; 20.2	5.8; 6.1; 6.9	
20.0	9.5	

<sup>a</sup>  
 $\phi^*$  Values for Some Polysubstituted Fluorobenzenes

61-47

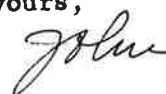
Substituents	$\phi^*$ Predicted	$\phi^*$ Observed	$\phi^*$ Corrected	$\Delta (P-O)^b$	$\Delta (C-O)^b$
2,4,5-Tri F, 3,6-DiCl	143	140	139	3	-1
2,3,4,6-Tet Cl, 5-F	117	109	109	8	0
2,6-DiCl, 3,5-DiF	112	110	110	2	0
2,4-DiCl, 3,5-DiF	113	112	112	1	0
2,6-DiCl, 3,4,5-TriF	119	119	117	0	-2
2,3,5-TriF, 4,6-DiCl	139	135	134	4	-1
2,4,6-TriF, 3,5-DiCl	167	161	161	6	0
2,4,6-TriCl, 3,5-DiF	116	113	114	3	1
2,3,4,5-TetCl, 6-F	141	131	131	10	0
2,3,4-TriF, 5,6-DiCl	143	136	132	7	-4
2,3,6-TriF, 4,5-DiCl	163	156	156	7	0
2,6-DiBr, 3,4,5-TriF	102	102	100	0	-2
2,3,5-TriF, 4,6-DiBr	130	125	125	5	0
2,4,6-TriF, 3,5-DiBr%	167	156	159	11	3
2-Br, 3,4,5-TriF	108	109	107	-1	-2
2,3,5-TriF, 6-Br	127	125	122	2	-3
2,3,5-TriF, 4-Br	135	133	131	2	-2
2,4,6-TriF, 3-Br	169	162	165	7	3
2,3-DiF, 5,6-DiBr	128	117	117	11	0
2,3-DiF, 4,5-DiBr	136	133	132	3	-1
2,6-DiF, 3,4-DiBr	165	156	161	9	5
2,3,4-TriF, 5,6-DiBr	135	125	124	10	-1
2,3,6-TriF, 4,5-DiBr	162	154	154	8	0
2-Br, 3,5-DiF	102	102	101	0	-1
3,5-DiF, 4-Br	109	109	109	0	0
2,6-DiBr, 3,5-DiF	96	94	94	2	0
2,4-DiBr, 3,5-DiF	104	103	103	1	0
2,4,6-TriBr, 3,5-DiF	98	95	96	3	1
2,5-DiBr, 3,4,6-TriF	134	132	129	2	-3
2,3-DiF, 4,6-DiBr	133	125	129	8	4
2,6-DiF, 3,5-DiBr	160	153	152	7	-1
2,3,5-TriF, 4-CF <sub>3</sub> , 6-Cl	131	126	126	5	0
2,6-DiCl, 3,5-DiF, 4-CF <sub>3</sub>	107	104	105	3	1

(a)  $\phi^*$  in ppm where CFC1<sub>3</sub> is taken as zero.

(b)  $\Delta (P-O) = \phi^* (\text{predicted}) - \phi^* (\text{observed})$ ;  $\Delta (C-O) = \phi^* (\text{corrected}) - \phi^* (\text{observed})$

Very truly yours,

J. J. Burke







TEXAS CHRISTIAN UNIVERSITY  
FORT WORTH, TEXAS

DEPARTMENT OF CHEMISTRY

October 23, 1963

Dr. Barry L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

Noting the recent interest on the part of your contributors regarding long range coupling constants, we thought they might be interested in a case which just turned up in the course of our work. The n.m.r. spectrum is given in the accompanying figure.

The coupling between the two methylene groups amounts to 1.3 c.p.s., and, as will be noted, there is an informal structural similarity between our case and that of santonin reported previously by Randall (MELLONMR 49-22). The splitting of the ring methylene group is quite obvious. However, the ethyl group methylene is somewhat more complicated presumably because of second order splitting by the methyl

Yours sincerely,

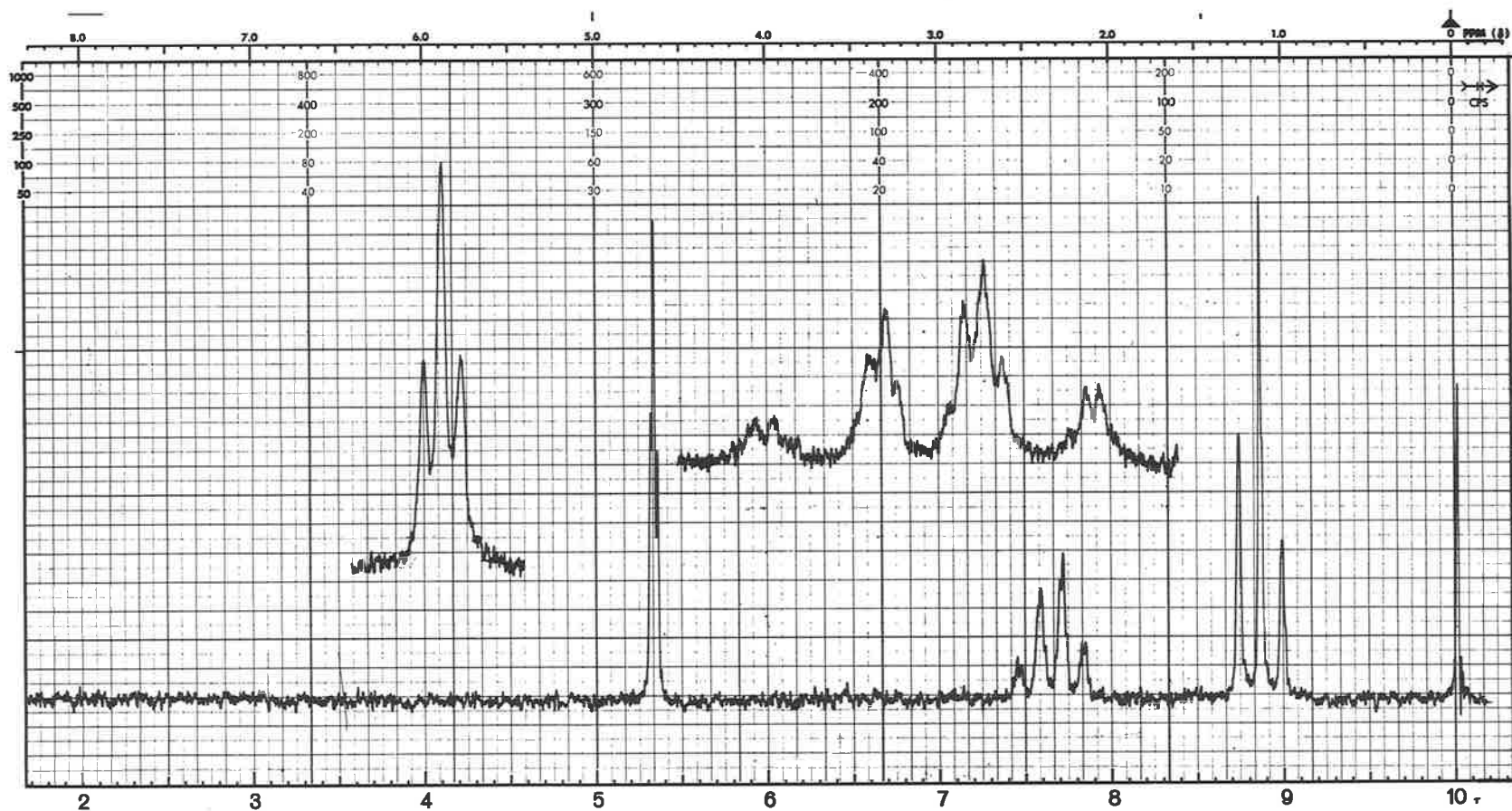
W. B. Smith

*W. B. Smith*

B. A. Shoulders

*B. A. Shoulders*

WBS/dc



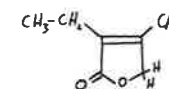
# 60 MC PROTON NMR SPECTRUM

DATE . . . . . SPECTRUM

TEMP. 42 °C OPERATOR BAS

SOLVENT. CCl<sub>4</sub> STD: Me<sub>4</sub>Si ✓

SAMPLE . . . . .



SWEEP WIDTH 500 CPS  
 SWEEP OFFSET 0.00 CPS  
 SWEEP TIME 5.00 SEC  
 FILT. BAND. 2 CPS  
 R.F. FIELD 9.12 MG  
 SPEC. AMP. 10X1.6  
 INT. AMP. . . . .  
 REMARKS: . . . . .

offset is 100 cps.  
 full scale;

NUCLEAR MAGNETIC



RESONANCE SPECIATIES

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- "Aucuparin and Methoxyaucuparin, Two Phenolic Biphenyl Derivatives from the Heartwood of *Borbus Aucuparia* (L.)"  
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