16. Sept. 64

Prenas

Illinois
Institute of
Technology
N – M – R
Newsletter

No. 71
AUGUST, 1964

Deadline for Next Issue: 21 September 1964

FAIRCHILD   300 ROBBINS LANE, SYOSSET, L. I., NEW YORK · 516 WE 1-4500 · TWX: 516 433-9121 · CABLE FAIRCAM SYOSSET NEW YORK

SPACE AND DEFENSE SYSTEMS
A DIVISION OF FAIRCHILD CAMERA
AND INSTRUMENT CORPORATION

July 23, 1964

Dr. B. L. Shapiro, Editor IIT-NMR
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

Asa Leifer and I have been looking at the N. M. R. spectra of some heterocyclic
compounds. In the case of 2-thiol-Δ^2-thiazoline - two different structures can
be written for the molecule. These structures are represented as follows:-

CH$_2$ ——— S   CH$_2$ ——— S
| | | |
CH$_2$ C ——SH   CH$_2$ C = S
   \   //   \   /
    N   N
                                            |
                                            H
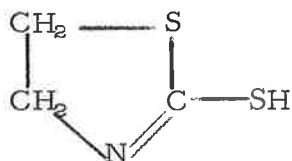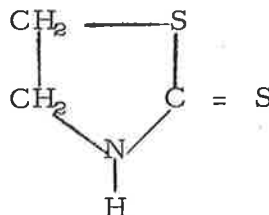
    (I)   (II)

The NMR spectrum of this compound was obtained in the mixed solvent (1:1)
consisting of CDCl$_3$ and (F$_2$ClC)$_2$CO· 2-1/2D$_2$O with TMS present as an internal
standard. There is a very broad band at 299 cps. upfield from TMS which is a result
of a single hydrogen absorption.

Since the absorption band is very broad it appears that the hydrogen is connected
to the nitrogen. That is, this absorption band is broadened by the quadrupole
moment of the nitrogen. If the hydrogen was connected to the sulfur the single
hydrogen absorption band would be sharp. On the basis of this data the structure
of this compound is II. i. e. the thiol form, if present, is in very low concen-
tration.

Sincerely yours,

Jim

Asa Leifer and J. E. LuValle

AL:JELV/mi

Koninklijke Shell-Laboratorium, Amsterdam

BADHUISWEG 3   AMSTERDAM - N.

TELEFOON (020) - 6 11 11

Dear Dr. Shapiro,

Contributions to relaxation in molecules such as HF, $CHFCl_2$ with two non-identical spins may be made by intra- and intermolecular interaction between identical and non-identical spins. It is possible to devise an experiment which allows the contributions from the various interactions to be determined. The nuclear spins (S and I) are supposed to be coupled through a small scalar interaction $J \bar{S}.\bar{I}$. For $S = I = \frac{1}{2}$ four lines are observed corresponding to four magnetizations. These magnetizations are proportional to differences in occupation numbers of the energy levels, e.g. $S_+ = const. (N_{++} - N_{-+})$, etc. Transition probabilities ω_0, ω_2, ω_1 and ω_1' are defined according to Solomon[1].

The equations of motion of the total S and I magnetizations are[1]:

$$\frac{dS}{dt} = \frac{d}{dt}(S_+ + S_-) = -(\omega_0 + 2\omega_1' + \omega_2)(S - S^0) - (\omega_2 - \omega_0)(I - I^0) \qquad (1a)$$

$$\frac{dI}{dt} = \frac{d}{dt}(I_+ + I_-) = -(\omega_2 - \omega_0)(S - S^0) - (\omega_0 + 2\omega_1 + \omega_2)(I - I^0) \qquad (1b)$$

where S^0 ($= S_+^0 + S_-^0$) is the equilibrium value of the S magnetization.

Shimizu and Fujiwara[2] also considered the decay of the difference between the magnetizations of each spin; this decay is purely exponential:

$$\frac{d}{dt}(S_+ - S_-) = -2(\omega_1 + \omega_1')(S_+ - S_-) \qquad (1c)$$

$$\frac{d}{dt}(I_+ - I_-) = -2(\omega_1 + \omega_1')(I_+ - I_-) \qquad (1d)$$

The relaxation equations for intramolecular interaction have to be modified for intermolecular relaxation. One then has to consider relaxation transitions within a collision complex of two molecules. This four-spin system has available 16 energy levels between which ω_2^*, ω_0^*, ω_1^* and $\omega_1^{*\prime}$ transitions are possible. The transition probabilities are starred to indicate that they originate from translation.

We distinguish between SI, SS and II relaxation processes. In the first type an ω_2^* process means a simultaneous transition of two spins due to interaction of an S and an I spin on different molecules, e.g. from the state $(++)_A(++)_B$ to $(+-)_A(-+)_B$, etc. for molecules A and B.

The equations of motion, when SI interactions are considered, analogous to (1), become:

$$\frac{dS}{dt} = -(\omega_2^* + 2\omega_1^{*\prime} + \omega_0^*)(S - S^0) - (\omega_2^* - \omega_0^*)(I - I^0) \qquad (2a)$$

$$\frac{dI}{dt} = -(\omega_2^* - \omega_0^*)(S - S^0) - (\omega_0^* + 2\omega_1^* + \omega_0^*)(I - I^0) \qquad (2b)$$

$$\frac{d}{dt}(S_+ - S_-) = -(2\omega_1^{*\prime} + 2\omega_1^* + 2\omega_2^* + 2\omega_0^*)(S_+ - S_-) \qquad (2c)$$

$$\frac{d}{dt}(I_+ - I_-) = -(2\omega_1^{*\prime} + 2\omega_1^* + 2\omega_2^* + 2\omega_0^*)(I_+ - I_-) \qquad (2d)$$

Thus the time constant of $(S_+ - S_-)$ (or $(I_+ - I_-)$) depends on whether the relaxation is intra- or intermolecular. The question whether the relaxation is due to interactions between like or unlike spins can be answered when the magnitude of the Overhauser effect is known.

The experiment has been performed at 56.4 MHz on liquid $CHFCl_2$ at $-135°C$, where the main relaxation mechanism is the dipole-dipole interaction[3]. In the steady-state Overhauser experiments an enhancement of 0.45 has been measured for both spins, showing that fluorine is relaxed by hydrogen and vice versa.

- 2 -

To study the total and difference magnetizations, S_+ is inverted by an adiabatic passage and the decays S_+ and S_- are simultaneously recorded; $(S_+ + S_-)$ and $(S_+ - S_-)$ can then be computed as a function of time. The same can be done for the I-spins. For a dipolar relaxation mechanism[1]:

$$\omega_2^* : \omega_0^* : \omega_1^{*\prime} : \omega_1^* = \omega_2 : \omega_0 : \omega_1^\prime : \omega_1 = 12 : 2 : 3 : 3$$

From this relation and the experimental decay of $(S_+ + S_-)$ the slope of $(S_+ - S_-)$ can be predicted for the two limiting cases of intra- and inter-molecular relaxation.

The experimental data have been collected in the figure. The full curve, $(S_+ - S_-)$, is a best fit of (1b) or (2b) to these points. The dashed lines are the decays of $(S_+ - S_-)$ predicted by (1d) (intra-) and (2d) (inter-molecular interactions). It is clear that the experimental data for $(S_+ - S_-)$ broadly follow the latter curve, so that $CHFCl_2$ at -135°C relaxes predominantly by intermolecular interaction between unlike spins.

Yours sincerely,

C. Maclean   E.L. Mackor

Amsterdam, 10th June 1964
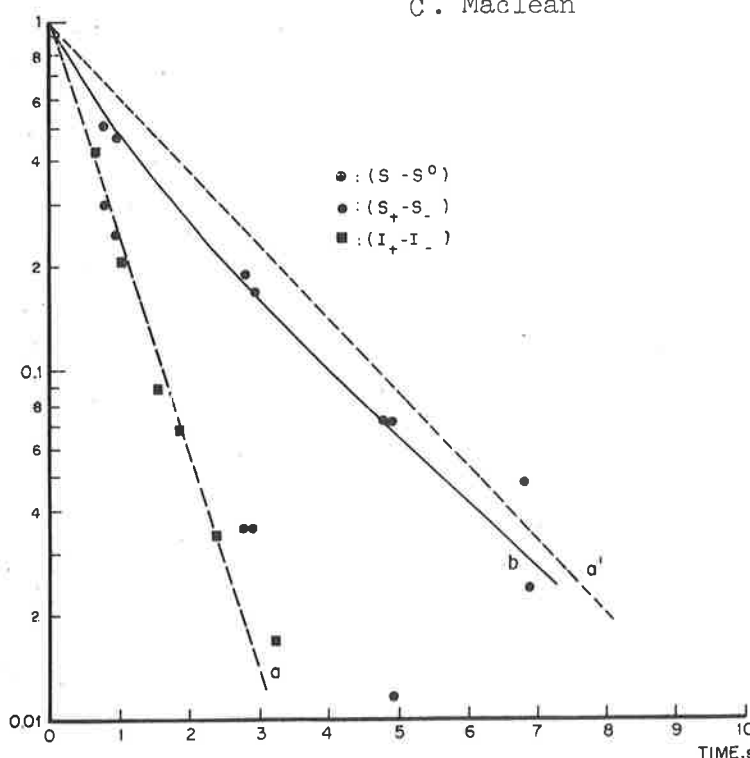
Decays of sum and difference magnetizations after an adiabatic flip through a fluorine line (S_+).
Initial values of S_-, I_+ and I_- correspond to equilibrium; the magnetizations have been scaled to $S° = I° = 1$.
a and a' : difference magnetizations calculated for inter- and intramolecular relaxation.
b   : sum magnetization of fluorine spins ($S-S°$); the solid curve has been fitted to the experimental points: ⊕

References:
1. I. Solomon, Phys. Rev. 99 (1955) 559
2. H. Shimizu and S. Fujiwara, J. Chem. Phys. 34 (1961) 1501
3. R.J.C. Brown, H.S. Gutowsky and K. Shimomura, J. Chem. Phys. 38 (1962) 76

UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY

COBB CHEMICAL LABORATORY   July 22, 1964   CHARLOTTESVILLE, VA.

Upfield Shifts Caused by Divalent Metal Ion
Binding to Amino Acids and Peptides

We have had occasion to note the effects of divalent transition metal ions on chemical shifts of ligand hydrogens in amino acids and peptides. Several workers have previously noted the downfield shifts caused by the addition of transition metal ion to solutions containing free base form of a ligand. We have verified this result in the case of the zinc (glycinate)$_2$ complex, for which the proton signal appears 0.17 ppm downfield from that of free glycinate anion. This shift is in the direction expected for additional positive charge near ligand hydrogens. More to the point, however, is a comparison of the shifts caused by complexed metal ions with ligands of the same net charge as those in the complex. Thus zero net charge zinc (glycinate)$_2$ exhibits an upfield shift of 0.22 ppm compared to dipolar ion glycine. Susceptibility corrections have been taken into account in all figures mentioned here.

Lesser upfield shifts have been observed in cadmium and zinc ion complexes of histidine and cysteine when compared with free ligand of the same net charge as that of ligand in the complex. For instance, for the zinc ion complexes of histidine and cysteine the upfield shifts are 0.03 and 0.17 ppm for the respective α hydrogens and 0.06 and 0.11 ppm for the β hydrogens. For the diamagnetic nickel (cysteinate)$_2$ complex the upfield shifts are much greater, 0.44 and 0.75 ppm for the α and β hydrogens, respectively.

A large shift is also observed in the yellow diamagnetic nickel ion complex of tetraglycine. On passing from cationic to anionic tetraglycine the total upfield shift per unit of charge of all four pairs of carbon bound hydrogens is 0.45 ppm. The total upfield shift on going from anionic tetraglycine to the -2 charged nickel-tetraglycine complex is 2.16 ppm, nearly five times greater than above. Since the pronounced upfield shifts induced by diamagnetic nickel ions occur in two different types of ligand, they appear to be a feature of diamagnetic nickel ion and not of the ligands involved.

Raj Mathur
R. Bruce Martin

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

July 20, 1964

Dear Professor Shapiro:

I am sorry that you had to remind me again for sending in our contribution to LITNMR Newsletter.

I have calculated the dependence of the line-shape of NMR spectrum on the rate of slow chemical exchanges of resonating nuclei, by treating the chemical exchanges in a quantum mechanical way. From the views of the quantum mechanics the nuclei-exchange processes may be regarded as a kind of quantum mechanical resonances. The main results of our treatment are: (1) The average rate of the exchange, $\overline{\omega}_e$, is decreased by applying an external magnetic field and is given by

$$\overline{\omega}_e = \frac{1}{2}\omega_e \left(1 + \frac{1}{\sqrt{1 + (\omega_s/\omega_e)^2}} \right).$$

The maximum decrease of the rate constant will be expected when $|\omega_e/\omega_s| \ll 1$, where ω_s is the chemical shift and ω_e is the original rate constant before the field is applied. (2) The collapse of two lines whose intensities are mutually same is qualitatively given as shown below, where we define as $\omega_e = 2K\sin 2\theta$ and $\omega_s = 2K\cos 2\theta$.
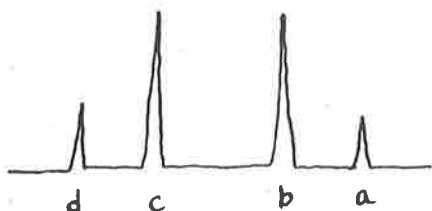
$$\omega_a = \frac{1}{2}\omega_e + K \quad ; \quad I_a = 1 - \sin 2\theta$$
$$\omega_b = -\frac{1}{2}\omega_e + K \quad ; \quad I_b = 1 + \sin 2\theta$$
$$\omega_c = \frac{1}{2}\omega_e - K \quad ; \quad I_c = 1 + \sin 2\theta$$
$$\omega_d = -\frac{1}{2}\omega_e - K \quad ; \quad I_d = 1 - \sin 2\theta$$

The collapse of NMR multiple lines due to other causes such as restricted motions and quadrupole relaxations are now being studied in a similar way under the collaboration of Dr. Y. Arata.

I have been invited from Professor Baldeschwiler to send the academic year 1964-1965 studing nuclear magnetic resonance phenomena in the Department of Chemistry at Harvard University. I would be happy if I could visit some of the contributers of the LIT NMR Newsletter.while I am in U. S. A.

Yours sincerely

H. Shimizu

H. Shimizu
Department of Chemistry
Chiba University
Chiba, Japan

FACULTE DES SCIENCES

DE MARSEILLE

Place Victor Hugo

(3 ème)

Laboratoire de Chimie Organique

Marseille, le 11 Juillet 1964

Tél. 64.11.60

J. METZGER

Professeur

Dans le cadre d'une étude par la R.M.N. de la molécule du Thiazole :
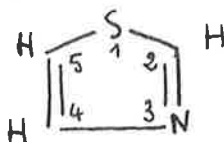
et de ses dérivés les plus simples (Alkoylés et Halogénés) nous avons prêté une attention toute particulière à une technique fort intéressante qui est la recherche des couplages du type C_{13}-H.

La difficulté de la méthode provient du fait que l'isotope C_{13} est relativement rare (1,1 %) et donc les signaux de couplages sont très faibles et cela d'autant plus s'il faut opérer en solution dans un solvant, ce qui est le cas pour les composés solides.

Néammoins nous sommes parvenus à dresser un tableau assez complet des couplages de cette sorte relatifs aux diverses positions 2,4 et 5 du cycle (voir tableau)

D'autre part, dans notre laboratoire, Monsieur H.A. BRAUN poursuit la synthèse de composés marqués à 60 % environ au carbone C_{13} en une des 3 positions. Ces produits enrichis nous ont permis de vérifier l'exactitude des valeurs avancées, puisque le couplage C_{13}-H en position 2 pour le thiazole est exactement de 210,2 cps.

D'autre part cela nous a permis de trouver un couplage C_{13}-H à longue distance entre le carbone 13 en position 2 et le proton en position 4 :

$$ J = 12,5 \text{ cps} $$

.../...

...$/$...
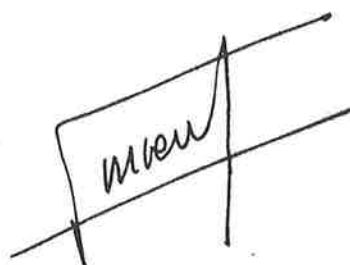
alors que le couplage entre le même carbonne et le proton 5 n'est semble-t-il que de 3 à 4 cps (mais cette dernière mesure a été entachée d'imprécision du fait de la forme de quadruplet du proton en 5, couplé avec les protons 2 et 4)

Les composés marqués en 4 et en 5 vont être bientôt disponibles, ce qui nous permettra, espérons-nous de compléter cette étude et d'en tirer des conclusions sur la nature des liaisons dans la molécule du Thiazole.

<u>COUPLAGES</u> C_{13}-H (en c.p.s.)

Composés	Position 2	Position 4	Position 5
Thiazole	210,2	184	189
Me$_2$ thiazole		183,8	187,5
Me$_4$ thiazole	212,0	-	185,5
Me$_5$ thiazole	212,5	183,5	-
Di-Me$_{24}$ thiazole	-	-	183,0
Di-Me$_{25}$ thiazole	-	179,5	-
Di-Me$_{45}$ thiazole	208	-	-
Cl$_2$ thiazole	-	189	189
Cl$_4$ thiazole	214	-	194
Cl$_5$ thiazole	214,5	190,0	-
Di-Cl$_{25}$ thiazole	-	193	-

E.J. VINCENT

Maître - Assistant

LABORATOIRE DE SPECTROSCOPIE HERTZIENNE

ANNEXE DU

LABORATOIRE DE RECHERCHES PHYSIQUES A LA SORBONNE

I, RUE VICTOR COUSIN, PARIS-V·

1762/RF/MNF

PARIS, LE **10 juillet 1964**

ODÉon : 24-13 POSTE 263

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

CHICAGO 16, Illinois
U. S. A.

Dear Professor B.L. Shapiro,

Researches in the field of nuclear magnetic resonance led to connect the chemical shift δ, or the spin-spin coupling constant J or line width to different physical constants (ε , μ , σ , pK...).

Likewise, infrared absorption spectroscopy pushed on to bind frequency band ν , or intensity |A|, or width L, to various physical constants (n, ε ,...).

The improvements of infrared (Perkin Elmer 125) and N.M.R. (Varian A 60) technics instigated us to unite infrared and N.M.R. results for some INTRA or INTER molecular bonds.

I. - INTRAMOLECULAR BONDS : Connection between shift δ (N.M.R.) and intensity |A|

P. JOUVE's results (Comptes Rendus Acad. Sc. France 1963, 256, 5120), are summarized in fig. 1 : there is a good connection between stretching band ν ($\equiv$ CH) intensity A and chemical shift δ, in various CCl_4 solutions of alkynes (concentration 0,4 mole/liter). These data were recently emphasized by other results on absolute intensity |A| for zero concentration solutions, in the case of the fondamental and 2nd and 3rd overtones of the streching vibration.

P. JOUVE has generalized fig. 1 data in comparing A (infrared) and δ (N.M.R.) measurements, which were realized by different authors, in the field of halogenated compounds (for example HF, HCl, HBr, HI or CH_3X series, or hydroxyl compounds (fig. 2).)

II. - INTERMOLECULAR BONDS

Variations $\Delta \nu$ (infrared) and variations $\Delta \delta$ (N.M.R.)

G. MAVEL (Thèse Paris 1960) had connected the infrared variations of water streching frequency to chemical shift variations $\Delta \delta_{H_2O}$, of water solutions in various organic solvents.

Mme Maryvonne MARTIN extended this result to organic solutes : she pointed out (''chloroform method'' Annales de Physique 1962) the advantage to enlarge for organic solutions the idea of ''basicity'' (i. e. pK in aqueous medium) with the idea of ''complexing power'' (i. e. $\Delta \delta_{\infty} CHCl_3$ in organic medium, for infinite dilution).

Drawing out her previous work concerning OH, OD, NH (Annales de Physique 1962), Mme Maryvonne MARTIN with Gérard MARTIN connected the infrared frequency variations $\Delta \nu$(C-Br) and the complexing power of solvents represented by $\Delta \delta_{\infty} CHCl_3$. Fig. 3 summarizes their results (saturated and vinylic bromides in many organic solvents).

These authors have also connected $\Delta \nu$ (C-Br) to the change of chemical shift $\Delta \delta$(C-H) of proton in the same bromide molecules (Comptes Rendus Acad. Sci. 1963, 257, 1048).

Variations $L\Delta \nu$ (infrared) and variations $\Delta \delta$ (N.M.R.)

P. JOUVE has studied acetylenic compounds in about 30 solvents and has showed, in this case, that infrared intensity |A| is little affected. He has introduced $L\Delta \nu$ (band width $\times$ variation of infrared frequency) better than $\Delta \nu$ alone. Fig. 4 summarizes his results.

Sincerely yours

R. FREYMANN

Top-left graph (INFRARED):

A . mole^{-1} cm^{-2}
INFRARED

HC≡C–◯–C≡CH

◯ C≡CH / C≡CH

◯–C≡CH

8000

CH$_3$–C–CH$_3$ / CH$_2$=C–C≡CH (CH$_3$)

7000

CH$_2$=C–C≡CH | CH$_3$ ⟶ ▱–C≡CH | –CHO–C≡CH

◯–C≡CH

6000

BrCH$_2$–C≡CH
ClCH$_2$–C≡CH

–CH$_3$OOC–C≡CH

HC≡C–(CH$_2$)$_3$–C≡CH
CH$_3$–(CH$_2$)$_2$–C≡CH

–CH$_3$–CH$_2$–O–CH$_2$–C≡CH

CH$_3$ / CH$_3$–C–C≡CH / CH$_3$

N.M.R.
δ∞ CCl$_4$ p.p.m.

5000

0   1   2   3   4

Top-right graph:

|A| cm.mole^{-1}
d'après
S.S.Penner et D.Weber
OKsengorn

×10^5

|A|=105×10^5
δ=2,5
HF

100

75

|A|=38×10^5
δ=–0,45
HCl

50

25

|A|=13×10^5
δ=–4,35 HBr

|A|=0,3×10^5
δ=–13
HI

δ R.M.N. d'après W.G.Schneider

–15   –10   –5   0   p.p.m.

Bottom-left graph:

Δν$_{C–Br}$ cm^{-1}

× CH$_3$/CH$_3$ CH–Br

o CH$_3$CH$_2$Br

H/H C=C Br/H

H/H C=C Br/CH$_3$

10

5

Δδ∞ (CHCl$_3$)   Δδ∞ (CHCl$_3$)

0,5   1,0   p.p.m.   0,5   1,0 p.p.m. 1,5

Bottom-right graph:

L Δν cm^{-2}
I.R.

2ν(≡C–H)
◯–C≡C–H

CH$_3$–C≡N

6000

C$_3$H$_7$–C≡N
CH$_3$NO$_2$

4500

ICH$_3$ +   CH$_2$I$_2$

CHBr$_2$–CHBr$_2$

3000

CHBr=CHBr   CHBr$_3$
CH$_2$Cl$_2$

HCCl$_3$
CS$_2$ CCl$_3$–CH$_3$

1500

CCl$_2$=CCl$_2$
CH$_2$=CH(CH$_2$)$_2$–CH$_3$ CCl$_4$
CCl$_2$F–CCl F$_2$ C$_{10}$H$_{18}$
CH$_3$–(CH$_2$)$_4$–CH$_3$ C$_6$H$_{12}$

δ∞ R.M.N.

0   2,50   2,75   9,00   3,25   p.p.m.

Top-left graph:

A mole^{-1}cm^{-2}
INFRARED

HC_3C ⬡ $-C\equiv CH$

$C\equiv CH$ / $C\equiv CH$ (⬡)

⬡$-C\equiv CH$

$CH_3-\overset{CH_3}{\underset{CH_2=C-C\equiv CH}{C}}-CH_3$

$CH_2=C-C\equiv CH$ → □$-C\equiv CH$ ⊣$-CHO-C\equiv CH$
$\overset{}{\underset{CH_3}{}}$

⬡$-C\equiv CH$

$BrCH_2-C\equiv CH$
$ClCH_2-C\equiv CH$ ⊣$-CH_3OOC-C\equiv CH$

$HC\equiv C-(CH_2)_3-C\equiv CH$ ⊣   ⊣$-CH_3-CH_2-O-CH_2-C\equiv CH$
$CH_3-(CH_2)_2-C\equiv CH$ ⊣

⊣$\overset{CH_3}{\underset{CH_3}{-CH_3-C-C\equiv CH}}$

δ_∞ CCl_4 p.p.m   N.M.R.

0   1   2   3   4

Top-right graph:

|A|cm. mole^{-1}
d'après
S.S.Penner et D.Weber
Oksengorn

×10^5

|A|=105×10^5
$\delta = 2,5$ HF

100

75

50

|A|=38×10^5
$\delta = -0,45$ HCl

25

|A|=13×10^5
$\delta = -4,35$ HBr

|A|=0,3×10^5
$\delta = -13$
HI

δ R.M.N. d'après W.G.Schneider

-15   -10   -5   0   p.p.m.

Bottom-left graph:

ν_{C-Br} cm^{-1}

× $\overset{CH_3}{\underset{CH_3}{}}$CH-Br

$CH_3 CH_2Br$

+ $\overset{H}{\underset{H}{}}C=C\overset{Br}{\underset{H}{}}$

□ $\overset{H}{\underset{H}{}}C=C\overset{Br}{\underset{CH_3}{}}$

$\Delta\delta_\infty$ (CHCl$_3$) $\Delta\delta_\infty$ (CHCl$_3$)

0,5   1,0   p.p.m.   0,5   1,0 P.p.m. 1,5

-7.64

Bottom-right graph:

$L\Delta\nu$ cm^{-2}
I.R.

$2\nu(\equiv C-H)$
⬡$-C\equiv C-H$

6000

$CH_3-C\equiv N$ +

$C_3H_7-C\equiv N$
CH_3NO_2

4500

ICH_3 +   + CH_2I_2

$CHBr_2-CHBr_2$

3000

$CHBr=CHBr$ $CHBr_3$
CH_2Cl_2

$HCCl_3$
CS_2 CCl_3-CH_3

1500

$CCl_2=CCl_2$

$CH_2=CH(CH_2)_2-CH_3$ CCl_4
$CCl_2F-CCl F_2$ ⬡⬡$C_{10}H_{18}$
$CH_3-(CH_2)_4-CH_3$ ⬡C_6H_{12}

δ_∞ R.M.N.

2,50   2,75   9,00   3,25   p.p.m.

July 29, 1964

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

Dear Dr. Shapiro,

An Uncommon Virtual Coupling Effect

I would like to draw your attention to a case of virtual coupling [1] involving a hydroxyl hydrogen. Hall [2] has commented on the spectrum of 1,3,5-tri-O-benzoyl-α-D-ribofuranose (I, R = H) and noted that the hydroxyl hydrogen appears as a doublet (9.7 cps.) at τ 7.14 in chloroform solution. As hydrogen 1 appears as a sharp doublet which does not change on treatment of the chloroform solution with D_2O, it follows that H^1 is not coupled with the hydroxyl hydrogen. Examination of the spectrum of I in mixtures of acetone and chloroform shows that as the % acetone increases, the doublet due to the hydroxyl hydrogen moves to low field, eventually merging into the complex of peaks due to hydrogens 2,4, and 5. At the same time, the doublet due to H^1 and the quartet due to H^3 become modified, the former changing to a triplet in 4:1 = $Me_2CO:CDCl_3$ and to a quartet in acetone itself, and the latter changing to a complex multiplet of 5 or 6 peaks in these solvents. An acetone solution spectrum of the O-deuterated compound (I, R = D) showed H^1 and H^3 as a doublet and a quartet respectively, identical with the signals observed for the chloroform solution, hence the "extra" multiplicity of the signals due to H^1 and H^3 in the acetone solution spectrum must be due to virtual coupling of these two protons to the strongly coupled system $\underline{H}^2$-C-O$\underline{H}$.

In the application of n.m.r. spectroscopy to structure problems, it's generally concluded that a multiplet which has its multiplicity reduced on exchanging a hydroxyl hydrogen for deuterium is most probably due to a proton in the environment $\underline{H}$-C-OH. The observations above show another instance in which this reasoning would not be valid, the other case being the obvious one (though not often observed) of long range coupling to a
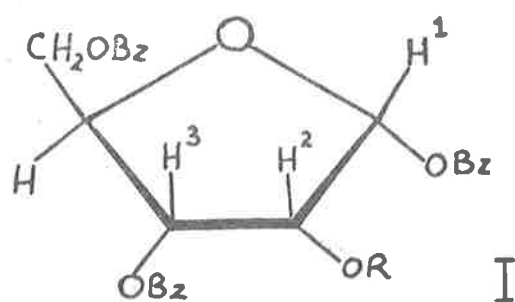
hydroxyl hydrogen[3].

1. J. I. Musher and E. J. Corey. Tetrahedron 18, 791 (1962).
2. L. D. Hall. Chem. & Ind. 1963, 950.
3. H. Ott, A. J. Frey, and A. Hofmann. Tetrahedron 19, 1675 (1963), foot-note No. 8.
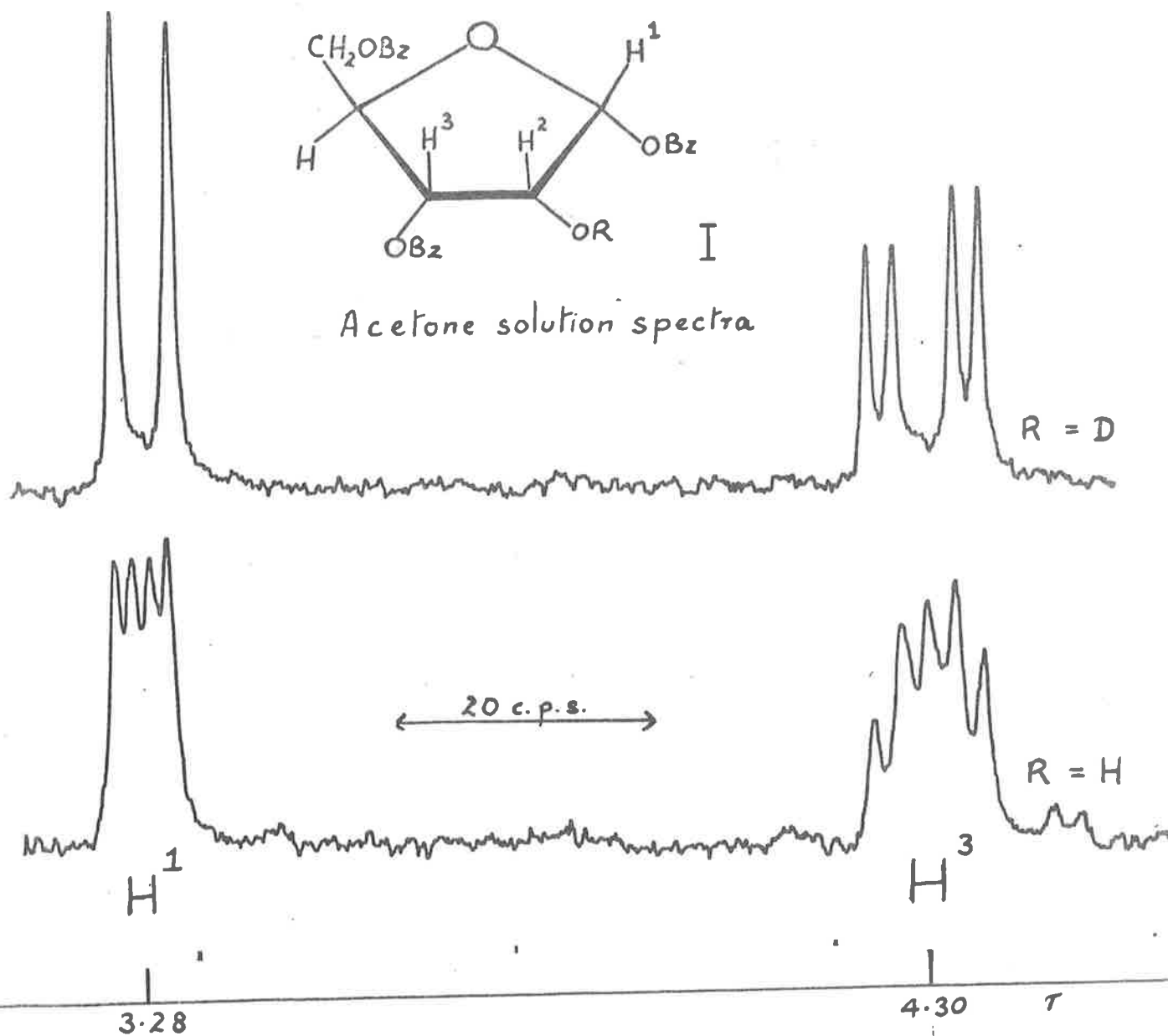
Yours sincerely,

John D. Stevens
Laboratory of Chemistry, NIAMD

Acetone solution spectra

I

R = D

R = H

H^1

H^3

20 c.p.s.

3.28

4.30

τ

71-14

CALIFORNIA STATE COLLEGE   **AT LOS ANGELES**

5151 State College Drive, Los Angeles, California 90032
(San Bernardino and Long Beach Freeways Interchange)
Telephone 225-1631 (Area Code 213)

Department of Chemistry

5 August 1964

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

Dear Barry:

Recently H-C-C-^{14}N and H-C-^{14}N coupling have been reported in a number of isonitriles[1]. The magnitudes of both these couplings are rather small

---

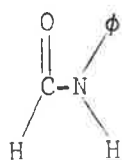(1) I. D. Kuntz, P. von R. Schleyer and A. Allerhand, J. Chem. Phys. 35, 1533 (1962).

---

and the H-C-^{14}N coupling is zero in some cases. We have performed double resonance studies on two of these compounds, ethyl and isopropyl isonitriles, and find that the signs of these two types of nitrogen-proton couplings are opposite. From ^{1}H-[^{14}N] decoupling we were able to relate the relative signs of these couplings to the H-C-C-H coupling in ethyl isonitrile. The experimental results are shown in the enclosed figures where increasing field is always to the right. In Fig. 1a and 2a are shown the undecoupled ethyl group of $CH_3CH_2N{\equiv}C$. In Figs. 1b and 2b a 4.3 Mc. r.f. field was placed somewhat downfield from the center of the low field triplet of the ^{14}N quartet of triplets. The decoupler which we used was a crystal controlled Varian V4210A. The crystal oscillator's center band could be adjusted to about $\pm$ 0.05 cps. over a range of about 1200 cps. Using several crystals we could cover the entire ^{14}N chemical shift range. The 4.3 Mc. r.f. was introduced at the sample by a second transmitter coil wound on a glass form which was placed coaxially with the probe receiver insert. This technique was first tried to our knowledge by John Baldeschwieler for some boron-proton decoupling where the lines are rather broad. From the results presented in Figs. 1 and 2 it is evident that the use of this technique does not result in any degradation of resolution. The changes observed in the proton spectrum of ethyl isonitrile on ^{14}N irradiation at the point indicated show that the ^{14}N-C-H coupling is opposite in sign to the ^{14}N-C-C-H and H-C-C-H couplings. This is the first result to our knowledge which relates the relative signs of nitrogen-proton spin-spin couplings to a proton-proton coupling. Because the H-C-C-H coupling is believed to be positive from other sign determination experiments[2] these

---

(2) P.C. Lauterbur and R.J. Kurland, J. Am. Chem. Soc., 84, 3405 (1962); A.D. Buckingham and K.A. McLauchlan, Proc. Chem. Soc., 144, 1963.
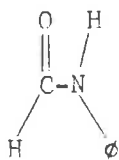

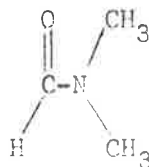results serve to establish the absolute signs of these nitrogen-proton couplings in this molecule.

Recently Ed Randall showed spectra of cis- and trans-phenylformamide-^{15}N in these letters (IITN-M-R #65). From his spectra it is evident that the directly bonded and geminal ^{15}N-proton couplings are the same sign and probably positive because the directly bonded ^{15}N-H coupling should be positive[3]. In a

$$
\underset{\text{I}}{
\begin{array}{c}
O \\
\parallel \\
C-N \\
\end{array}
}
\qquad
\underset{\text{II}}{
\begin{array}{c}
O \quad H \\
\parallel \\
C-N \\
\end{array}
}
\qquad
\underset{\text{III}}{
\begin{array}{c}
O \quad CH_3 \\
\parallel \\
C-N \\
CH_3
\end{array}
}
$$

I   II   III

(3) M. Karplus and D. M. Grant, Proc. Nat. Acad. Sci., 45, 1269 (1959);
M. Karplus, J. Am. Chem. Soc., 84, 2458 (1962).

recent paper he also reported that in II the geminal nitrogen-proton coupling to the proton on the carbonyl carbon is a different sign than the other two geminal nitrogen-proton couplings[4]. The changes in signs and magnitudes observed

(4) A. J. R. Bourn and E. W. Randall, J. Mol. Spectroscopy, 13, 29 (1964).

for the ^{15}N-C-H coupling appear to be strongly dependent on (a) the hybridization of the carbon atom bonding orbitals, (b) the presence of adjacent π-electron centers and (c) the hybridization of the nitrogen atom. We hope to discuss the geminal coupling situation in terms of these factors more fully in the future.

Joseph Casanova, Jr.

Daniel D. Elleman*

Claude D. Pearce*

Stanley L. Manatt*

P.S. One of us (J.C.) would like to ask that this contribution be used to add his name to the IITN-M-R mailing list.

* Space Sciences Division, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Fig. 1. 60 Mc. frequency sweep spectra of the methylene group of $CH_3CH_2N\equiv C$.
a) Undecoupled, b) ^{14}N slightly perturbed, c) ^{14}N completely.
Increasing field to the right.
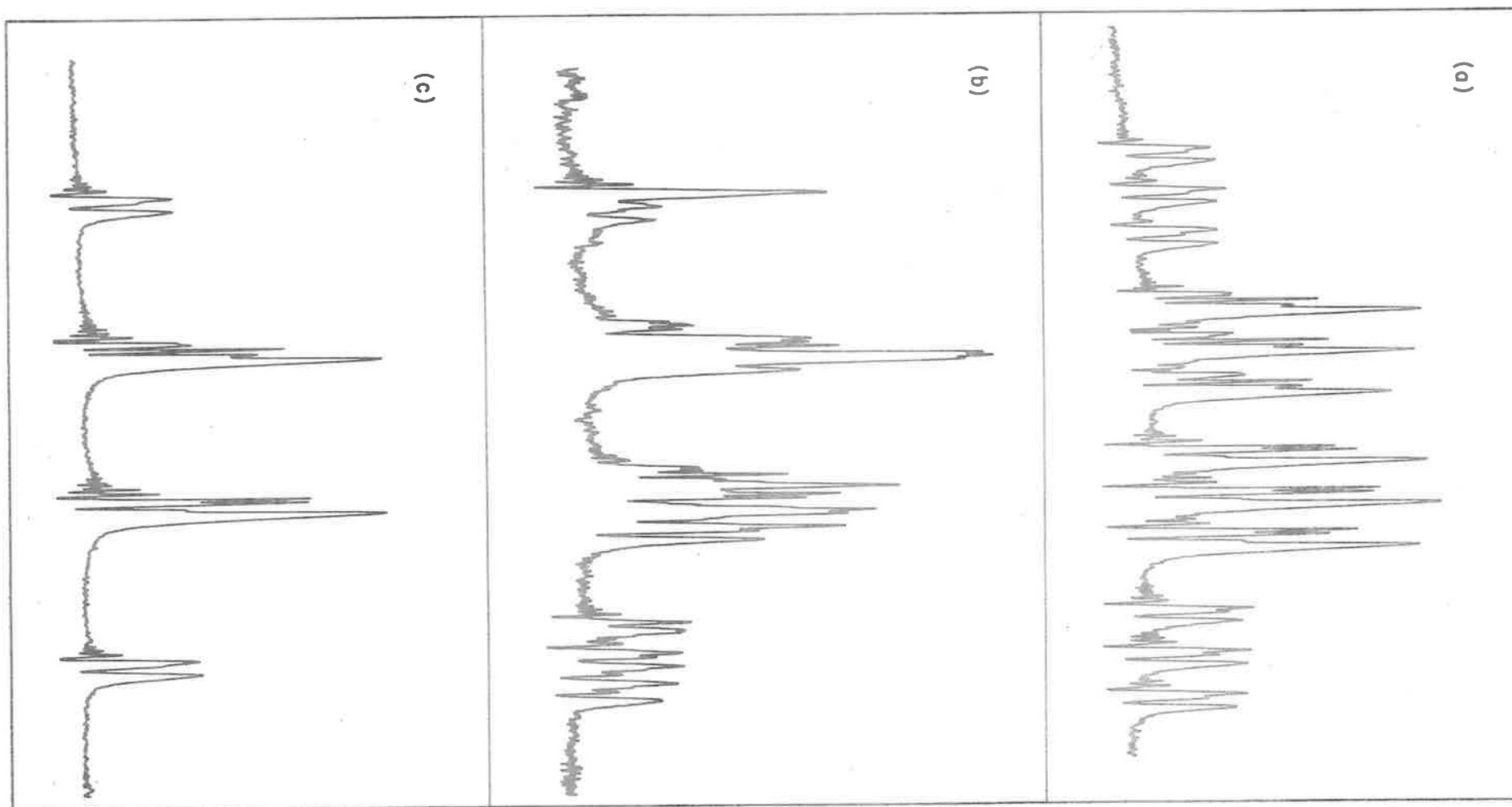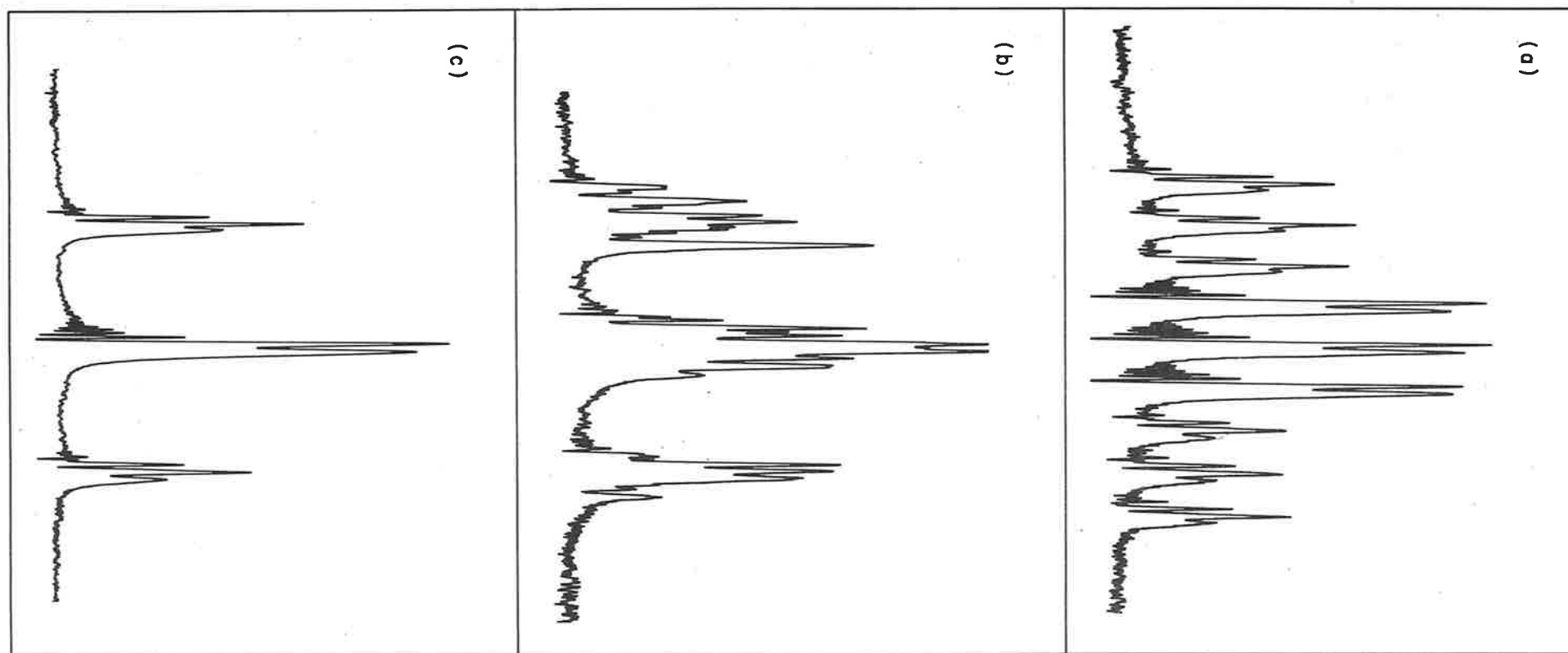
Fig. 2. 60 Mc. frequency sweep spectra of the methyl group of $CH_3CH_2N{\equiv}C$.
a) Undecoupled, b) ^{14}N slightly perturbed, c) ^{14}N completely
decoupled. Increasing field to the right.

Professor Bernard L. Shapiro

Illinois Institute of Technology
Department of Chemistry

C h i c a g o   60616

Dr. G. Englert, c/o
F.Hoffmann-La Roche & Co.AG.
Grenzacherstrasse 124, Basle
(Switzerland)

Dear Professor Shapiro,

I should like to report on the <u>ANISOTROPY of the CHEMICAL SHIFTS of</u>
<u>SOME AROMATIC 4-SPIN SYSTEMS.</u>

As it has been shown elsewhere [1], [2], [3], [4], the "liquid-crystal-
line matrix-technique" (solution of a suitable compound + tetramethyl-
silan, TMS, in a nematic phase, e.g. 4,4-di-n-heptyloxyazoxy-benzene)
can be used to obtain reliable experimental values of the anisotropy of
chemical shifts. This can be done by a comparison of the chemical shifts
of the different proton signals of the isotropic phase (random orienta-
tion of the dissolved aromatic molecules) and of the nematic phase
(partial orientation), provided the following conditions are fulfilled:

1) The spectrum can be analysed: direct and eventually indirect
dipole-dipole couplings and chemical shift-values are obtainable from the
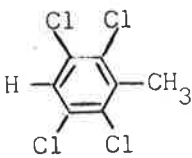experimental spectrum of the nematic phase.
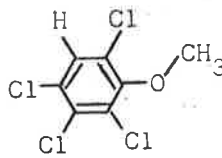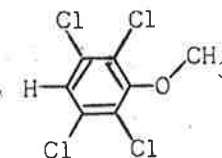
2) The degree of the molecular ordering described by the S-matrix
(see ref. 2) can be derived from the direct dipole-dipole couplings if
reasonable values for the interproton distances are known.

By this method, Dr.Saupe and I have determined the anisotropy of
the chemical shift of benzene and of 1,3,5-trichlorobenzene [3], [4].

In the following less favorable cases of 2,3,5,6-tetrachlorotoluene
(I), 2,3,4,6-tetrachloroanisole (II) and 2,3,5,6-tetrachloroanisole (III)
only condition 1) was fulfilled. The chemical shifts obtained are given
in the table below. From these data the following qualitative conclusions
can be drawn:

The high-field shifts of the aromatic proton in these compounds in
the nematic phase indicate that the molecular plane is preferably orien-
ted parallel to the magnetic field (contribution of the π-current effect
because of the preferred molecular orientation; see other examples given
in ref. 3). The same shift direction is expected for the methyl-signal of
(I), since the rotating CH_3 group is fixed in the molecular plane. The
methyl-signals of (II) and (III) do not show appreciable changes of the
chemical shift, and it is concluded, therefore, that in these compounds
the methyl groups are forced out of the molecular plane by the bulky ortho-
substituents. The influence of the π-current effect is then expected to
be small (or may even turn in the opposite direction).

- 2 -

Compound	Chemical shift in cps below TMS $\Delta_{isotropic}$	$\Delta_{nematic}$	Difference $\Delta_{iso}-\Delta_{nem}$
(I)	H_4: 432.5±0.3 CH_3: 141.7±0.2	371.0±0.5 126.0±0.5	+61.5 +15.7
(II)	H_5: 432.5±0.3 CH_3: 224.8±0.3	392.0±0.5 225.0±0.5	+40.5 ~0
(III)	H_4: 429.5±0.5 CH_3: 225.8±0.3	392.5±0.5 231.0±0.5	+37.0 -5.2

Similar conclusions have been drawn in the case of 2,6-dimethyl-anisole by measurement of the dielectric relaxation time [5].

With all best regards,

Yours sincerely,

G. Englert

References:

1) A.Saupe and G.Englert, Phys.Rev.Letters 11, 462 (1963)

2) A.Saupe, Z.f.Naturf. 19a, 161 (1964)

3) G.Englert and A.Saupe, Z.f.Naturf. 19a, 172 (1964)

4) G.Englert, Symposium on High Resolution NMR of Oriented Molecules, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1964

5) F.K.Fong and C.P.Smyth, J.Chem.Phys. 40, 2404 (1964).

UNIVERSITY OF SOUTH FLORIDA

TAMPA, FLORIDA 33620

AREA CODE 813: 988-4131

July 31, 1964

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

Dear Barry:

The occurrence and stereospecificity of long range coupling constants across four or more bonds in saturated and unsaturated hydrocarbons is of great interest in NMR spectroscopy. I would like to report the results of some calculations of the angular dependence of long range proton coupling constants, $^4J_{HH'}$, across four bonds.

Using a ten electron fragment of the type

$$H_1 \diagdown \underset{C_1}{} \diagup \overset{C_2}{} \diagdown \underset{C_3}{} \diagup H_3$$
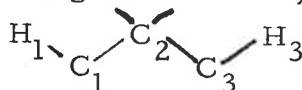
as a model for a Karplus and Anderson type coupling constant calculation, and a first order perturbation VB calculation to approximate the coefficients of an orthonormal set of basis functions, $^4J_{HH'}$ is written as the sum of a direct contribution, $^{4D}J_{HH'}$, and an indirect contribution, $^{4I}J_{HH'}$. The direct contribution involves exchange integrals associated with the bonds containing the coupled protons, whereas the indirect contribution,

$$^{4I}J_{HH'} = -\frac{1.395 \times 10^3}{\Delta E} \frac{3}{16} \sum_j \left\{ \frac{\left[K(C_1, \gamma_j') - K[C_1, \gamma_j(\underline{C}_2)] \right]\left[K(C_3, \gamma_j') - K[C_3, \gamma_j(\underline{C}_2)] \right]}{\left[K(C,H) + K[\gamma_j', \gamma_j(\underline{C}_2)] \right]^2} \right\},$$

involves exchange integrals associated with the j hybrid orbitals, $\gamma_j[C_2]$ on carbon C_2. Semi-empirical estimates of these integrals are based on their relation to vicinal H-H and C^{13}-C-H coupling constants in unsubstituted hydrocarbons. A similar procedure does not appear to be feasible for the integrals which occur in the expression for $^{4D}J_{HH'}$. Calculated value of $^{4I}J_{HH'}$ are plotted in Fig. 1 as a function of the dihedral angles, ϕ_1' and ϕ_3' ($\phi_1' = \phi_3 = 180°$ corresponds to the completely staggered conformation). The positive absolute maximum at ϕ_1' and $\phi_3' = 180°$ and the sharp decrease in value as one or both protons are moved out of the plane are consistent with the experimental results (1).

By combining the above expression for the "sigma" contribution, $^{4I}J_{HH'}^\sigma$,

- 2 -

with the expression of Karplus for the pi contribution, $^{4I}J^{\pi}_{HH}$, the angular dependence of the indirect contribution to the allylic coupling constant was calculated as a function of the dihedral angle, ϕ (Fig. 2). The upper and lower curves correspond to transoid and cisoid coupling, respectively. This difference and the calculated angular dependence agree with a variety of experimental data (1). In particular, positive allylic (and meta) coupling constants are obtained in those cases in which the coupled protons are in the nodal plane of the pi electrons. [norbornadiene (2); norbornenes (3)].

(1) S. Sternhell, Rev. Pure and Appl. Chem. 14, 15 (1964).
(2) F. S. Mortimer, J. Mol. Spectry. 3, 528 (1959).
(3) E. I. Snyder and B. Franzus, J. Am. Chem. Soc. 86, 1166 (1964);
P. Laszlo and P. Von R. Schleyer, J. Am. Chem. Soc. 86, 1171 (1964).

Sincerely,

Mike

Michael Barfield

Figure 1.

Figure 2.

$^{4}J_{HH''}$(cps)

DIHEDRAL ANGLE, ϕ
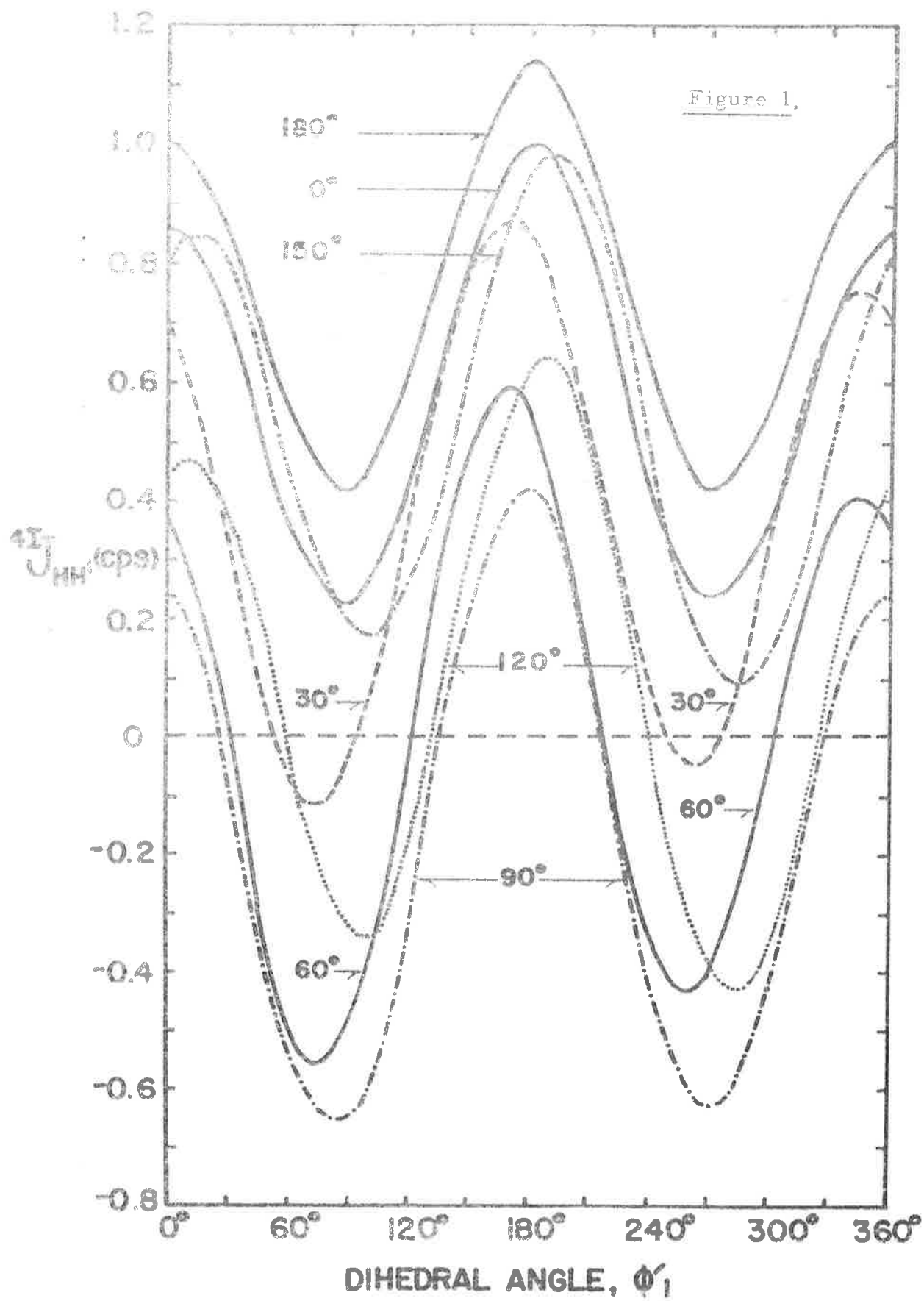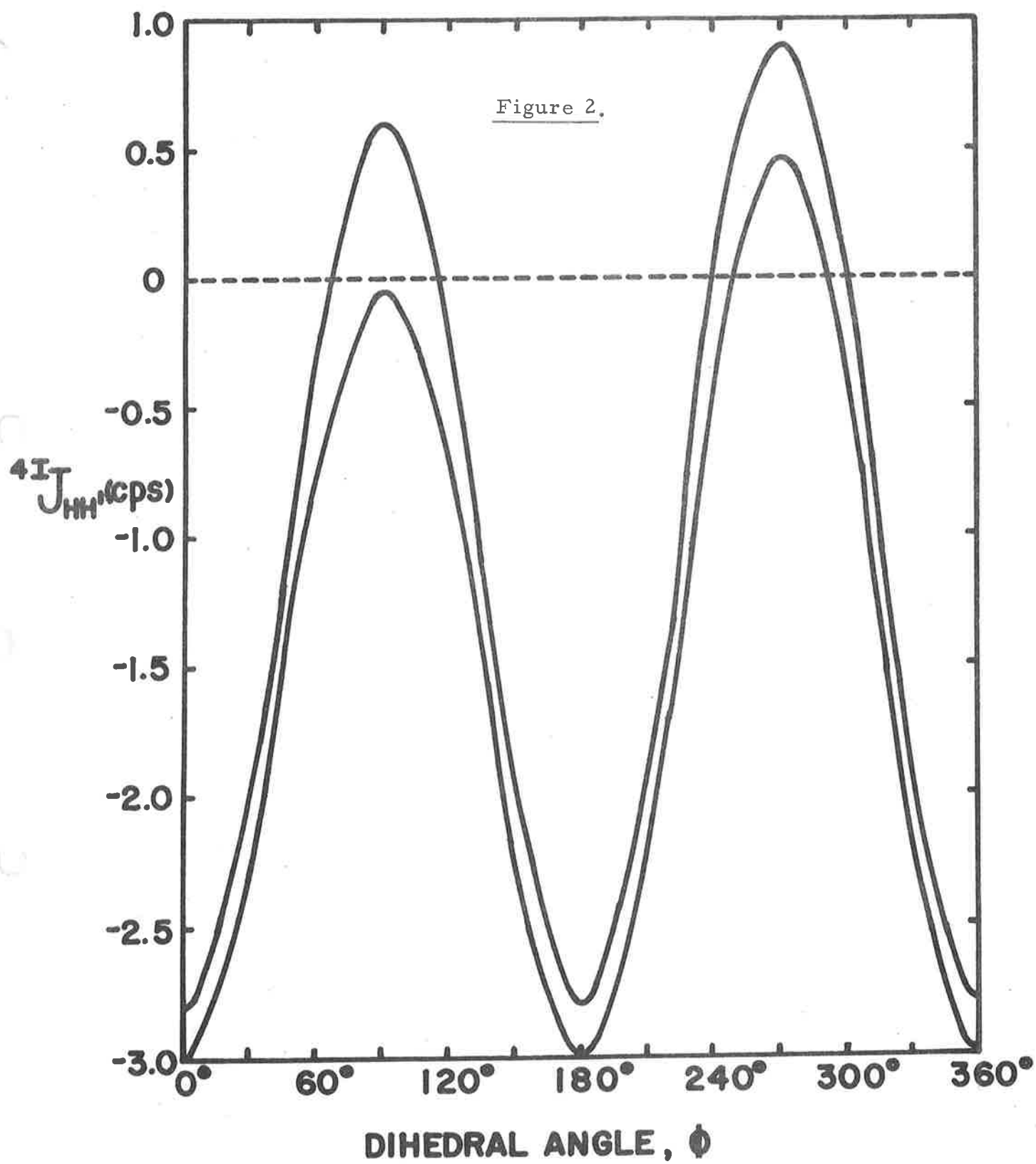
INSTITUT FÜR ANORGANISCHE CHEMIE

DER

UNIVERSITÄT MÜNCHEN

Herrn
Professor Dr. B.L.Shapiro
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
C h i c a g o, Ill. 60616
U.S.A.

Sehr geehrter Herr Professor Shapiro!

Im Verlauf unserer Arbeiten über Rhodium-Alkyl-Verbindungen konnten wir - unseres Wissens - erstmals Kopplungskonstanten zwischen Rh^{103} und Protonen von Methylgruppen festlegen. Untersucht wurden die Verbindungen:

$RhCl_3 \cdot 3 S(CH_3)_2$ [I], $Rh_2J_2[S(CH_3)_2]_3(CH_3)_4$ [II],

π-$C_5H_5Rh(CH_3)_2S(CH_3)_2$ [III] und "$(\pi$-$C_5H_5)_2Rh_2(CH_3)_4S(CH_3)_2$"[IV].
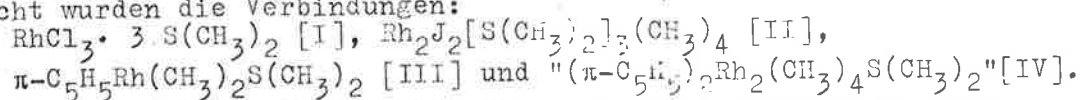
Kopplung über S-Atome hinweg wurde stets beobachtet. Auch an diesen Beispielen fand sich, daß Metall-Proton-Kopplungskonstanten bei Alkylen größer sind als bei Cyclopentadienylen.

Substanz	τ-Werte				$J_{Rh^{103}-H^1}$ [Hz]				Lösungsmittel	Konzentration
	CH_3	$S(CH_3)_2$	$S(CH_3)_2$ (Brücke)	π-C_5H_5	CH_3	$S(CH_3)_2$	$S(CH_3)_2$ (Brücke)	π-C_5H_5		
I	-	7.15*	-	-	-	1.0	-	-	D_2O	ges.
II	8.92	7.55	7.48	-	2.5	1.6	1.25	-	$CDCl_3$	40%
III	9.22	8.28	-	5.10	2.7	1.5	-	0.6	C_6D_6	40%
IV	9.28	-	8.06	5.08	2.6	-	1.0	0.4	C_6D_6	20%

*Von H_2O auf TMS umgerechnet.

Da Rhodium-Alkyl-Verbindungen zunehmendes Interesse finden, dachten wir, daß die erwähnten Resultate einigen Lesern der IIT NMR Newsletters eine Hilfe sein könnten.

Mit freundlichen Grüßen und herzlichem Dank für die IIT NMR Newsletters

Ihre

(H.P.Fritz) und (K.-E.Schwarzhans)

UNIVERSITY OF PITTSBURGH

PITTSBURGH, PENNSYLVANIA 15213

DEPARTMENT OF CHEMISTRY

29 July, 1964

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

Dear Barry:

Victor Mark of Hooker Chemical and I are collaborating on a review chapter on the proton spectra of organophosphorus compounds for Topics in Phosphorus Chemistry. We hope to make this review as inclusive as possible and should appreciate receiving preprints or other unpublished data from readers of this newsletter and other workers in the field. Our particular interest at the moment is in phosphorus-proton coupling constant data, but we should also appreciate chemical shift data, especially for the more exotic types of compounds.

Myra Gordon and I have recently carried out a study of the spectra of a number of benzylphosphonium salts and found the geminal PCH coupling to be strongly solvent dependent. Variations of J_{PCH} from 14.0 (CF_3COOH) to 15.6 c.p.s. (DMSO) were observed for the benzyl-triphenylphosphonium cation. This article has been accepted by J. Chem. Phys. and preprints are available.

Sincerely,

Claibourne E. Griffin

CEG:m

August 5, 1964

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

Dear Barry:

NMR Spectrum of a Multi-Layered Cyclophane

In the NMR spectra of [2.2] paracyclophanes (e.g., I) the aromatic protons appear at abnormally high fields ($>3.5\tau$). This phenomenon has been attributed both to impairment of ring currents due to ring deformations and transannular shielding effects. It is likely that the latter explanation is generally the correct one.

We have prepared the multi-layered [2.2] paracyclophane II. Its spectrum, with that of I as a model, is "abnormal." Much like I (see table), the bridge methylene protons appear as an A_2B_2 multiplet centered at 7.4τ and the methyl protons as a singlet at 8.19τ. While the aromatic protons in I appear as a singlet at characteristically high field (3.77τ), in II both sets of aromatic protons (inner and outer rings) appear as singlets at very high fields, 4.38 and 4.48τ. These chemical shifts are concentration insensitive ($CDCl_3$).

We had anticipated that the two structurally equivalent pairs of protons on the inner rings of II (each shielded by two adjacent aromatic rings) would be found at ca. 4.5τ while the protons on the outer rings would appear close to 3.8τ. Clearly, transannular shielding due to induced ring currents cannot alone account for the nearly identical chemical shifts. A qualitative explanation might be offered by simply assuming disruption of ring currents due to severe puckering of all aromatic rings; however, this argument does not appear attractive to us. Until a crystallographic structure analysis becomes available we cannot adequately explain the observed chemical shifts.

. . .

Dr. B. L. Shapiro   -2-   August 5, 1964
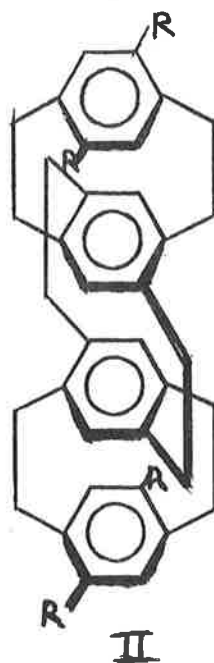
R = CH$_3$

	Ar<u>H</u>	Ar<u>CH</u>$_2$	Ar<u>CH</u>$_3$
I	3.77(s)	7.19(m)	8.04(s)
II	4.38(s), 4.48(s)	7.44(m)	8.19(s)

Sincerely yours,

Daniel T. Longone

H. S. Chow
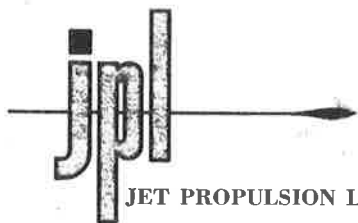
DTL:tb

JET PROPULSION LABORATORY *California Institute of Technology • 4800 Oak Grove Drive, Pasadena, California 91103*

4 August 1964

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

Dear Barry:

I am in the process of writing up some of our coupling constant
relative sign work and after looking at a large amount of data on various
coupling constants relative signs I have noted a very consistent pattern
regarding the relative signs and magnitudes of the geminal coupling in
the H-C-X fragment. All available data on magnitudes and absolute signs
of geminal couplings <u>without exception</u> can be qualitatively described by
the following four simple rules:

     1. <u>In a H-C-X fragment the geminal coupling will become either
more positive or less negative as the s character of the carbon bonding
orbitals to H and X increases.</u>

     2. <u>In a H-C-X fragment the geminal coupling will become either
less positive or more negative as the s character of the X atom bonding
orbitals to carbon increases.</u>

     3. <u>A π-electron orbital on the X atom or adjacent to the H-C-X
fragment gives a significant negative contribution to the H-C-X coupling
unless the H-C-X plane lies close to the nodal plane of the π-orbital.</u>

     4. <u>If X is ^{19}F the positive contribution to the geminal coupling
predominates but rules 1-3 still are obeyed.</u>

These rules not only apply to the proton-X case but also to the proton-
proton case.

     It appears that certain series of geminal couplings are crudely
describable by the relation:

$$J = A + B\, s_x s_{c_1} s_{c_2}$$

where A contains constants plus some function of the X to H bond order
(M.O. definition) in the H-C-X fragment, and the <u>s</u>'s are the % <u>s</u> character
in the appropriate bonding orbitals. This model is obviously very crude
but it is useful at the moment until more involved quantum mechanical
calculations such as John Pople's M.O. theory (IITN-M-R #69) have been
put thoroughly to the test. As regards the geminal coupling in allene
the simple relation give above would predict a coupling more positive

JET PROPULSION LABORATORY *California Institute of Technology* • *4800 Oak Grove Drive, Pasadena, California*

Prof. B. L. Shapiro
8/4/64   Page 2

than that of ethylene while John Pople's M.O. theory suggests that the
allene geminal coupling should be more negative than ethylene. Probably
to any empirical relationship a term embodying the effect of hyperconjugative
electron withdrawal should be added. Maybe Dave Grant will come up with
a relative sign which will settle this point.

                              With best regards,

                              Stan

                              Stanley L. Manatt
                              Chemistry Section

SLM:jas
Air Mail

P.S. - Possible title could be "Geminal N.M.R. Couplings and Bonding
       Orbital s Character".

UNIVERSITY OF CALIFORNIA, BERKELEY

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO   SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY   BERKELEY, CALIFORNIA   94720

August 5, 1964

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

Dear Barry:

Following is a short report on some work that is just being
finished in this laboratory. This, I hope, will soon be in pre-
print form and I shall be glad to send same out to anyone who is
interested.

RATES OF INTERNAL CONVERSION FROM NMR SPECTRA
OF HIGHLY COUPLED SPIN SYSTEMS

Much work has been done in microwave spectroscopy to measure
the barriers to internal rotation in substituted ethanes. However,
this work has been by necessity limited to molecules with a symmetric
top rotating on a rigid framework. Hence, barriers to internal
rotation in highly substituted ethanes have not been available by
this method. These barriers are however, obtainable by investi-
gation of the rates of intraconversion between the various rotamers
by use of NMR spectroscopy.

Kaplan has formulated a self-consistent density matrix theory
which describes a system of interconverting highly coupled magnetic
spins. This general theory has been expanded and applied to
calculating the NMR spectra of a system of substituted ethane
molecules which are undergoing internal rotation. The theory is
applicable to molecules with several nuclear spins which are strongly
coupled.

A computer program has been written which uses this expanded
theory to calculate the NMR spectra of molecules undergoing internal
rotation as a function of the temperature and the barriers to
internal rotation. Using this program, spectra are calculated
making various estimates for the barriers and the resulting spectra
at various temperatures are compared with the experimental spectra.
The fit between the experimental and calculated spectra is excellent
in those cases tried; and the barriers to internal rotation have
been estimated to ± 0.2 kcal/mole. They are 9.6 kcal/mole in
$CFCl_2-CFCl_2$; 7.7 and 9.9 kcal/mole in $CF_2Br-CCl_2Br$; and 10.8 and
11.3 kcal/mole in $CF_2Br-CFBr_2$.

Dr. Bernard L. Shapiro   -2-   August 5, 1964

The rate of internal rotation is the quantity which is determined by the experimental spectra. The conversion of this rate to a barrier height involves several assumptions in the field of absolute reaction rate theory. In particular, it has not been clear what value should be used for the transmission coefficient. Stated in another way, after a molecule obtains sufficient energy in the internal rotation mode to overcome the barriers to internal rotation, is that molecule, on the average, capable of making many rotations before it is deactivated, or is it always deactivated in a time short with respect to its period of internal rotation. In fitting the observed spectrum for $CF_2Br-CCl_2Br$, the second assumption above does a substantially better job than the first.

In addition to this, we have been having great fun recently interfacing an A-60 spectrometer to a Scientific Data Systems 910 computer. This should be going very shortly. The 910 in turn is going to be interfaced to the campus 7094. When all of this is going, we should have the world's best, and most expensive, CAT. However, the unlimited number of channels available, and the capability of registering each scan as it is made should make this endeavor quite worth while. In addition, with "good" data in digital form, we are going to make some effort at curve decomposing, i.e., fitting a sum of Lorentzian curves to the experimental one. In this endeavor, we have found that by slowing down our A-60 scan by a factor of 10 from the standard rates, we can achieve true slow passage spectra (without any ringing on peaks with a 0.1 cps width at half height). Previous to this, we have often had a hard time differentiating between true multiplet structure and ringing. This modification was very trivial. We simply replaced the drive motor with one which runs one-tenth as fast. I would strongly suggest that other people try this when they are interested in very high resolution spectra on the A-60.

Sincerely,

C. H. Sederholm

INSTITUT FÜR ORGANISCHE CHEMIE

DER UNIVERSITÄT KÖLN

Dr. H. Günther

KÖLN, August 5, 1964
ZÜLPICHER STRASSE 47
TELEFON: 2024 239

Associate Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center

Chikago, Illinois

USA

A-60 Performance

Dear Barry,

In recent weeks we had difficulties with our A-60
spectrometer. Several times we did not get the desired
resolution. Instead, the acetaldehyde quadrublett was ob-
served as demonstrated by the enclosed figures. Sweeping
the field in one direction, for instance upfield, one would
observe excessive ringing, whereas sweeping in the opposite
direction, downfield, would yield only poor "resolution".
Next time this behaviour could be reversed. Also the line-
shapes differed completely. No adjustment to normal beha-
viour was possible with curvature and/or Y-gradient con-
trols. At the same time all testswitch positions were in
the right range. The phenomena would disappear by itself
eventually after some days.

We thought, that perhaps one of your readers has
observed similar facts and could relate these to one or
several specific malfunctions. Sofar we were not able to
establish such a relationship.

In the meantime we had to replace the chopper of
the phase detector integrator and the crystal of the trans-
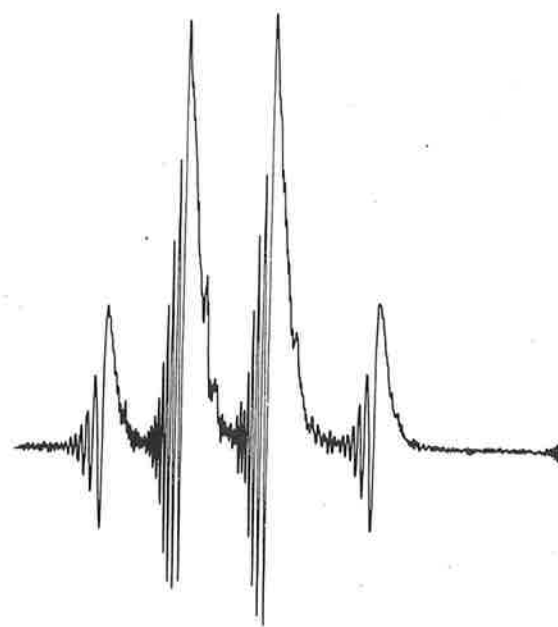mitter. The instrument, at least until now, operates nor-
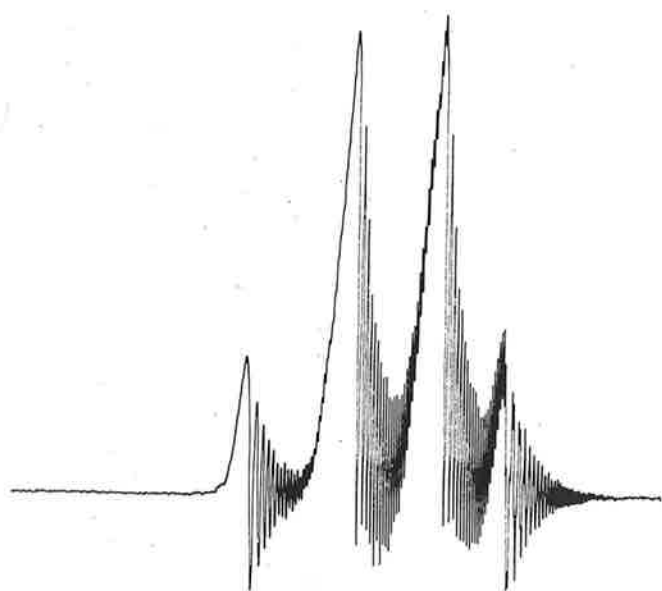mally.

Sincerely yours,

Dr. H. Günther
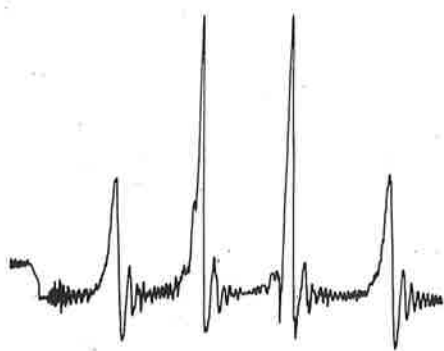
UPFIELD

DOWNFIELD

UPFIELD
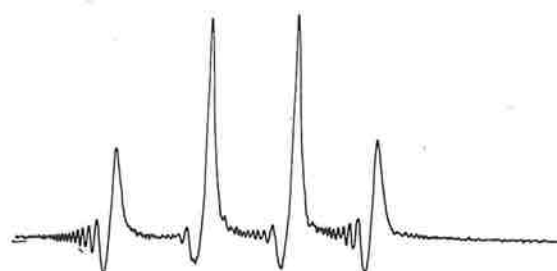
DOWNFIELD

BRYN MAWR COLLEGE
BRYN MAWR, PENNSYLVANIA
19010

DEPARTMENT OF CHEMISTRY

7 August 1964

Prof. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60615

Dear Prof. Shapiro:

I'd like to call to the attention of the IIT NMR
Newsletter readers the availability of some convenient
gadgets for degassing NMR tubes.

Polytechnical Products, Inc., P. O. Box 571, Vineland,
New Jersey, manufactures a series of fluorocarbon-aluminum
adapters that allow one to use a vacuum system without grease,
but maintain a vacuum of 10^{-6} mm or so. Since less than this
is sufficient for degassing NMR samples, these adapters make
the degassing operation very simple. The NMR tube (5 mm,
presumably) is held in place by an O-ring deformed by an
aluminum nut. This assembly is screwed onto a threaded glass
tube by means of a fluorocarbon nut.

Using Polytechnical's adapters and threaded glass
connectors, one can walk up to a vacuum system, and with
nothing more than a few turns of the wrist, place an NMR sample
on the line for degassing. The adapters thus eliminate the
need for attatching ⪰ joints or using messy black wax.
There is one drawback: one must be careful in sealing off an
NMR tube close to the fluorocarbon adapter. With care one
can seal of a 7" tube and not melt the adapter.

We have also used other of Polytechnical's adapters
instead of 24/40 ⪰ equipment in some synthetic maneuvers..
They work very well, and are probably cheaper in the long run
than the usual standard-taper equipment.

Sincerely yours,

Jay Martin Anderson

DEPARTMENT OF ORGANIC CHEMISTRY,

THE UNIVERSITY,

WOODLAND ROAD,

BRISTOL 8.

Dr. Bernard L. Shapiro,
Associate Professor,
Department of Chemistry,
Illinois Institute of Technology,   23rd July, 1964
Technology Centre,
Chicago,
Illinois 60616,
U.S.A.

Dear Dr. Shapiro,

Here at Bristol, one of our main interests is the application
of NMR to the determination of the conformations of carbohydrate
derivatives.   Recently, we have been looking at the proton spectra
of a number of methyl 4,6-O-benzylidene-α-D-aldohexopyranosides,
variously substituted at the 2 and 3 positions.   It was of particular
interest to examine some compounds with the α-D-altro configuration
in order to see if the presence of a non-hydrogen bonded 1,2,3-triaxial
system in the Cl chair conformation (e.g. A) would cause any con-
formational modification.   In the course of this work we have observed
several further examples of the 1:3 equatorial:equatorial type of
long-range coupling in saturated systems, in addition to those reported
previously between H_1 and H_3 of certain 1,6-anhydrohexopyranoses[1], and
more recently for H_2 and H_4 of some substituted 1,2-O-alkylidene-α-D-
glucopyranoses[2].

For example, methyl 2,3-di-O-acetyl-4,6-O-benzylidene-α-D-
altropyranoside (I) (whose $CDCl_3$ spectrum is reproduced in the
accompanying figure with spectrum amplitude reduced as necessary to
put all resonances on the chart) showed spacings $J_{1,2}$ 0.9, $J_{1,3}$ 0.9,
$J_{2,3}$ 3.0, and $J_{3,4}$ 2.9 c.p.s.   Similarly, methyl 3-acetamido-2-O-acetyl-
4,6-O-benzylidene-3-deoxy-α-D-altropyranoside in pyridine, displayed
spacings $J_{1,2}$ 1.0, $J_{1,3}$ 0.9, and $J_{2,3}$ 2.7 c.p.s.   Because of the
trans-fused benzylidene ring the number of possible conformations of the
pyranose ring is necessarily limited.   From the magnitudes of the
splittings listed above, it appears that the conformation of (I) is
essentially a Cl chair (A), but somewhat distorted in that the proton
dihedral angle $\phi_{1,2}$ is greater than 60°.

It seems unlikely, however, that this distortion is due to
1:3 diaxial repulsion since the α-D-manno isomer of (I) (equatorial
acetoxy group at C_3) also showed a small splitting $J_{1,2}$ = 1.2 c.p.s.

(A)
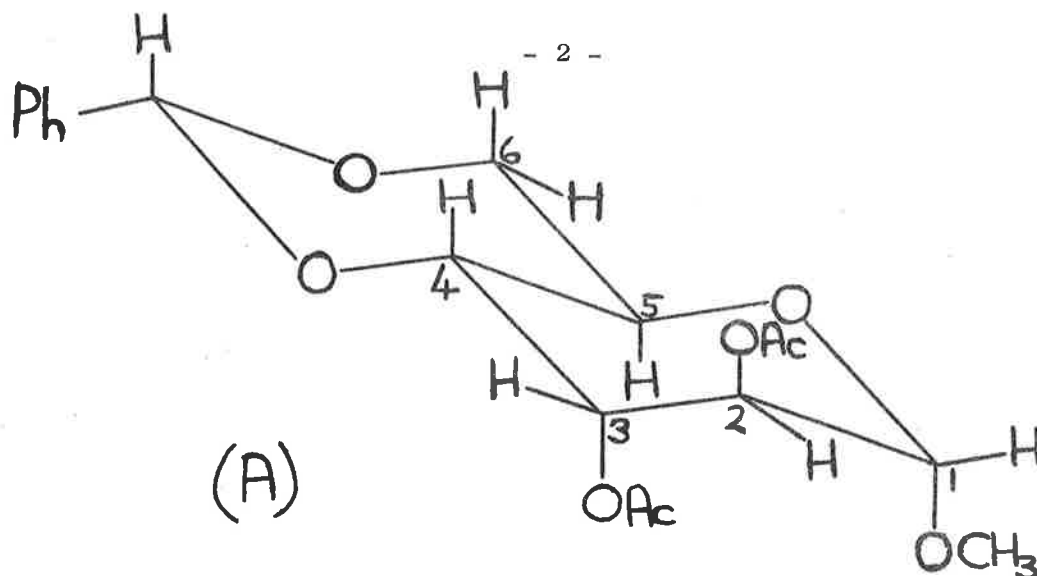
In general, compounds with the α-D-altro and α-D-manno configurations gave spectra with first-order $J_{1,2}$ = 1.2 c.p.s. or less so that the signal for H_1 frequently appeared as a singlet, whereas several derivatives possessing the α-D-gluco configuration had $J_{1,2}$ = 3.1 - 3.6 c.p.s.   Since all three of these configurations would have a theoretical dihedral angle $\phi_{1,2}$ of 60° when in perfect Cl chair conformations, these results suggest that $\phi_{1,2}$ in the α-D-altro and α-D-manno derivatives is appreciably larger than it is in the α-D-gluco compounds.*

In connection with long range coupling, it is of interest that compound (I) in conformation (A) contains a five bond planar zig-zag system

as mentioned by Lynden-Bell and Sheppard[3].   Unfortunately, the signal due to H_3 is already complicated by long range coupling with H_1.   This could presumably be removed by double resonance (we do not have this at Bristol yet), or we could probably synthesise the β-anomer of (I).

Yours sincerely,

Bruce Coxon
Leslie Hough

References
1. Hall and Hough, Proc. Chem. Soc., 1962, 382
2. Coxon and Hall, Tetrahedron, 1964, 20, 1685
      (See also Lemieux and Nagarajan, Canad. J. Chem., 1964, 1270.
3. Lynden-Bell and Sheppard, IITNMRN, 68, 22.
4. Williams and Bhacca, J. Am. Chem. Soc., 1964, 86, 2742.

* However, our results are in accord with the view[4] that vicinal coupling constants are dependant upon the configuration of the electronegative substituent at C_2.

Ph

H₃C⟨O O Ph⟩O

H₃

H₂

H₁

OCH₃

OAc

H₄ + H₅ + 2H₆

⟶ H₀ ⟶

(structure labels: O–CH₂ 6, 5, H, Ph, 4, O, H, Ac O, 3, Ac O, H, H, 2, O, Ac O, 1, H, OCH₃)

(I)

IN   CDCl₃

| 2.60 | 4.40 | 4.76 | 4.97 | 5.40 | 6.62 | 7.90 | 7.92 | τ |
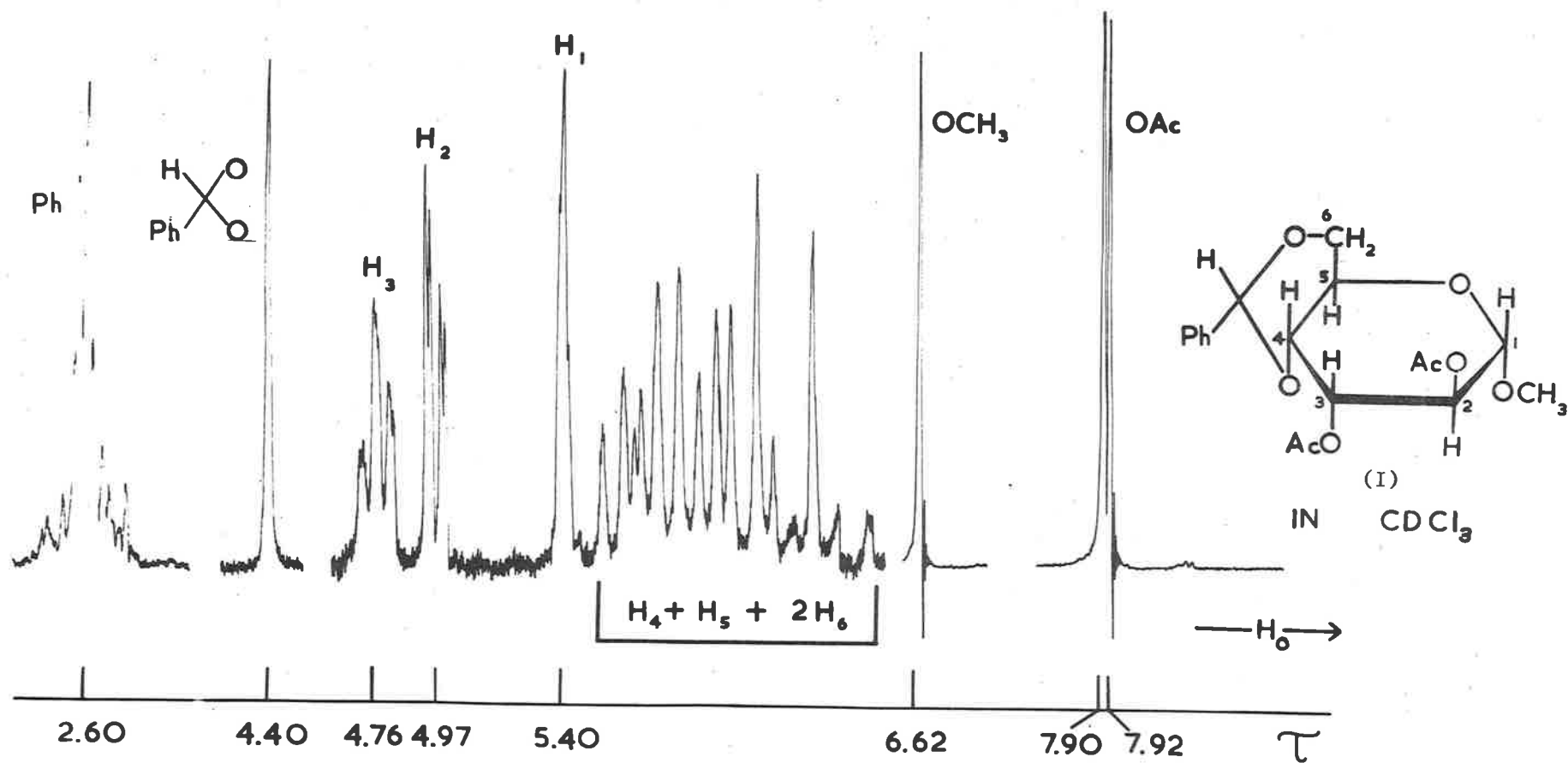
A-60 Proton Magnetic Resonance Spectrum of Methyl 2,3-di-O-acetyl-4,6-O-benzylidene-α-D-altropyranoside.

71-37

Please address any reply to
THE DIRECTOR
and quote: BP.5/7/01
Your reference:

BASIC PHYSICS DIVISION

20th July, 1964.

Dear Barry,

POLYMER CHAIN CONFORMATIONS

We have started a programme of investigation of the chain conformations of polymers, and would like to report some preliminary measurements on polyethylene oxide, $\{CH_2 - CH_2 - O\}_n$, of molecular weight 6000, i.e. a chain with $\sim$ 136 monomer units.   To obtain information we have looked at the C^{13} satellites for this polymer at different temperatures in the melt and in chloroform and water as solvents.   Although the resolution is not as good as that obtained with small molecules (Line widths $\sim$ 1.25 cps at room temperature in solution) we have found it possible to measure accurately the splitting $J + J^1$ between the outermost lines of the satellite spectra, which approximate to half an A_2X_2 pattern.   The splitting $J - J^1$, which is present in the inner lines of the satellite is not resolved.   A sample of the spectra obtained at 60 Mc/s is shown in the figure and is for a solution in chloroform at 87°C and shows that it is possible to make quite accurate measurements of $J + J^1$.   We have found that the value of $J + J^1$ increases with temperature by about 1 cps in the temperature range 30 to 125°C for this solution.   A similar increase occurs in aqueous solution.   Unfortunately, it is not possible to make accurate measurements in the melt until a temperature of $\sim$ 150°C is reached, i.e. 80°C above the polymer melting point, so that a restricted temperature range is available.   Also, the signal to noise ratio falls, leading to less reliable measurements.   However, $J + J^1$, appears to increase as the temperature rises.   This fact implies that in all these cases the gauche configuration of the chain is more stable than the trans.

We have also made similar measurements on a number of smaller molecules which are more or less satisfactory as model compounds.   These are ethylene glycol, 1,2 - dimethoxyethane and 1,2 - dichloroethane.   The last shows no appreciable variation of $J + J^1$ with temperature which is in agreement with previous measurements which indicate that the energy difference, ΔE, between the gauche and trans forms is $\sim$ 0 k/cal[1].   Also, the value of $J + J^1$ is much greater than in the other cases studied. $J + J^1$ shows an increase with temperature for pure ethylene glycol and 1,2 - dimethoxyethane, although the increase is not so large as that found for the polymer.   Again, it appears that the gauche conformation is the most stable, a result also found for the related compound, 2 - methoxyethanol[2].   Unfortunately, one needs to know rather accurate values of J_g and J_t, the couplings expected for gauche and trans configurations of the hydrogen nuclei, before good values of ΔE can be obtained.   Alternatively values of ΔE may be obtainable from independent measurements by other techniques[3].

We have hopes that we may be able to use C^{13} satellite spectra in investigations of other polymers although the satellite bands become more complicated and harder to observe in other cases.   However, these bands are fundamentally less mixed than the C^{12}

/spectrum

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

Dr. B. L. Shapiro   -2-   CONTINUATION

spectrum and thus are more amenable to interpretation.   The difficulties in ob-
servation do not appear to be insuperable, particularly with the aid of irradiation
in the C^{12} region and so this method may become a useful source of information on
the conformations of polymer chains in the melt and in solution.

    With best wishes,

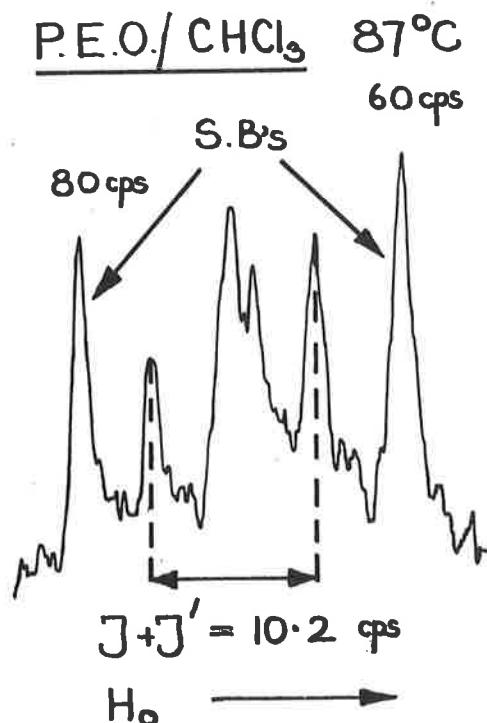   Yours sincerely,

Tom.

K. A. McLauchlan
T. M. Connor.

References

1. Mizushima. S. 1954 "Structure of Molecules and Internal Rotation" p. 41
   New York Academic Press.

2. Sheppard, N., and Turner, J. J. Proc. Roy. Soc. A. 252, 506, 1959.

3. Abraham, R. J., and Pachler, K. G. R., Mol. Phys., 7, 165, 1963.

P.E.O./ CHCl₃ 87°C

LEDERLE LABORATORIES

(Lederle)

A Division of AMERICAN CYANAMID COMPANY

PEARL RIVER, NEW YORK   (AREA CODE 914) 735-5000

August 11, 1964

Dr. B. L. Shapiro
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Dear Dr. Shapiro:

Thank you for the reminder. I wish I knew how ten months passed so quickly.

We'd like to report on two separate items:

1. <u>Conditions for active hydrogen exchange with deuterium</u>

We are investigating the experimental conditions necessary for maximum exchange of active hydrogen with minimum effect on the remainder of the n.m.r. spectrum. We want to avoid excessive dilution and intrusion of extraneous peaks due to the deuterating agent.

Based on our experiments to date, hydrogen on nitrogen in amides and urethanes will not exchange out readily, especially in dimethyl sulfoxide. We have found that very small amounts of an acid such as F_3CCOOD or D_2SO_4 in the D_2O used as a deuterating agent will expedite the exchange for about two-thirds of the natural protons on the amide or urethane nitrogen. This two-thirds exchange occurs in about three minutes with stoichiometric quantities of deuterium present. Increasing the amount of acid or deuterium does not greatly improve the exchange ratio so far as we can determine at this point.

2. <u>Improved signal to noise ratio on an A-60</u>

We have been plagued with a poor signal to noise ratio on our A-60 for months. The trouble seemed to narrow down to the Phase Detector Integrator (Fig. 4-55 in the A-60 Maintenance Manual). Our instrument technician, George Pastre, decided to attempt adjustment of the trimmer capacitors C-804 through C-834.

An improvement by a factor of three in the signal to noise ratio was achieved by observing the noise level and carefully adjusting C-834 (Fig. 4-55 in the A-60 Maintenance Manual). The other trimmers were adjusted, but only changing C-834 helped.. At this time our A-60 is in better condition than it has ben in a long time; perhaps this adjustment may help others.

Very truly yours,

W. Fulmor, V. L. Canady, G. O. Morton
Organic Chemical Research Section

WF:sao

NATIONAL RESEARCH COUNCIL
CANADA

DIVISION OF APPLIED CHEMISTRY

OTTAWA 2,

6th August, 1964

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

Dear Barry:

It has been a long time since there has been any
mention of 304TL tubes in these letters. When we switched
to 23,500 gauss operation it was necessary to have tubes in
better condition than those which were adequate previously.
Enclosed is a circuit diagram of a tube tester which was
constructed to determine the characteristics of these tubes.
With a plate voltage of 650 V. and a grid bias of -20 V., a
new tube should have a plate current of 250 milliamps.
Provided the sum of the plate currents for all 8 tubes is
greater than 1,100 milliamps under these conditions, the
magnet power supply will function adequately. We have found
this device very useful in matching used 304TL's to get
maximum usage from them.

The letter of P. Bladon and N.M.D. Brown (IITNMR
#70) prompts me to report the following chemical shifts, which
I interpret as evidence for the absence of a ring current in
the difluoroboron acetylacetone chelate. Proton shifts are
τ values and fluorine shifts are in p.p.m. to high field of
CFCl_3 as internal reference. Solvent is liquid SO2.

........Cont'd......

$$
\begin{array}{cc}
-1.73 & 144.6 \\
H & BF_3 \\
O & O \\
\end{array}
$$

7.41 3.85

$CH_3-C-CH = C-CH_3$

$$
\begin{array}{cc}
6.43 \\
H \\
O \quad O \\
\end{array}
$$

7.98 4.42

$CH_3-C-CH = C-CH_3$

$$
\begin{array}{cc}
132.3 \\
F \quad F \\
B \\
O \quad O \\
\end{array}
$$

7.70 3.90

$CH_3-C-CH = C-CH_3$
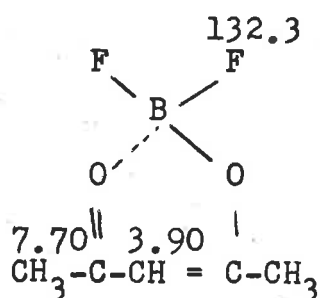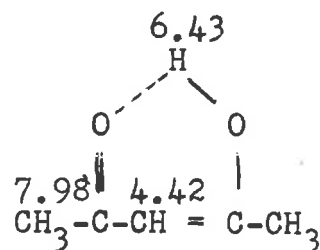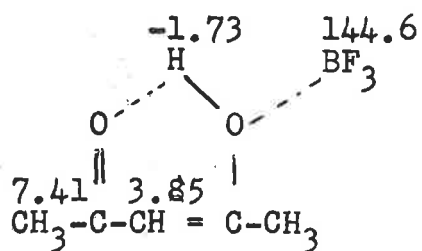
If moisture and air are rigorously excluded the co-ordination compound formed initially slowly changes to the chelate compound. The similarity in chemical shift of the =C-H suggests that no ring current is produced by chelation.

Yours truly,

Syd.

S. Brownstein

SB/jar

117V @ 60~

HAMMOND #1144X60
10V, 10AMP.

HAMMOND #715X60
510-0-510 V @ 300MA

ALL DIODES
1N2071

10MFD
900V

1CM

5MFD
900V

100K
4W

20K

BIAS ADJ.

PLATE CURRENT

I 0-500MA

6AP

TUBE 304TL

5

GRID CURRENT

I 0-1MA

2

3

1 4

GRID BIAS
0-10V
OR
0-100V

V

71-43
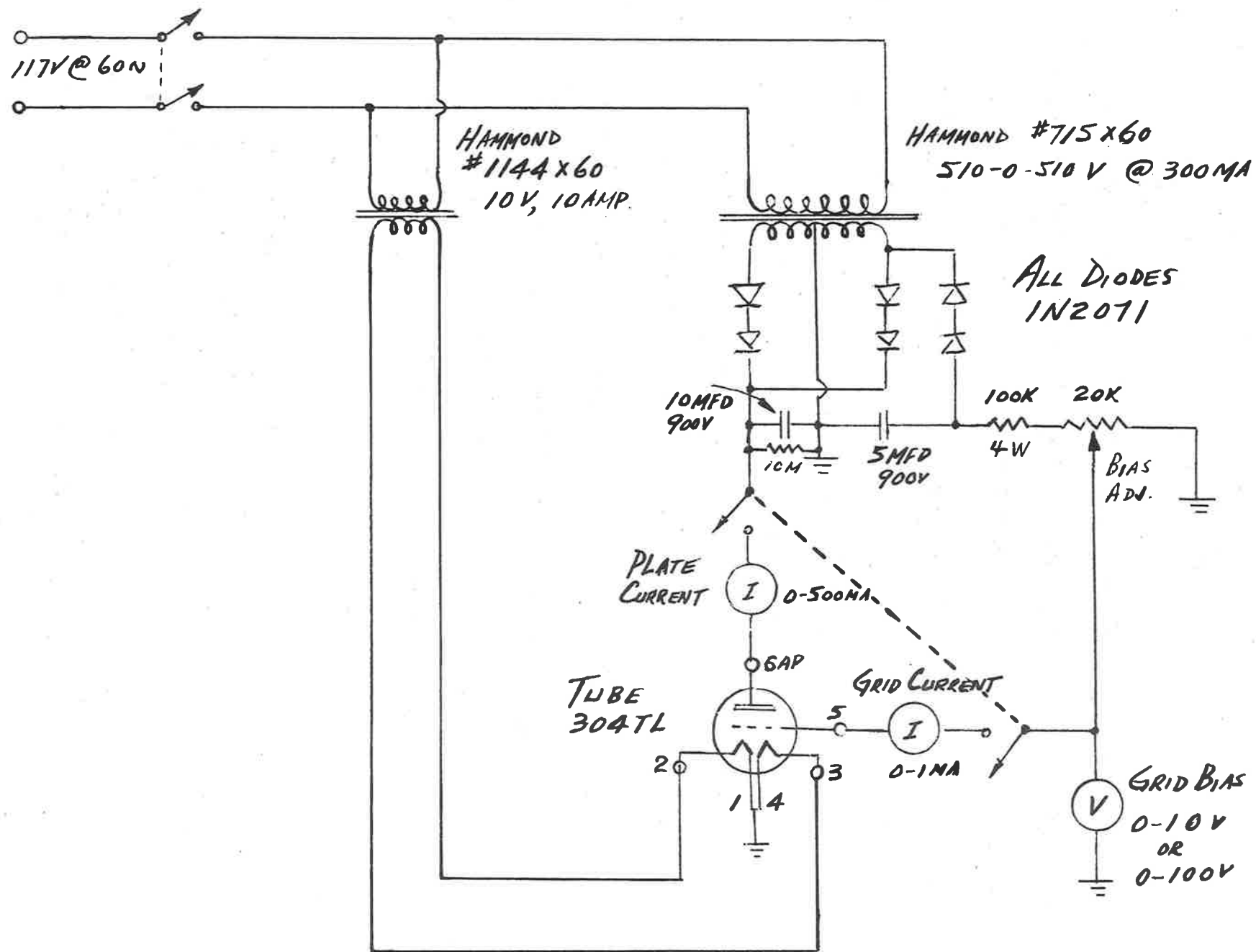
Physical Chemistry Laboratory
South Parks Road,
Oxford.

Aug 10
1964.

Dear Barry,

I am temporarily without the services of a typist and hope that my poor handwriting will reproduce and be legible. Your recent reminder about my lack of contribution came as rather a shock but on checking I realise it is issue 61 which contains our last effort. We have shown recently a square root law dependence for reduced coupling constants $J/\delta\delta$ versus atomic number. (e.g. Mellon News 61) which is obeyed very well, providing variations of bond ionicity are not extreme, for couplings J_{X-H} and J_{X-C-H} where 'X' is a second or higher period element. (J. Chem. Phys. $\underline{40}$ p's. 2128, 2132 and 2425).

It occured to us that the regular deviations from the square root law in the first period – shown in figure 1 accompanying – were very close to a linear dependence. (Figure 2) Without going into the justifying details which would take up too much space, it is clear that the earlier dependence

② on bond 's' character dependence noticed by shoolery and Muller (J. Chem. Phys. <u>31</u> p1427 1959)) (J. Chem. Phys. <u>31</u> p768 (1959).). might be combined with a simple proportionality dependence on atomic number in the following empirical equation;-

$$\left(\frac{J_{X\ldots Y}}{\gamma_X \gamma_Y}\right) = K \, \alpha_X \alpha_Y Z_X Z_Y \quad \underline{\hspace{2cm}} \quad (1)$$

$J_{X\ldots Y}$ is the spin-spin coupling constant of the X nucleus to Y nucleus in a directly bonded state or bridged by a common intermediate atom in a series. 'α_X' and 'α_Y' are respectively the 'S' electron character in the bonding electrons at atoms 'X' and 'Y'. K is a simple proportionality constant.

The above equation is tested for J_{X-H} and J_{X-C-H} by plotting $\left(\frac{J_{X-Y}}{\gamma_X \gamma_Y Z_X Z_Y}\right)$ versus $\alpha_X \alpha_Y$ as shown in figures 3 and 4. A remarkable linearity is evident passing through the origin. The coupling constants used are indicated on the diagrams. From figure 4 one can predict values of $J_{C^{13}-C-C^{13}}$, $J_{C^{13}=C-C^{13}}$ and $J_{\equiv C^{13}-C-C^{13}}$

to an uncertainty of ± 20%. The numerical values predicted are 18 c.p.s., 24 c.p.s. and 36 c.p.s. respectively.

This contribution is also to be associated with the name Ted Wells apart from legibility and spelling.

Best Regards.

L.W. Reeves.

L. W. REEVES.

E. J. WELLS.

Fig.1

Fig.2.

$$\frac{J_{X-Y}}{\gamma_X \gamma_Y Z_X Z_Y}$$

10

5

H–H

$\equiv C^{13}-H$

$=C^{13}-H$

$-C^{13}-H$

$C^{13}=C^{13}$

$\equiv C^{13}-C^{13}-$

$C^{13}-C^{13}$

$-C^{13}-C^{13}=$

·1 ·2 ·3 ·4 ·5 ·6 ·7 ·8 ·9 1·0

$\alpha_X . \alpha_Y \longrightarrow$

Fig 3

71–48

$$\frac{J_{\underline{X}-C-\underline{H}}}{\gamma_X \gamma_Y Z_X Z_Y}$$

$H-C-H$

$\equiv C^{13}-C-H$

$=C^{13}-C-H$

$-C^{13}-C-H$

$\alpha_X \alpha_Y \longrightarrow$

Fig 4

10 August,1964

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

Dear Professor Shapiro,

Enclosed please find our contribution to IITNMRN.

Study of Some Cyano-Metal Complexes by Nuclear Magnetic Resonance. I. Chemical Shifts and linewidths of N^{14} and C^{13} resonances.

M. Shporer, G. Ron and A. Loewenstein, Department of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel
and
G. Navon, Department of Physical Chemistry, The Hebrew University, Jerusalem.

Abstract: Chemical shifts and linewidths of N^{14} nmr in aqueous solutions of various paramagnetic and diamagnetic complex cyanides are reported. The C^{13} resonance was detected in one paramagnetic complex ($K_3Fe(CN)_6$) and in several diamagnetic ones. Temperature and concentration dependence of the resonances for some compounds are also included. The results indicate that in both para-and diamagnetic complexes the linewdith is determined primarily by the quadrupolar relaxation. Line positions in the diamagnetic complexes do not vary much from complex to complex. In the paramagnetic complexes, on the other hand, considerable shifts have been detected and these are ascribed to the contact term. $K_3Cr(CN)_6$ forms an exception both with respect to the N^{14} chemical shift and the linewidth.

2/...

Study of Some Cyano-Metal Complexes by Nuclear Magnetic Resonance. II.
Kinetic of Electron Transfer between Ferri- and Ferrocyanide Ions.
Same authors as above.

Abstract: The kinetics of the electron transfer reaction between
$K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ in aqueous solutions was studied by measuring
the ^{14}N nmr linewidth. The reaction obeys a rate equation: rate = k
$\left[Fe(CN)_6^{-3}\right]\left[Fe(CN)_6^{-4}\right]$ with k = 9.2 ± 1.3x10^4 sec^{-1} M^{-1} at 32°C and an
Arrhenius activation energy of 4.2 kcal/mole in the temperature range of
25 to 40°C.
The effect of replacing the potassium by other alkali and alkaline-earth
cations is reported. The rate increases from H$^+$ to Cs$^+$ and from Mg^{++}
to Sr^{++}. Possible mechanisms, in view of the catalytic effect of the
cations, are discussed.
The effect of the presence of various cations on the N^{14} linewidth is
reported and discussed.

Sincerely yours,

A. Loewenstein

A. Loewenstein

AL:dn

UNIVERSITÉ D'OTTAWA

FACULTÉ DES SCIENCES PURES ET APPLIQUÉES

UNIVERSITY OF OTTAWA

FACULTY OF PURE AND APPLIED SCIENCE

OTTAWA 2, CANADA

DÉPARTEMENT DE CHIMIE
365, RUE NICHOLAS

DEPARTMENT OF CHEMISTRY
365 NICHOLAS ST.

August 12, 1964.

Conformational Differences in the Bicyclo[2.2.1]heptane System

Dear Barry,

In response to the receipt of # 70, IIT NMR I felt I should submit the following contribution which should elevate me to a member in good standing.

In collaboration with Dr. R.T. Lalonde at the State College of Forestry at Syracuse University, the proton spectra of a series of nine norbornadienes I and nine corresponding norbornenes II were examined
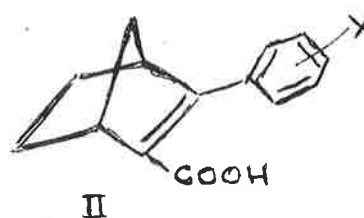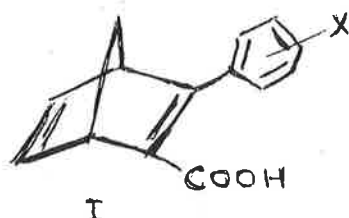
$X = H$, ortho − (CH_3, NO_2, Cl, OCH_3); para − (CH_3, NO_2, Cl, OCH_3).

The spectra were in general uneventful except for one notable feature, the chemical shifts of the bridgehead protons H_A and H_B. In all the derivatives studied, the bridgehead proton at lower field moved upfield by 0.07 − 0.09 p.p.m. more than the other bridgehead proton upon removal of the double bond. For example where $X = H$, protons A and B in I occurred at 4.11 and 3.88 δ whereas in II their δ values were 3.42 and 3.27. Thus one proton moved upfield 0.69 p.p.m., the other 0.61 p.p.m. The effect of removal of a double bond can be estimated from the chemical shift data for the bridgehead protons in norbornadiene and norbornene which occur at 3.57 and 2.85 respectively. Thus they move upfield 0.72 ppm upon hydrogenation, whereas the average upfield shift in our series is 0.68 for proton A and 0.60 for proton B.

... 2

We have attributed this observation to the presence of a secondary effect, paramagnetic in nature and of unequal intensity at the two bridgehead protons. This causes a downfield shift of 0.04 p.p.m. upon one proton and 0.12 p.p.m. on the second. The origin of the effect is most logically attributed to the fact that the two substituents, phenyl and carboxyl can attain a greater degree of coplanarity with the double bond between them in II than in I. Thus this rotation of the substituents towards planarity with the double bond would place the two bridgehead protons under a greater influence of the ring current effects of the substituents. The resultant effect on the chemical shifts of the bridgehead hydrogens must be paramagnetic, as long as the angle between the substituents and the hydrogens in question decreases on hydrogenation. The interpretation of the ultraviolet spectra of the same compounds reinforces this somewhat tenuous conclusion that there is a greater degree of coplanarity of phenyl and carboxyl with the double bond in II.

P.S. I would welcome any recommendations regarding standardization of chemical shift units. I like τ values but would prefer even more strongly the common use of either one of them, δ or τ. I would suggest you propose adoption of one of the units for IIT NMR and see if it is followed by the contributors. I feel discussion of the relative merits of the two systems would be fruitless.

Yours sincerely,

Robert R. Fraser

RRF/vb

Robert R. Fraser,
Associate Professor of Chemistry.

PRINCETON UNIVERSITY
DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY

Frick Chemical Laboratory

August 11, 1964

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

Dear Dr. Shapiro:

We would like to follow up our recently reported work[1] and record further observations of <u>solvent effects on diastereomeric methylene proton resonances</u>.

As shown in Table I, only two of numerous solvent systems were effective in separating the diastereomeric proton resonance signals in the diketone! While benzene and thiophene are exceptional in this respect, they are not so in the case of the sulfide. Both biphenyls are conformationally stable under the conditions of measurement (room temperature, A-60 spectrometer, about 5% w/v solutions with internal tetramethylsilane).

Sincerely yours,

Barbara Singer

Barbara Singer

Kurt Mislow

Kurt Mislow

(1) K. Mislow, M.A.W. Glass, H.B. Hopps, E. Simon and G.H. Wahl, Jr., J. Am. Chem. Soc., <u>86</u>, 1710 (1964).

Table I

Methylene Proton Magnetic Resonance Absorption
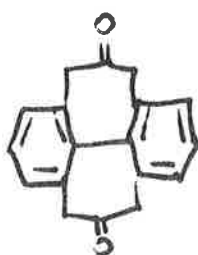
Solvent	Signals[a]	J_{AB} [b]	Signals[d]	J_{AB} [b]
$CDCl_3$ [c]	6.43 (1.8)		6.75 (1.8)	
CCl_4 [c]	6.48 (1.9)		6.81 (1.5)	
CS_2 [c]	6.56 (1.8)		6.88 (2.0)	
C_5H_5N [c]	6.39 (1.9)		6.70 (1.4)	
$C_6H_5NO_2$ [c]	6.42 (2.1)		6.78 (2.0)	
C_6H_5CN	6.44 (1.8)		6.72;6.83	12.2
$C_6H_5COOCH_3$	6.49 (1.9)			
$CH_3COC_6H_5$	6.52 (1.7)		6.78 (1.3)	
$p\text{-}C_6H_4F_2$	6.50 (1.7)		6.79 (1.5)	
$m\text{-}C_6H_4Cl_2$			6.80 (1.8)	
$o\text{-}C_6H_4Cl_2$	6.52 (1.6)		6.81 (1.5)	
$m\text{-}C_6H_4F_2$	6.53 (1.6)		6.80 (1.7)	
$o\text{-}C_6H_4F_2$	6.54 (1.7)		6.82 (1.8)	
C_4H_4O	6.58 (1.6)			
$C_6H_5CCl_3$	6.59 (2.0)		6.77 - 6.83	
C_6H_5I			6.81 (1.9)	
C_6H_5Br	6.60 (1.9)		6.81-6.85	
C_6H_5Cl	6.62 (1.5)		6.80;6.91	12.2
C_6H_5F	6.62 (1.6)		6.78-6.85	
$C_6H_5OCH_3$	6.64 (1.8)			
$C_6H_5CF_3$	6.65 (1.8)		6.78;6.88	12.1
$m\text{-}ClC_6H_4CH_3$	6.65 (1.5)		6.83-6.89	

Table I (cont'd)

Solvent	Signals	J_{AB} [b]	Signals	J_{AB} [b]
p-ClC$_6$H$_4$CH$_3$	6.66 (1.6)		6.85-6.91	
o-FC$_6$H$_4$CH$_3$	6.66 (1.5)		6.79;6.92	12.3
m-FC$_6$H$_4$CH$_3$	6.66 (1.5)		6.81-6.90	
p-FC$_6$H$_4$CH$_3$	6.67 (1.7)			
o-ClC$_6$H$_4$CH$_3$	6.67 (1.6)		6.81;6.94	12.3
C$_4$H$_4$S	6.65;6.73	15.6	6.79;6.95	12.2
1-C$_{10}$H$_7$F			6.71;6.91	12.1
C$_6$H$_6$ [c]	6.69;6.81	15.5	6.75;7.00	12.4
C$_6$H$_5$CH$_3$	6.77 (2.0)		6.81;7.01	12.1
m-C$_6$H$_4$(CH$_3$)$_2$	6.81 (2.0)		6.83;7.03	12.1
p-C$_6$H$_4$(CH$_3$)$_2$	6.83 [e]			
C$_6$H$_3$(CH$_3$)$_3$	6.83 [e]		6.85;7.05	12.5
1-CH$_3$C$_{10}$H$_7$			6.72;6.98	12.1

[a]Chemical shifts are reported in p.p.m. on the τ-scale. Values reported as two numbers separated by a semicolon refer to the centers of gravity obtained by analysis of the AB system. Numbers in parentheses are peak widths at half height given in c.p.s.

[b]c.p.s.   [c]Reported in ref. (1)

[d]Ranges refer to broad peaks and give peak width at half height.

[e]Measurement was precluded by extensive overlap of the ^{13}C satellite of the solvent peak.

THE UNIVERSITY OF CONNECTICUT
STORRS, CONNECTICUT
06268

August 12, 1964

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

Dear Barry:

Although we have not done any n.m.r. work recently, our A-60 will, hopefully, be installed and operative imminently. Before leaving Esso I had done some variable temperature studies on $CH_2BrCHBrCO_2CH_3$ which afforded the data reproduced below. Unfortunately, the sensor was acting up that day so the recorded temperatures are subject to large uncertainties. This prevents determination of conformer distribution a la Gutowsky, but the data nevertheless are qualitatively significant.

Data

Recorded Temperature	1	2	3	J_{12}	J_{13}	J_{23}
-47	9.19	29.00	70.00	11.72	4.04	-9.43
-35	9.20	30.53	69.10	11.73	4.15	-9.50
-24	8.92	31.09	67.05	11.38	4.13	-9.46
-11	8.91	32.37	66.01	11.31	4.18	-9.57
+4	9.12	34.65	66.11	11.43	4.35	-9.68
+33	8.92	35.65	64.76	11.26	4.44	-9.83

The temperature dependence of the vicinal couplings, J_{12} and J_{13}, and the direction of the change is to be expected because of a shift in conformer population. Note that the sum, $J_{12} + J_{13}$, seems to be temperature independent. One way this could arise is if the mole fraction of one of the conformers, viz., the one with Br gauche to both Br and CO_2CH_3, were negligible at all temperatures. This explanation is not unique. What is totally unexpected, to me at least, is the temperature dependence of the geminal coupling constant, J_{23}. Although the change is small, the trend seems unmistakable.

We intend to pursue similar variable temperature studies in the immediate future.

Sincerely,

Eugene I. Snyder
Assistant Professor of Chemistry

EIS/lsj

GOOD/YEAR

The Goodyear Tire & Rubber Company

AKRON 16, OHIO

RESEARCH DIVISION
142 GOODYEAR BLVD.

August 17, 1964

Dr Barry L Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Dr Shapiro:

Thank you for the subscription reminder. First, I would like
to ask for some assistance. Recently we have completed the
cooling system for the magnet of our A-60 Spectrometer. It
consists of a Heat-X air cooled water cooler (Freon 12 refrigerant)
and an Eastern Industries centrifugal water pump for circulating
distilled water in an enclosed system. We would appreciate
having information from any magnetic resonator who has found an
effective, long lasting, and non-corrosive additive for the
cooling water, which will prevent clogging of the cooling system
due to the growth of microorganism inside it.

Before I left U S Industrial Chemicals Co, we had installed an
International Rectifier Zener voltage reference pack, Type 6RV8-A,
for the magnet power supply of the Varian DP-60 Spectrometer to
replace its 8 volt mercury reference batteries as suggested by
Dr C A Reilly (MELLONMR 58-12). I would like to report that the
Zener voltage reference pack works quite satisfactorily in a
high-resolution spectrometer also.

With kind regards,

Hung Yu Chen
cm

Spectroscopy Section
RESEARCH DIVISION

P S: The title of the contribution is "Soliciting information on
anti-clogging additive for magnet cooling water system and
Zener voltage reference pack for magnet power supply".

"Fluorocarbon Derivatives of Metals. Part VIII. Spectro-
    scopic Studies"
P. M. Treichel and F. G. A. Stone
Adv. Organometallic Chem. 1, 206, Academic Press (1964)

"The Synthesis and Configurational Analysis of 2-Amino-1,3-
    cyclohexanediol"
T. Suami and S. Ogawa
Bull. Chem. Soc. Japan 37, 194 (1964)

"The Concentration Effect of the Long-range Proton Spin-spin
    Coupling Constant in Ketones"
K. Takahashi
Bull. Chem. Soc. Japan 37, 291 (1964)

"Die Reaktion von Natrium-bis-trimethylsilyl-amid mit
    Carbonylchloriden"
J. Pump und E. G. Rochow
Chem. Ber. 97, 627 (1964)

"α-Eliminierungen bei alkalimetallorganischen Verbindungen.
    III. Alkoxycyclopropane aus Alkoxycarbenen und Olefinen"
U. Schöllkopf und W. Pitteroff
Chem. Ber. 97, 636 (1964)

"Reaktionen acylierter Aldehydaminale mit ungesättigten
    Kohlenwasserstoffen. II. Reaktionen von N-acylierten
    Salicylaldehydaminalen. Eine neue Synthese für 4-Substi-
    tuierte Chromanderivate"
R. Merten und G. Müller
Chem. Ber. 97, 682 (1964)

"Polyacetylenverbindungen. LII. Über den Mechanismus der
    Oxydativen Dimerisierung von Acetylenverbindungen"
F. Bohlmann, H. Schönowsky, E. Inhoffen und G. Grau
Chem. Ber. 97, 794 (1964)

"NMR-Spektroskopische Untersuchungen an Trimethylsilanol"
H. Schmidbaur
Chem. Ber. 97, 830 (1964)

"Tetramethylstibonium-tetrakis-trimethylsiloxy-alanat,
    -gallanat und -ferrat(III)"
H. Schmidbaur
Chem. Ber. 97, 842 (1964)

"α-Eliminierungen bei Alkalimetallorganischen Verbindungen.
    IV. Synthese von Phenylmercaptocyclopropanen aus Phenyl-
    mercaptocarben und Olefinen"
U. Schöllkopf, G. J. Lehmann, J. Paust und H.-D. Härtl
Chem. Ber. 97, 1527 (1964)

"Über das intermediäre Auftreten von Benzocycloheptenin und
    Indin"
G. Wittig und H. Heyn
Chem. Ber. 97, 1609 (1964)

"Die Struktur des 1.5-Diamino-naphthochinons-(2.6); ein
    Quadrupol-Merocyanin"
S. Dähne und H. Paul
Chem. Ber. 97, 1625 (1964)

"Die PMR-Spektren der Methylsilane und -germane"
H. Schmidbaur
Chem. Ber. 97, 1639 (1964)

"α-Colubrin aus Strychnin"
P. Rosenmund und H. Franke
Chem. Ber. 97, 1677 (1964)

"Über Kumulene, XVII. Darstellung von Pentatetraenen"
R. Kuhn, H. Fischer und H. Fischer
Chem. Ber. 97, 1760 (1964)

"Über eine Retroaldolumlagerung in der Steroid -Reihe"
F. Bohlmann und C. Rufer
Chem. Ber. 97, 1770 (1964)

"Structure of Eseramine"
B. Robinson and G. Spiteller
Chem. Ind. 459 (1964)

"Synthesis of "Thiothiophthens" and Related Compounds from
    Dithiolium Salts"
D. Leaver and D. M. McKinnon
Chem. Ind. 461 (1964)

"Studies of the Conversion of Podocarpic Acid into Atisine"
L. H. Zalkow and N. N. Girotra
Chem. Ind. 704 (1964)

"Iron Tricarbonyl Adducts of Dihydroanisoles: an Adduct of
    a Tautomer of Phenol"
A. J. Birch, P. E. Cross, J. Lewis and D. A. White
Chem. Ind. 838 (1964)

"Reaction of Diazomethane with Cyclopropenones"
P. T. Izzo and A. S. Kende
Chem. Ind. 839 (1964)

"Étude par Résonance Magnétique Nucléaire (R.M.N.) de la
    Molécule Polaire HCl en Phase Gazeuse à l'état pur et
    Perturbé par le gas Étrangers"
G. Widenlochen, E. Dayan et B. Vodar
Compt. Rend. 258, 4242 (1964)

"Tuboxenin, ein Nebenalkaloid aus Pleiocarpa tubicina.
    5. Mitteilung über Pleiocarpa-Alkaloide[1]"
C. Kump, J. Seibl und H. Schmid
Helv. Chim. Acta 47, 358 (1964)

"Odeur et constitution XXII[1] Les cis- et trans-p-men-
    thènes-8"
A. F. Thomas et M. Stoll
Helv. Chim. Acta 47, 413 (1964)

"Verdoppelungserscheinungen beim Ringschluss von Peptiden.
    V. Relative Bedeutung der sterischen Hinderung und der
    Assoziation über Wasserstoff-Brucken bei Tripeptiden.
    Spektroskopische Versuche zur Konformationsbestimmung
    12.Mitteilung uber homodet cyclische Polypeptide[1]"
R. Schwyzer, J. P. Carrión, B. Gorup, H. Nolting und A.Tun-Kyi
Helv. Chim. Acta 47, 441 (1964)

"Deuteronen-Kernresonanzspektroskopie"
P. Diehl und Th. Leipert
Helv. Chim. Acta 47, 545 (1964)

"Zur Kenntnis des Kohlenstoffringes. 78. Mitteilung [1].
    Untersuchung von trans-1-Methyl-cyclodecen-(1)-on-(6) auf
    Atropisomerie mittels einer asymmetrischen Synthese aus
    (1S, 9R, 10R)-10-Hydroxy-1-methansulfonyloxy-9-methyl-decalin"
H. H. Westen
Helv. Chim. Acta 47, 575 (1964)

"Zur Darstellung von Tetrahydropyran- und Tetrahydrofuran-
    derivaten aus 1,7-bzw. 1,6-Allyldiolen durch Dehydration
    in der Allylstellung"
G. Ohloff, K.-H. Schulte-Elte und B. Willhalm
Helv. Chim. Acta 47, 602 (1964)

"Zur Konfiguration des natürlichen Capsanthins und Capsoru-
    bins"
J. W. Faigle, H. Müller, W. von Philipsborn und P. Karrer
Helv. Chim. Acta 47, 741 (1964)

"Weitere Reaktionen an Acylchinonen und verwandten Verbindun-
    gen"
P. Bosshard, S. Fumagalli, R. Good, W. Trueb, W. von Philips-
    born und C. H. Eugster
Helv. Chim. Acta 47, 769 (1964)

"Die Strukturen von C-Fluorocurin, C-Mavacurin and Pleiocar-
pamin. 57. Mitteilung uber Curare-Alkaloide [1]"
M. Hesse, W. von Philipsborn, D. Schumann, G. Spiteller,
M. Spiteller-Friedmann, W. I. Taylor, H. Schmid und
P. Karrer
Helv. Chim. Acta 47, 878 (1964)

"Über π-Allyl-acyl-Eisencarbonyl-Verbindungen"
H. D. Murdoch
Helv. Chim. Acta 47, 936 (1964)

"Etude Spectroscopique d'oxadiazoles-1,2,4 en relation avec
leur degré d'aromaticité"
C. Moussebois et J. F. M. Oth
Helv. Chim. Acta 47, 942 (1964)

"Über Buxamin, Nor-buxamin und Buxaminol, neue Alkaloide aus
Buxus sempervirens L"
D. Stauffacher
Helv. Chim. Acta 47, 968 (1964)

"Zur Struktur der ATP -Komplexe zweiwertiger Kationen. IV.
Koordinative Besetzung des Adeninrings"
P. W. Schneider, H. Brintzinger und H. Erlenmeyer
Helv. Chim. Acta 47, 992 (1964)

"Methylvinylfulvene"
M. Neuenschwander, D. Meuche und H. Schaltegger
Helv. Chim. Acta 47, 1022 (1964)

"6-Methyl- $\Delta^{8,9}$-ergolen-8-carbonsäure, ein neues Ergolinderi-
vat aus Kulturen eines Stammes von Claviceps paspali Stevens
et Hall. 60. Mitteilung über Mutterkornalkaloide 1 "
H. Kobel, E. Schreier und J. Rutschmann
Helv. Chim. Acta 47, 1052 (1964)

"Additionen von Organometallverbindungen an die C≡N-Bindung"
A. Marxer und M. Horvath
Helv. Chim. Acta 47, 1101 (1964)

"Zero-Field Exciton Magnetic Resonance"
D. D. Thomas, A. W. Merkl, A. F. Hildebrandt and H. M.
McConnell
J. Chem. Phys. 40, 2588 (1964)

"Proton Relaxation in Dilute Solutions of Cobalt(II) and
Nickel(II) Ions in Methanol and the Rate of Methanol Ex-
change of the Solvation Sphere"
Z. Luz and S. Meiboom
J. Chem. Phys. 40, 2686 (1964)

"ERRATUM: Fast Exchange Width of Nuclear Magnetic Resonance
Spectra. [J. Chem. Phys. 38, 1787 (1963)]"
S. Alexander
J. Chem. Phys. 40, 2741 (1964)

"Nuclear Magnetic Resonance in Molten Salts. I. Chemical
Shift of Crystalline and Molten Thallium Salts"
S. Hafner and N. H. Nachtrieb
J. Chem. Phys. 40, 2891 (1964)

"Nuclear Magnetic Resonance Spectrum of ^{11}B and B-Si Order
in Danburite, $CaB_2Si_2O_8$"
E. Brun and S. Ghose
J. Chem. Phys. 40, 3031 (1964)

"Nuclear Free Precession in Very Low Magnetic Fields"
D. D. Thompson, R. J. S. Brown and M. Bloom
J. Chem. Phys. 40, 3076 (1964)

"NMR Study of Rotational Barriers and Conformational Prefer-
ences. I. Cyclohexyl Fluoride"
F. A. Bovey, E. W. Anderson, F. P. Hood and R. L. Kornegay
J. Chem. Phys. 40, 3099 (1964)

"ENDOR of a Free Radical in Solution"
J. S. Hyde and A. H. Maki
J. Chem. Phys. 40, 3117 (1964)

"Perturbed Hartree-Fock Calculations. III. Polarizability
and Magnetic Properties of the HF Molecule"
R. M. Stevens and W. N. Lipscomb
J. Chem. Phys. 41, 184 (1964)

"Preparation and Properties of Dimethylaminodifluorophosphine"
R. G. Cavell
J. Chem. Soc. 1992 (1964)

"Synthesis and Properties of Some Hydroxycinnamoyl Esters of
Quinic Acid"
E. Haslam, G. K. Makinson, M. O. Naumann and J. Cunningham
J. Chem. Soc. 2137 (1964)

"Synthetic Studies in the Diterpene Series. Part VI.
Synthesis of Some Hydrophenalene Derivatives"
D. Nasipuri, G. Pyne, D. N. Roy, R. Bhattacharya and P. Dutt
J. Chem. Soc. 2146 (1964)

"Organic Photochemistry. Part I. The Irradiation of some
Charge-transfer Complexes of Cyclohexene"
R. Robson, P. W. Grubb and J. A. Barltrop
J. Chem. Soc. 2153 (1964)

"The Reaction of Enamines with Electrophilic Olefins. A
Synthesis of Cyclobutanes"
I. Fleming and J. Harley-Mason
J. Chem. Soc. 2165 (1964)

"The cis- and trans-α β-Dicyanostilbenes. Part II. Authen-
tic cis-α β-Dicyanostilbene"
M. V. Sargent and C. J. Timmons
J. Chem. Soc. 2222 (1964)

"The Alkaloids of Phylica rogersii Pillans"
R. R. Arndt and W. H. Baarschers
J. Chem. Soc. 2244 (1964)

"Proton Magnetic Resonance of Hydrogen-bonded Chelate Rings"
R. W. Hay and P. P. Williams
J. Chem. Soc. 2270 (1964)

"Proton Resonance Spectra of Some Derivatives of Monogermane"
E. A. V. Ebsworth, S. G. Frankiss and A. G. Robiette
J. Mol. Spectr. 12, 299 (1964)

"An NMR Study of Several Alkyl Nitrites and Nitrosamines"
H. W. Brown and D. P. Hollis
J. Mol. Spectr. 13, 305 (1964)

"The NMR Spectra of Some Halopropenes"
M. Y. DeWolf and J. D. Baldeschwieler
J. Mol. Spectr. 13, 344 (1964)

"The Preparation of Organolithium Compounds by the Trans-
metalation Reaction . Part VIII. β-Styryllithium"
D. Seyferth, L. G. Vaughan and R. Suzuki
J. Organometal. Chem. 1, 437 (1964)

"Di- π-Azulen-Komplexe des Chroms und Eisens"
E. O. Fischer und J. Müller
J. Organometal. Chem. 1, 464 (1964)

"O-Silyl-Substituted Enols"
C. R. Krüger and E. G. Rochow
J. Organometal. Chem. 1, 476 (1964)

"Methylgermanylazide"
I. Ruidisch and M. Schmidt
J. Organometal. Chem. 1, 493 (1964)

"Nuclear Magnetic Resonance Studies of Adsorption on Thorium
   Oxide"
W. S. Brey, Jr. and K. D. Lawson
J. Phys. Chem. 68, 1474 (1964)

"Calculated Effect of Bond Magnetic Anisotropy on the Methyl
   Group in Some Cyclohexanes"
I. Yamaguchi and S. Brownstein
J. Phys. Chem. 68, 1572 (1964)

"Long-Range Proton Spin-Spin Coupling in Dimethyl Sulfone"
G. M. Whitesides and J. D. Roberts
J. Phys. Chem. 68, 1583 (1964)

"Proton Magnetic Resonance Spectrum of 4-Chloro-1,2-butadiene"
R. C. Ferguson
J. Phys. Chem. 68, 1594 (1964)

"The Activation Energy to Hindered Internal Rotation in
   Some Thionamides"
A. Loewenstein, A. Melera, P. Rigny and W. Walter
J. Phys. Chem. 68, 1597 (1964)

"Nuclear Magnetic Resonance Coupling Constants in Maleic and
   Itaconic Acids and Their Anhydrides"
H. M. Hutton and T. Schaefer
J. Phys. Chem. 68, 1602 (1964)

"Effects of Swelling on Proton Relaxation in Vinyl Polymers"
G. Bonera, A. Chierico and A. Rigamonti
J. Polymer Sci. A2, 2963 (1964)

"Proton Magnetic Resonance Study of Sorption of Water and
   Alcohols by Wool"
J. H. Bradbury, W. F. Forbes, J. D. Leeder and G. W. West
J. Polymer Sci. A2, 3191 (1964)

"Stereoregular Diene Polymerization with Inorganic Catalysts.
   II. Magnetic Resonance Optical and X-Ray Study of Catalysts
   Containing Cobalt"
D. E. O'Reilly, C. P. Poole, Jr., R. F. Belt and H. Scott
J. Polymer Sci. A2, 3257 (1964)

"Remarks on the Hydrochlorination of 1,4-Polyisoprene"
M. A. Golub and J. Heller
J. Polymer Sci. B2, 723 (1964)

"Nuclear Magnetic Resonance Absorption in Polycarbonate"
I. Murakami, A. Kawai and H. Yamamura
J. Sci. Hiroshima Univ., Ser.A-II., 27, 141 (1964)

"Synthesis of 4-Methylene-DL-proline: a Naturally Occurring
   Racemic Amino-acid"
A. W. Burgstahler, M. L. Trollope and C. E. Aiman
Nature 202, 388 (1964)

"Dynamic Nuclear Orientation for Nuclei of Spin I = 1"
M. D. S. Breitbart and W. A. Barker
Nuclear Phys. 52, 641 (1964)

"Nuclear Magnetic Resonance in Intermetallic Compounds"
G. W. West
Phil. Mag. 9, 979 (1964)

"Nuclear Magnetic Resonance of La^{139} and Al^{27} and Electron
   Paramagnetic Resonance of Fe^{3+} in Lanthanum Aluminate"
K. A. Müller, E. Brun, B. Derighetti, J. E. Drumheller and
   F. Waldner
Phys. Letters 9, 223 (1964)

"Proton Spin Relaxation in Water"
J. G. Powles and D. W. G. Smith
Phys. Letters 9, 239 (1964)

"Nuclear Magnetic Resonance Line Shift in Cadmium"
E. F. W. Seymour and G. A. Styles
Phys. Letters 10, 269 (1964)

"Nuclear Magnetic Resonance and Magnetic Susceptibilities of
   Alloys of V with Al"
D. O. Van Ostenburg, D. J. Lam, H. D. Trapp and D. W. Pracht
   and T. J. Rowland
Phys. Rev. 135, A455 (1964)

"Nuclear Spin-Lattice Relaxation in Polyacetaldehyde"
T. M. Connor
Polymer 5, 265 (1964)

"Proton NMR Spectra and the Conformation of Δ^3-Carene Oxide"
B. A. Arbuzov, Y. Y. Samitov and Z. G. Isaeva
Proc. Acad. Sci. USSR. Chem. Sect. (English Transl.) 150,
   475 (1964)

"Absolute Configuration of Some Carbohydrate Benzylidene
   Derivatives"
N. Baggett, K. W. Buck, A. B. Foster, M. H. Randall and
   J. M. Webber
Proc. Chem. Soc. 118 (1964)

"Apparatus for Nuclear Electron Double Resonance at 12500
   gauss"
R. E. Richards, F.R.S., and J. W. White
Proc. Royal Soc. Ser.A, 279, 474 (1964)

"Nuclear Electron Double Resonance at 12500 Gauss"
R. E. Richards, F.R.S., and J. W. White
Proc. Royal Soc. Ser.A, 279, 481 (1964)

"The Protonation of Pyrid-4-One"
P. J. Van Der Haak and Th. J. De Boer
Rec. Trav. Chim. 83, 186 (1964)

"Applications of Proton Resonance Spectroscopy to Structural
   Problems. Part X. Disulphonyl Derivatives of 2-Amino-
   pyridine"
G. R. Bedford, H. Dorn, G. Hilgetag and A. R. Katritzky
Rec. Trav. Chim. 83, 189 (1964)

"Alkaloidy Strychnos nux Vomica. VIII. O Katalitycznej
   Wodorolizie Metylooctanu Strychnidyny"
O. Achmatowicz i S. Achmatowicz
Roczniki Chem. 38, 613 (1964)

"Telomerization Reactions in the Synthesis of Models for
   Some Fluorocarbon Polymers"
R. D. Chambers, J. Hutchinson, R. H. Mobbs and W. K. R.
   Musgrave
Tetrahedron 20, 497 (1964)

"The Piloty Cyclization of Biscyclohexanone Azine and the
   Methylation of 1,2,3,4,5,6,7,8,-Octahydrocarbazole"
B. Robinson
Tetrahedron 20, 515 (1964)

"Methylenation Studies of Hydroxyflavonoids and Derivatives
of Resorcinol. Syntheses of Biflavonyls of Novel Types"
S. K. Grover, A. C. Jain and T. R. Seshadri
Tetrahedron 20, 555 (1964)

"Total Synthesis of the Calycanthaceous Alkaloids"
J. B. Hendrickson, R. Goschke and R. Rees
Tetrahedron 20, 565 (1964)

"Modified Steroid Hormones. XXXIII. Steroidal 6-Formyl-3-
Alkoxy-3, 5-Dienes and Some of their Transformations"
D. Burn, G. Cooley, M. T. Davies, J. W. Ducker, B. Ellis,
P. Feather, A. K. Hiscock, D. N. Kirk, A. P. Leftwick,
V. Petrow and D. M. Williamson
Tetrahedron 20, 597 (1964)

"Acetolysis of trans-1,2-Dibromobenzocyclobutene"
H. Nozaki, R. Noyori and N. Kôzaki
Tetrahedron 20, 641 (1964)

"Conformational Effects in Compounds with Six-Membered Rings.
I. Synthesis of the Stereoisomers of 5-Alkylcyclohexane-
1,3-Dicarboxylic Acids"
B. J. Armitage, G. W. Kenner and M. J. T. Robinson
Tetrahedron 20, 723 (1964)

"Reaction of Phenylcarbene Formed from Benzaldehyde Tosyl-
hydrazone in Certain Solvents"
H. Nozaki, R. Noyori and K. Sisido
Tetrahedron 20, 1125 (1964)

"Stereoisomerism of Quaternary Salts of 5-Nitrotetrahydro-
1,3-Oxazines"
D. Gürne, T. Urbański, M. Witanowski, B. Karniewska and
L. Stefaniak
Tetrahedron 20, 1173 (1964)

"NMR Spectroscopy of Benzocyclobutene and Biphenylene"
G. Fraenkel, Y. Asahi, M. J. Mitchell and M. P. Cava
Tetrahedron 20, 1179 (1964)

"Mass Spectra and Organic Analysis. II. Mass Spectra of
Aromatic Ethers in Which the Oxygen Forms Part of a Ring"
B. Willhalm, A. F. Thomas and F. Gautschi
Tetrahedron 20, 1185 (1964)

"The Preparation of 14β, 18-Cyclosteroids from N-Desmethyl-
N(20)-Conene Derivatives and 18-Aminosteroids"
W. G. Dauben and P. Laug
Tetrahedron 20, 1259 (1964)

"Axial and Equatorial Thiols. 3α- and 3β-Thiol Derivatives
of Cholestane and Androstanone"
D. A. Swann and J. H. Turnbull
Tetrahedron 20, 1265 (1964)

"Oxidation of Steroidal Ketones. IV. Reinvestigation of
Selenium Dioxide-Hydrogen Peroxide of Ring A Saturated
3-Ketones"
E. Caspi, Y. Shimizu, and S. N. Balasubrahmanyam
Tetrahedron 20, 1271 (1964)

"Configuration of Some 17a-Alkyl-17a-Hydroxy-D-Homosteroids"
S. N. Ananchenko, V. N. Leonov, V. I. Zaretskii, N. S. Wulf-
son and I. V. Torgov
Tetrahedron 20, 1279 (1964)

"Terpenoids. XLVIII. Structure and Stereochemistry of
Hydroxyvaleranone and Acetylhydroxyvaleranone"
K. S. Kulkarni, S. K. Paknikar and S. C. Bhattacharyya
Tetrahedron 20, 1289 (1964)

"Terpenoids. L. Transformation Products of Costunolide"
G. H. Kulkarni, G. R. Kelkar and S. C. Bhattacharyya
Tetrahedron 20, 1301 (1964)

"The Extractives of Piscidia Erythrina L. I. The Constitu-
tion of Ichthynone"
J. S. P. Schwarz, A. I. Cohen, W. D. Ollis, E. A. Kaczka
and L. M. Jackman
Tetrahedron 20, 1317 (1964)

"The Extractives of Piscidia Erythrina L. II. Synthetical
Evidence Concerning the Structure of Ichthynone"
S. F. Dyke, W. D. Ollis, M. Sainsbury and J. S. P. Schwarz
Tetrahedron 20, 1331 (1964)

"Oxymercuration of Endo- and Exo-Dicyclopentadienes"
J. K. Stille and S. C. Stinson
Tetrahedron 20, 1387 (1964)

"Heartwood Constituents of Sciadopitys Verticillata Sieb. Et
Zucc. -- II. The Structure of Methyl Sciadopate"
M. Sumimoto and Y. Tanaka and K. Matsufuji
Tetrahedron 20, 1427 (1964)

"Über 2 Alkaloide aus der Rinde von Symplocos Celastrinea
Mart"
R. Tschesche, P. Welzel, R. Moll und G. Legler
Tetrahedron 20, 1435 (1964)

"The Structure of Oxycolchicine"
G. L. Buchanan, A. McKillop, A. L. Porte and J. K. Sutherland
Tetrahedron 20, 1449 (1964)

"The Structure of Loliolide. A Terpene from Lolium Perenne"
R. Hodges and A. L. Porte
Tetrahedron 20, 1463 (1964)

"Über Digitanolglykoside --X. Zur Konstitution des Digini-
genins und Digifologenins"
R. Tschesche und G. Brügmann
Tetrahedron 20, 1469 (1964)

"Zur Stereochemie der Mycarose der Ihrer 3- und 4-Epimeren"
F. Korte, U. Claussen und G. Snatzke
Tetrahedron 20, 1477 (1964)

"Applications de la Spectrographie de Resonance Magnetique
Nucleaire (R.M.N.) Dans le Domaine des Derives Polycycliques
a Caractere Aromatique. VI. Dérivés Aza-Aromatiques Poly-
condensés"
E. V. Donckt, R. H. Martin et F. Geerts-Evrard
Tetrahedron 20, 1495 (1964)

"Applications de la Spectrographie de Resonance Magnetique
Nucleaire (R.M.N.) Dans le Domaine des Derives Polycycliques
a Caractere Aromatique. VI. Dérivés Aza-Aromatiques Poly-
condensés"
E. Vander Donckt, R. H. Martin et F. Geerts-Evrard
Tetrahedron 20, 1495 (1964)

"Applications de la Spectrographie de Resonance Magnetique
Nucleaire (RMN) Dans le Domaine des Derives Polycycliques
a Caractere Aromatique. VII. Cétones Cycliques Aroma-
tiques"
R. H. Martin, N. Defay et F. Geerts-Evrard
Tetrahedron 20, 1505 (1964)

"Isomeric Nitropropenes and their Nuclear Magnetic Resonance
Spectra"
Yu. V. Baskov, T. Urbański, M. Witanowski and L. Stefaniak
Tetrahedron 20, 1519 (1964)

"Phospholin-Derivate. II. Untersuchung Über die Lage der
Doppelbindung in Phospholinen"
K. Hunger, U. Hasserodt und F. Korte
Tetrahedron 20, 1593 (1964)

"Free Radical Addition Reactions. I. The Reaction of Tri-,
Di- and Mono-Chloromethanesulphonyl Chlorides with Alkenes"
H. Goldwhite, M. S. Gibson and C. Harris
Tetrahedron 20, 1613 (1964)

"Synthesis and Chemistry of Several Fluorinated p-Xylenes
  Designed as Precursors for $\alpha,\alpha,\alpha',\alpha'$-Tetrafluoro-p-
  Xylylene"
S. A. Fuqua, R. M. Parkhurst and R. M. Silverstein
Tetrahedron 20, 1625 (1964)

"Free Radical Addition Reactions. II. The Reaction of
  Trichloromethanesulphonyl Chloride with Styrene, and
  Chemistry of the Adducts"
H. Goldwhite, M. S. Gibson and C. Harris
Tetrahedron 20, 1649 (1964)

"The Conformations of Cyclic Compounds in Solution. II.
  Some 1,2-O-Alkylidene-Pyranose Derivatives"
B. Coxon and L. D. Hall
Tetrahedron 20, 1685 (1964)

"Tetracyclische α-Amino-Indoline. Eine Neue Verbindungsklasse
  mit Ring-Ketten-Tautomerie Sowie die Synthese Eines Modi-
  fizierten C-Curarins-III"
H. Fritz und O. Fischer
Tetrahedron 20, 1737 (1964)

"The Volatile Constituents of Coffee. III. The Structures
  of Two Heterocyclic Compounds and the Synthesis of Tetra-
  hydrofuranones"
M. A. Gianturco, P. Friedel and A. S. Giammarino
Tetrahedron 20, 1763 (1964)

"Two New Antibiotic Cyclopentanoid Monoterpenes of Plant
  Origin"
W. H. Tallent
Tetrahedron 20, 1781 (1964)

"The Constitution of Two New Sesquiterpenic Ketones. Furo-
  pelargones A and B"
G. Lukas, J. C. N. Ma, J. A. McCloskey and R. E. Wolff
Tetrahedron 20, 1789 (1964)

"A New Synthesis of ($\pm$)-3-Carone"
F. Medina and A. Manjarrez
Tetrahedron 20, 1807 (1964)

"Chemistry of α-Diazosulphones. A Sulphonylcarbene"
A. M. van Leusen, R. J. Mulder and J. Strating
Tetrahedron Letters 543 (1964)

"NMR Studies of Bridged Ring Systems. IV. Epoxides"
K. Tori, K. Kitahonoki, Y. Takano, H. Tanida and T. Tsuji
Tetrahedron Letters 559 (1964)

"Spin-Spin Coupling Constants for Methylene Groups Adjacent
  to Carbonyl Groups"
T. Takahashi
Tetrahedron Letters 565 (1964)

"Formation and Decomposition of Tetrasubstituted Phosphonium
  Salts"
D. B. Denney and H. M. Relles
Tetrahedron Letters 573 (1964)

"Fragmentation of Substituted Norbornadienone Ketals"
D. M. Lemal, E. P. Gosselink and A. Ault
Tetrahedron Letters 579 (1964)

"Claisen Rearrangements in the Xanthone Series and Synthesis
  of Dihydroisojacareubin"
E. D. Burling, A. Jefferson and F. Scheinmann
Tetrahedron Letters 599 (1964)

"Organic Syntheses by Means of Noble Metal Compounds. V.
  Reaction of Butadienepalladium Chloride Complex with
  Carbon Monoxide"
J. Tsuji, J. Kiji and S. Hosaka
Tetrahedron Letters 605 (1964)

"Canaric Acid - A 3,4-Secotriterpene Acid from Canarium
  Muelleri"
R. M. Carman and D. E. Cowley
Tetrahedron Letters 627 (1964)

"Carbon-13 Carbonyl Shielding and Steric Inhibition of Reso-
  nance. A New and Better Method for Estimating Angles of
  Twist in Conjugated Systems"
K. S. Dhami and J. B. Stothers
Tetrahedron Letters 631 (1964)

"Incorporation of a C_2 Fragment in the Course of Photolysis
  of Some Aromatic Shiff's Bases in Ethanol"
J. S. Shannon, H. Silberman and S. Sternhell
Tetrahedron Letters 659 (1964)

"The Diterpene Alkaloids. The Structure of Heteratisine"
R. Aneja and S. W. Pelletier
Tetrahedron Letters 669 (1964)

"Coupling Constants in 1,3-Dioxolans and 1,3-Dioxans: The
  Structure of Delphinium Alkaloids Containing a Methylene-
  dioxy Group"
T. A. Crabb and R. C. Cookson
Tetrahedron Letters 679 (1964)

"Claisen Rearrangement to a Meta Side Chain in the Quinoline
  Ring System"
Y. Makisumi
Tetrahedron Letters 699 (1964)

"Long Range Spin-Spin Coupling and the Mills-Nixon Effect"
P. Madhavan Nair and G. Gopakumar
Tetrahedron Letters 709 (1964)

"The Structure of Lyconnotine: A Novel Lycopodium Alkaloid"
F. A. L. Anet, M. Z. Haq, W. A. Ayer, R. Hayatsu, S. Valverde-
  Lopez, P. Deslongchamps, W. Riess, M. Ternbah, Z. Valenta
  and K. Wiesner
Tetrahedron Letters 751 (1964)

"Opening of Steroid Methyl Ethers with BF_3-Etherate"
C. R. Narayanan and K. N. Iyer
Tetrahedron Letters 759 (1964)

"Moleküle Mit Schneller und Reversibler Valenzisomerisierung.
  II. Synthese und Eigenschaften von Brombullvalen und Tert-
  Butyl-Bullvalyläther"
G. Schröder, R. Merényi, and J. F. M. Oth
Tetrahedron Letters 773 (1964)

"Further Studies on the Structure of Tetrodotoxin"
T. Goto, Y. Kishi, S. Takahashi and Y. Hirata
Tetrahedron Letters 779 (1964)

"The Nuclear Magnetic Resonance Spectra of Cyclopropane
  Derivatives"
T. Shono, T. Morikawa, A. Oku and R. Oda
Tetrahedron Letters 791 (1964)

"Stereospecific Additions to Olefins. The Iodonium Ion"
A. Hassner and C. C. Heathcock
Tetrahedron Letters 1125 (1964)

"Lead Tetraacetate Oxidation of Unsaturated Alcohols. Oxide
  Formation and Fragmentation"
R. M. Moriarty and K. Kapadia
Tetrahedron Letters 1165 (1964)

"The Diterpenoids of Erythroxylon Monogynum. I. Monogynol"
A. H. Kapadi and S. Dev
Tetrahedron Letters 1171 (1964)

"The Diterpenoids of Erythroxylon Monogynum. II. Devadarool,
a New Type in Tetracyclic Diterpenoids"
R. Soman and S. Dev
Tetrahedron Letters 1181 (1964)

"Structure of the Sesquiterpenic Hydrocarbon Cyperene"
B. Trivedi, O. Motl, J. Smolíková and F. Sorm
Tetrahedron Letters 1197 (1964)

"Studies of the Structure of Scandenin"
A. Pelter and P. Stainton
Tetrahedron Letters 1209 (1964)

"Structure of Tauranin"
K. Kawashima, K. Nakanishi, M. Tada and H. Nishikawa
Tetrahedron Letters 1227 (1964)

"An N. M. R. Study of 4-Ethylthio-4-En-3-Oxo Steroids: The
Unique Deshielding Effect of a Thio-Function"
M. Tomoeda, M. Inuzuka, T. Furuta and T. Takahashi
Tetrahedron Letters 1233 (1964)

"The Constitution and Stereochemistry of Enmein"
T. Kubota, T. Matsuura, T. Tsutsui, S. Uyeo, M. Takahashi,
H. Irie, A. Numata, T. Fujita, T. Okamoto, M. Natsume,
Y. Kawazoe, K. Sudo, T. Ikeda, M. Tomoeda, S. Kanatomo,
T. Kosuge and K. Adachi
Tetrahedron Letters 1243 (1964)

"The Structure of Robustic Acid"
A. P. Johnson, A. Pelter and M. Barber
Tetrahedron Letters 1267 (1964)

"Serratenediol: A New Skeletal Triterpenoid Containing a
Seven Membered Ring"
Y. Inubushi, T. Sano and Y. Tsuda
Tetrahedron Letters 1303 (1964)

"Elektrochemische Reduktionen an Prophyrinen"
H. H. Inhoffen und P. Jäger
Tetrahedron Letters 1317 (1964)

"The Full Stereochemistry of the Grayanotoxins and a Novel
Rearrangement"
T. Kozima, K. Nakanishi, M. Yanai and H. Kakisawa
Tetrahedron Letters 1329 (1964)

"The Structure and Stereochemistry of Some Condensation
Products of Pulegone"
Y.-L. Chow
Tetrahedron Letters 1337 (1964)

"Homoallylic Rearrangements of 19-Substituted Steroids"
J. Tadanier and W. Cole
Tetrahedron Letters 1345 (1964)

"Übertragung von Dimethoxy-Carben-Resten aus Tetramethoxy-
Äthylen"
R. W. Hoffmann und H. Häuser
Tetrahedron Letters 1365 (1964)

"A Photochemical Synthesis of Dehydrocamphor from Eucarvone"
D. I. Schuster, M. J. Nash and M. L. Kantor
Tetrahedron Letters 1375 (1964)

"Steroid Alkaloids of Pachysandra terminalis (Buxaceae)"
W. F. Knaack, Jr. and T. A. Geissman
Tetrahedron Letters 1381 (1964)

"The Epimeric 1-Cyano-5α-Cholestan-3-Ones"
A. T. Glen and J. McLean
Tetrahedron Letters 1387 (1964)

"The Structure of Some N-Aryl Glucosylamines"
B. Capon and B. E. Connett
Tetrahedron Letters 1391 (1964)

"Correlation of ^{13}C-H Spin-Spin Coupling Constants and Inter-
nuclear Angles in Cyclic Molecules"
K. Mislow
Tetrahedron Letters 1415 (1964)

"The Constituents of Harungana Madagascariensis Poir.
E. Ritchie and W. C. Taylor
Tetrahedron Letters 1431 (1964)

"N.M.R. Evidence for the Twist Conformations of Some cis-1,4-
Disubstituted Cyclohexanes"
H. Booth and G. C. Gidley
Tetrahedron Letters 1449 (1964)

"Chemical Shifts of Carbohydrates"
L. D. Hall
Tetrahedron Letters 1457 (1964)

"Stereospecific Synthesis and Oxidative Transformation of a
Synthetic 1,4-Thiazepine from D-Penicillamine"
N. J. Leonard and G. E. Wilson, Jr.
Tetrahedron Letters 1465 (1964)

"A Synthesis of 3-Isothiazolones"
W. D. Crow and N. J. Leonard
Tetrahedron Letters 1477 (1964)

"ERRATUM: Stereospecific Additions to Olefins. The Iodonium
Ion. Tetrahedron Letters, 1125-1130 (1964)"
A. Hassner and C. C. Heathcock
Tetrahedron Letters 1502 (1964)

"The Structure of Lobinaline"
M. M. Robison, W. G. Pierson, L. Dorfman, B. F. Lambert and
R. A. Lucas
Tetrahedron Letters 1513 (1964)

"Über die Katalysierte Homologisierung von Naphthalin und
Phenanthren mit Diazomethan"
E. Müller, H. Fricke und H. Kessler
Tetrahedron Letters 1525 (1964)

"On Lac Acids"
R. G. Khurana, M. S. Wadia, V. V. Mhaskar and S. Dev
Tetrahedron Letters 1537 (1964)

"Meso-Nitro- and Amino-Aetioporphyrins"
A. W. Johnson and D. Oldfield
Tetrahedron Letters 1549 (1964)

"New Lignans from Phyllanthus Niruri Linn"
L. R. Row and C. Srinivasulu, M. Smith and G.S.R. Subba Rao
Tetrahedron Letters 1557 (1964)

"Reinvestigation de la Synthèse Diénique Comme Moyen D'Obten-
tion des 2H-Oxazines-1,2"
J. Rigaudy, G. Cauquis et J. Barrane-Lafont
Tetrahedron Letters 1569 (1964)

"Photoreactions of Azidoformates with Ethyl Azidoformate and
  with Diethyl Azodiformate"
W. Lwowski, T. W. Mattingly, Jr. and T. J. Maricich
Tetrahedron Letters 1591 (1964)

"A New Synthesis of Thiophenes"
B D. Tilak, H. S. Desai and S. S. Gupte
Tetrahedron Letters, 1609 (1964)

"The Structure of Xanthorrhoein"
A. J. Brich, M. Salahud-Din and D. C. C. Smith
Tetrahedron Letters 1623 (1964)

"Yellow Alkaloids of Atherosperma Moschatum Labill"
I. R. C. Bick and C. K. Douglas
Tetrahedron Letters 1629 (1964)

"Studies on the Alkaloids of Pachysandra Terminalis Sieb.
  Et Zucc. (2). : Structure of Pachysamine -A and -B"
M. Tomita, S. Uyeo, Jr. and T. Kikuchi
Tetrahedron Letters 1641 (1964)

"Über Kurchi-Alkaloide, VII. Die Konstitution des Kurcholes-
  sins"
R. Tschesche, W. Meise und G. Snatzke
Tetrahedron Letters 1659 (1964)

"Ein am Bor Alkyliertes Carboran-2,3"
R. Köster und G. W. Rotermund
Tetrahedron Letters 1667 (1964)

"Thermal Rearrangements of Substituted Vinylcyclopropanes"
A. D. Ketley
Tetrahedron Letters 1687 (1964)

"Die Umsetzung von Diphenylchlormethan mit Grignard-Verbin-
  dungen"
F. Bohlmann und K. Junghans
Tetrahedron Letters 1701 (1964)

"Synthese des 9-Oxa-Bicyclo-[3.3.1]-Nonanons-(3)"
F. Bohlmann, H. J. Schulz und J. Riemann
Tetrahedron Letters 1705 (1964)

"Reaction of Duroquinone with Diazomethane: Formation of
  Tricyclo[5,1,0,0^{3,5}] Octane Derivatives"
W. C. Howell, M. Ktenas and J. M. MacDonald
Tetrahedron Letters 1719 (1964)

"Reaktionen von Benzol-Derivaten mit Nitrenen"
K. Hafner, D. Zinser und K.-L. Moritz
Tetrahedron Letters 1733 (1964)

"Two Photochemical Reactions of Cyclocamphanone"
P. Yates and L. Kilmurry
Tetrahedron Letters 1739 (1964)

"1,2-Diphenylphenanthro[1]Cyclobutadiene: A Highly Unstable
  Condensed Aromatic Cyclobutadiene"
M. P. Cava and D. Mangold
Tetrahedron Letters 1751 (1964)

"The Structure of Dolabradiene"
Y. Kitahara and A. Yoshikoshi
Tetrahedron Letters 1755 (1964)

"Total Synthesis of Dolabradiene"
Y. Kitahara, A. Yoshikoshi and S. Oida
Tetrahedron Letters 1763 (1964)

"The Structure of Hibaene"
Y. Kitahara and A. Yoshikoshi
Tetrahedron Letters 1771 (1964)

"Interpretation of the Proton and Nitrogen Chemical Shifts of
  Pyridine and Pyridinium Cation"
V. M. S. Gil and J. N. Murrell
Trans. Faraday Soc. 60, 248 (1964)

"The N.M.R. Spectra of Silicon Hydrides and Derivatives.
  Part 4. Disilane and Trisilane"
E. A. V. Ebsworth and J. J. Turner
Trans. Faraday Soc. 60, 256 (1964)

"Protonmagnetische Resonanzspektren von Methylderivaten des
  Isothialens (Cyclopenta[c]thiopyran)"
R. Radeglia und R. Wagner
Z. Chem. 4, 145 (1964)