

24.8.1965

*Prentiss*

Illinois  
Institute of  
Technology  
**N - M - R**  
Newsletter

**No. 82**  
JULY, 1965

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



UNITED STATES  
DEPARTMENT OF THE INTERIOR  
BUREAU OF MINES

PITTSBURGH  
COAL RESEARCH CENTER

4800 FORBES AVENUE  
PITTSBURGH, PENNSYLVANIA 15213  
June 23, 1965

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

Dear Dr. Shapiro:

Request for N<sup>14</sup> spectra

We are interested in obtaining the N<sup>14</sup> chemical shifts and spectral line-widths of the pyridine signal in a few pyridine solutions of coal and coal derivatives. Unfortunately the lowest frequency r.f. unit we have operates at 15.1 mc/sec. Anyone interested in making these measurements for us in exchange for some C<sup>13</sup> work or on a contract basis is urged to write to me.

Sincerely,

H. L. Retcofsky

LABORATORY OF PHYSICAL CHEMISTRY

The University

Bloemsingel 10, Groningen

The Netherlands

Groningen, June 15, 1965

Dr. B.L.Shapiro

Illinois Institute of Technology

Department of Chemistry

Chicago 60616

Illinois, U.S.A.

Deuterium Resonance in Collagen Hydrated with D<sub>2</sub>O

Dear Dr. Shapiro:

We have exchanged the water in hydrated oriented collagen (a fibrous protein) with D<sub>2</sub>O by exposing the samples to a D<sub>2</sub>O atmosphere of constant relative humidity (70 to 90 %). Deuterium resonance at 10 Mc/s then showed a well-defined splitting in the range of 10 to 20 gauss, due to quadrupole effects (Figure 1). The magnitude of the splitting varies according to  $(3 \cos^2 \theta - 1)$  with the angle  $\theta$  between direction of the fibers and magnetic field (Figure 2). The splitting decreases with increasing D<sub>2</sub>O content, a typical value being 14 gauss at a D<sub>2</sub>O content of 50 gram per 100 gram collagen.

In analogy with earlier proton resonance measurements in hydrated collagen [J.Chem.Phys. 36, 3297 (1962); Annals N.Y.Acad.Sci, in press], we presume that the splitting of the deuterium resonance is due to anisotropic rotation of D<sub>2</sub>O molecules, such that the electric field gradients at the D nuclei are not averaged out to zero. Compared with Ba(ClO<sub>3</sub>)<sub>2</sub>.D<sub>2</sub>O at low temperatures, where the D<sub>2</sub>O molecule does not rotate, [Chiba: J.Chem.Phys. 39, 947 (1963)] the field gradient is reduced by a factor of thirty. We are now trying to calculate average field gradients for certain models of hydration.

Yours sincerely,

*C. Migchelsen*

(C. Migchelsen)

*H. J. C. Berendsen*

(H. J. C. Berendsen)

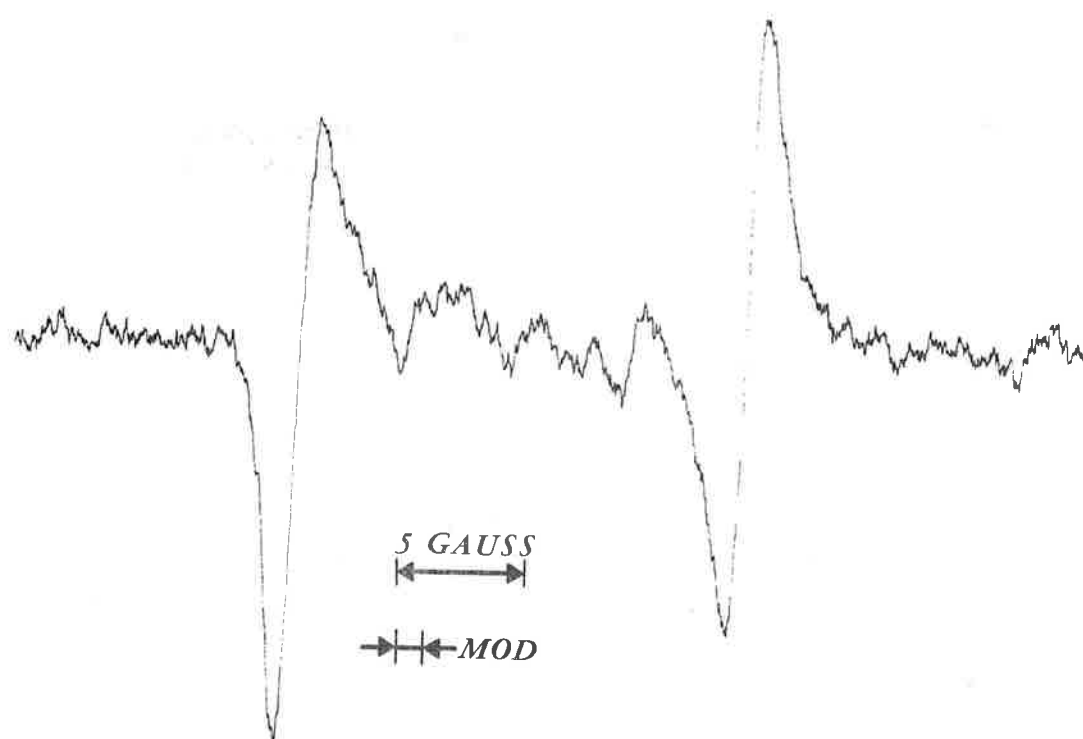


Fig. 1. Quadrupole splitting of  $D_2O$  on collagen with a  $D_2O$  content of 42 gr. per 100 gr. collagen.

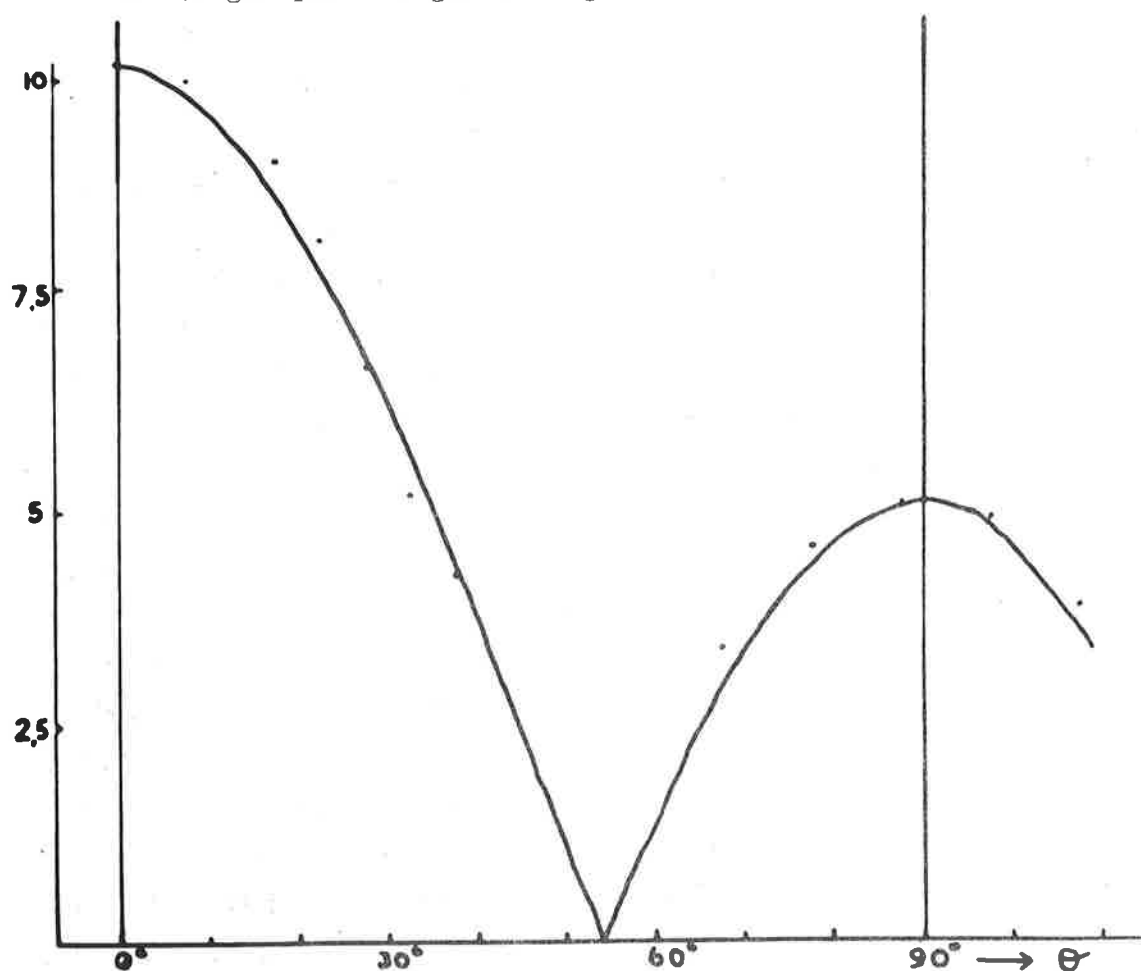


Fig. 2. Splitting in gauss as a function of the angle  $\theta$  between the fiber and magnetic field direction. The drawn curve is the theoretical  $(3 \cos^2 \theta - 1)$  curve.

CHEMISCHES LABORATORIUM  
DER UNIVERSITÄT MÜNCHEN

INSTITUT FÜR ORGANISCHE CHEMIE

Prof. Dr. Herbert Zimmermann

© MÜNCHEN 2, 18. Juni 1965  
Karlsruhe 23 - Telefon 55 79 76

Herrn Prof. Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Ill. 60616  
USA

Sehr geehrter Herr Dr. Shapiro!

Wir haben in der letzten Zeit einige NMR- und IR-spektroskopische Untersuchungen an Wasserstoffbrückenbindungen durchgeführt. Imidazol und seine Derivate bilden in geeigneten Lösungsmitteln Assoziate, in denen benachbarte Moleküle durch  $\text{NH} \cdots \text{N}$ -Wasserstoffbrückenbindungen verknüpft sind. Die NH-Signale der Brückenbindungen werden bei extrem niedrigen Feldstärken beobachtet, z.B. für 4(5)-Methylimidazol in Toluol als Lösungsmittel bei  $\tau = -5,4$  ppm. Die NH-Signale zeigen im allgemeinen keine Verbreiterung durch Kopplung des Protons mit den Stickstoffkernen, wodurch auf intermolekularem Protonenaustausch in der Brückenbindung hingewiesen wird. Um zu prüfen, ob ähnliche Befunde auch bei anderen Systemen zu beobachten sind, haben wir eine größere Anzahl von Brückenbindungen zwischen Pyrrol und verschiedenen Elektronendonatoren untersucht. Folgende Verbindungen B wurden verwendet: 1. 1-Methylimidazol, 2. Triäthylamin, 3. Tetramethyläthylendiamin, 4. 2.6-Luditin, 5. 2.4-Luditin, 6. 2.4.6-Collidin, 7. Tri-n-butylamin, 8. Pyridin, 9. Dioxan, 10. Diäthyläther, 11. Diisopropyläther, 12. Tetrahydrofuran, 13. Cyclohexanon, 14. Aceton, 15. Diäthylketon, 16. Acetophenon, 17. Acetonitril, 18. Butyronitril, 19. Nitromethan, 20. Chloroform, 21. Schwefelkohlenstoff, 22. Tetrachlorkohlenstoff, 23. Cyclohexan, 24. n-Hexan. Bei keinem System konnte ein scharfes NH-Signal bei extrem niedrigem

Feld beobachtet werden.

Es besteht eine Korrelation zwischen der Lage der Banden im NMR- und IR-Spektrum (Abb.1). Die aromatischen Moleküle wurden auf Ringstrom korrigiert. - Ebenso besteht eine Korrelation zwischen den spektroskopischen Daten und den  $pK$ -Werten der verwendeten Basen B. Wie man der Abbildung entnehmen kann, sind die Meßwerte für Moleküle mit gleichen funktionellen Gruppen im Diagramm dicht benachbart.

Mit freundlichen Grüßen

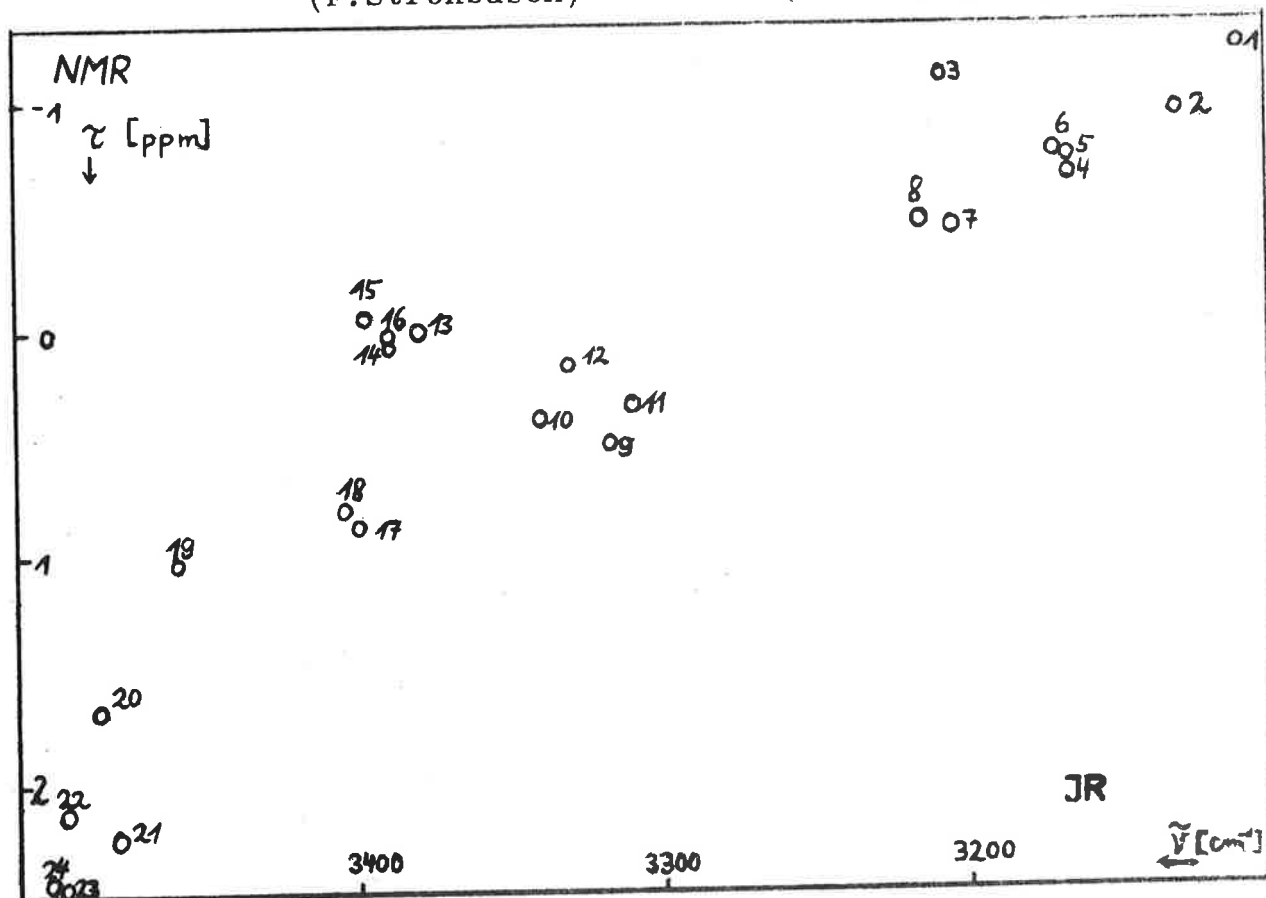
Ihr

F. Strohbusch

H. Zimmermann

(F. Strohbusch)

(H. Zimmermann)



## Koninklijke Shell - Laboratorium, Amsterdam

BADHUISWEG 3 AMSTERDAM - N.

TELEFOON (020) - 6 11 11

Dear Dr. Shapiro:

Modified Carr-Purcell method to measure  $T_2$  of a system of two non-identical spins

The nmr spectrum of a molecule with two non-identical spins ( $S = I = \frac{1}{2}$ ) consists of two doublets, one of each spin species. To measure the transverse relaxation time  $T_2$  of such a spin system one may use the Carr-Purcell method, in which a  $90^\circ$  pulse is applied to the spins followed by a sequence of  $180^\circ$  pulses.

The free induction signal of such a two-spin system is caused by a superposition of two precessions at frequencies differing by  $J$  c/s, in which  $J$  is the coupling constant between the  $S$  and  $I$  spins in the molecule. The induction signal is

$$I = A(t)\sqrt{2} \cdot \cos \pi Jt \cdot \exp -t/T_2^* ,$$

where  $A(t)\exp -t/T_2^*$  is the signal in the absence of the spin-spin interaction. The duration of the free precession signal depends on the homogeneity of the magnetic field.

In liquids one usually introduces an intentional inhomogeneity to shorten the duration of the free precession;  $180^\circ$  pulses are here applied at short time intervals. If the viscosity of the liquid is low, molecular diffusion may influence the echoes and it may be necessary to enhance the frequency of the  $180^\circ$  pulses beyond the possibility of one's apparatus. In these situations the following approach may be useful.

The  $T_2$  measurements may be performed in a homogeneous field, the free precession signal then being of long duration. Following this the series of  $180^\circ$  pulses is applied during the free precession. In order to obtain a simple resultant signal, from which the "real"  $T_2$  can be directly determined, the  $180^\circ$  pulses are given in the minima (or the maxima) of the free precession. The minima occur at times  $t = (2n + 1)/J$  s after the  $90^\circ$  pulse ( $n = 0, 1, 2, \dots$ ). One may apply the  $180^\circ$  pulses at times corresponding with  $n = 1, 2, 3, \dots$ , or, depending on convenience, at times corresponding with  $n = 1, 3, 5, \dots$ , etc. An advantage of this method is that the influence of diffusion does not easily come into play on account of the homogeneity of the external field.

$T_2$  measurements have been made according to the above method using a modified<sup>1</sup> DP 60 A nmr spectrometer. The maximum available output of the V 4311 transmitter is applied during a pulse; the duration of a  $90^\circ$  pulse is then 0.3 ms, which is adequate for experiments on most organic molecules ( $T_2^{-1} \leq 10 \text{ s}^{-1}$ ). Fig. 1 illustrates an experiment on  $\text{CHFC}_2$  at  $-142^\circ\text{C}$  (56.4 Mc/s). The coupling constant  $J = 54$  c/s; the minima in the free precession are 38 ms apart, which, in this particular experiment, is also the interval between  $180^\circ$  pulses.

Yours sincerely,

Amsterdam, 21st May 1965

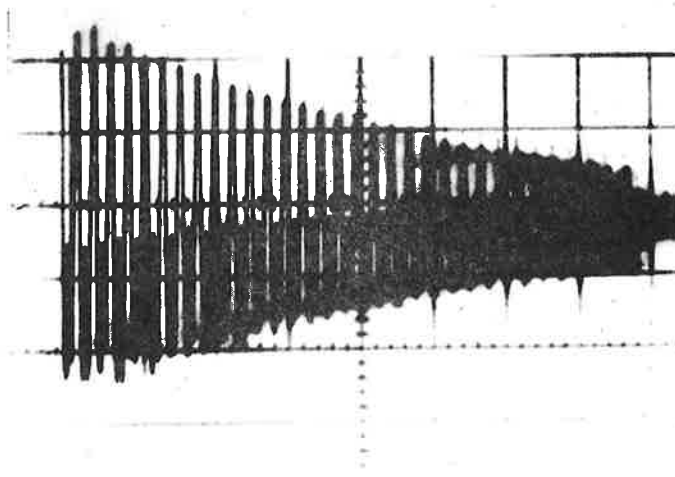
C. Maclean

E.L. Mackor

1. E. Grunwald, C.F. Jumper and S Meiboom, J. Am. Chem. Soc. 84 (1962) 4664.



- 2 -



Example of  $T_2$  measurement of  $\text{CHFCl}_2$  at  $-142^\circ\text{C}$  (fluorine resonance at  $56.4 \text{ Mc/s}$ ). The induced signal is detected with a phase-sensitive detector. The  $180^\circ$  pulses are applied in the minima of the free precession.  $T_2$  can be obtained directly from the time dependence of the maxima.

THE UNIVERSITY OF CONNECTICUT  
THE COLLEGE OF LIBERAL ARTS AND SCIENCES

June 14, 1965

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

Dear Dr. Shapiro:

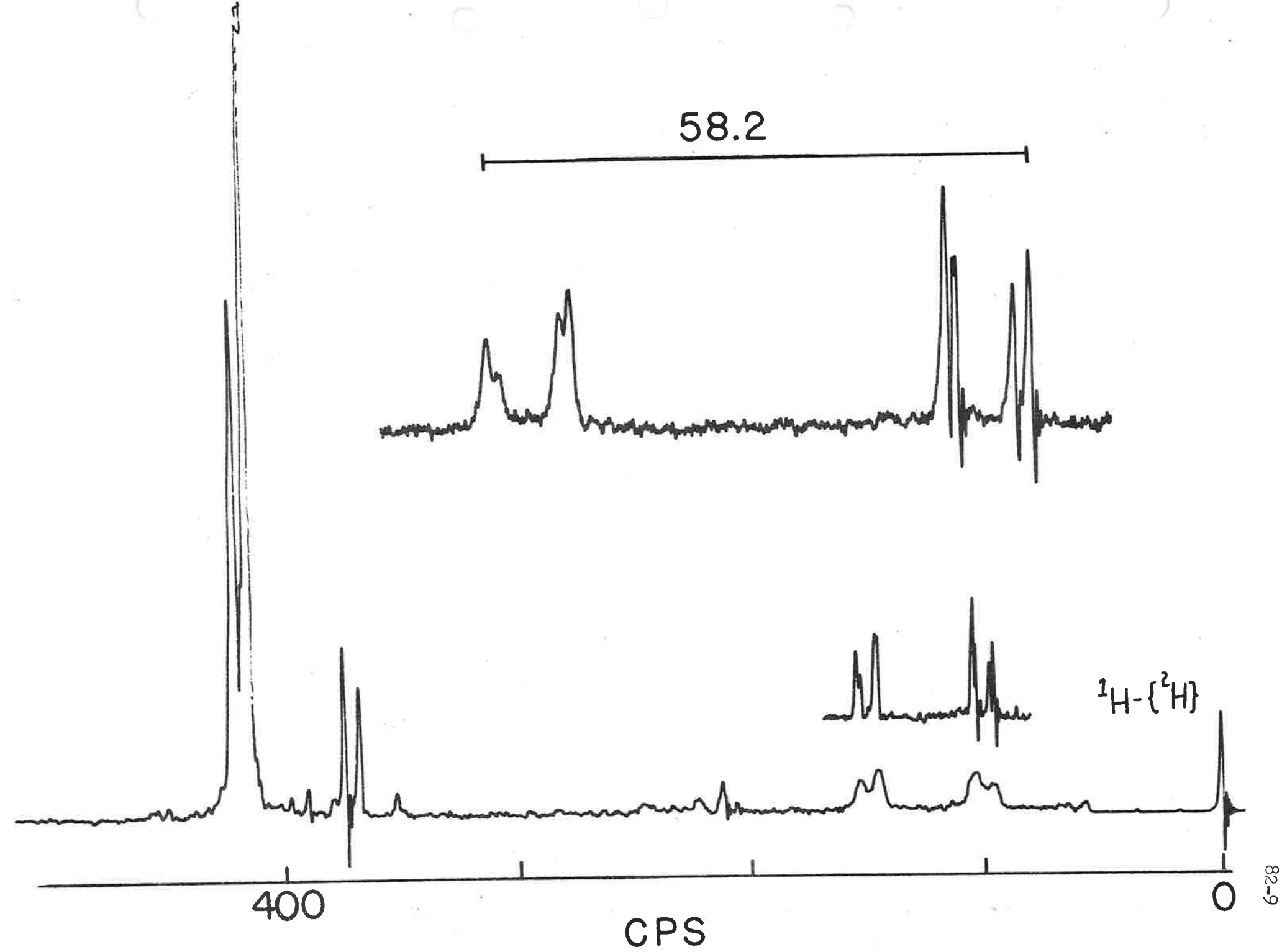
We have gotten quite a bit of experience with the NMR Specialties Heteronuclear Decoupler HD-60A on our A-60 since the decoupler became operational about 6 months ago. The resolution seems completely unaffected by the probe modification, and sensitivity is within Varian specifications although it is somewhat lower than before. Our major difficulty is in eliminating spinning sidebands; the best we have done is reduction to about 3% of signal height with considerable day-to-day variability. Tom Hill of NMR Specialties will, hopefully, soon resolve this problem.

We have investigated the n.m.r. spectrum of various deuterated hydrocinnamyl alcohols and show the aliphatic proton spectrum for an (almost) equimolar mixture of erythro- and threo-  $C_6H_5CHDCHDCD_2OD$ . The benzylic protons remain broadened upon deuterium irradiation because of small couplings with the ring hydrogens. From the two AB patterns one finds (1) the chemical shift,  $\Delta\delta$ , is 2 cps. less than the corresponding shift in  $C_6H_5CH_2CH_2CD_2OD$ , a whopper of a deuterium isotope effect, and (2) the chemical shift difference in the two isomers is not the same. We've looked at several different samples in different solvents at different times, and invariably the chemical shift in that isomer with the larger (9.1 cps) vicinal coupling constant is greater by 0.2 - 0.3 cps. than that in the isomer with the smaller (6.3 cps) coupling. We're reasonably confident that this effect is real since we've observed it in every spectrum recorded.

Sincerely,

*Eugene I. Snyder*

Eugene I. Snyder  
Assistant Professor  
Department of Chemistry



## University of Bristol

## School of Chemistry

Professor F. G. A. Stone

Telephone: Bristol 24161 Ext. 311

Department of Inorganic Chemistry  
Bristol 8.  
EnglandProfessor B.L. Shapiro,  
Department of Chemistry,  
Illinois Institute of Technology,  
Chicago,  
Illinois 60616,  
U.S.A.

21st June, 1965

Dear Barry,

Platinum-Fluorine Coupling Constants, and  
 $F^{19}$  Chemical Shifts in Pentafluorophenyl-  
platinum Complexes

We have recently prepared a number of cis and trans complexes of the type  $(Et_3P)_2Pt(C_6F_5)_2X$  using  $^1H$  NMR spectra to determine their stereochemistry as described in our previous contribution (IITNMR No.75). The  $^{19}F$  spectra of the complexes have now been studied and we would like to report some of the parameters obtained.

Table I provides values of  $^{195}Pt/^{19}F$  coupling constants. Coupling of the metal to the ortho fluorine ( $F_o$ ) is always observed but in certain cases coupling to the meta fluorine ( $F_m$ ) cannot be estimated because of the complexity of the spectrum and the low intensity of the resonance signals. The constant  $J_{Pt-F_{para}}$ , which was expected to be very small, if not zero, was never observed.

The chemical shifts of the ortho, meta and para fluorine atoms are shown in Table II. Parshall (J. Amer. Chem. Soc., 86,

- 2 -

5367 (1964)) by studying the spectra of some meta- and para-monofluorophenylplatinum complexes has shown that their  $F^{19}$  shifts depend on the nature of the ligand X in the trans position to the  $C_6H_4F$  group. He has suggested that  $|\delta_p - \delta_m|$  is a measure of the  $\pi$ -acceptor capability of X. The ability of the ligand to accept electrons in  $\pi$  or  $\pi^*$  orbitals is thought to be one of the two electronic factors which contribute to the "trans-effect" in square planar complexes. In our pentafluorophenyl complexes we have been able to study simultaneously the variation of the meta and para fluorine chemical shifts with ligand X. The figures in the last column of Table II clearly suggest correlation of  $|\delta_p - \delta_m|$  with the  $\pi$ -acceptor nature of X. Strong  $\pi$ -acceptor ligands such as CN produce large values for Z, the  $\pi$ -acceptor series being  $CN^- \sim SCN^- > I^- > Br^- > Cl^- > CH_3^-$ .

One of us (F.G.A.S.) would like to thank Dr. Parshall for a stimulating discussion.

Yours sincerely,

*F. J. Hopton*

F.J. Hopton,

*A. J. Rest*

A.J. Rest,

*Gordon*

F.G.A. Stone.

TABLE I.  $^{195}\text{Pt}$ - $^{19}\text{F}$  Coupling Constants in  $(\text{Et}_3\text{P})_2\text{Pt}(\text{C}_6\text{F}_5)\text{X}$  Compounds

<u>Trans compounds</u>	X	$J_{\text{Pt-F}_o}$ (cps)	$J_{\text{Pt} - \text{F}_m}$ (cps)
	Cl	492	106
	Br	490	105
	I	470	100
	SCN	470	103
	CN	370	76
	$\text{CH}_3$	300	-
<u>Cis compounds</u>	$\text{C}_6\text{F}_5$	377	-
	Cl	360	-

TABLE II.  $^{19}\text{F}$  Chemical Shifts in Trans  $(\text{Et}_3\text{P})_2\text{Pt}(\text{C}_6\text{F}_5)\text{X}$  Compounds

<u>X</u>	$\delta_o^\dagger$	$\delta_p^\dagger$	$\delta_m^\dagger$	$\pi$ -Bond criterion Z $ \delta_p - \delta_m $
$\text{CH}_3$	123.7	174.2	174.2	0
Cl	125.1	173.3	174.6	1.3
Br	124.7	172.6	174.1	1.5
I	125.3	172.1	173.7	1.6
SCN	124.9	171.4	173.7	2.3
CN	124.3	171.0	173.3	2.3

$^\dagger$  Chemical shift in p.p.m. from  $\text{CCl}_3\text{F}$  (0.0 p.p.m.)  
as internal reference.

## ROHM &amp; HAAS COMPANY

WASHINGTON SQUARE



PHILADELPHIA 5, PA.

Reply to

ROHM & HAAS RESEARCH LABORATORIES  
 SPRING HOUSE, PENNSYLVANIA 19477  
 MITCHELL 3-0200  
 CHESTNUT HILL 2-0400

June 23, 1965

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

Dear Professor Shapiro:

In course of checking an Org. Syn. preparation for a mixture of cis- and trans-2,2'-dichloro- $\alpha,\alpha'$ -epoxybibenzyl we had occasion to measure the n.m.r. spectrum of these oxiranes. The values for the oxirane protons, as may be seen from a long list of similar epoxides prepared by Mark,<sup>1</sup> always show cis-H > trans-H. That this should be so arises from the difference in the dihedral angles of the aromatic rings with the C-C single bond causing different diamagnetic shifts.<sup>2,3</sup> Similar chemical shifts were found in the necessarily cis-configuration "phenanthrene epoxide".<sup>4</sup> This lengthy introduction is meant to point out an unfortunate error appearing in the Varian Catalog, Nos. 625 and 626, where the cis- and trans-stilbeneoxide structures are assigned to the opposite spectra.

With this letter I hope to get on your mailing list.

Yours sincerely,

ROHM &amp; HAAS COMPANY

*George A. Frank*  
 George A. Frank  
 Senior Chemist

GAF:ma

1. V. Mark, J. Am. Chem. Soc., 85, 1884 (1963).
2. L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, New York, 1959, Chapter 7.
3. M. H. Gianni, E. L. Stogryn, and C. M. Orlando, J. Phys. Chem., 67, 1385 (1963).
4. M. S. Newman and S. Blum, J. Am. Chem. Soc., 86, 5598 (1964).

# TECHNISCHE HOGESCHOOL TE EINDHOVEN

POSTBUS 513 - TEL. (04900) 68000 - GIROREKENING 1076326 - BANKIER: F. VAN LANSCHOT - EINDHOVEN

Prof. B. Shapiro,  
Department of Chemistry,  
Illinois Institute of Technology,  
Chicago 16,  
Illinois,  
USA

UW BRIEF

LETTER EN NUMMER

EINDHOVEN, INSULINDELAAN 2

ONDERWERP

Dear Prof. Shapiro,

For one of us (F.H.A.R.) this is the first contribution to "Mellon Letters", and he hopes hereby to be admitted to your mailing list.

During my 2 year stay at the National Research Council in Ottawa we engaged in a renewed attack on medium effects in NMR, and gas-to-liquid shifts in particular. The literature on the latter subject is not very encouraging [1,2]. The quantitative agreement between calculated and experimental shifts usually being poor even for isotropic, nonpolar molecules, where the Van der Waals  $\sigma_w$  term is the only operative one. It occurred to us that two factors have been neglected so far

a) Repulsive forces between molecules influence the screening in a similar way (but with opposite sign) as attractive forces do [3]. We propose this leads to an extra factor  $[1-(r_0/r)^6]$  in the expression for  $(\sigma_{\text{pair}})_w$  ( $r$  is the distance between the molecules,  $r_0$  is the distance of zero interaction energy in the Lennard-Jones (6-12) potential).

b) The field square term,  $\bar{F}^2$  (which causes the van der Waals shift) should be evaluated not at the center of the solute molecule but at the site of the measured nucleus (which is usually peripheral). After proper averaging over tumbling it turns out that in the expression for  $\bar{F}^2$ ,  $(1/R)^6$  must be replaced by  $\langle \frac{1}{R^6} \rangle = \frac{1}{r^6} \frac{1+g^2}{(1-g^2)^4}$  where  $g = d/r$

$d$  being the distance from measured nucleus to the center of the molecule.

VERZOEK EEN ONDERWERP PER BRIEF TE BEHANDELEN EN DIJ BEANTWOORDING LETTER, NUMMER EN DATUM TE VERMELDEN



These two improvements were applied to the earlier work on medium effects in gases by Bernstein and coworkers [4,5], in order to calculate new (and hopefully better) values for the bond parameters  $B$  ( $(\sigma_{\text{pair}})_w = -B\bar{F}^2$ ). The new and old  $B$  values are compared in the Table

Bond type and number of solute-solvent systems investigated		Old B values $\times 10^{18}$ esu [4,5]		New B values $\times 10^{18}$ esu	
C - H (non polar)	3	1.0	$\pm 33\%$	1.35	$\pm 20\%$
C - F in $\text{CF}_4$	5	16.4	$\pm 13\%$	24.1	$\pm 8\%$
Si - F in $\text{SiF}_4$	4	43.5	$\pm 12\%$	59.2	$\pm 7\%$
S - F in $\text{SF}_6$	4	29.5	$\pm 8\%$	40.0	$\pm 5\%$

It is clear that the new  $B$  values are more internally consistent by a factor 2 from one solute-solvent system to another, which is taken as evidence for the correctness of the two proposals. We also measured the gas-to-liquid shifts of the five  $\text{X}(\text{CH}_3)_4$  compounds ( $\text{X} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) and their 20 binary combinations (infinite dilution). They range from 10 to 22 cps at 60 Mc. The simple binary-collision gas model of Raynes, Buckingham and Bernstein [4] extended to include the site- and repulsion corrections is a surprisingly good basis for the calculation of (van der Waals) gas-to-liquid shifts. A plot of calculated versus

experimental  $\sigma_w$  values for the solutions mentioned above gives a straight line through the origin. The standard deviation is  $\pm 1.5$  cps which is within the error limits of experiment and calculation. The slope of this line is 1.44, the deviation from unity being attributed to triple and higher order collisions in the liquid. Measurements on the temperature dependence of  $\sigma_w$  corroborate this interpretation.

1. B. B. Howard, B. Linder, M.T. Emerson, J.C.P. 36 (1962), 485
2. N. Lumbroso, T. K. Wu, B. P. Dailey, J.Phys.Chem. 1963, 2469.
3. T. W. Marshall, J.A. Pople, Mol. Phys. 3, (1960), 339
4. W. T. Raynes, A. D. Buckingham, H. J. Bernstein, J.C.P. 36 (1962) 3481.
5. L. Petrakis, H.J. Bernstein, J.C.P. 37 (1962), 2731.

*H. J. Bernstein*

H. J. Bernstein

*F. H. Rummens*

F. H. Rummens

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RESEARCH & DEVELOPMENT DEPARTMENT  
RESEARCH DIVISION

500 SOUTH RIDGEWAY AVENUE  
P. O. BOX 85  
GLENOLDEN, PA.

June 29, 1965

File: 002

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

Dear Dr. Shapiro:

Plastic Caps

For the benefit of those people that have been having trouble with the plastic caps sold by Varian, I would like to suggest an alternate source, Protective Closure Co., Inc., 2207 Elmwood Ave., Buffalo, N. Y. These caps have two O-rings on the inside and will hold up to about 2 atms. Cost \$5.00/1000.

The following papers are in the process of being published and a few preprints are available.

NMR of Polymers

(1) NMR Study of Polymers of Ethyl, Isopropyl, Isobutyl, and t-Butyl Vinyl Ethers.

(2) Tacticity of Poly( $\alpha$ -Methylstyrene) by NMR.

(3) Effect of Solvent upon High Resolution NMR Spectra of Polymers.

Aluminum Alkyls

(4) NMR Study of Aluminum Alkyls.

Very truly yours,

  
Kermit C. Ramey

KCR:LH

## UNIVERSITÉ D'OTTAWA

FACULTÉ DES SCIENCES PURES ET APPLIQUÉES



OTTAWA 2, CANADA

## UNIVERSITY OF OTTAWA

FACULTY OF PURE AND APPLIED SCIENCE

DÉPARTEMENT DE CHIMIE  
365, RUE NICHOLASDEPARTMENT OF CHEMISTRY  
365 NICHOLAS ST.

June 28th, 1965

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

Dear Barry,

We have just completed the analysis of the  $A_2B_2$  portion of the spectrum of 2,3-dichloro-1,4-dioxane, m.p.  $52^\circ$ . Summerbell (1) originally assigned the cis configuration to this compound, since it was observed to be the less stable of the two diastereomeric 2,3-dichlorodioxanes and since the other isomer, m.p.  $31^\circ$  was capable of kinetic resolution and therefore possessed the trans configuration. Dipole moment measurements and X-ray analysis corroborated this conclusion and further provided evidence that the chlorine atoms in the trans compound were diaxial (2).

Caspi and co-workers (3), from a qualitative examination of the spectra of both isomers, concluded that the  $52^\circ$  isomer was cis and occupied a rigid boat conformation, while the  $31^\circ$  isomer was trans and in a rigid chair form. Both conclusions were of a highly speculative nature and were unfortunately accepted in part by Le Fevre (4). Le Fevre remeasured the dipole moments and Kerr constants of the two isomers and in conjunction with Caspi's data arrived at the modified conclusion that the isomer m.p.  $52^\circ$  was trans diequatorial, the isomer m.p.  $31^\circ$  trans diaxial. We thus felt that a rigorous analysis of the compound m.p.  $52^\circ$  was warranted.

The  $A_2B_2$  analysis was carried out in the usual manner, as was recently well delineated by Abraham (5). We used the Frequent IV A program kindly provided by Paul Lauterbur to calculate the theoretical spectrum on an IBM 1620 computer. The parameters were adjusted until agreement to within 0.15 c. p. s. in calculated and observed line positions was obtained for spectra measured in benzene and in chloroform. The comparisons are shown in Fig. 1. The coupling constants and chemical

- 2 -

shifts obtained from the analysis are as follows:

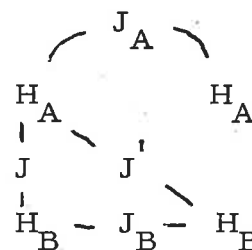
$$J_A = J_B = 3.05 \text{ cps (M = O)}$$

$$J = -12.3 \text{ cps}$$

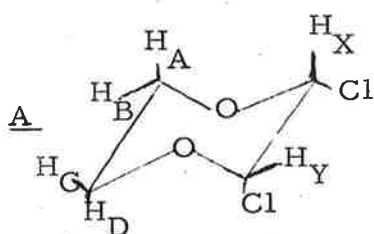
$$J' = 6.4 \text{ cps}$$

$$\delta = 22.95 \text{ cps in CHCl}_3$$

$$= 31.0 \text{ cps in benzene}$$

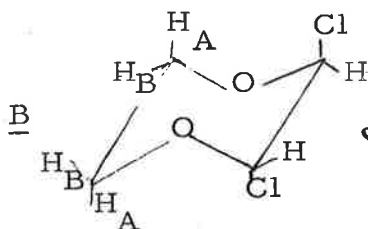


Let us now consider the most probable configurations and conformations for the compound



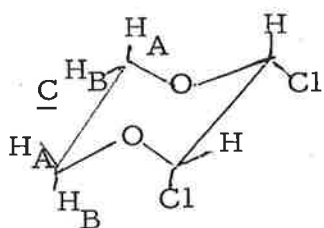
cis-rigid chair

Spectrum Expected  
ABCD  
XY



trans-rigid chair

$$J_A = J_B$$

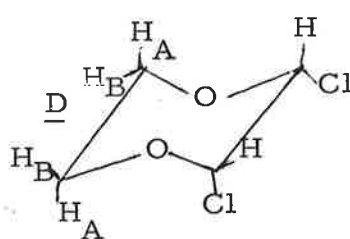


cis-inter-converting chairs

$$J_A = J_B = J_{60^\circ}$$

$$J = J_{\text{Gem}}$$

$$J' = \frac{J_{160} + J_{180}}{2}$$



trans-inter-converting chairs

$$J_A = J_B = \frac{J_{60} + J_{180}}{2}$$

$$J = J_{\text{Gem}}$$

$$J' = J_{60} \text{ for equal populations}$$

or  $J_A \neq J_B$  for unequal populations.

... 3

- 3 -

- A can be eliminated since the observed  $\text{CH}_2$  absorption is not an ABCD and more important,  $\text{H}_\text{X}$  and  $\text{H}_\text{Y}$  gave a single sharp peak
- B can be eliminated since we found  $J_\text{A} = J_\text{B}$
- D for unequal populations can be eliminated for same reason. For equal populations, we would require  $J_{60} = 6.4$  and

$J_\text{A} = \frac{J_{60} + J_{180}}{2} = 3.05$ . This completely revokes the Karplus relationship between  $J_\text{vic}$  and  $\phi$ . Although the equation is far from quantitative it is completely reliable in predicting that  $J_{180} > J_{60}$ . Thus D is eliminated.

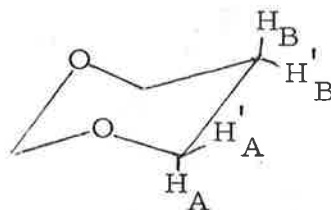
For C our parameters compare favorably with coupling constants in the 1,3-dioxane system reported by Barbier et al (6). They found

$$J_{60} = J_{\text{A'B}} = 3.8 \text{ cps}$$

$$\frac{J_{60} + J_{180}}{2} = \frac{J_{\text{A'B'}} + J_{\text{AB}}}{2} = 6.7$$

$$J_{\text{AA'}} = -11 \text{ (a better model in this case might be } \text{CH}_3\text{CH}(\text{OH})\text{-CH}_2\text{OH}$$

in which  $J_{\text{Gem}} = -11.9$  (7)).



In view of the good agreement between the model and experimental coupling constants, any detailed consideration of the high energy boat form is entirely unwarranted. We therefore conclude that the  $52^\circ$  isomer of 2,3-dichloro-dioxane has the cis configuration and undergoes rapid chair-chair interconversion at room temperature.

We are currently investigating several other 2,3-disubstituted dioxanes both by analysis and low-temperature measurements.

#### References:

- (1) R.K. Summerbell and H.E. Lunk, J. Am. Chem. Soc. 79, 4802 (1957).
- (2) C. Altona, C. Romers and E. Havinga, Tetrahedron Letters 10, 16 (1959).
- (3) E. Caspi, T.A. Wittstruck and D.M. Piatak, J. Org. Chem. 27, 3183 (1962).

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- (4) C.Y. Chen and R.J. Le Fevre, J. Chem. Soc. 1965, 558.
- (5) K.J. Abraham, J. Chem. Soc. 1965, 256.
- (6) C. Barbier, J. Delmau, and J. Rånft, Tetrahedron Letters, 45, 3339 (1964).
- (7) Varian Associates Spectra Catalog, p. 45.

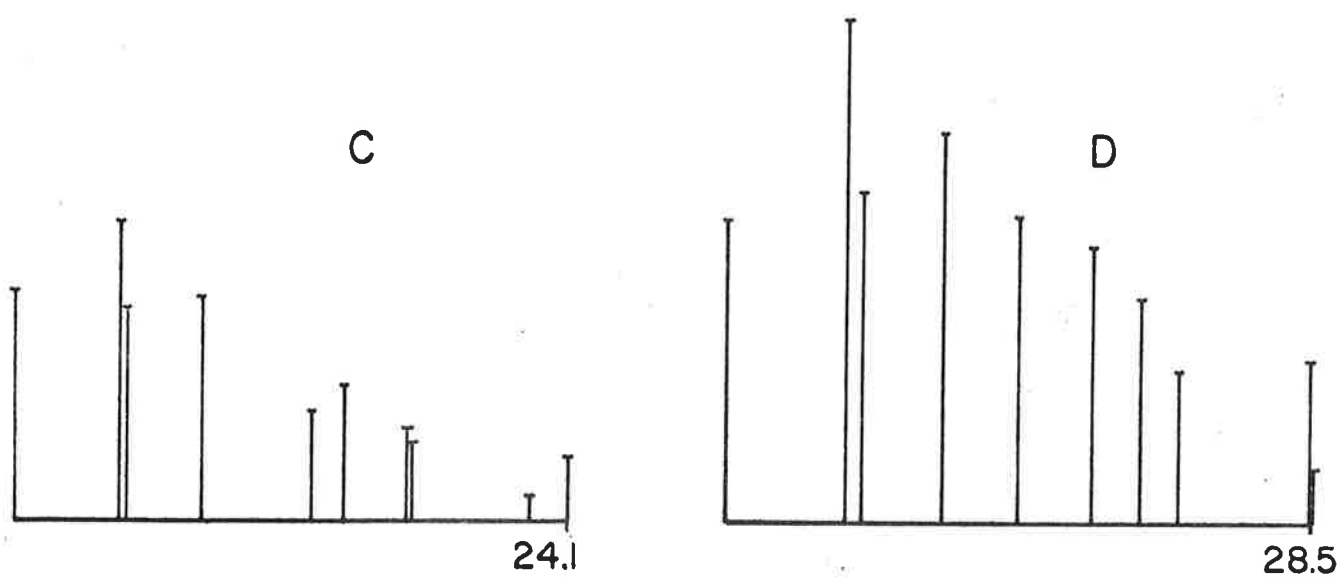
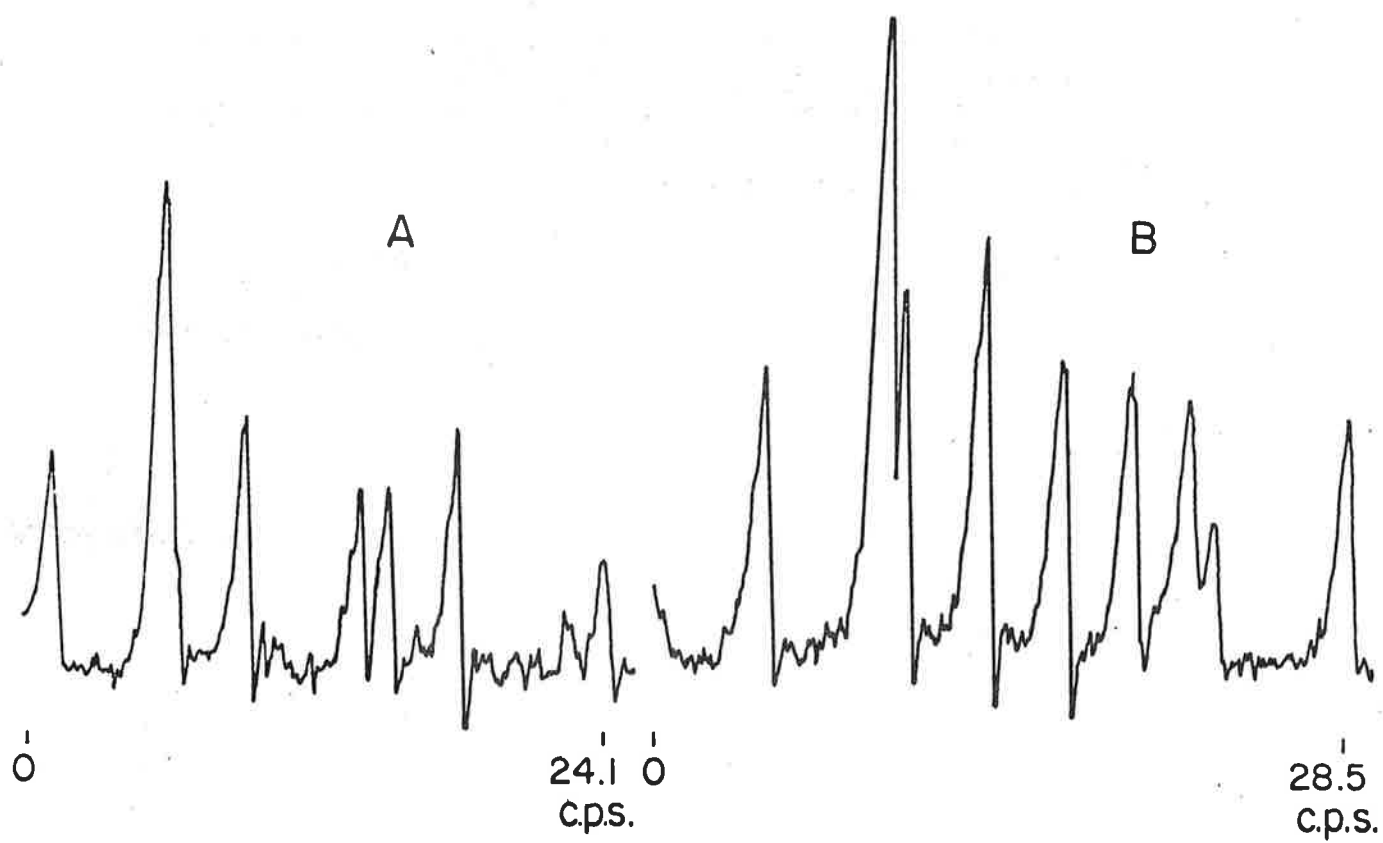
Yours sincerely



RRF/cg

*please entitle "Proof of Structure of 2,3-dichloro-  
1,4-dioxane."*

FIGURE 1





Nuclear Magnetic Resonance Studies with the Gallium-71 Isotope

By J.W. Akitt, N.N. Greenwood and A. Storr  
Department of Inorganic Chemistry, University of Newcastle upon Tyne  
England.

Abstract

The  $^{71}\text{Ga}$  nuclear magnetic resonance signals of a series of symmetrical gallium ions have been located at 20 Mc./sec. Chemical shifts over a range of 1367 p.p.m. were noted with resonance line-widths between 90 and 6000 c./sec. A  $^{71}\text{Ga}$  n.m.r. study of the gallium trichloride-hydrochloric acid indicates that there is a critical concentration of acid below which the tetrachlorogallate anion is increasingly replaced by the hexa-aquogallium cation  $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$  together with some intermediate species. Similar results are reported for the bromide and iodide systems though the latter shows less tendency to form intermediate species.

Solutions and melts of gallium dichloride and dibromide have also been examined and the results confirm the presence of two types of gallium.

The  $^{71}\text{Ga}$  resonance positions of the species  $\text{GaH}_4^-$ ,  $\text{Ga}(\text{OH})_4^-$ , and  $\text{Et}_2\text{OGaCl}_3$  are also reported. The increased line widths of the species  $\text{Ga}(\text{OH})_4^-$ ; and  $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$  as compared with  $\text{GaCl}_4^-$ ,  $\text{GaBr}_4^-$  are interpreted as being due to hydrogen bonding of the former species with the solvent.

Preprints not yet available



*Fysiska Institutionen, Uppsala July 2, 1965*

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

Dear Barry:

Line-width variations in spectra of the ABMX type.

During the past academic year Mr. A.A. Khan, a scientist from Aligarh Muslim University (India) has been a member of our group and participated in double-resonance work on signs of long range proton spin couplings.

One of our samples, viz. N-methyl-2-pyrrolealdehyde displayed a rather peculiar spectrum. The 3- and 5- ring hydrogens were very strongly coupled but the 4-hydrogen was shifted far away from all other protons and its resonance band consisted of 4 lines of roughly equal intensity and with splittings close to the known values of  $J_{34}$  and  $J_{45}$  in the pyrrole ring. The "inner" lines in the 4-hydrogen quartet were however appreciably broader than the two outer lines.

For a happy moment we believed that these line-width differences were related to some peculiar relaxation phenomena. On second thought this exciting idea could however be discarded in favour of yet another "virtual coupling" (J.I. Musher and E.J. Corey, Tetrahedron, 18, 791-809, 1962) effect.

The shift between the 3 and 5 hydrogens is small enough to allow the degree of mixing of their spin states to be influenced by the spin state of the aldehyde proton, (because of the finite value of  $J_{\text{CHO}-5} \approx 1\text{cps}$ ). The "inner" transitions of the 4-hydrogen correspond to transitions between mixed spin states and must therefore contain (unresolved) doublet splittings which may be attributed to a partial (since it affects only some of the 4-hydrogen lines) virtual coupling between the 4-hydrogen and the aldehydic hydrogen.

The correctness of this explanation was verified by a double resonance experiment in which the aldehyde proton was decoupled (and thus could no longer influence the mixing of 3- and 5- proton spin states). Spin decoupling of the aldehyde led to a sharpening of the "inner" 4-hydrogen lines and thus the original broadening could be ascribed to unresolved splittings.

A similar series of experiments was carried out with 2-thiophene-aldehyde where the doublet structure of the "inner" 4-hydrogen lines could be resolved (at 40 Mc/sec.)

Theoretical single- and double-resonance spectra of the M-hydrogen in an ABMX system are depicted in Fig. 1.

The parameters of the spectrum are  $\nu_M$  (large),  $\nu_X$  (large)

$$\nu_A - \nu_B = 1.6$$

$$J_{AB} = 1.4$$

$$J_{AM} = 5.0$$

$$J_{BM} = 3.4$$

$$J_{AX} = 1.2$$

$$J_{BX} = J_{MX} = 0$$

These parameters are similar to - but not identical with - those of 2-thiophenealdehyde (the spectrum of the latter compound is complicated by second order effects due to a finite  $\nu_M$  and an additional finite real coupling  $J_{MX} = +0.10$  cps).

It is apparent from figure 1 that not only the "mixed" transitions 5, 6, 7 and 8 are split, but also the "combination" lines 3, 4, 9 and 10 are split by the coupling  $J_{AX}$ . All these splittings collapse in the double resonance spectrum which appears as a normal ABM (or ABX) spectrum.

Best regards

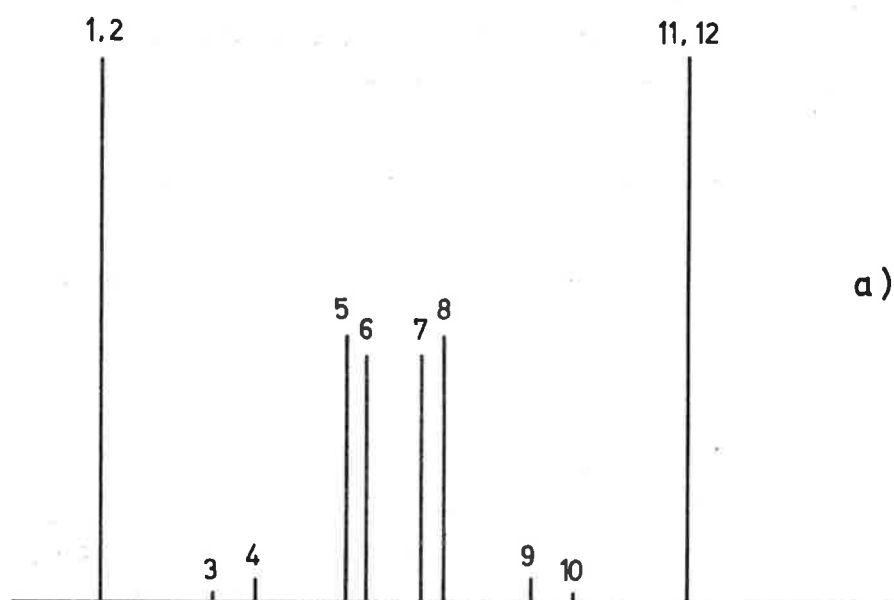
*Ragnar A. Hoffman*

Ragnar A. Hoffman

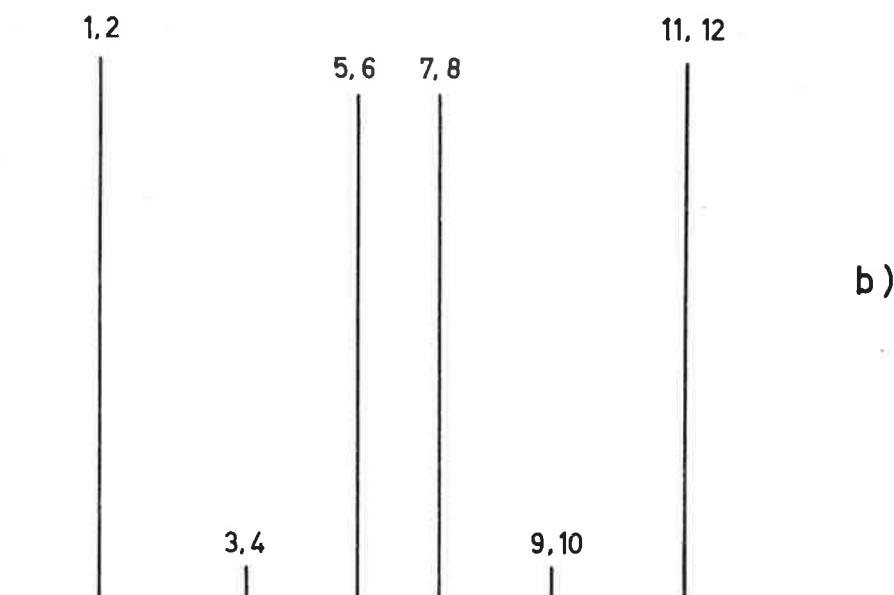


*Fysiska Institutionen, Uppsala*

single  
resonance



double  
resonance  
(X decoupled)



**ABMX**

Hoffman

Fig. 1 The M-part spectrum of an ABMX system with  $J_{MX} = 0$



# BP RESEARCH CENTRE

SUNBURY-ON-THAMES

MIDDLESEX

ENGLAND

## COMPUTER PROGRAMS

During the past few months we have been translating or adapting some existing NMR computer programs for use with our Elliott 803 computer.

We have an Algol version of Frequent IV (non-reiterative). The original program has been modified so that the calculated energy levels are printed out together with the frequencies and intensities. The original version of this program we obtained from Dr. Sekuur (IITNMR, No. 67, 15).

Further we have Algol versions of NMREN 1 and 2 for up to 6 spins. The original Fortran program was devised by Reilly and Swalen for the calculation of energy levels. The program is best used in conjunction with an energy level diagram for the spin system of interest. Labelling some of the transitions in the spectrum can be uncertain, but a calculation using approximate parameters (using, say the modified Frequent IV described above) plus some decoupling ("tickling" type) experiments usually provides sufficient information to get the correct energy level numbering required for NMREN.

Finally we have an almost complete Algol version of NMRT. When we have completed and checked the translation we will put a note in IITNMR and send a copy to anyone who is interested. If anyone requires our versions of Frequent IV or NMREN 1 and 2 we will gladly send them a listing.

## Acid and Phenol Characterisation

Frequently one is asked to examine by NMR samples of organic acids and phenols. Quite often examination of the NMR spectrum reveals no obvious bands characterising these types of hydrogen, usually due to band overlap or broadening or, with small samples of high molecular weight, due to the band being lost in background noise. A convenient technique found for detecting this type of hydrogen is to methylate the sample when a sharp singlet, due to  $-OCH_3$ , appears in the 6 - 7 region. Any of the normal methylation techniques can be used although we have found diazomethane (ethereal solution) to be particularly suitable. Small quantities of the reagent can be prepared from N-methyl-p-toluenesulphonylnitrosamide which is readily obtainable from most chemical suppliers.

S.A. Knight

D.C. Bonner

## THE ROCKEFELLER INSTITUTE

*A Graduate University and Research Center*

NEW YORK, N.Y. 10021

July 2, 1965

Prof. B. L. Shapiro  
 Dept. of Chemistry  
 Illinois Institute of Technology  
 Chicago, Illinois 60616

Dear Barry:

Sorry to be so tardy in sending my contribution, although your letter was a bit premature since Pierre Laszlo and I sent in a note supposedly to my "credit" in September on axial-axial  $^4J$ 's which has since appeared in Bull. Soc. Chim. (France).

Anyway, I have now calculated in closed form the zeroth-order Fermi-contact spin-spin coupling constant in HD for an unsymmetrical wave function

$$\psi_0 = (\alpha^3/\pi) e^{-\alpha(r_{1A} + r_{2B})}$$

$J_F^0$ , the leading term in an expansion for  $J_F$  is <sup>\*</sup>

$$J_F^0 = -\hbar^{-1} (16\pi\beta^2/3)^2 \gamma_H \gamma_D e^{-2\alpha_0^5} (\alpha a_0)^4 \left[ \frac{5}{2} - \mathcal{E} - \log(2\alpha a_0) \right. \\ \left. - \left( -\frac{1}{\alpha R} + 2 \log(R/a_0) + 2\alpha R \right) e^{-2\alpha R} + \frac{1}{2} \left( \frac{1}{\alpha R} + 2 + 2\alpha R \right) e^{-4\alpha R} \right]$$

and for  $\alpha a_0 = 1$   $J_F^0 = -50.3$  cps with the one-electron contribution +7.8 cps and the two-electron contribution -58.1 cps. Thus, once again - see Mellonmr 63-25 - a real calculation, and this time exact and in closed

<sup>\*</sup>  $\mathcal{E}$  = Euler's const. 0.57

2--Prof. B. L. Shapiro

form gives a negative  $J_F^0$ . Despite its being a great surprise, I hope that maybe this time it will be taken seriously. As I said in 63-25 for some reason noone believes a negative  $J$  in  $HD$ , but when John Pople later does a calculation for  $J$  in  $CF$  and gets a negative result it's believed. I hope to get this published in Phys. Rev. or Phys. Rev. Letters, and hope to break through the skepticism; maybe someone will do the experiment some day.

Pierre Laszlo and I are writing a non-review article on the chemical shift. I am doing the theory and Pierre is doing the inadequate experimental interpretations of the theory (if my description does him justice). If anyone has preprints or sketches of exact solutions, of model problems, or detailed Hartree-Fock, or other solutions of chemical shifts I would appreciate receiving them by the middle or end of September. Likewise if anyone has new (better or worse) interpretations of experiment, Laszlo would appreciate receiving them with about the same deadline.

With best regards,

Yours sincerely,



Jeremy I. Musher

JIM/kss

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

Basel, July 3rd, 1965

Prof. B.L. Shapiro  
Illinois Institute of Technology  
Chicago 60616  
USA

Dear Barry,

We have recently tried to modify the formula for the correlation time used e.g. in quadrupole relaxation. There exists the well known Debye-formula<sup>(1)</sup>, modified for the magnetical case.

$$\tau_D = \frac{4\pi \eta a^3}{3kT}$$

But as e.g. Agishev<sup>(2)</sup> as well as Moniz and Gutowsky<sup>(3)</sup> have shown the value of  $\tau_D$  is on the average too large about a factor of ten.

This discrepancy can be explained using a theory of dielectric relaxation published by Hill<sup>(4)</sup>. This theory takes into account the shape of molecules and the conservation of angular momentum. Its disadvantage lies in the fact, that moments of inertia of molecules have to be calculated numerically. On the other hand it turns out that if the shape is neglected but the conservation of angular momentum still observed one finds a formula which differs from the Debye-formula only by a constant numerical factor. We obtain

$$\tau^* = \frac{(3-\sqrt{2})}{5} \cdot \frac{\eta a^3}{kT}$$

Comparing the three correlation theories with experimental values

$\tau_e$  we find the following factors:

Debye	$\tau_D/\tau_e = 9,5 \pm 2,0$
Hill	$\tau_H/\tau_e = 1,1 \pm 0,3$
our value	$\tau^*/\tau_e = 0,7 \pm 0,2$



- 2 -

Of course our approximation must break down for molecules with extreme shapes, whereas the Hill theory should still give a good approximation. More details will be published.

Yours sincerely,

Peter

Th. Leipert

P. Diehl and  
Th. Leipert

- (1) P. Debye, "Polar Molecules", New York, 1945, Reinhold Publishing Company
- (2) A.Sh. Agishev, JETP, 16, 815 (1963)
- (3) W.B. Moniz & H.S. Gutowsky, J.Chem.Physics, 38, 1155 (1963)
- (4) N.E. Hill, Proc.Phys.Soc., B 67, 149 (1954)

CALIFORNIA STATE COLLEGE



AT LOS ANGELES

Department of Chemistry

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

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

Dear Barry,

I have often been amused by the high frequency of opening lines in these Letters which intimate that the communication is submitted under duress in order to assure continued subscription. This note is no exception.

About two years ago we observed that the proton resonance spectrum of phenylcyclopropane underwent dramatic changes when observed at a series of low temperatures, suggesting that rotations about the bond connecting the two rings was decreasing in frequency at a rate which invited speculation that the thermodynamically more stable conformer might be observable at the low temperature limit of our instrument ( $-60^{\circ}\text{C}.$ ), and thus permit an assignment of this conformation, since of the two extreme orientations of the rings relative to each other (1a and 1b), only one (1a) should possess an identical



1a



1b

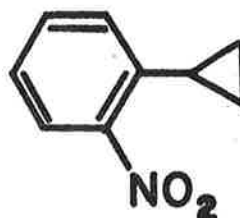
magnetic environment for both ortho protons. Inferences could then be advanced with regard to conjugative overlap of the  $\pi$ -electrons of these rings, for examination of scale molecular models of 1a and 1b suggested that H-H non-bonded interactions would be rather small and very similar for both conformers, thus stereoelectronic considerations should be the determining factor. This proved not to be the case -- an observation confirmed recently by G. Closs<sup>1</sup>, who has estimated the energy barrier to this rotation to be roughly 1 - 2 kcal./mole.

- 2 -

Substitution of a functional group that would be conjugatively electron withdrawing in the para position of the aromatic ring should serve both to lower the energy of 1b relative to 1a and the energy maximum between 1a and 1b, and to greatly simplify the aromatic portions of the spectrum. p-Nitrophenylcyclopropane(2) had been reported by Ya Levina and coworkers, who had oxidized "2" to p-nitrobenzoic acid (76%) and also converted it in three steps to phenylcyclopropane, thus confirming the structural assignment. An examination



2



3

of the  $^1\text{H}$ -spectrum of this compound which we prepared and purified by preparative GLC revealed an aromatic  $^1\text{H}$ -spectrum which induced an immediate excitement in us, for it could by no means be construed as an  $\text{A}_2\text{B}_2$  pattern (Fig. 1). The spectrum underwent little change at temperatures as high as  $120^\circ\text{C}$ , rendering suspect the original structural assignments as the para isomer.

There appeared at this time a correction by the Russian workers identifying the major mono nitration product (75%) as the ortho isomer(3) and the minor one (18%) as the para. Subsequent chromatographic isolation of the minor component by us gave a yellow solid (m.p.  $30^\circ$ ) which displayed an aromatic  $^1\text{H}$ -resonance signal consistent with an  $\text{A}_2\text{B}_2$  system (Fig. 2). The temperature dependence studies on this compound are now in progress.

Sincerely yours,

Joseph Casanova, Jr.

*Joseph Casanova, Jr.*

H. R. Kiefer

*Hansruedi Kiefer*

#### References

1. G. L. Closs, Paper 11, Organic Section, 149th National A.C.S. Meeting, Detroit, April 5-9 (1965), and private communication.
2. R. Ya Levina, Yu. S. Shabarov and V. K. Potopov, Zh. Obshch. Khim, 29, 3197 (1959).
3. Yu. S. Shabarov, V. K. Potapov, and R. Ya Levina, *ibid.*, 34 (9) 3127 (1964).

10 cps.

Fig. 1

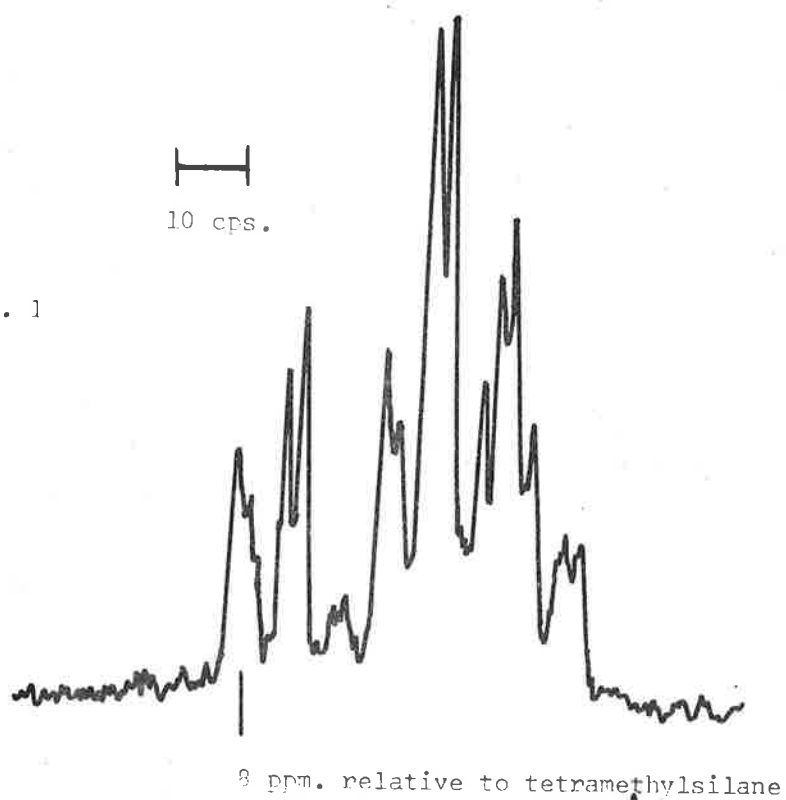
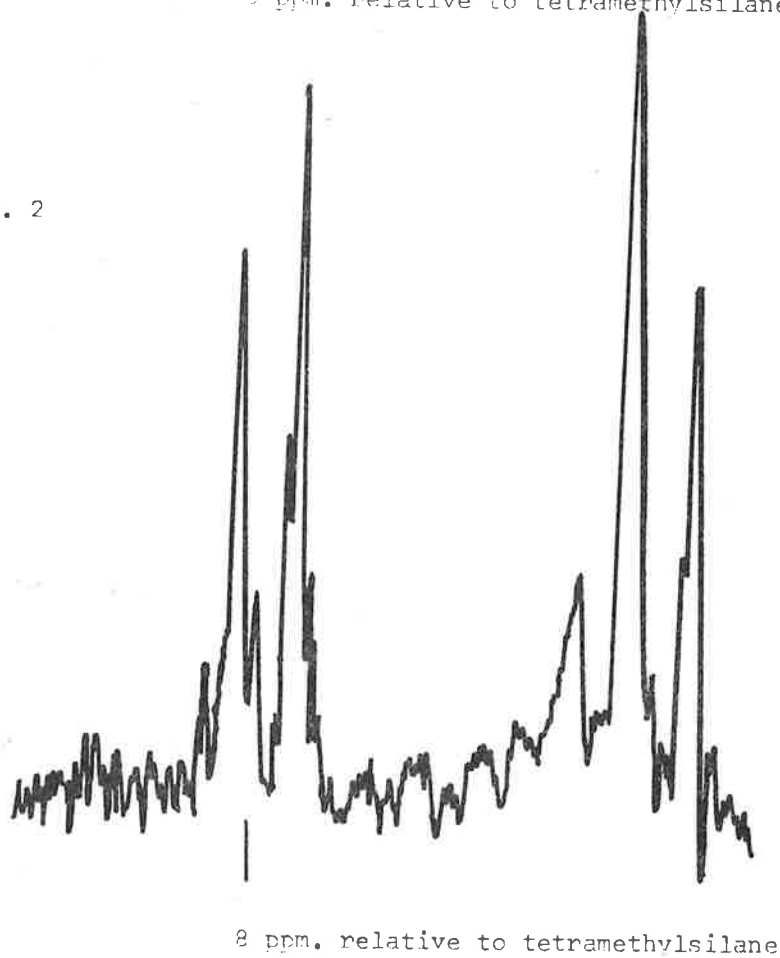


Fig. 2



DEPARTMENT OF CHEMISTRY  
THE UNIVERSITY OF MICHIGAN • ANN ARBOR, MICHIGAN

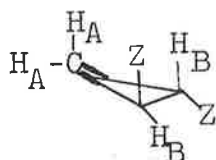
July 6, 1965

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

Dear Barry:

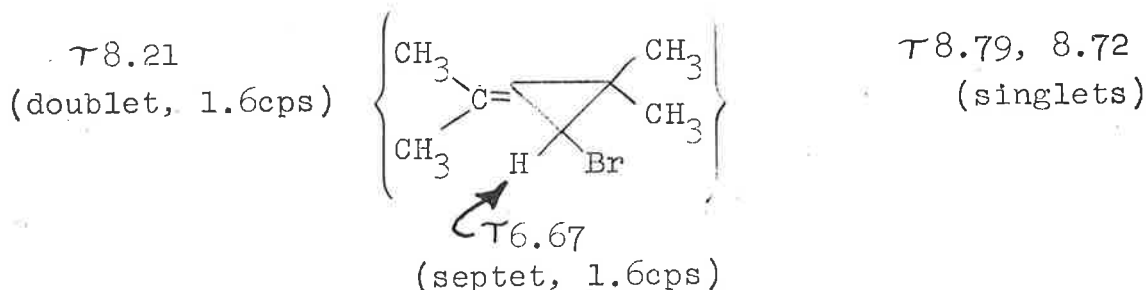
Long-Range Coupling in Methylenecyclopropanes

As our current contribution we summarize some long-range (four- and five-bond) couplings we have noted in several methylenecyclopropane derivatives. The four-bond couplings are tabulated below.



Z	SOLVENT	$H_2C=C \left( J_{H_A H_B} \right)$	$H_B$	OTHER
-CH <sub>2</sub> Br	CCl <sub>4</sub>	$\tau 4.43$ (triplet, 2.2cps)	$\tau 8.14$ (nonet)	$\tau 6.62(CH_2Br)$ (doublet, 7.4cps)
-CH <sub>2</sub> OH	CDCl <sub>3</sub>	$\tau 4.57$ (triplet, 2.0cps)	$\tau 7.5-9.2$ (multiplet)	$\tau 6.0-7.0(-CH_2O-)$ (multiplet) <sup>2</sup>
-CH <sub>2</sub> OT <sub>s</sub>	CDCl <sub>3</sub>	$\tau 4.46$ (triplet, 2.1cps)	$\tau 8.0-8.6$ (multiplet)	$\tau 6.0$ (multiplet)
-CO <sub>2</sub> Et	CCl <sub>4</sub>	$\tau 4.42$ (triplet, 2.4cps)	$\tau 7.23$ (triplet)	---
-C(=O) <sub>2</sub> OH	CDCl <sub>3</sub>	$\tau 4.46$ (triplet, 2.2cps)	$\tau 7.50$ (triplet)	---

For the five-bond case:



Sincerely yours,

*Dan*  
Daniel T. Longone

*Richard F. Smith*  
Richard F. Smith

*Richard R. Doyle*  
Richard R. Doyle

Dr. G. ENGLERT



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

LIMITED COMPANY

DEPARTMENT Phy.A.  
Eng/to

Basel, July 7, 1965

Professor B.L. Shapiro  
 Illinois Institute of Technology  
 Department of Chemistry  
CHICAGO, Ill. (USA)

Dear Professor Shapiro,

I am very sorry that you had to remind me again and I do hope that the following short note will renew our subscription:

PMR-Spectrum of Oriented 3,5-Dichlorobenzoic Acid

In my talks given at the 5<sup>th</sup> ENC and at the 1964 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy I have discussed the PMR-spectrum of 3,5-dichlorobenzoic acid oriented in a nematic matrix of p-butoxybenzoic acid. Because of the small concentration of the solute molecules the signal to noise ratio of the spectrum was very poor. Furthermore the given interpretation of the spectrum was incomplete since we have neglected the effect of the chemical shift.

In the meantime I have re-investigated the spectrum of this compound at 100 Mc using the nematic phase of 6-n-hexyloxy-2-naphthoic acid (mp: 142°, clearing point: 194°C) as a solvent. Both compounds were partly deuterated (COOD). The comparison of the experimental (127°C) and theoretical 100 Mc-spectra shows that one line (no. 3) is hidden by the strong COOH-signal. At higher temperatures the COOH-signal moves downfield and line no. 3 can clearly be detected.

The parameters used in the theoretical analysis were:

$$\begin{aligned}
 \text{direct dipolar couplings: } & A_{2,6} = \frac{h \gamma^2}{4 \pi^2 r^3} = -316 \text{ cps} \\
 & A_{2,4} = A_{4,6} = \frac{h \gamma^2}{4 \pi^2 r^3} \left( \frac{3}{4} S_{\parallel} + \frac{1}{4} S_{\perp} \right) = 541 \text{ cps} \\
 \text{indirect coupling assumed: } & J_{2,4} = J_{4,6} = 1,6 \text{ cps} \\
 \text{chemical shift: } & \Delta \nu = \frac{\gamma}{2 \pi} H_0 (\sigma_4 - \sigma_{2,6}) = -226 \text{ cps}
 \end{aligned}$$

-2-

Here the S-values<sup>(1)(2)</sup> denote the degree of ordering of the molecular axis  $\xi, \eta$  and  $\zeta$  (see figure).

Assuming a H-H-distance of 4.3 Å the following values are obtained:

$$S_{\xi} = 0.55 \quad / \quad S_{\eta} = -0.21 \quad / \quad S_{\zeta} = -0.34$$

The following conclusions can be drawn from these parameters:

The molecular  $\xi$ -axis is oriented preferably parallel to the magnetic field direction. The mean orientation is clearly asymmetrical with respect to the  $\zeta$ -axis, since the degree of orientation of the  $\eta$ -axis is much smaller than that of the  $\zeta$ -axis. The respective values for p-chlorobenzoic acid were:

$$S_{\xi} = 0.71 \quad / \quad S_{\eta} = -0.345 \quad / \quad S_{\zeta} = -0.365 \quad (2)$$

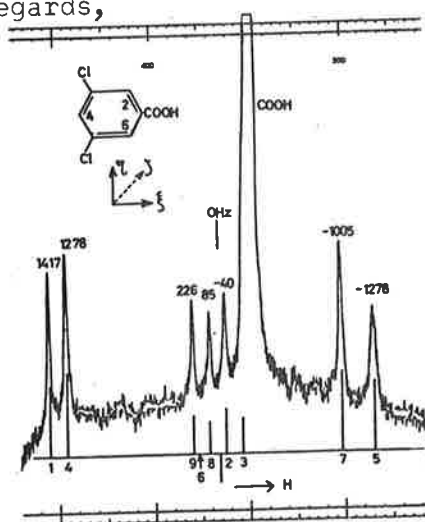
A qualitative comparison shows that the replacement of the p-chloroatom by the 3,5-dichlorosubstituents markedly change the molecular orientation.

Since the line widths of the signals and therefore the experimental error in the line positions are relatively large the magnitude and the sign of the indirect coupling could not be confirmed with certainty. A comparison of the chemical shifts of the isotropic ( $\Delta\nu \sim +30$  cps) and anisotropic phase indicates that even the sign of  $\Delta\nu$  is changed by the molecular orientation. This is probably due to the isotropic and anisotropic contributions of the substituents.

Dr. Saupe and I are presently preparing a publication containing some further results on the PMR-spectra of oriented molecules.

With best regards,

Yours sincerely,



(G. Englert)

#### References

- See e.g. 1) Z. f. Naturf. 19a, 161 (1964)  
2) Z. f. Naturf. 19a, 172 (1964).

UNIVERSITY OF KENTUCKY  
LEXINGTON, KENTUCKY

COLLEGE OF ARTS AND SCIENCES  
DEPARTMENT OF CHEMISTRY

July 7, 1965

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

Dear Dr. Shapiro:

Please accept our apologies for neglecting our obligations. Hopefully, the following will suffice to restore our subscription.

SOLVENT AFFECTS ON GEMINAL H-H COUPLING CONSTANTS

I. CORRELATION BETWEEN SOLVENT SHIFTS AND SIGNS OF COUPLING  
CONSTANTS

Reports by a number of investigators<sup>1</sup> clearly establish the solvent dependence of  $J_{gem}$  in double bonded systems. Recently we have reported the solvent dependence of the couplings in the non-double bonded compound styrene oxide<sup>2</sup>. It appeared to us (and has been suggested or implied by Goldstein and others) that there might be a correlation between the sign of the coupling constant and the change in  $J_{gem}$  as a function of solvent parameters. The three membered ring systems styrene oxide (I) and styrene sulfide (II) are well suited for a test of this hypothesis;  $J_{gem}$  being positive in the former and negative in the latter<sup>3</sup>. Since the rigid molecules differ only in the replacement of O by S one might expect whatever solvent phenomena occur to be qualitatively the same for both species.

The change in  $J_{gem}$  for I and II as a function of the dielectric constant of the solvent is shown below.



Associate Professor Bernard L. Shapiro  
 Page Two  
 July 7, 1965

<u>Solvent</u>	<u><math>\epsilon</math></u>	<u>Styrene oxide (I)</u>	<u>Styrene sulfide (II)</u>
Cyclohexane	1.99	+6.00	-1.15
CCl <sub>4</sub>	2.20	+5.85	-1.18
C <sub>6</sub> H <sub>6</sub>	2.26	+5.81	-1.37
Toluene	2.35	+5.79	-----
CDCl <sub>3</sub>	4.55	+5.55	-1.52
Pyridine	12.3	+5.69	-1.41
Acetophenone	16.99	+5.67	-----
Acetone-d <sub>6</sub>	19.8	+5.56	-1.46
o-nitrotoluene	25.15	+5.68	-----
Nitrobenzene	32.22	+5.53	-1.47
Nitromethane	35.0	+5.42	-1.61
Acetonitrile-d <sub>3</sub>	35.1	+5.40	-1.54
DMSO-d <sub>6</sub>	46	+5.31	-1.55
NEAT	---	+5.63	-1.34

The geminal coupling constant in I decreases from 6.00 cps in cyclohexane to 5.31 cps in DMSO. The corresponding change in II is from -1.15 in C<sub>6</sub>H<sub>12</sub> to -1.61 in nitromethane and -1.55 in DMSO. In both cases  $J_{\text{gem}}$  decreases (becomes more negative).

In every case we know of for which solvent shifts of  $J_{\text{gem}}$  have been reported and for which signs are either known or can be assumed with some certainty the same decrease is observed. We thus propose as a working hypothesis that "geminal H-H coupling constants always become more negative as the dielectric constant of the solvent increases". If this hypothesis proves valid it implies that absolute signs of  $J_{\text{gem}}$  may be determined (at least for polar molecules) by noting the change of  $J$  as a function of solvent.

We hope to report on the theoretical justification for this suggestion in the near future.

## II. SOLVENT AFFECTS ON $J_{\text{gem}}$ ACROSS $\text{sp}^3$ HYBRIDIZED CARBONS:

### POLARIZATION REQUIREMENTS

All reported solvent induced changes of  $J_{\text{gem}}$  have been observed in systems in which the carbon involved is  $\text{sp}^2$  hybridized. For numerous reasons it is necessary to know if similar effects can be observed in cases where the carbon is  $\text{sp}^3$  hybridized. We have examined a number of compounds

Associate Professor Bernard L. Shapiro  
 Page Three  
 July 7, 1965

having magnetically non-equivalent hydrogens on  $sp^3$  hybridized carbons, but were unable to observe any appreciable change in  $J_{gem}$  as a function of solvent (although a solvent induced change of  $J_{H-F}$  has been reported for dichlorofluoromethane<sup>4</sup>). Recently we examined the spectrum of 4-methyl-1,3-dioxolane in a variety of solvents. The results listed below represent so far as we know the first case of a solvent dependent geminal  $J_{HH}$  across an  $sp^3$  hybridized carbon.

<u>Solvent</u>	<u><math>\epsilon</math></u>	<u><math>J_{gem}</math> (C<sub>2</sub>)</u>
Cyclohexane	1.99	0.79
CCl <sub>4</sub>	2.20	0.69
CS <sub>2</sub>	2.64	0.68
isopropyl ether	3.88	0.73
p-chlorotoluene	6.08	0.61
CH <sub>2</sub> Cl <sub>2</sub>	9.09	0.0
Pyridine	12.3	0.0
Acetone	19.8	0.0
DMSO	46	0.0
D <sub>2</sub> O	80	0.0
NMA	129	0.0
NEAT	---	0.0

The decrease of  $J_{gem}$  from 0.79 cps in C<sub>6</sub>H<sub>12</sub> to approximately zero in solvents of high dielectric constant suggests on the basis of our previous hypothesis that this coupling is positive. (Line widths were checked in all cases and the observed effect is not due to homogeneity changes.) Offers to check this assignment by Cl<sup>35</sup> decoupling would be appreciated.

The existence of a solvent induced change of  $J_{gem}$  in the dioxolane (and of  $J_{HF}$  in dichlorofluoromethane), but the absence of such changes in similarly substituted molecules (e.g. styrene carbonate) is significant. Watts and Goldstein<sup>1c</sup> suggested on the basis of their work with vinyl halides that polarization of the solute molecule may be involved in those cases where  $J_{gem}$  is solvent dependent. In the dioxolane the dipole moment and thus presumably the polarization axis must lie in (or very close to) the H-C-H plane. The same is true for dichlorofluoromethane and all the double bond systems studied to date. This is not the case for many  $sp^3$  hybridized systems.

Associate Professor Bernard L. Shapiro  
Page Four  
July 7, 1965

These facts suggest that polarizability of the H-C bond is a key requirement for the existence of solvent induced changes of geminal coupling constants. This idea is appealing since it is consistent with the current theories of substituent affects on coupling constants<sup>5</sup>. Increased polarization might also explain why some solvent changes of coupling constants correlate better with solvent acidities or basicities than with the dielectric constants of the solvents.

Extension of the above concept to solvent induced changes of vicinal couplings would explain the large variations reported by Laszlo<sup>6</sup> for cis ClHC=CHOEt. The dipole vector must be at approximately right angles to the double bond, thus producing considerable polarizability in the same direction for both C-H bonds and little or no effect along the C-C bond. In other cases one might expect to find competing effects canceling each other.

We are presently conducting experiments to test this hypothesis.

#### References

1. a. B. L. Shapiro, et al., J. Chem. Phys., 39, 3154 (1963).  
b. B. L. Shapiro, et al., J. Mol. Spectry, 11, 325 (1963).  
c. V. S. Watts and J. H. Goldstein, J. Chem. Phys., 42, 228 (1965).
2. S. L. Smith and R. H. Cox, J. Mol. Spectry, 16, 216 (1965).
3. S. L. Manatt, et al., J. Am. Chem. Soc., 87, 2220 (1965).
4. D. F. Evans, J. Chem. Soc., p. 5575 (1963).
5. J. A. Pople and A. A. Bothner-By, J. Chem. Phys., 42, 1339 (1965).
6. P. Laszlo, Tetr. Letters, (No. 18) 1325 (May 1965); NMR Abstracts No. 65-1871.

*Stanford L. Smith*

Stanford L. Smith

*Richard H. Cox*

Richard H. Cox

SLS:dd

**Technische Hogeschool Delft, Laboratorium voor Technische Natuurkunde**

Geadresseerde

Lorentzweg 1, Delft, Nederland  
Ons kenmerk JS/MWS Datum 7th July 1965

Blad 1

**C<sup>13</sup>-H COUPLING IN THE ACETONE-WATER SYSTEM.**

Associate Professor Bernard L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
CHICAGO, Illinois 60616  
U.S.A.

Dear Professor Shapiro,  
In our magnetic resonance group Mr. de Jeu and Mr. Angad Gaur have done some work on the dependence of the C<sup>13</sup>-H coupling in acetone and dimethylsulphoxide on the solvent. As little or no attention has been given to this subject (as far as we know only Evans<sup>1)</sup> has made an investigation into this matter), we think it worthwhile to do some research in this field.

One of our results is the concentration dependence of the C<sup>13</sup>-H coupling in the acetone-water system. As for this system the chemical shift of O<sup>17</sup> has been measured by Christ and Diehl<sup>2)</sup> we can plot our J<sub>C<sup>13</sup>H</sub> values against their  $\tau_{O^{17}}$  values (fig. 1)

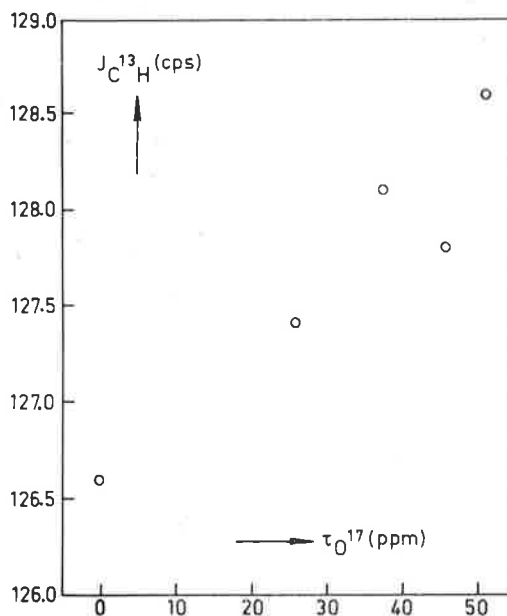


Fig. 1

- 1) D.F. Evans: J. Chem. Soc. 5575 (1963)
- 2) H.A. Christ and P. Diehl: Helv. Phys. Acta 36, 170 (1963)
- 3) N. Muller and D.E. Pritchard: J. Chem. Phys. 31, 768 (1959); 31, 1471 (1959).

An almost linear relationship is found. It seems likely, that a similar - if not the same - mechanism is responsible for the variations in  $J_{C^{13}H}$  and  $\tau_{O^{17}}$ . Hydrogen bridges may increase the relative importance of polar resonance structures of the C=O group, resulting in a larger electron withdrawal experienced by the CH<sub>3</sub> groups, which causes an increase of  $J_{C^{13}H}$ .

We hope to publish these and other results, indicating the same tendency, in the near future.

Yours sincerely,

Prof. Dr. Ir. J. Smidt



# OKLAHOMA STATE UNIVERSITY • STILLWATER

Department of Chemistry  
Frontier 2-6211, Ext. 7215-7218

July 8, 1965

74075

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

Dear Dr. Shapiro:

We are continuing our work on NMR studies of organophosphorus compounds. Organophosphorus acids are soluble with difficulty in most organic solvents, (acetone is fair but its volatility can be troublesome) but we have found that tetramethylurea is very useful. In TMU with TMS as internal standard, the following coupling constants were obtained:

	$\delta$ (J)		
	<u>P-O-H</u>	<u>Aryl Protons</u>	<u>-CH<sub>2</sub>-</u>
$(C_6H_5)_2P(O)(OH)$	6.46	7.6 (m)	
$(HOCH_2)_2P(O)OH$	6.85	3.87 (5)	
$C_6H_5P(O)(OH)_2$	12.36	7.55 (m)	
$HOCH_2P(O)(OH)_2$	9.52		3.78 (7.5)

We feel TMU is a very valuable solvent for many other organic compounds. The methyl resonance is a singlet and is observable down field from TMS.

Short title: Tetramethylurea - A Solvent for Phosphorus Acids.

Sincerely yours,

*K. D. Berlin*

K. D. Berlin  
Associate Professor

KDB:ih

Telephone: (0C03) 68905

From Dr. J. A. S. Smith.

School of Molecular Sciences  
University of Warwick, Coventry  
England.

8th July, 1965.

NMR spectra of some  $\beta$ -diketone complexes of Sn(IV).

Dear Professor Shapiro,

We have recently observed some quite long-range spin-spin splittings in tin (IV)  $\beta$ -diketone complexes. Whereas the  $\text{CH}_3$  and CH groups of the  $\beta$ -diketone ring in  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$  show no coupling to the  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  nuclei (McGrady & Tobias, J.A.C.S., 1965, 87, 1909), in the dihalo complexes of the type  $\text{SnX}_2(\text{acac})_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) there is a clearly-resolved splitting as the following table shows:

Compound	Solvent	$\tau(\text{CH}_3)$	$\tau(\text{CH})$	$J(\text{Sn}.. \text{CH}_3)$	$J(\text{Sn}.. \text{CH})$
$\text{SnCl}_2(\text{acac})_2$	$\text{CDCl}_3$	7.79, 7.88	4.29	7.2, 5.8	6.0
	$\text{C}_6\text{H}_6$	8.41, 8.43	4.93	6.8, 5.4	5.6
$\text{SnBr}_2(\text{acac})_2$	$\text{CDCl}_3$	7.79, 7.90	4.28	6.2, 5.8	4.9
	$\text{C}_6\text{H}_6$	8.41, 8.44	4.91	6.6, n.r.	5.0
$\text{SnI}_2(\text{acac})_2$	$\text{CDCl}_3$	7.83, 7.93	4.24	4.2, 4.0	2.8
	$\text{C}_6\text{H}_6$	8.45, 8.47	4.88	4.4, 4.2	2.8

We think we may have prepared a difluoro complex, in which  $J(\text{Sn}.. \text{CH})$  is 8.5 c/s (consistent with the steady increase from I to Cl) but this has yet to be confirmed. Several interesting conclusions may be drawn from these spectra. Firstly, the dihalo complexes all seem to prefer the cis- configuration, with two methyl peaks but one CH peak, rather than the trans- configuration typical of  $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ . Secondly, the two methyl groups show different spin-spin splitting constants to the Sn nucleus, the difference increasing with increasing electronegativity of the halogen, suggesting the possibility of a "trans effect" in the transmission of these effects. Thirdly, the complexes are interesting in showing a well-resolved  $^{117}\text{Sn}$ ,  $^{119}\text{Sn}$  splitting to the CH group of the chelate ring; we have observed a similar splitting of 2.5 c/s between

Continued...

2.

Cont'd...

<sup>195</sup>Pt and the CH group of (acac) in  $(\text{CH}_3)_3\text{Pt}(\text{acac})(\text{isoquinoline})$ , but we have failed to resolve any splitting from <sup>203</sup>Tl in  $(\text{CH}_3)_2\text{Tl}(\text{acac})$ , nor do any other examples appear to have been reported in the literature.

Thanking you for our copy of the ILLTNMR newsletter, which is always read with the greatest interest.

Yours sincerely,

*John K. S. Smith*  
J. J. E. J. Wilkins.

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

## IOWA STATE UNIVERSITY

of Science and Technology



AMES, IOWA 50010

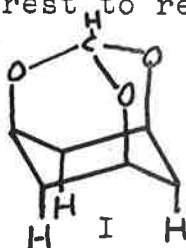
July 13, 1965

Department of Chemistry

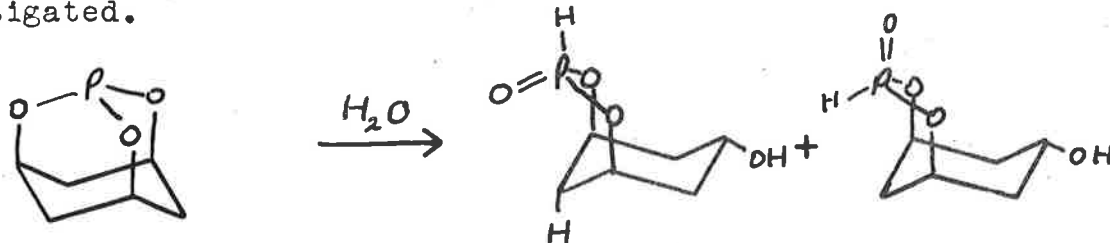
Professor B. L. Shapiro  
 Department of Chemistry  
 Illinois Institute of Technology  
 Chicago Illinois 60616

Dear Dr. Shapiro:

We have found a few examples of long-range coupling in saturated systems of fixed geometry which may be of interest to readers of IITNMR.



In the course of a study of some cage phosphorus esters by Dr. J. G. Verkade of this department the trioxaadamantane I was prepared as a model compound. The apical proton turned out to give a 1:3:3:1 quartet of spacing 1.2 c.p.s. due to coupling to the three axial methylene protons only. We expected the bicyclo 2.2.2 octane derivative II to show a much greater coupling, but the value observed was 1.7 c.p.s. between apical protons. There was no detectable HCOCH coupling in either case. It may be fortuitous that the three-path coupling in II is 1.5 times as great as the two-path coupling in I, but in any case there seems to be no dramatic effect on coupling of rotation about the central C-O bond. The only common factor is that the C-H bonds involved are opposed and parallel, not unlike the condition observed for five-bond couplings in unsaturated systems. Relative signs are being investigated.

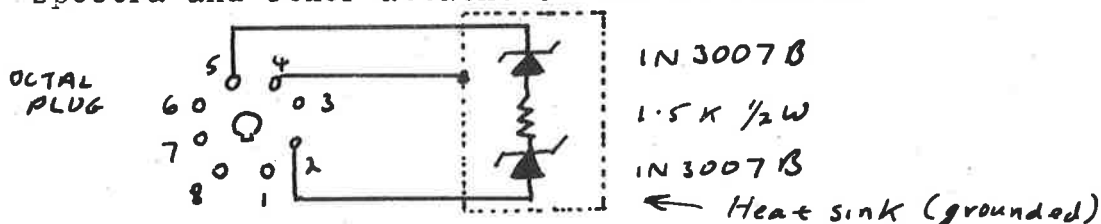


The Arbuzov reaction of the above phosphite with water gives two products showing P-H doublets of splitting 730 and 781 c.p.s. respectively. However, each member of the 781 c.p.s. doublet is a 1:3:3:1 quartet of about 0.8 c.p.s. spacing, the other doublet being of slightly broadened singlets. Spin decoupling shows that



(2)

the quartets are caused by coupling to two equivalent protons whose chemical shift places them at the bridgehead positions and one unique proton at the high-field end of the methylene region, suggesting an axial proton. Mechanistically the above structures are probable for the products and I would like the long-range coupling to be across the boat-form ring as shown. We are now working on the  $P^{31}$  spectra and other attacks on the structures.



Finally, having grown tired of replacing flickering OC3 tubes in our V-2100B power unit, I threw them out and replaced one with a shorting plug and the other with a pair of zener diodes on an aluminum fin. The 1.5 K resistor was necessary to prevent a violent sawtooth oscillation that set in when the diodes were tried alone. The reason for it is obscure. Since this modification the unit has been perfectly happy, as I wish all our machines were.

Sincerely yours,

*Roy W. King*

Roy W. King

P.S. Our prize P-H multiplet has splittings of 781 and 0.8 c.p.s., a ratio of about  $10^3$ . Is this a record?

DIVISION OF PURE CHEMISTRY  
DIVISION DE CHIMIE PURE



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NATIONAL RESEARCH COUNCIL  
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CANADA

OTTAWA 2,  
July 12, 1965

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

Dear Barry:

Some time ago K. Frei investigated some compounds containing  $C^{13}-C^{13}$  carbon carbon bonds and we reported (1) the  $C^{13}-C^{13}$  coupling constants for a variety of bond types. Subsequently we attempted the measurement of the coupling constant in the central bond of  $HC\equiv C^{13}-C^{13}\equiv CH$  with only partial success. I mention that we only partially succeeded because the accuracy of the spectra left something to be desired and before we could get suitable spectra, the sample exploded. The results of our analyses of the  $H^1$  and  $C^{13}$  measurements are given below:-

	<u><math>H^1</math> spectrum</u>	<u><math>C^{13}</math> spectrum</u>
$J_{\overline{CCH}}$	$52.4 \pm .3$	$51.8 \pm .5$
$J_{\overline{CCCH}}$	$6.8 \pm .6$	$6.6 \pm .5$
$J_{\overline{HCCCCH}}$	$2.2 \pm .2$	Not resolved
$J_{CC}$	$147 \pm 14$	$155 \pm 15$

All in C/S

The experimental value of  $J_{C^{13}C^{13}}$  is not inconsistent with the value of 140 C/S previously estimated<sup>(1)</sup> for the coupling constant in an sp-sp type of CC singlebond.

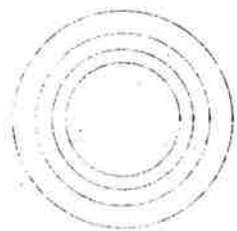
(1) K. Frei and H. J. Bernstein, J. Chem. Phys. 38: 1216 (1963)

Yours sincerely,

*Harold Bernstein*

H. J. Bernstein

HJB:tn

**VARIAN associates**

611 HANSEN WAY • PALO ALTO, CALIFORNIA • 326-4000

14 July 1965

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

Dear Barry:

"The Phase-Sensitive Eyeball"

The internally locked HA-100 instrument has a continuous display of the field-frequency error signal observable as a sine wave on the oscilloscope when the usual sawtooth horizontal deflection waveform is used. Some owners may find an alternative mode of display useful. This is simply to generate a single-loop Lissajous figure on the scope by running a cable to the 'Horizontal Deflection' plug at the rear of the oscilloscope from either 'Manual Oscillator Out' on the V4354 (for frequency sweep) or from 'Sweep Oscillator Out' (for field sweep), and by disabling the repetitive sweep of the oscilloscope.

The information content of the signal on the Y plates of the scope remains of course the same, but the eye much more easily appreciates two more parameters: frequency and phase. Signals excited by sidebands other than that used for control cannot produce the single-loop Lissajous pattern and are thus readily distinguished when the operator is searching for a lock. The human eye is here functioning as a synchronous detector. When the system is locked, the opening-out of the loop is a measure of the dephasing of the error signal, anticipating any tendency to pull out of the locked condition. In frequency sweep double resonance experiments, where there is often a very large signal excited by  $H_2$  that swamps out the smaller error signal on the scope, reassurance that the lock is holding comes from a slight tilt of the total pattern.

Adjustment of the current shim coils for optimum resolution by observing the signal height is equally feasible in either mode of display.

Yours sincerely,

Ray

Ray Freeman  
Analytical Instrument Research

RF:iw

CYANAMID

AMERICAN CYANAMID COMPANY  
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1937 WEST MAIN STREET, STAMFORD, CONN. 06904  
AREA CODE 203 348-7331

July 19, 1965

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

Dear Barry:

In examining some ABC systems, we noticed a relationship between the single and double quantum spectra which may be worth mentioning since it can be useful in an ABC analysis.

Anderson, Freeman, and Reilly (J. Chem. Phys. 39, 1518, 1963) have pointed out the importance of identifying the "terminal" transitions in the construction of the complete energy level scheme. The "terminal" transitions are those which terminate on the levels  $M = \pm 3/2$  (six in all). Their procedure for the assignment involves finding the two or three pairs of lines which are symmetrically disposed about each double-quantum line. In a table of such line-pairs, any terminal transition appears three times while the non-terminal (inner) transitions appear only twice.

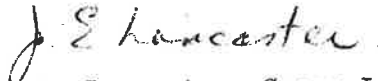
However, if the center of gravity of the spectrum is known, the terminal transitions can be identified directly without constructing the table of line-pairs. The center of gravity is usually available, either from having identified a complete set of 12 lines which satisfy the repeated spacings requirement, or from having observed the triple-quantum line or all six double-quantum lines.

If the center of gravity is set equal to zero, then, as in the method of Castellano and Waugh (J. Chem. Phys. 34, 295, 1961),  $E_1 = E_8$ , where  $E_1$  and  $E_8$  are the  $+ 3/2$  and  $- 3/2$  levels, respectively. If  $E_i$  ( $i = 2, 3, 4$ ) and  $E_j$  ( $j = 5, 6, 7$ ) are the  $+ 1/2$  and  $- 1/2$  levels, the terminal transitions are  $E_1 - E_i$  and  $E_j - E_8$ . The double-quantum transitions are  $(E_1 - E_j)/2$  and  $(E_i - E_8)/2$ . But since  $E_1 = E_8$ , the double quantum lines are also given by  $-(E_1 - E_i)/2$  and  $-(E_j - E_8)/2$ . In other words, for each double quantum line observed, there is a corresponding single quantum line (which must be a terminal transition) located at twice the distance of the double quantum line from the center of gravity, but on the opposite side of the spectrum. Referring to the cube analogy for the ABC system, these two transitions are the cube edge and face diagonal which lead from  $E_1$  to  $E_8$ .

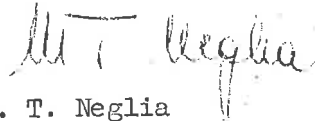
-2-

It can be seen that the rule concerning the sum of the couplings and the input data for a Castellano and Waugh treatment (which does not require the correct ordering for the  $E_i$  and  $E_j$ ) follow equally well from the double quantum spectrum alone.

Very truly yours,



J. E. Lancaster, Group Leader



M. T. Neglia  
Nuclear Magnetic Resonance Group  
Research Service Department

cab

## THE LILLY RESEARCH LABORATORIES

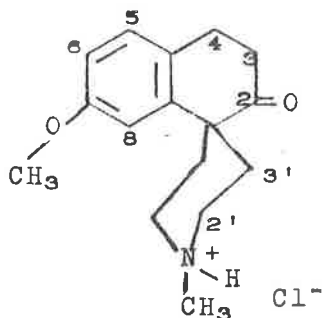
ELI LILLY AND COMPANY · INDIANAPOLIS 6, INDIANA · MELROSE 6-2211

July 15, 1965

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

Dear Dr. Shapiro:

We have observed a pair of equatorial protons on the piperidine ring of compound I at higher field than the geminal axial ones. This, we believe, arises primarily from the fact that the carbonyl in the adjacent ring is sufficiently close to the 3'-axial protons to deshield them in preference to the 3'-equatorial ones. Consideration of the Dreiding model of the spiro compound in the conformation shown below is in agreement with this requirement.



From a study of related compounds and a decoupling experiment, the protons of compound I measured in  $\text{CDCl}_3$  were assigned the following shift values (position,  $\tau$ ) 3,  $\sim 7.3\text{t}$ ; 4,  $6.94\text{t}$  (from deuteration study); 5,  $2.98\text{d}$ ; 6,  $3.23\text{q}$ ; 7- $\text{OCH}_3$ ,  $6.13\text{s}$ ; 8,  $2.62\text{d}$ ; N- $\text{CH}_3$ ,  $7.15$ ; 2' envelope,  $6.4\text{--}6.8$ ; and 3' eq.,  $7.92\text{d}$ ; 3' ax.,  $\sim 6.9$ . The aromatic protons 5 and 6 had the same shift values in the free base and the hydrochloride salt form, but the 8 proton was 28 c.p.s. lower in the salt. Thus, we favor the fixed conformation I for the salt in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$ , where the paramagnetic shift of the 8 proton compared with the base is due to the spatial anisotropy of the charged nitrogen center.

The NMR spectrum of salt I measured in  $\text{D}_2\text{O}$  and  $\text{CD}_3\text{OD}$  showed the 3'-protons as a compact triplet indicating that under these conditions the piperidine ring, in addition to the keto ring, is in rapid equilibration.

Please keep the Lilly copy coming.

Sincerely yours,

C. Ainsworth

H. Boaz

R. Hackler

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