Institute of
Technology
N-M-R
Newsletter

No. 70

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Deadline for Next Issue: 20 August 1964

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".

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*



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Professor B.L. Shapiro Department of Chemistry

Illinois Institute of Technology Technology Center

CHICAGO, Illinois 60616

YOUR REF.

YOUR LETTER OF

2954 CL - N 5

the 17th June 1964

Measurement of T_1 on Varian DP-60.

Dear Dr. Shapiro,

Pending the completion of our spin-echo apparatus, we did some experiments on the use of our Varian DP-60 spectrometer for the determination of spin-lattice relaxation times.

At first we tried measuring T_1 in fast adiabatic passage and found that our spectrometer at least is not well suited for this kind of measurement. The snag is a phenomenon we can neither explain nor remedy: racing through resonance at a few dB below. 5 Watts at the maximum speed our slow sweep allows, we get signals that are neither u- nor v-mode. In particular it is impossible to determine with the accuracy requisite for the determination of T_1 whether the signal is upside down or not.

Probably related to this phenomenon is the fact that our DP-60 is unable to give a pure dispersion signal at values of the radio frequency field higher than 20 dB attenuation. We feel that some non-linearity in the detector is responsible but do not know how to overcome this. We would be very grateful to anyone able to offer suggestions for making our spectrometer behave.

Afterwards we had more success with the determination of relaxation times by means of signal recovery after saturation. For these measurements we derive the linear sweep from the time base of a Tektronix 545 A oscilloscope at a rate of about one passage through resonance per second

PAGE NR 2

DATE the 17th June 1964

OUR REF. 2954 CL - N 5

(reproducibility 1 %; 16 microamps through the linear sweep coils gives a shift of 1 milligauss). The signal is recorded on a Sanborn Recording System Model 128. This works well with relaxation times from about one second upwards, the usual range encountered in high-resolution work. In order to get reproducible peak heights it is essential to stop the spinner and to switch off the field homogeneity control. An increase of 20 dB in H, is sufficient to go from negligible to almost complete saturation. As an example we enclose the recorded recovery of the aldehyde group resonance of the Varian acetaldehyde sample for field homogeneity testing. The astonishing T_1 of 44 seconds shows the care Varian spent on the preparation of this sample. The relaxation times found in this way are reproducible within a few percent. As an independent test on the validity of our procedure we determined some of the longer relaxation times by recording signal growth after an unmagnetized sample is introduced into the probe. T, 's found in this way are not noticeably different from those found from the recovery procedure.

Yours sincerely,

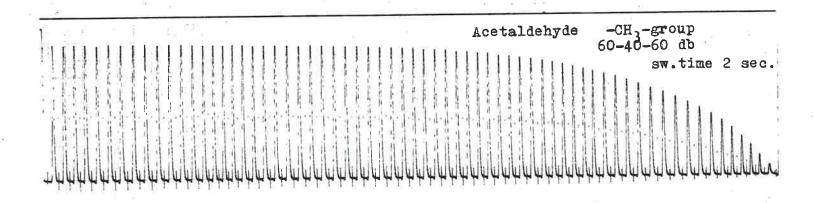
1 minumbul

(E. Konijnenberg)

(W. van Raaven)

(J. Schrama)

Enclosure: 2 spectra



THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

May 11, 1964

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

Dear Dr. Shapiro:

There is some historical precedent for using carbohydrate derivatives as model systems for P.M.R. conformational studies. We (L. D. Hall and J. F. Manville at U. B. C. and D. H. Buss and L. Hough at Bristol University) have recently studied the A.60 spectra of the two series of carbohydrates shown below

and find that compounds having configuration (I) (i.e. H_1H_2 trans) show $J_{1,2}=0$ c.p.s. whilst those having configuration (II) show $J_{1,2}=2.5-4.5$ c.p.s. Indene oxide shows similar couplings (J ≈ 0 and 2.5.c.p.s.) as also do some steroidal epoxides (Page, Green and Staniforth (I.I.T. NMR 67) and if this stereospecificity is at all general it may aid spectral and configurational assignments (compare the letter from Nadlander, Ritchey and Sable).

Yours sincerely,

L.D. Hall.

L. D. Hall

WESTERN RESERVE UNIVERSITY

CLEVELAND 6, OHIO

SCHOOL OF MEDICINE
DEPARTMENT OF BIOCHEMISTRY

June 8, 1964

Dr. Barry Shapiro Illinois Institute of Technology

Dear Barry:

We have been keeping in touch with Dr. L. D. Hall about our study of cyclic epoxides. He very thoughtfully suggested that it would be a good idea for the Cleveland and Vancouver groups to write to you at about the same time. Our interest in epoxides began with compound I. We hoped to determine the

configuration by measuring $J_{1,2}$. Unfortunately we obtain deceptively simple spectra for this substance and its dibenzoate, and there is always a sharp singlet for H_2 and H_3 with no evidence of coupling. Fortunately, John Franks and Hank have proved the configuration by classical chemistry, so we feel that this is a case in which $J_{1,2}=0$ for the same stereochemistry for which Hall observes a small coupling. We are also studying the spectrum of II. Here we have only preliminary data. $J_{2,3}$ is about 3 cps and there seems to be coupling $J_{1,2}$ and $J_{3,4}$ but we would rather not give any figures until we can carry out triple resonance experiments and analyze the data in Bill's 7090 computer program (slightly modified from the one supplied by Reilly and Swalen).

The spectrum we really want to tell you about is that of the epoxybromohydrin III. This compound was first made by Young, H. K. Hall and Winstein, and has turned out to give a great deal of useful information. Every signal in the spectrum can be explained completely by a first order analysis. We assign the methylene protons on the basis of the relation of internal chemical shifts in an ABX system that Williamson reported for substituted norbornanes. Parenthetically we should say that Williamson's results have been of the greatest value in interpreting our

spectra. At any rate, we are convinced that the highest field signal belongs to H_5 and the next one to H_6 . From these two signals we obtain $J_{4,5}$ and $J_{4,6}$. We thought at first that the additional small splitting of H_5 might be long-range coupling with H_3 (the triplet at 4.43 δ). However, Bill carried out a double-irradiation study, using the Varian integrator and Johnson's technique. By irradiating at the H_1 H_2 frequency (the tall signal at 3.65 δ) he was able to collapse the H_5 signal to a series of sharp singlets. We therefore assign that small splitting to J_1 , 5 which has a value of 1.1 cps. The small splitting in the H_3 signal is therefore due to J_2 which has a value of 1.3 cps. The dihedral angles (H_1 -C-C- H_5 and H_2 -C-C- H_3) measured from Dreiding models are 30 \pm 30 in both cases, if the molecule is nearly planar. This same dihedral angle is also present in compound I.

The triplet signal for H_3 arises because J_3 , 4 and J_3 , 7 are very nearly equal. H_7 shows up as a clean doublet at 3.99 δ . This is a rather low field for an OH proton, but it occurs because of strong H-bonding to the epoxide (confirmed by the IR spectrum). The proof that the signal at 3.99 δ is indeed due to H₇ is the following: a different preparation of compound III was used to measure the spectrum in Eric's A-60, at a somewhat higher temperature. The 3.99 δ signal disappeared and was replaced by a new signal at about 2.8 δ , nearly overlapping the lowest of the four lines of the ${\rm H_6}$ signal. At the same time the ${\rm H_3}$ triplet became a doublet of two rather wide lines; the widening was due to some residual coupling with the OH proton which was no longer so strongly bonded. Next the sample was fully deuterated by shaking the $CDCl_3$ solution with D_2O_{\bullet} The H_7 signal disappeared and an HDO signal appeared at 4.61 δ . The H_3 signal became a sharp doublet with each line showing the small doubling due to J_{2,3}. We may now proceed with the analysis of the H_4 signal. $J_{3,4}$ is computed as follows: in the spectrum shown $J_{3,7} = 7.1$ cps. The total width of the H_3 signal* is $J_{3,7} + J_{3,4} = 14.2$ cps, and consequently $J_{3,4}$ must be 7.1 cps. The methylene signals give $J_{4,5} = 9.1$ cps and $J_{4,6} = 7.5$ cps. First-order theory predicts 8 lines spaced as shown above the spectrum, and we have labeled these lines in the signal which is centered at 3.70 δ . The separations of the lines and the total width of the signal agree almost perfectly with the first order predictions.

We have a whole boatload of substituted cyclopentanes and we re having a good time studying them. We still have a long way to go before our final publication but we wanted to send this message along to you so our friends would know what we're doing.

Best regards,

H. Z. SABLE, Biochemistry Department

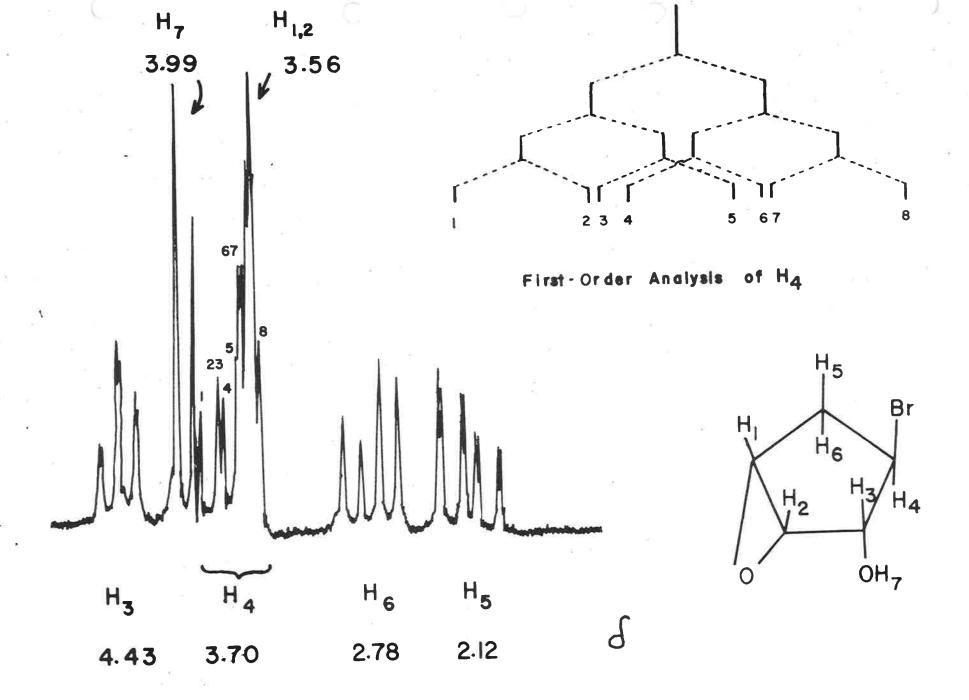
Western Reserve University

W. M. RITCHEY, Research Department,

The Standard Oil Go. (Ohio)

J. E. NORDLANDER, Chemistry Department

Western Reserve University





Eidg. Technische Hochschule

für Organische Chemie

Zürich

Dr. D. Meuche / eh

Zürich 6, Universitätstrasse 6 Tei. (051) 32 73 30 June 16, 1964

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

Illinois 60616

USA

Dear Professor Shapiro,

Good luck to IITNMRN!

Since our Mellon-letter 48 - 19 we have extended our studies on acid-base equilibria of substituted azulenes and investigated sixteen compounds of this group 1). The protonation of alkylsubstituted l-azulene-aldehydes I (R=H) and of l-acetyl-azulenes I (R=CH3) leads to the species II, III, IV and V (Rn: H- or CH3-). The cations of type III and II are protonated on the carbonyl group in syn- and anti-planar position, respectively, to the seven-membered ring, the cation of type IV on C-3 and the cation of type V on C-1 of the five-membered ring.

Data for five of the studied compounds ²), which illustrate that steric hindrance influences strongly these equilibria, as mentioned in the earlier letter, are given in the table. Evidence for the existence of the conjugate acids of types II, III and IV in the equilibria of the unsubstituted 1-azulene-aldehyde can be derived from figg. 1 and 2.

The spectrum 1 is that of a solution of 1-azulene-aldehyde in $\mathrm{F_{3}CC00H}$ to which I equivalent conc. $\mathrm{H_{2}SO_{4}}$ has been added. In the absence of conc. $\mathrm{H}_2\mathrm{30}_4$ the spectrum shows broad signals at the mean resonance frequencies of the corresponding protons of the cations a and b. The exchange rate decreases monotonically with stepwise addition of conc. H,SO4 on passing to the equimolar mixture. During this process the signals of the two cations a and b become resolved and move towards their δ -values (neglecting normal solvent effects). Finally the lines become sharp and fine splittings can be observed. The coupling constant $J_{\mathrm{H}\,2}$, $_{\mathrm{H}\,3}$ is 5,0 cps for the cations a and b. The long-range coupling of the cation b $J_{\rm H1syn}$, H3 is about 0,8 - 1,0 cps over the trans-trans path. This value is strikingly larger than the coupling constant $J_{\rm H1}$ trans, H_3 of the cation a 3) which is less than 0,5 cps. The spectrum of a freshly prepared solution of 1-azulene-aldehyde in F_3 CCOOD to which conc. D_2 30 $_4$ has been added (ca. 90% D) indicates complete proton-deuterium exchange on C-3 (see fig.2), suggesting that the conjugate acid of type IV is rapidly formed. On deuteration (i) the signals previously assigned to ${
m H}_3$ of the cations a and b have only about one tenth of the intensity, (ii) the splittings $\rm J_{H2},~D_3$ and $\rm J_{H1syn},~D_3$ are so small that the signals belonging to $\rm H_2$ of the cations a and b and belonging to H_1 of the cation b are practically singlets.

8-Methyl-1-azulene-aldehydes protonate in the same acid solution preferentially on the carbonyl group in anti-planar position to the seven-membered ring giving a cation of type II. In fig. 3 the typical trans-trans long-range coupling $J_{\mbox{H}_{\mbox{Syn}}}$, H_3 = 1,0 cps is nicely resolved.

The smaller steric interaction between the proton on C-8 and the hydroxyl group in the cation of the type III is the reason why this cation is formed preferentially. In this series, the protons of C-COH, C-2 and C-8 of the cation type II and III give different 1-values depending on their relative positions in the induced magnetic field of the molecule.

In two cases with an acetyl group on C-l and a methyl group on C-8 steric hindrance between the peri-substituents is so large that cations of type V predominate, as in the previously mentioned conjugate acids of l-nitro-4,6,8-trimethyl-azulene ⁴) and of guaiazulene-3-sulfonic acid ^{1b}).

Sincerely yours,

Dom Keuche

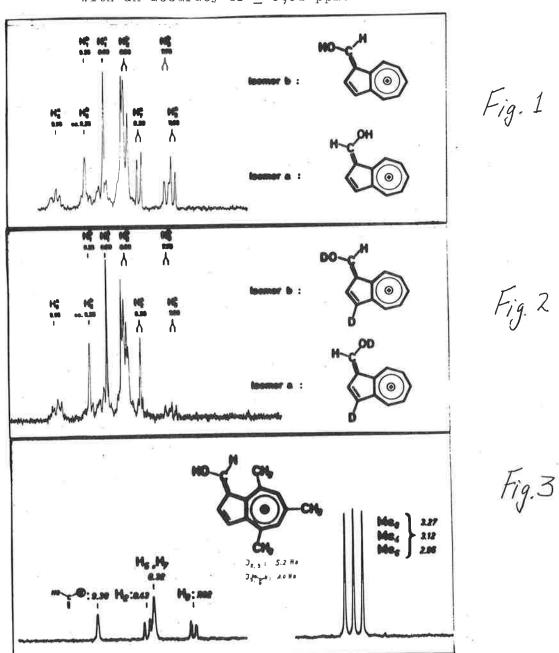
Doris Meuche

values of the conjugate acids of 1-azulene-aldehydes and 1-acetyl-azulenes

(Solvent: F3COOH/H2SO4, internal standard TMS)

Compound	R	R ₂	R ₃	R ₄	R ₅	R ₆	^R 7	R ₈
HO	н: 9,25	н: 8,53	н: 7,75		H ₅ , H ₆ , H ₇ :	t about 8,6	<u> </u>	н: 9,25
H-CONT	н: 8,90	H: 8,28	H * 7,63	ADOD	-spectra a			н: 9,95
HAY!	н: 9,13	Н: 8,35	Me: 2,73 2,65	1	H ₅ , H ₆ , H ₇ :	t about 8,5	0	н: 9,21
H YON	н: 8,77	н: 8,03		ADOD	-spectra a	c about 6,5	0	н: 9,88
HOZH	н: 9,13	H : 8,40	i-Pr:	,	H ₅ , H ₆ , H ₇ :		0	н: 9,07
H ON CHS	н: 8,78	н: 8,10	1,55/3,52	ABCD-spectra at about 8,58		8	н: 9,90	
HO H CH3	н: 9,30	H : 8,43	H: 7,62	Me: 3,12	H : 8,32	Me: 2,96	Н: 8,32	Me: 3,27
CH _S	Me: 3,05	H: 8,23	Me: 2,65	H: 8,85	ABC-spec	tra at abo	ut 8,50	н: 9,95

- la) Doris Meuche & E. Heilbronner, Helv. 45, 1965 (1962)
- b) Doris Meuche, W. Meier & E. Heilbronner, Helv. 46, 1929 (1963);
- c) Doris Meuche, B.B. Malloy, D.H. Reid & E. Heilbronner, Helv. 46, 2483 (1963)
- 2) Doris Meuche, D. Dreyer, K. Hafner & E. Heilbronner, Helv. in preparation
- 3) R. Freeman & N.S. Bhacca, Mellon No. 42, 47; W. Brügel, ibid No.59
- 4) J. Schulze & F.A. Long, Proc.chem.Soc. 364 (1962)
- 5) The spectra were measured on a Varian A-60 Spectrometer with an accuracy of \pm 0,02 ppm.



National Chemical Research Laboratory



of the South African Council for Scientific & Industrial Research

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AIR MAIL

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

Our file 4 NMR Our letter

Your file

Your letter

P.O. Box 395, Pretoria

24. JUN. 1964

Dear Dr. Shapiro,

N.M.R. Data of 2,6-Dialkyl Naphthalene Derivatives

We have recently measured the N.M.R. spectra of some 2,6-dialkyl-derivatives of naphthalene and their 4-sulphonic acids. These data may be of interest to some of the readers of IITNMRN in so far as substituent effects on the chemical shifts may be derived. It is particularly interesting to note the difference between the effects of straight chain and branched chain alkyl substituents. The table below gives the substituent pattern and the coupling constants (first order analysis, accuracy ±0.2 c.p.s.), and the enclosed figure gives the chemical shifts (dilute CDCl₃ solutions with internal TMS, accuracy ±0.01 p.p.m.).

Commonad	Substituents i	n Positions	Coupling Constants in c.p.s.		
Compound	2 and 6	4	Occiping constants in copes.		
1*	2 - 0	-	$J_{\alpha\beta} = 8.6 J_{\alpha\beta'} = 1.4 J_{\beta\beta'} = 6.0$		
2	n-hexyl	-	$J_{13} = J_{57} = 1.5$ $J_{34} = J_{78} = 8.1$		
3	n-octyl	ē -	$J_{13} = J_{57} = 1.8$ $J_{34} = J_{78} = 8.6$		
4	t-butyl	-	$J_{13} = J_{57} = 1.7$ $J_{34} = J_{78} = 8.7$		
5	i-octyl	-	$J_{13} = J_{57} = 1.5$ $J_{34} = J_{78} = 8.8$		
6	n-octyl	-so ₃ h	$J_{13} = 1.6$ $J_{57} \simeq 1.5$ $J_{78} = 8.9$		
7	n-decyl	-S0 ₃ H	$J_{13} = 1.6$ $J_{57} = 1.7$ $J_{78} = 8.6$		
8	i-octyl	-so ₃ h	$J_{13} \simeq 1.5$ $J_{57} = 1.6$ $J_{78} = 8.7$		

Data for naphthalene are from: Bernstein, Schneider, Pople, Proc. Roy. Soc. (London) <u>A236</u>, 515 (1956) and J. Chem. Phys. <u>26</u>, 957 (1957).

Yours sincerely,

Kranker

K. Pachler
SENIOR RESEARCH OFFICER
CHEMICAL PHYSICS GROUP
NATIONAL CHEMICAL RESEARCH LABORATORY

c. Dr. Herbstein

KP/ED

T-VALUES OF 2,6-ALKYL NAPHTHALENE DERIVATIVES 2.6 22 2.0 2.4 comp 1.4 1.6 1.8 7 3,7 1,5 4,8 2 3,7 4,8 1,5 3 48 15 4 3,7 5 85 6 58 8 2,6 2,2 2,0 1,8 1,6

INSTITUT FÜR ANORGANISCHE CHEMIE

DER

UNIVERSITÄT MÜNCHEN

(a) MÜNCHEN 2, den 29.6.1964

MEISERSTR. 1

FERNSPRECHER 55 79 76

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!

In der letzten Zeit haben wir eine interessante Beobachtung gemacht. über die wir Ihnen kurz berichten möchten.

"Anomale Abschirmung in π -Indenyl-Metall-Komplexen"

Im allgemeinen beobachtet man, daß die Ringprotonen von freien Aromaten weniger stark abgeschirmt sind, als die jenigen von entsprechenden ungeladenen Aromat-Metall- π -Komplexen. Ferner erfahren nicht-äquivalente Protonen bei der Komplexbildung etwa gleiche Verschiebungen.

Bei π -Komplexen, in denen ein Indenylligand mit dem Fünfring an das Zentralmetall gebunden ist, wie π -C9H7Ir(C0)2 und π -C9H7Rh(C0)2, zeigen die beiden Signale der drei Fünfringprotonen gegenüber dem freien Indenylanion eine gleichartige Verschiebung nach höheren Feldern. Die Abschirmung der 1,3-Protonen ist dabei jeweils größer als die des 2-Protons.

Völlig anders liegen die Verhältnisse bei π -Komplexen mit zwei Indenylliganden. In den Di-indenyl-Verbindungen des Fe, Ru und Co, cf. Tabelle, ist die Abschirmung der 2-Protonen stärker als die derjenigen in 1,3-Stellung.

Wir führen diese unerwartet höhere Abschirmung der 2-Protonen in Di-indenyl- π -Komplexen auf die in trans-Stellung der Liganden mögliche Felderniedrigung in diesen Positionen durch in den Sechsringen induzierte Ringströme zurück. Ähnliche Effekte wurden früher an 1,4-Polymethylenbenzolen[1] beobachtet. Die trans-Stellung der beiden π -Indenylliganden im gelösten Zustand wurde bereits zur Erklärung der verschwindend kleinen Dipolmomente von $(\pi$ -CoH7)2Fe[2] und $(\pi$ -CoH7)2Ru[3] gefordert. Im Kristall fand sich für die Eisen-Verbindung eine verdrehte cis-Konfiguration[4].

 $\,$ Mit freundlichen Grüßen und herzlichem Dank für die IIT NMR Newsletters

Ihre

Heing P. Fitz E.f. Weiter

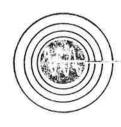
(H.P.Fritz) und (C.G.Kreiter)

Substanz	ν _{1.3} ν ₂	٧4 , 7	ν _{5,6}	Lösungsmittel
(C ₉ H ₇)-Na+	356.9< 395	5.1 437.2	387.5	Dimethylsulfoxyd
π-C ₉ H ₇ Ir(CO) ₂	334.1< 360	430.2	430.2	$cycle-C_6H_{12}$
π - C_9 H_7 Rh(CO) ₂	339.5< 360	.3 422.0	422.0	CS ₂
$(\pi - C_9 H_7)_2$ Fe	275.8> 241	.9 411.7	411.7	DCC1 ₃
$(\pi - C_9 H_7)_2 Ru$	292.0> 274	.3 398.0	398.0	DCC13
$[(\pi - C_9 H_7)_2 Co]^+ NO_3^-$	371.9> 347	7.9 456.4	415.6	D ₂ 0 *)

Die Frequenzen sind positiv nach tieferen Feldern, bezogen auf int. TMS. bei 60 MHz.

*) Frequenzen umgerechnet auf TMS-Standard

- [1] J.S. Waugh und R.W. Fessenden, J. Amer. Chem. Soc. 79,846(1957)
- [2] E.O.Fischer und S.Schreiner, Chem. Ber. 92,938(1959)
- [3] E.Weiss, Z.anorg.allg.Chemie 287,223(1956)
- [4] J.Trotter, Acta Cryst. 11,355(1958)



VARIAN AG · SWITZERLAND

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ZUG TELEPHONE 042 / 4 45 66 TELEX 58 444

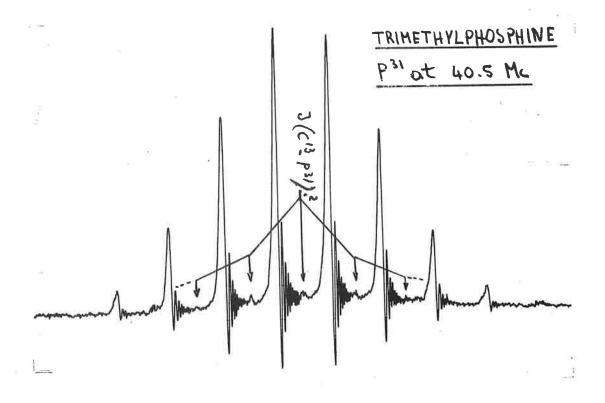
THE RESEARCH LABORATORY ZÜRICH 8 KLAUSSTRASSE 43 TELEPHONE 051/47 24 20 30 June, 1964

Prof. Barry L. Shapiro
Dept. of Chemistry
Illinois Institute of Techn.
Technology Center
C h i c a g o
Illinois 606/6

Dear Barry,

together with IITNN No 68 I have received your second "caveas!" calling for a long overdue contribution.

I am thus entering the P³¹ resolution contest announced by S.L. Manatt and G.L. Juvinall with a trimethylphosphine spectrum run at 40.5 Mc during my stay in Palo Alto last March.



One is tempted to assign the small satellitelines pointed out in the spectrum as arising from the J $(C^{13} - P^{31})$ but their intensities -ca. 4% of the main signals - seem to indicate an impurity.

Last time we met you were interested to know how long it takes for IITNN to reach Europe by normal mail; I have checked into this matter and can now tell you that it takes about three weeks.

Best wishes

A. Melera Research Chemist

VARIAN AG

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA

91109

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

June 30, 1964

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

RE: 1. Clogging of A-60 magnet cooling coils.

2. Fluorine-fluorine decoupling technique.

Dear Barry:

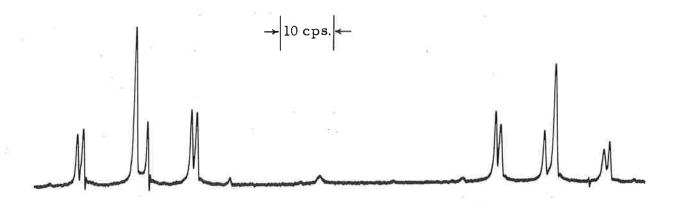
1. The news is spreading but perhaps not rapidly enough about the clogging of our (and other) A-60 magnet with magnetic iron oxide. Ours was so completely plugged that it had to be returned to the factory and when the coil was cut open, oxide was found to be the major constituent of the plug.

The obvious conclusion is that we were using pretty raw water but in fact we have a recirculating system of our own design. The real problem is that the A-60 shuts off the water when the power is shut off. Accumulated magnetic oxide which would then be swept out of an HR-60 stays behind and is held when the magnet is energized again. We noted an accumulation of this kind a long time ago when we happened to back-flush the magnet as part of another overhaul job. At the time we did not stop to figure out what happened although we were especially perplexed because the filter looked clean. Apparently the oxide particles are so small they pass right through the filter.

We suggest that A-60 owners who find that their magnets seem to be running hot should flush out their magnets occasionally with the field off by defeating the automatic valve. The repair job for replacement of a coil is expensive—about \$1,000 and shipping charges and time out of service.

2. In perfluoro-1, 2-dimethylenecyclobutane, the ring fluorines (F_r) and the vinylic fluorines (F_v) are strongly coupled $(J \sim 8 \text{ cps})$; attempts to obtain field-sweep $F_v^{19} - \{F_r^{19}\}$ spectra were unsuccessful. Fluorine-fluorine decoupling has been accomplished by a previously unreported technique. The center-band frequency was first adjusted to precisely the F_r^{19} resonance frequency; the field was then locked on the hexafluorobenzene resonance (internal) using an audio side-band, phase-detection, field-lock system; the F_v^{19}

spectrum was observed by frequency sweep using audio side-band phase detection (see below). Another audio side-band was used to perform double-irradiation tickling experiments. The assistance of Drs. S. L. Manatt and D. D. Elleman in obtaining these spectra on the HR-60 at JPL is greatly appreciated. The iterative analysis yields the parameters: $v_{\rm A}$ - $v_{\rm B}$ = 1.391 ppm; $J_{\rm AA}$ = +23.2 cps; $J_{\rm AB}$ = +14.7 cps; $J_{\rm AB}$ = +6.7 cps; $J_{\rm BB}$ = +7.6 cps.



With all good wishes,

Very truly yours

John D. Roberts

Kenneth L. Servis

JDR:KLS/bi

STEVENS INSTITUTE OF TECHNOLOGY

HOBOKEN, NEW JERSEY

Department of Chemistry and Chemical Engineering

July 2, 1964

Subject: Chart Calibration

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

Dear Dr. Shapiro:

Some readers who do not have access to precalibrated systems might be interested in the rapid chart calibration technique we have been using in our laboratory during the past three years.

The method is essentially the same I described in an earlier letter (MELLONMR Dec., 1961). The accompanying diagram is almost self explanatory. The graphical scale is drawn on a piece of paper 30" x 30". Each of the ten divisions (shown on the diagram) is further subdivided into twenty equally spaced divisions (not shown on the diagram). The horizontal lines are merely to help properly position the NMR spectrum.

After a spectrum has been obtained light pencil lines are drawn thru the major peaks perpendicular to the base line. The spectrum is then positioned on the graphical scale so that the T.M.S. peak lines up on the zero cps line and its image upon whatever frequency was used for calibration.

Our reproducibility has been better than ± 0.01 p.p.m. using this technique and, of course, we have saved many hours of tedious labor.

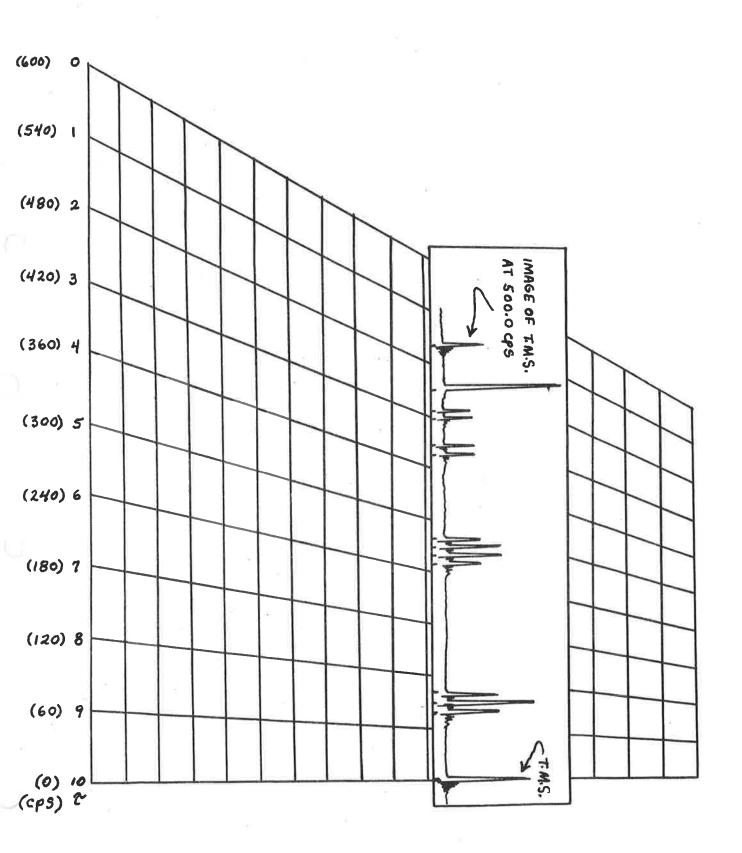
Sincerely yours,

Edmund R. Malinowski Assistant Professor of

Edmund R. Malinowski

Chemistry

ERM/ar



FACULTÉ DES SCIENCES ECOLE PRATIQUE DES HAUTES ETUDES

PARIS, LE 16 juin

1964

Laboratoire de Synthèse Organique

1. Rue Victor-Cousin PARIS (VE)

ODÉON 24-13

Sur la stéréospécificité des magnésiens vinyliques

Cher Professeur Shapiro,

Nous vous remercions très vivement de notre admission sur votre liste d'envoi.

Notre première contribution concerne le problème de la stéréospécificité de la réaction de Normant (1). Nous vous adressons quelques résultats relatifs au groupement propényle.

Les spectres des motifs CH₃CH=CH- étudiés, de type ABX₃ sont analysés au second ordre (tableau).

Nous avons séparé les bromo-I propènes <u>cis</u> et <u>trans</u> (par chromatographie en phase gazeuse) et les avons caractérisés par leurs couplages J23 (tableau). Les spectres RMN permettent d'écrire deux séquences réactionnelles au départ de ces bromures isomères :

Dans le magnésien formé à partir du bromure <u>cis</u>, le couplage J23 est de 14,9 Hz. Cette valeur élevée est cependant inférieure au couplage <u>cis</u> déterminé dans les dérivés vinyliques métalliques ${}^{-M}_{H'}C=C_{H'}^{H}$, (lithien (3) et magnésien (J<u>cis</u> = 17,7 Hz (2)).

Le spectre du magnésien résultant du bromure $\underline{\text{trans}}$ est caractérisé par une valeur élevée de J23/ $\sqrt{3}$ 2 - $\sqrt{3}$ 3, et n'a pas été analysé, la partie X_3 du spectre étant masquée par le solvant.

Ces résultats montrent que le magnésien retient la configuration du \

bromure de départ. Nous avons vérifié que l'équilibre naturel des bromo-I propènes (70 % cis et 30 % trans) conduit à un mélange des magnésiens cis et trans. Dans ces systèmes, on constate toutefois que la température et la basicité du solvant influent sur l'isomérisation.

Par ailleurs, la nature du réactif opposé au magnésien semble jouer un rôle dans la rétention de configuration. En effet, si la carbonatation du magnésien <u>trans</u> ne modifie pas la géométrie du motif propényle, l'acylation du mélange naturel ne nous a conduit jusqu'ici qu'à une cétone <u>trans</u> (J23 = 15,9 Hz).

Ce comportement peut être rapproché des résultats de Seyferth (4), relatifs à des propényl-Ge, Sn ...

*		- Tableau	- CH ₃	-CH=CH-X (2) (3)	
x X	isomère	12-13	J12	J13	J23
-Br	cis trans	1,50 7,50	+6,55 +6,85	-1,70 -1,65	+6,95 +13,40
-Mg-	cis trans	37,5	5,75 non	0,85 analysable	14,90
-COOH	trans	69,6	6,9	1,0	15,70
-COCH ₃	trans	47,6	+6,55	-1,45	+15,90

- (1) H. Normant C. R. Ac. Sc. 1954, <u>239</u>, 1510 H. Normant et P. Maitte - Bull. Soc. Chim. 1956, 1439
- (2) G. Martin et M. Martin C. R. Ac. Sc. 1963, <u>256</u>, 5099 J. Organometal. Chem. 1964
- (3) C.S. Johnson, M.A. Weiner, J.S. Waugh et D. Seyferth J.Am. Chem. Soc. 1961, <u>83</u>, 1706
- (4) D. Seyferth et L. G. Vaughan J. Organometal. Chem. 1963, 1, 138

Bien cordialement,

Gérard Martin

Maryvonne Martin (Laboratoire de Spectroscopie Hertzienne) The N.M.R. Spectra of Some 1,4-Diheterocyclohexanes.



TEXAS CHRISTIAN UNIVERSITY

Fort Worth, Texas

July 7, 1964

Department of Chemistry

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

Dear Dr. Shapiro:

Below is an abstract of a paper which we are in the process of submitting somewhere for possible publication sometime. The accompanying figure is the upfield half of the morpholine ring hydrogen spectrum (N-CH₂). This is one half of the A₂B₂ system. The line assignments from left to right are 4,3,12,11, 8, 5,10,9, 2, and 1. This case is similar to those discussed by Hirst and Grant(J.Chem. Phys., 40,1909(1964). The spectrum was taken in benzene solution. The frequencies are in c.p.s. from the A₂B₂ band center. The instrument was an A-60.

Abstract

The n.m.r. spectra of morpholine, N-methylmorpholine, N-phenylmorpholine, and thioxane have been analyzed and the pertinent chemical shifts and coupling constants determined. The spectra are all of the A₂B₂ type. The C(13)-H spectrum of dioxane has been re-examined. A comparison of these results with data in the literature is made.

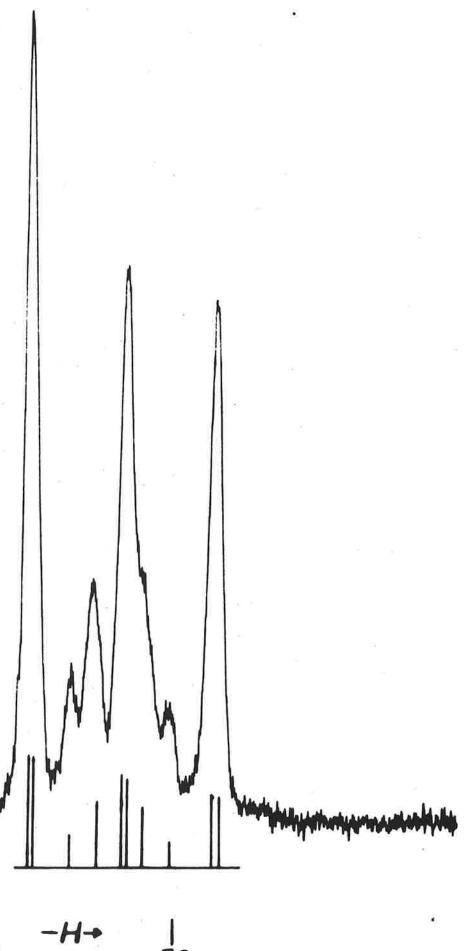
Thioxane Morpholine N-Methylmorpholine N-Phenylmorpholine Dioxane Morpholinium ion Diwethylmorpholinium	N 10 0 9 7 9 7 9 9	Jaa 12.05 10.28 10.25 9.66 10.2	Jae 2.65 3.04 3.05 3.38	1.97 1.47 0.16 0.60	83.60 54.24 87.57 48.50
Dimethylmorpholinium iodide	9•7				33

Yours sincerely,

William B. Smith Sen A. Shouldes

William B. Smith

Ben A. Shoulders



20

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

INSTITUT DE CHIMIE DES SUBSTANCES NATURELLES GIF-SUR-YVETTE (s.-&-o.)

Gif, le 7 Juillet 1964

TÉL.: 928.46.76

Associate Professor B. L. SHAPIRO Illinois Institute of Technology Chicago, Illinois 60616

Cher Barry,

Les comparaisons des déplacements chimiques entre molécules voisines, si utiles pour les déterminations de structure, bien qu'effectuées dans le même solvant et à la même concentration, ne sont pas obligatoirement licites. En particulier, le chloroforme (ou le deutériochloroforme), solvant très généralement employé (80% des articles comportant des spectres de RMN sur 10 livraisons mensuelles d'un périodique international de Chimie Organique), a des capacités reconnues d'association avec les molécules comportant des hétéroatomes ou une insaturation, de type liaison hydrogène. Afin d'isoler les perturbations des déplacements chimiques des divers groupes de protons des molécules de solutés dues au chloroforme, en tant que donneur de proton par liaison hydrogène, nous avons choisi comme solvant de référence le tétrachlorure de carbone, qui :

- 1) n'est pas un donneur de proton, et dont la différence avec le chloroforme consiste seulement dans le remplacement d'un hydrogène par un chlore; les volumes moléculaires sont équivalents, et l'on peut ainsi espérer minimiser les différences de stabilité des complexes par transfert de charge avec les solutés de ces 2 molécules halogénées.
- 2) a une constante diélectrique du même ordre que celle du chloroforme.
- 3) a été employé concurremment avec celui-ci dans un grand nombre de cas.

Nous avons choisi comme solutés une série de molécules saturées, insaturées, aromatiques ou polaires. Les déplacements chimiques mesurés pour un type déterminé de protons dans le chloroforme (CHC13) ou le tétrachlorure de carbone (CC14) diffèrent de -0,15 ppm à +0,30 ppm³ (CHC13 CHC13 CCC14), une valeur souvent observée étant +0,10 ppm.

.../

NSTITUT DE CHIMIE DES SUBSTANCES NATURELLES GIF-SUR-YVETTE (s.-&-o.)

TÉL.: 928.46.76

-2 -

/...

Les comparaisons intramoléculaires et les comparaisons intermoléculaires risquent donc d'être faussées dès lors que les différences de déplacements chimiques sont inférieures à 0,50 ppm.

Nous n'avons pas soulevé ce problème dans un esprit de pointille, mais pour indiquer que le choix d'un système adéquat de plusieurs solvants est une conditions nécessaire pour que l'importante qualité d'information présente dans un spectre de RMN soit communiquée sans ambiguité. Le cyclohexane, qui semble être un solvant de choix, devrait être utilisé maintenant que les problèmes de solubilité sont considérablement diminués par l'emploi des processus de sommation des spectres, du type CAT. Un mémoire détaillé paraîtra dans le Bulletin de la Société Chimique de France.

Veuillez croire, Cher Barry, à mon amical souvenir,

- Pierre Laszlo -

INSTITUTE FOR CHEMICAL PROCESS FUNDAMENTALS CZECHOSLOVAK ACADEMY OF SCIENCE PRAHA 6, NA CVIČIŠTI 2

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

June 26, 1964

Dear Dr. Shapiro:

We would greatly appreciate, if you could put us on the mailing list of Mellonmr. As our first contribution we would like to describe some of our recent results.

Vinyl-silicon compounds have been studied by several authors $^{1-4}$. These authors found out for about twenty vinyl-silicon compounds all coupling constants ($J_{gem} = 3.6$, $J_{trans} = 20.3$, and $J_{cis} = 14.6$ cps) to be approximately constant.

We have had the possibility to measure N.M.R. spectra (at 40Mc) of the compounds listed in the table. In this series we expected some changes in the coupling constants because of the greater changes in the substituent electronegativity and $(p \rightarrow d)$ bonding ability. (Spectra were analysed by Castellano - Waugh method⁵. Assignment was done on the bases of the results of the paper¹).

As may be seen from the table the coupling constants here remain also constant (within the experimental errors), but are of greater spread than in the series of vinylsilanes 1-4 or 1-propene derivatives 6-8. (The greatest deviation occurs in ViSiMe₂Cl).

Also the similar collaps of ViSiCl₃ (see¹), ViSiCl(t-BuO)₂, and ViSi(OSiMe₃)₃ spectra is of interest. ViSiMeCl₂ gives also the singlet but broadened. This collaps seems to be quite general in the cases of strongly electronegative sunstituents, but on the other hand ViSi(OEt)₃ gives a complex pattern.

Summitt etc. ³ found the vinyl peak in ViSiCl₃ to be at the same position as the signal of HSiCl₃. For tris-trimethylsiloxy and t-butoxy derivatives this is not true /the signals of HSi(OSiMe₃)₃ and HSi(Ot-Bu)₃ were found at 112 and 121 cps, resp., downfield to cyclohexane/.

We hope that this contribution will be acceptable for Mellonmr.

Sincerely yours,

J.Schraml, V.Chvalovský

1 Schula (Maler lorolg)

Table of NMR parameters of
$${}^{H}_{A}$$
 $c = c {}^{H}_{C}$ compounds at 40Mc Si ${}^{R}_{1}$ ${}^{R}_{2}$ ${}^{R}_{3}$

D	D	D	Chemical	shifts of	protons a)	Coup	ling	constants b)	b) <i>Z</i> 'J
R ₁	R ₂	R ₃	A	В	С	J _{AB}	J _{AC}	J _{BC}	۷ ۵
Мө	Мө	Ме	167.3	176.9	186.5	3.8	20.4	14.5	38. 8
Ме	Ме	OSiMe ₃	176.8	184.0	193.5	4.5	21.8	14.9	41.2
Мө	Мө	0- t-Bu	170.0	177.1	188.3	3.9	20.7	14.8	39.4
Me	Ме	Cl	177.2	183.8	188.8	2.8	21.1	15.9	39.8
Me	Же	OEt	171.1	179.7	185.7	3. 8	21.0	15.4	40.3
M e	OSiMe ₃	OSiMe ₃	178.7	184.1	188.2	4.6	21.4	15.0	41.1
Me	0-t-Bu0	0-t-Bu0	172.6	176.6	183.7	4.1	20.6	15.2	39.9
Мө	Cl	Cl	~ 187.5	~ 187.5	~187.5	,			l
Иe	OEt	OEt	~180.0	~180.0	~180.0				1
OSiMe ₃	OSiMe ₃	OSiMe ₃	~112.3	~112.3	~112.3				1
C1	Cl	C1	~190.3	~190.3	~190.3				
0-t-Bu	0- t-Bu	0-t-Bu	~176.2	~176.2	~176.2			·	
Cl	0-t-Bu	0-t-Bu	~179.5	~179.5	~179.5		8		

a) downfield to cyklohexane as internal standard, in cps. The mean deviation for the center of gravity + 1 cps. Error in chemical shift differences +0.5 cps

Literature:

- 1. Hobgood R.T.Jr., Goldstein J.H., Reddy G.S.: J.Chem.Phys. 35, 2038 (1961).
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- 5. Castellano S., Waugh J.S.: J.Chem.Phys. 34, 295 (1961).
- 6. Brügel W., Ankel Th., Krückeberg F.: Z.Elektrochem. 64, 1121 (1960).
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b) calculated, in cps. Error, ± 0.5 cps.

THE ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY

Chemistry Department



GLASGOW, C.1 TELEPHONE: BELL 4400

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

Dear Barry,

Thank you for the reminder. We hope that the following jottings will be acceptable.

Spectra of Pyrones and Thiopyrones.

We have recently run spectra of $\mbox{$\chi$}$ -pyrone and its three derivatives in which one or both oxygens have been replaced by sulphur. The spectra (at 40 Mc/s in CDCl $_3$) are all $A_2\,X_2$ or $A_2\,B_2$ type showing at least 20 of the 24 expected lines clearly resolved. Algebraical analysis gave the results shown below.

H _B	H _B '	(II)	S (III)	S (IV)
Chemical shifts	(ralues)			
Ha Hb	3.62 2.08	2.95 2.15	2.85 2.48	2.40 2.10
Coupling Constan	ts (c.p.s.)			
JAB JAB JAA JBB	5.85 0.35 2.85 1.05	10.60 0.50 4.12 1.88	5.71 0.49 2.34 0.56	10.21 0.59 3.33 1.17
Dipole moments	(Debye Units	from ref. 1)		
	3.72	3.96	4.08	4.41

The assignment of the ortho (J_{AB}) and the para (J_{AB}) coupling constants presented no difficulty. We assign the larger of the two meta coupling constant (J_{AA}) to the cross ring coupling of the α -hydrogens since by analogy with coupling constants of the α -hydrogens of furans and thiophenes this shows an increase when oxygen is replaced by sulphur. The smaller meta coupling constant (J_{BB}) shows a decrease when the carbonyl oxygen is replaced by sulphur. This can be rationalized if we assume that coupling, in this instance, is through the π -electrons of the γ -c=X bond; increase in polar character on going from γ -c=0 to γ -c=S being evidenced by increase in dipole moment and decrease in coupling constant.

Spectra of difluoroboron chelates.

Hester² found that the resonance of the C-3 protons ('para' protons) in tris (acetylacetonato) silicon dichloride was shifted downfield compared with that of the parent β -diketone. The shift was on much greater magnitude than in diamagnetic transition metal chelates, and he attributed this to 'benzenoid' resonance in the chelate rings. We have prepared some analogous difluoroboron chelates by reaction of boron trifluo/ide etherate with β -diketones. These all show para proton resonance at low fields, comparable with the resonance position in the silicon compounds.

Chemical shifts (7 values in CDC13)

I restrict to the last to the			1 10
R	R ^{† †}	Parent diketone	Chelate
Me	Me t-Bu	4.60	3.95 3.84
Me Me n-Pr	Ph Ph	3.90 3.88 3.88	3.39 3.36 3.35
iso-Pr t-Bu Ph	Ph Ph Ph	3.80 3.20	3.30 2.80

While in the silicon chelates d-orbital participation in the stabilization of a because of ring current can be envisaged, such a situation is extremely unlikely with boron. In the boron compounds the low field shift of the para proton is due to the low electron density near this hydrogen atom, and the high dipole moment $(6.7 \ D.)$ of the chelate (V, R' = R'' = Ph) supports this.

We suggest that the whole subject of 'benzenoid' ring currents in chelates is open to question.

Filtering of solutions.

Dr. J.K. Becconsall's observations on solution filtering (MELLONMR 63, 2) prompt us to record our more primitive technique. We use 'one-time-only' filters made by drawing out small (3'' x 3/8'') soda glass test tubes. These are fitted with cotton-wool plugs pushed hard into the constriction which is broken off to give a fine tube which reaches to the bottom of the NMR tube. The solution is filtered directly into the NMR tube using positive pressure from the mouth or from a small rubber bulb. This technique removes suspended particles with very little solution loss (<5%). Frequently, and in particular with organometallic compounds, filtration through cotton wool alone does not remove traces of paramagnetic impurities. In these cases we filter the solution immediately before running the spectrum through a similar tube, having a 5 mm. layer of decolorising charcoal, on top of 5 mm. layer of Celite on top of cotton wool.

Yours sincerely,

Peter Bladen.

Peter Bladon.

Morman M. D. Brown.

N.M.D. Brown.

References.

- 1. M. Polli, G. Traverso, and M. Senesi, <u>Ann. Chem.</u>, (<u>Rome</u>), <u>42</u>, 673 (1952). <u>C.A. 47</u>, 11934b.
- 2. R.E. Hester, Chem. and Ind., 1397 (1963).

CA	BLE A	DDRESS	"RESE	ARCH
IÑ	YOUR	REPLY	PLEASE	QUOT

NATIONAL RESEARCH COUNCIL CANADA

DIVISION OF PURE CHEMISTRY

OTTAWA 2. June 30, 1964

FILE No.

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

Dear Barry,

In response to your dunning letters to pay the 'price' for a subscription to IITNMR I am writing to you about some work that has just been finished here.

Dr. R. Jones has been involved in the analysis of the A_3X_3 spectrum and found the result, at first sight surprising, that the A spectrum although very similar is not identical to the X spectrum. This difference has indeed been observed in the H and F spectra of sym trifluorobenzene.

Dr. P. Diehl, who is a visiting scientist at N.R.C. for 5 months, has just completed the analysis of an A_2X_2 spectrum for spin $A = \frac{1}{2}$, spin X = 1 and has obtained the NMR spectra (D and C_{13}) of $C_2^2D_2$ to compare with the theory.

Any reader interested in the details can write us directly.

Yours sincerely,

Haroes Berustein

H. J. Bernstein

1< 4 Jones

R. Jones

P. Diehl

HJB) amd

TELEPHONE 34 0484

LMJ:BE



University of Melbourne

Department of Organic Chemistry. Parkville, N.2, Victoria

23rd June, 1964.

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

Dear Barry,

We, the undersigned, would like you to accept this contribution as our "subscription" to I.I.T.N.M.R.N. At the same time we hasten to assure you that we do not intend to try and get away with joint subscriptions in the future. The fact is that the work described below was begun independently at Melbourne University (with Dr. Q.N.Porter and Mr. G.R. Underwood) and Monash University (with Mr. P.J. Black) and subsequently became a collaborative project.

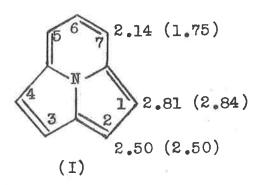
We have been interested for some time in the possibility of using chemical shift data for establishing the aromaticity of partially aromatic systems1. This work has lead to attempts to calculate the contribution of the ring current to the shielding of protons in such systems and Hall and Hardisson2 have developed an S.C.F. treatment for this purpose. In relating such calculations to experiment data it is necessary to allow for the effects of partial charges (also calculated by the S.C.F. method). A semi-empirical method3 appears to be best for this purpose. In dealing with heterocyclic aromatic systems, it is necessary to choose parameters (analogous to a in Hückel M.O.) for the hetero-atoms.

We have examined several systems containing nitrogen as a betero-atom and compared the experimental results with those calculated for various values of the nitrogen parameter. An example of the sought of agreement one obtains is provided by the molecule [3,2,2]cyclazine.

Boekelheide, Gerson, Heilbronner, and Meuche⁴ have examined the spectrum of this molecule and the dideutero-derivative prepared by acid catalysed exchange. We have also examined the spectra of these two compounds and determined the chemical shifts at infinite dilution in carbon tetrachloride. In addition we have established the position of deuteration from an examination of the spectra of methylcyclazine and dimethyl cyclazine-4-a 1,2-dicarboxylate, so that the assignments of chemical shifts in cyclazine itself are independent of calculated charge densities.

The annexed results (I) show reasonable agreement. The calculated values (given in parenthesis) were obtained using the S.C.F. treatment for ring current contributions⁵. A value of the parameter for nitrogen (giving two γ -electrons to the γ -system) equivalent to $\alpha_N = \alpha_C + 1.5\beta$ in a Huckel treatment was used and the shift due to the ring current in benzene was taken to be 1.55 p.p.m. The effects of the charge densities were calculated by the semi-empirical equation of Schiseizer, Chan, Helmkamp, and Ts'o⁶.

2.41 (2.05)



Obviously, many more compounds have to be examined. It appears that heterocyclic compounds in which nitrogen contributes two π -electrons provide the most sensitive test. To this end, we have just completed the analysis of the spectrum indolizine II data for which are given in the table. The theoretical and experimental spectra are also included. Interesting features are the various cross ring coupling constants, in particular $\underline{J}_{2,6}$.

We have also examined the l,- , 2- , and 3-azaindolizines (kindly supplied by Pr. Armarego) which exhibit similar features.

Finally, the Hall-Hardisson method has been incorporated into the V.E.S.C.F. model. The programs have just been written and we eagerly await the results, as the present indications are that the V.E.S.C.F. treatment gives the best account of the charge distribution in azulene?.

We hope that this account will keep readers up-to-date with one aspect of n.m.r. research in Melbourne.

With best regards,

Yours sincerely,

Glora est factions ...

L. M. JACKMAN.

Michael . L. Hoffernan

M.L. HEFFERNAN.

References

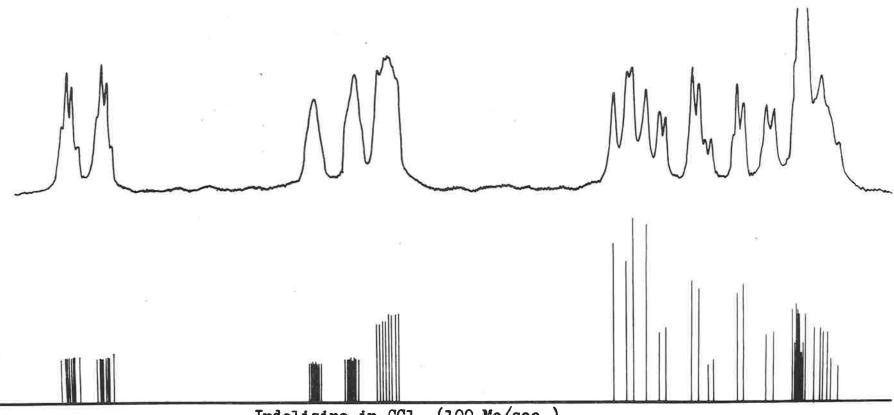
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- 3. G.G. Hall, A. Hardisson and L.M. Jackman, Tetrahedron, 1963, 19 (Suppl. 2), 101.
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Table

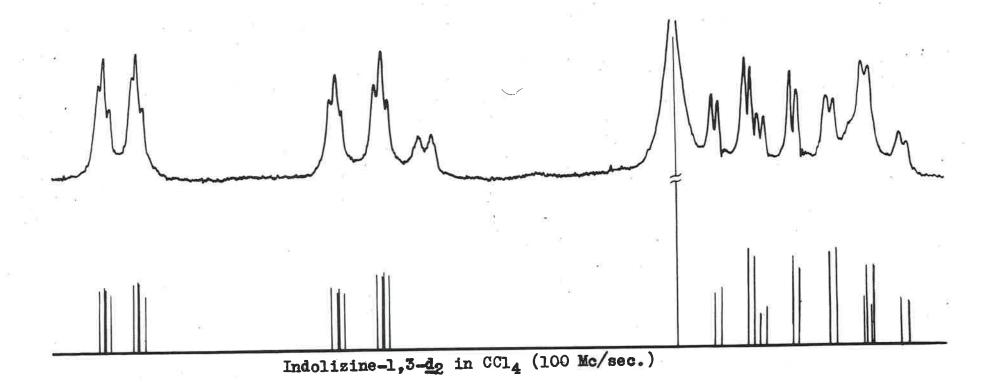
Chemical Shifts and Coupling Constants for Azaindolizines

Derived from 100 Mc/s. Spectra.

	r_1	72	$ au_3$	75	τ ₆	77	7 0					
INDOPIZINE	3.72	3.36	2.86	2,24	3.69	3,50	2.75					
1-AZAINDOLIZINE		2.52	2 52	1.91	3.35	3.97	2.49		ř.			
2-AZAINDOLIZINE	2.73	*	2.03	2.12	2.59	3.42	2.66					
3-AZAINDOLIZIME	3.62	2 . 20		1.61	3. 38	3.03	2.56					
	<u>J</u> 12	<u>J</u> 13	J 15	<u>J</u> 23	<u>J</u> 26	<u>ქ</u> ყვ	<u>J</u> 56	<u>J</u> 57	<u>∓</u> 53	<u>J</u> 67	<u>1</u> 68	<u>I</u> ng
INDOLISINE	3.90	~1.2	~ 1	2.74	~ 0.5	~0.5	6.82	1.02	1.15	6.39	J.02	2.98
1-AZAINDODIZINE					~0.5	0.5	6.89	1.19	1.02	6.77	0.95	9.29
2-AZAINDOLIZINE		0	~0.5			~1.0	7.13	0.88	1.11	6 .3 8	1.05	2.21
3-AZAINDOLIZINE	2.18		~0.º		~0.5		6.93	1.00	1.02	6.79	1.17	8.94



Indolizine in CCl₄ (100 Mc/sec.)



70-39

MONASH UNIVERSITY DEPARTMENT OF CHEMISTRY

P.O. BOX 92, CLAYTON, VICTORIA. TELEPHONE 544 0611

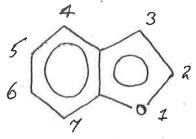
HEAD OF DEPARTMENT: PROFESSOR R. D. BROWN INORGANIC CHEMISTRY: PROFESSOR B. O. WEST

9th July, 1964.

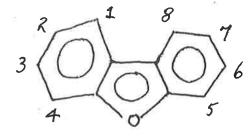
Professor Bernard L. Shapiro, Illinois Institute of Technology, Technology Centre, CHICAGO 16 U. S. A. Illinois,

Dear Dr. Shapiro,

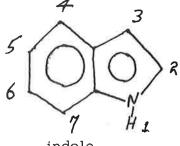
We have been continuing the determination of the spectral parameters in a number of heterocyclic molecules, mainly for the purpose of making detailed comparison between their measured chemical shifts and the values predicted by molecular orbital calculations. We are still working on this latter problem; however, perhaps some of the interim parameters are of some interest. The present note deals with the series of related heterocycles, benzofuran, dibenzofuran, indole, 7-azaindole, carbazole and 4-azacarbazole. All the spectra were run at 100 Mc/s and the parameters were assigned by a combination of, inter alia, already existing results, solvent effects, field sweep double irradiation and finally, by use of an iterative computer programme of the Reilly and Swalen type. The numbering systems used for these heterocyclics are shown below.



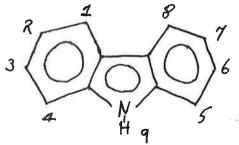
benzofuran



dibenzofuran



indole



carbazole

The data obtained are summarized in the following three tables.

TABLE 1.

Chemical Shifts and Coupling Constants (c/s) for benzofuran, indole and 7-azaindole.

Parameter	Benzofuran pure liquid	Benzofuran in acetone	Benzofuran in CCl ₄	Indole in acetone	7-Azaindole in acetone	7-Azaindole in CCl ₄
$ au_{1}$	-			-0.12	a *	=
$ au_2^{}$	2.73	2.22	2.48	2.74	2.53	2.64
$ au_3^-$	3.60	3.24	3.34	3.55	3.52	3.59
$ au_4$	2.59	2.37	2.51	2.45	2.05	2.11
$ au_{5}^{ au}$	2.90	2.77	2.87	3.01	2.95	2.99
$ au_6$	2.90	2.70	2.81	2.91	1.73	1.71
$ au_7$	2,56	2.49	2.58	2.60	, -)
J ₁₂	<u>, . =</u>	; ; =		2.5	-	-
J ₁₃	=		100 ×	2.0	-	0 0
J ₁₄	=		-	0.8	- ,	i -
J ₂₃	2.3	2.2	2.2	3.1	3.4	3.3
J ₃₇	1.0	0.9	0.9	0.7	-	₩.
J ₄₅	(8.0)*	7.8	7.9	7.8	7.8	7.7
J ₄₆	1.1	1.3	1.3	1.2	1.6	1.5
J ₄₇	0.7	0.7	0.8	0.9	· ·	-
J ₅₆	7.3	7.3	7.3	7.1	4.7	4.8
J ₅₇	1.2	0.9	0.9	1.3		. 4
J ₆₇	(8,0)*	8.4	8.4	8.1	(-)	÷-

^{*} Values unreliable because of near equality of au_5 and au_6

TABLE 2. Chemical Shifts and Coupling Constants (c/s) for dibenzofuran and carbazole.

Parameter	Dibenzofuran in CCl ₄	Dibenzofuran in acetone	Carbazole in acetone
$ au_{\uparrow}$	2.16	1.93	1.92
τ_2	2.77	2.63	2.84
$ au_3$	2.65	2.49	2.64
$ au_{l_+}$	2.52	2.39	2.51
τ ₉	<u>~</u>		-0.25
J ₁₂	7.6	7.9	7.8
J ₁₃	1.3	1.4	1.2
J ₁₄	0.6	0.6	0.7
J ₂₃	7.3	7.6	7.1
J ₂₊	0.9	0.7	0.9
J ₃₄	8.5	8.4	8.2
^J 19	ř :=	_	0.7

TABLE 3.
Chemical Shifts and Coupling Constants (c/s) for 4-azacarbazole in acetone.

τ_1	= 1.57	J ₁₂ = 7.7*	$J_{58} = 0.7$
τ 2	= 2.82	J ₁₃ = 1.6*	$J_{67} = 7.6$
$ au_3$	= 1.57	J ₂₃ = 4.9*	J ₆₈ = 1.2
⁷ 5	= 2.42	$J_{56} = 8.3$	$J_{78} = 7.9$
τ_6	$= 2_{1}.55$	$J_{57} = 0.8$	
τ_7	= 2.77		
$ au_8$	= 1.88		

^{*} Values obtained in dioxane.

It is not appropriate here to go into a detailed justification of these assignments, the work will be written up in due course in the Australian Journal of Chemistry. Several brief comments can be made on these results.

- Long-range coupling constants now seem to be the rule, rather than the exception and our results support the recent determinations of $J_{\mbox{\footnotesize{37}}}$ by Elvidge and Foster for benzofuran and indole 2. The cross-ring coupling involving the NH proton in indole (J_{14}) and carbazole (J_{19}), occurs over a similar conjugation path to J_{37} and is analogous to a coupling involving the NH proton in acridine reported by Kokko and Goldstein.
- The NH proton in 7-azaindole and 4-azacarbazole is undergoing exchange, (b) presumably involving the tertiary N atom and hence couplings involving this proton are unobserved in these compounds.
- The ortho-coupling constant for protons respectively, to a ring (c) atom, is considerably reduced. Other, smaller, regularities may be discerned for the effect of a heteroatom on various coupling constants.
- El Vidge J.A. and Foster R.G., J. Chem. Soc.; 590; (1963)
- Elvidge J.A. and Foster R.G., J. Chem. Soc.; 981; (1964)
- Kokko J.P. and Goldstein J.V., Spectrochim Acta. 19; 1119; (1963).

Needless to say, IIT NMR Newsletter continues to be an extremely valuable link with the world "up above".

Yours sincerely,

Peter J. Black

Peter J. Black

Michael L. Heffernan

Michael. L. Heffernan

UNIVERSITY OF FLORIDA GAINESVILLE

DEPARTMENT OF CHEMISTRY

July 13, 1964

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

Dear Barry:

I trust this contribution will reach you in time to maintain active our subscription to your very valuable Newsletter. One reason our report has been delayed somewhat is that we have been very busy setting up and getting ready to operate several pieces of new equipment, including an NMR Specialties nitrogen spin-decoupler and a series of Tektronix units for pulse work.

We have also added a new Varian outfit, the arrangement of which may be of some interest to Newsletter readers. It is essentially an EPR spectrometer, but provided with a 12-inch magnet which was planned to take some of the wide-line load from our DP-60. The magnet has low-impedance coils and a solid-state power supply, which greatly reduces the problem of heat dissipation in the laboratory. However, it is provided with tapered pole pieces which were shimmed at 14,000 gauss, insulation jacket, field trimmer, and homogeneity coils, in order to increase its capabilities for NMR.

To find out how the outfit might work, we did some boron chemical shift determinations, using the 19.3 mc. rf. unit and probe. The results turned out to be unexpectedly good. The Fieldial unit appears to be very convenient to operate as a sweep unit. Although the field drifts somewhat, it is possible to work rapidly enough when only shift measurements are involved to obtain results which are correct within a few cycles, which is as good as justified by the peak shape for many of the boron absorptions we were looking at. We were not looking for fine structure, but the rather widely separated doublet for a boron atom attached directly to a hydrogen was resolved nicely enough to indicate that we could obtain 5-cycle resolution or better without magnet cycling or use of the homogeneity coils. Unfortunately, results with P-31 at about 11,000 gauss and 19.3 mc. were much less satisfactory, chiefly because the probe leakage could not be nulled at this field. We have not yet had time to track down the reason why this difficulty occurred in the new magnet but had not been noticed with the high-resolution magnet.

Turning to another subject, I would like to report one of our more interesting recent results, which concerns the hydrogen spectrum of aluminum borohydride. This compound was found (Ogg and Ray, Farad. Soc. Disc. 19, 239 (1955)) to give a broad absorption band. Irradiation of Al collapsed the band to an equal-intensity quartet resulting from coupling with B. It was also found that heating the sample gave a

product which had a similar quartet, and it was proposed that ${\rm Al}_2{\rm B}_4{\rm H}_1{\rm 8}$ had been formed with the elimination of diborane. Calvin Maybury, of the University of South Florida, set out to study this reaction, and we have had the opportunity of collaborating with him on the NMR aspects of the problem.

The first thing he discovered was that no diborane or other byproduct of the reaction could be found. It was then observed that
samples in sealed tubes seemed to display erratic behavior—the pattern
changed back and forth from broad band to quartet in what seemed at
first to be a random fashion. Dr. Maybury was finally able to show that
any sample of aluminum borohydride which had been recently in the gas phase
gave the broad spectrum. Of course it is reasonable to transfer a
volatile material of this sort to a sample tube by distilling a portion
from a vacuum line. This produces the broad band, which everyone had
supposed to be characteristic of the liquid. In fact, if one allows
the liquid sample to stand for a period of time, some days or weeks, the
spectrum slowly reverts to the resolved quartet. Heating the liquid in
the sealed tube serves merely to greatly accelerate this process, rather
than producing any chemical reaction.

Two experiments served to confirm this hypothesis as to the changes occurring. A sample of gaseous aluminum borohydride of about 200 mm. pressure mixed with 5 atmospheres of argon gave a spectrum which, although weak, was clearly the broad band rather than the quartet. On the other hand, a sample of material poured directly from the original container without distillation gave the sharp quartet.

Although we can not yet say exactly what the nature of the change in bonding is that may be involved here, it is tempting to speculate on some possibilities. Perhaps there is an "ionic" form which is stabilized in the liquid state, while the gaseous species is a single covalent molecule. An alternative explanation is that there is some sort of monomer-polymer equilibrium which is reversible. Neither of these explanations fits quite all the experimental data, and the problem is still under investigation.

Cordially yours,

Wallace S. Brey, Jr. Professor of Chemistry

Wallace & Bry

WSB:la

TELEPHONE 549-8111 RESEARCH TRIANGLE PARK BOX 731, DURHAM, NORTH CAROLINA



July 13, 1964

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

Dear Dr. Shapiro:

Conformational Studies on 2,4 Disubstituted Pentanes.

We have continued our investigation of 2,4-disubstituted pentanes first discussed in MELLONMR #51. As we pointed out two different vicinal coupling constants between the β (-CH₂-) and α (-CH<) protons are evident in the spectra of the racemic isomers. One expects from steric considerations that only two conformers of the racemic dichloride, dibromide, and dicyanide (the compounds investigated) are energetically favorable [Shimanouchi and Tasumi, Spectrochim. Acta., 17, 755, 1961]. This conclusion is further supported by energy calculations based upon interactions between nonbonded atoms and groups as characterized by a Lennard-Jones potential function.

Assuming a Boltzmann distribution between the two conformers, it was possible to express the separation between the two central β peaks [see MELIONMR #51] as a function of the conformeric energy difference and the absolute temperature. A study of this separation as a function of temperature then yielded the energy differences (ΔE 's) for the three compounds. The experimentally observed ΔE 's are 1.5 \pm 0.3, 1.4 \pm 0.4, and 1.2 \pm 0.3 Kcal./mole respectively, for the dichloride, dibromide and dicyanide. It is impossible to determine from the coupling constants which of the two conformers is energetically favored, however, we are carrying out chemical shift measurements and calculations which should provide this information.

Consideration of the <u>meso</u> isomers has also been extended. We have found that two different α - β coupling constants (they differ by approx. 0.5 c/s) are evident in the spectra of the <u>meso</u> dichloride

To: Dr. B. L. Shapiro

July 13, 1964

and dibromide. As pointed out by Shimanouchi and Tasumi (and again confirmed by calculations based on nonbonded interactions) only two conformers of the <u>meso</u> isomer are expected to be significantly populated and these two are mirror images which are equal in energy. The presence of only these conformers (possessing the classical trans and gauche dihedral angles of 180° and 60°) predicts equal α - β coupling constants.

The observation of two distinct α - β coupling constants in the <u>meso</u> spectra can best be explained by deformations of the dihedral angles away from the classical 60°, 180°, gauche and trans values and/or by different C-C-C bond angles. These deformations are predicted by additional calculations based on nonbonded interactions.

A limited number of preprints of a paper (to appear in the Journal of Molecular Spectroscopy) describing this study in more detail are available and will be furnished upon request to those especially interested in this area of investigation.

Sincerely yours, P.E. M. Molow

P. E. McMahon

W. C. Tincher

FS/64-180/DS

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July 15, 1964

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

Dear Dr. Shapiro:

We offer the following data for consideration by readers of the Newsletter.

ON CALCULATING ACTIVATION ENERGIES FOR INVERSION PROCESSES IN SPIN-COUPLED SYSTEMS

In some cases, the Piette and Anderson fast exchange approximation has been used to calculate Ea for inversion processes where the exchanging protons are spin-coupled. In this manner, $_{\Delta}H^*=9.0\pm0.2$ kcal/mole was calculated for the chair-chair interconversion of cyclohexane, although more recent studies of C_6HD_{11} have given more accurate values for this parameter 3 . We have been studying the conformational inversion of 7,12-dihydropleiadenes 4 in which the -CH2- signals go from sharp singlets under fast exchange conditions to AB quartets on cooling. $_{\Delta}H^*$ is generally quite large (20-80cps depending on the compound) when rotation is hindered; because the protons lie in different shielding regions with respect to the aryl rings, and $_{\Delta}H^*$ is ca. 15 c.p.s. 1-Methyl-7,12-dihydropleiadene gives a single -CH2- peak at room temperature, but two AB quartets at -30°, indicating a difference in geometry of the CH2 groups when the molecule is frozen.

8A8=73 H H H JAB=15 cps.

JA8=15 H H H JAB=15 cps.

CH2 protons

-30°

It is unlikely that this difference is due to long-range shielding by the CH_3 group since only a single $-\mathrm{CH}_2$ - signal appears under fast exchange conditions. When the above molecule was selectively deuterated at each $-\mathrm{CH}_2$ - group, we were able to study the temperature dependence of each

Dr. B. L. Shapiro July 15, 1964

Page 2

-CH2 - signal separately and calculated AF* from the rate constant at T_c for each isomer. A value of 13.5 kcal/mole was obtained in each case, there being no reason to expect substantial differences due to steric isotope effects4. However, when we attempted to calculate Ea for the two compounds, using lime-width data above Tcl, substantially different activation energies were obtained. Although we are not certain what the experimental errors amount to, we feel that the major difference in the values arises from inconsistencies in the fast exchange approximation when applied to AB systems. Ea calculated for isomer I with $\mathcal{E}_{AB}/J_{AB} \simeq 5$ (ca. 12 kcal/mole) seems to give a more reasonable value for as* than the other isomer (II) where J&S. The pertient data are summarized below:

30.	H CO CH3	D
	I	II
8 _{AB}	73 cps.	18,5
J _{AB}	15 cps.	15
$T_{\mathbf{c}}$	» 8°	-10°
∆F*	13.5	13.5
Ea	12.0 ± 1 (?)	9.1±1 (?)

Any comments pertaining to these results will be most welcome.

Yours sincerely

P. T. Lansbury

Associate Professor of Chemistry

PTL:bjv

References:

- Piette and Anderson, J. Chem. Phys. 30, 899 (1959)
- 2. Harris and Sheppard, Proc. Chem. Soc. 418 (1961)
- 3. Anet et al, Bovey et al, Proc. Chem. Soc. 145, 146 (1964)
- 4. c.f. P. T. Lansbury and J. F. Bieron, JACS, 84, 2524

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H. Dreeskamp, E. Sackmann

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Telefon 29978393

July 14, 1964

Dear Dr. Shapiro:

The sign of the geminal H-H coupling in formaldehyde

Reading the most interesting letter by Prof. Pople on "A molecular orbital theory of geminal H-H coupling" in the last issue (No 69-32) prompts us to make this contribution:

Prediction 1) of that letter says: the H-H coupling in formaldehyde, whose absolute value is known to be 42.4cps [B.L.Shapiro, R.M.Kopchik, S.S.Ebsole, J.C.P. 39 3154 (1963)] should have positive sign.

We found the following: In acetaldehyde the coupling of the aldehyde-proton to the methyl- c^{13} is $|J_{C-C-H}|=26.6$ cps [H.Dreeskamp, E.Sackmann, Z.Phys.Chemie N.F. $\underline{34}$ 273 (1962)]. By H- {H} decoupling we found that this constant has the same sign as the one-bond c^{13} -H

coupling of the methyl-group, i.e. $J_{C-C-H} = +26.6$ cps. Similarly we found the signs of the other long-range couplings as given in the attached graph:

Furthermore a large empirical material confirms that the geminal J_{H-C-H} and J_{C-C-H} of two molecules which differ by the replacement of a hydrogen by a methyl-group are in the ratio of:

$$\frac{J_{H-C-H}}{J_{C-C-H}} \simeq 2 \quad \left[\text{interpreted as} = \frac{\chi_{H} \cdot S_{A}^{2}(0) \cdot \Delta \in (C-C-H)}{\chi_{C} \cdot S_{C}^{2}(0) \cdot \Delta \in (H-C-H)} \right]$$

An analoguous relation seems to hold not only for C but for all group IV elements as shown in Z.Naturf. 19a 139 (1964).

Therefore we think we have very good reason to carry the findings of acetaldehyde to formaldehyde and thus confirmed the positive sign for $J_{\rm HH}$ in formaldehyde as predicted by Prof.Pople.

Best regards

4. Fres amy

The Sign of $J_{H-H}(\underline{\text{gem}})$ in Formaldehyde

In last month's Newsletter, Professor Pople predicted a large positive geminal H-H coupling constant in CH₂O (see IITNMRN <u>69</u>, 32-34). It has previously been reported (B. L. Shapiro, R. M. Kopchik and S. J. Ebersole, J. Chem. Phys., <u>39</u>, 3154 (1963)) that the absolute magnitude of this coupling is indeed large (ca. 41 c/s). In the immediately above letter from Dr. Dreeskamp, he, too, infers that this coupling is positive.

By means of $H^1(C^{13})$ experiments on 13 CHDO, we have shown that $J(H-C^{13})$ and J(H-D) have the same sign, and that therefore by the usual arguments J(H-H) in CH_2O is in fact positive.

The details of this work will be published shortly.

B. L. Shapiro
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MELLON INSTITUTE

4400 FIFTH AVENUE PITTSBURGH, PA. 15213

July 15 1964

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

Dear Barry:

Recently Dr. D. Jung wrote a sub-routine to plot the calculated spectra obtained from the LAOCOON II program. We think it may be of interest to the readers of IITNMR to see the results of an analysis performed by the now complete program.

The example given here refers to the NMR spectrum of benzophenone run as a 20% (W/V) solution in CCl_h .

The chemical shifts and coupling constants giving the best fit are:

```
Chemical shifts: W(1) = 462.145 c.p.s. from TMS
                   W(2) = 441.785
                   W(3) = 447.096 "
                   W(4) = 441.785 "
                   W(5) = 462.145
Coupling constants: A(1,2) = 7.809 c.p.s.
                   A(1,3) = 1.293
                   A(1,4) = .685
                   A(1,5) = 1.780
                   A(2,3) = 7.527
                   A(2,4) = 1.320
                   A(2,5) = .685
                   A(3,4) = 7.527
                   A(3,5) = 1.293
                                    11
                   A(4,5) = 7.809
```

and were obtained after 3 consecutive iterations. The labeling of the protons is the following:

MELLON INSTITUTE

Dr. B. L. Shapiro

15 July 1964

and the experimental and calculated spectra are shown in the accompanying figure.

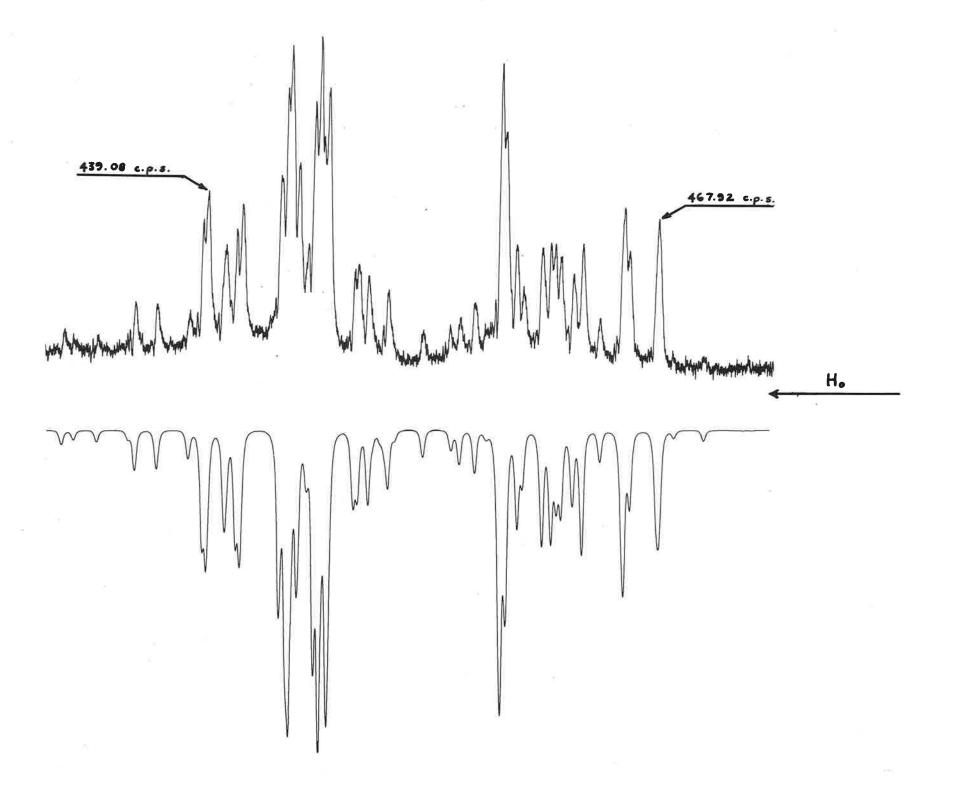
We hope that our next contribution to IITNMR will not require as much prodding as this one.

Cordially yours,

S. Castellaus
S. Castellano

A. A. Bothner-By

P. S.Distinti saluti e cordiali ringraziamenti alla tua segretaria per aver tradotto in un dignitoso Italiano le mille contumelie sicuramente da te dettatele in Inglese nei miei confronti.





LABORATORIUM VOOT ORGANISCHE CHEMIE

Dir.: Prof. Dr. F. GOVAERT

GENT, July 15th 1964. Tel. 25,26.02 J. Plateaustraat, 22

Associated Prof. Bernard L. SHAPIRO. Department of Chemistry, Illinois Institute of Technology, Technology Center,

> CHICAGO. Illinois 60616.

Concerning: ${}^4J_{HH}$ and J_g in dioxolanes.

Dear Professor,

In connection with two communications to the ITTNMR letters, one about long range interactions (1), and another about f_{gem} in 1,3-dioxanes and 1,3-dioxolanes (2), we wish to report some results we have at these laboratories on 1,3-dioxolanes.

We are interested in structural features of those components. Of several dioxolanes, we finished a comparative study about shielding effects and the related analysis of $^{A}2^{B}2$ system (3), and note at the same time some features related with magnetic anisotropy (4). Another program concerning J_{nem} and $^4J_{\text{HH}}$ is started.

Long range 4 coupling: This is frequently observed especially in rigid systems (5) when a specific "W" or "M" arrangement saturated c-bonds can be recognised (6)(7) and when the "straight" zig-zag set is planar (9). The phenomenon can thus inform us about conformation. Therefore we took the spectra of a few dioxolanes such as

I, II and IIIa.
$$H_{A}$$
 H_{A}
 $H_{$

In compound I the low field proton resonance of the C2-methylene group at $\tau = 5.03$ is a triplet (fig. 1) with a relative surface of 1. As it was recognised that this must be attributed to the proton trans to a β C-C bond (4), this must be attributed to H_B of I. At the same time the pattern at $\tau = 5,61$ for the methine H_C protons shows that the long-range coupling of H_{B} occurs with these H_{C} protons. It is thus confirmed that only the proton which fits a """ pattern shows long range, while H_A on the contrary has about the same band width as TMS, and thus does not couple at all. Therefore $J_{\text{confirm}} = 0$. (vide infra). From the figure it is seen that ${}^4J_{\text{HH}} = 0,5^{\text{gem}}$ c/s.

As the normal value is somewhat between 1 à 2 c/s (5) one can assume that either (a) there is a distortion of the ideal bond angles fitting the "W" pattern (so that the small lobes of the bond orbitals H_B and H_C do not overlap each other quite nicely) and/or

(b) that some flexibility of the ring (s) disturbs this

special arrangement.

To our surprise the compound II does not show a long range coupling, although the W-pattern in both possible conformers should be more ideal than in compound I. In IIIa, where conformation is not influenced by a fused ring, we again find $|{}^4J_{\rm HII}| \leq 0.5$ cps (fig. 3). We

feel that these facts are only the beginning of a yet unresulved problem and should be happy to get a few hints.

 $\frac{J_{\text{gem}}}{1.174_{-}^{+}}$ 0.03 is observed (sideband modulation technique, number of measurements N = 28). The French investigation (2) mention $J_g = 0$,

for the monocyclic derivatives IIIb and IIIc. We found for IIIa (meso compound) on the contrary a /J / = 0.63 $^{\pm}$ 0.05 c/s (N = 6). This value was found, measuring the gactual separation between peak-maxima and can be too low (7).

We hope to prepare in the near future more dioxolanes, especially bicyclic ones analogous with I or II, to obtain some more information. Litterature:

R.Lynden-Bell, N.Sheppard; ITTNMR letters, 68, 22(1964).

C.Barbier, J.Delman; ITTNMR letters, 69, 30 (1964).

F.Alderweireldt, M.Anteunis; Part. V, To be published.

M. Anteunis, F. Alderweireldt; NMR experiments on ketals, Part. III and IV., Bull. Soc. Chim. Belg., in press.

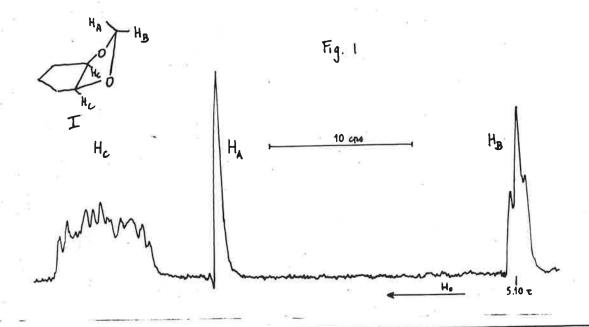
see f.i. A.Rassat, C.Jefford, J.Lehn, B.Waegell; Tetrahedron Letters, nr. 5, 233 (1964).

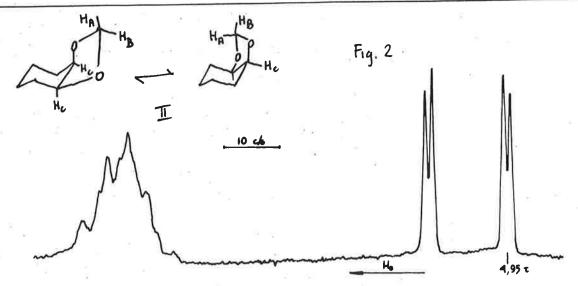
J.Meinwald, A.Lewis; J.Am.Chem.Soc., 83, 2769 (1961).

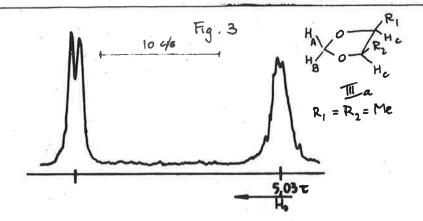
For some other examples see f.i. VARIAN Spectra catalogue II, products nr.

^{0.}Jardetzky; ITTNMR <u>69</u>, 31/32 (1964).

Banwell, N. Sheppard; Disc. Faraday Soc., 34, 115 (1962).







Sincerely yours,

Mereve Prof. Dr. F. Alderweireldt.

Assoc.Prof. N.Anteunis.



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE

BETHESDA, MD. 20014

17th. July, 1964.

NATIONAL INSTITUTES OF HEALTH Area Code 301 Tel: 656-4000

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

Dear Dr. Shapiro,

In the hope that a very short note will at least lessen, if not remove the obligation that our institute has to the IITNMR Newsletter, we should like to report an observation we made during the NMR study of some ring interconversions in the cyclohexane series.

As a result of the rapid interconversion of the chair forms of 2,2-dimethyl cyclohexanone, the six methyl protons are identical and give a singlet at 1.08 ppm. (in CCl₄, relative to TMS) which integrates for six protons. A bulky substituent will tend to take up an equatorial configuration, thus "locking" the ring with the result that one methyl group acquires an axial identity and the other becomes equatorial. The latter, by virtue of its greater proximity to the carbonyl group would be expected to give a signal at lower field than that of the axial methyl group.

This is observed in the spectrum of 2,2-dimethyl-5-bromocyclohexanone, which was measured in CDCl₃. At 37°, two methyl peaks are observed at 1.200 and 1.225 ppm. (relative to TMS) i.e. separated by 1.5 cps. As the temperature of the probe is decreased, these peaks separate and at -10° are 6.5 cps. apart. Raising the temperature above 37° has the reverse effect and at about 50°, the peaks coalesce. This is only a little higher than the normal operating temperature of the probe and may be subject to a small error. We hope to pursue this further with 100 megacycle spectra.

Yours sincerely,

G.Milne.

M.A. Oxman.

M. a. Clyman

MICHIGAN STATE UNIVERSITY EAST LANSING

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

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

July 20,1964

Dear Barry:

Readers of IITNMR may be interested in details of a symposium on "The Interpretation of NMR Chemical Shifts and Spin Coupling Constants" to be held Wed.Sept.30 -Thurs.Oct.1,1964, as part of the 3rd National Meeting of the Society of Applied Spectroscopy in Cleveland, Ohio.

The program is as follows:

Wednesday Sept.30, Morning Session

Introductory Remarks, Max T. Rogers 10:10 "Concerning Geminal Coupling Constants in sp²-Type Methylene Systems", 10:20 Bernard L. Shapiro, Dept. of Chemistry, Illinois Institute of Technology, Chicago. "A Molecular Orbital Theory of Spin Coupling", John A. Pople, Dep't of Chemistry, 11:10 Carnegie Institute of Technology, Pittsburgh, Pa. Wednesday Afternoon Introductory Remarks, Prof. J. B. Stothers, Dep't of Chemistry, University of 2:00 Western Ontario, London, Ont. "Carbon Shieldings and the Electronic Structures of Unsaturated Molecules", 2:05 Paul C.Lauterbur, Dep't of Chemistry, State University of New York, Stony, Brook, L.I. "On the Interpretation of C13_H1 Coupling Constants", Jeremy I. Musher, 2:40 The Rockefeller Institute, New York, N.Y. 3:20 Intermission "Factors Affecting Proton-C13 Coupling", G.J.Karabatsos, Dep't of Chemistry, 3:30 Michigan State University, East Lansing, Mich. "Fluorine NMR Shielding in Organic Ions", Robert W. Taft, Dep't of Chemistry, 4:10 Pennsylvania State University, University Park, Pa.

Thursday Morning, Oct. 1

"Broad Line Nuclear Magnetic Resonance Studies; Structure of Biscyclo-10:10 pentadieny Rhemium Hydride", L.N.Mulay, Materials Research Laboratory, Pennsylvania State University, University Park, Pa.

"NMR Studies on Novel Organometallic Compounds", W.M.Ritchey and D.P.Tate, 10:50 The Standard Oil Company(Ohio), Cleveland, Ohio.

"Tacticity Studies of Polypropylene by NMR", F.J.Knoll, W.M.Ritchey and 11:25 D.B.Emrick, The Standard Oil Company (Ohio), Cleveland, Ohio.

"Proton Magnetic Resonance Studies of Some Organosulfur Compounds", James 11:45 M.Purcell, Eastern Regional Research Laboratory, U.S.D.A., Philadelphia, Pa.

In addition there will be two papers on biological applications of NMR in another symposium (Wed.morning 9:00-10:10) and several papers on EPR on Thursday afternoon. Anyone interested is invited to attend.

Yours sincerely.

Max T. Rogers, Prof. of Chemistry

Max-Planck-Institut für Biochemie

Dr.J. Sonnenbichler

8 München 15, den 17.7.1964
Goethestraße 31
Fernruf 59 42 61/62
Postschließfach 64

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

Dear Dr. Shapiro:

You say that the IITNMR Newsletters shall not be used only for information of scientific results but also for exchange of opinions. So I will use this possibility.

- 1) Has any of your readers knowledge of PMR publications about charge-transfer-complexes? I should be pleased if one could give me some tips.
- 2) In the literature you find in the NMR-spectra the Tor confacts (related on TMS) which we all know. Both of these counting ways have their advantages and their adherents. But if you are used to a scale you are often forced to think round to another counting way. It is surely not very difficult but I ask you: couldn't we bypass ist? The scientific editorial offices have also no uniform and international principle in this matter, however, one should wish this. Do we all really want two scales, as it is now unfortunately the case in IR. (μ or cm $^{-1}$)? An international standard would surely help all of us and at least every one would accept it. Someone has to start looking for a way out and I may as well be it. Nearly most of all NMR men nowadays read the IITNMR Newsletters; therefore, I have a proposal: Ask all your readers and make use of the answers. The system which is most acceptable (? or frelated on TMS) should be generally appreciated and everyone should use it. I think there is enough good will to help us all in this aspect.
- 3) At last I have a short technical note. Nearly one year ago we noticed at our A 60 a not unimportant deposit of limestone; we had to remove the cooling-spirals and to clean them with acid. Since this time we use equipment manufactured in Germany for decalcification that makes a limestone deposit at the tube system unpossible. The limestone is currently washed out as a fine powder. A metal casing is flushed with tap water and contains a high-frequency tube which burns for about 60 000 hours. The case is hooked up with the cooling-system through a metal tube connection. This small supplement is very cheap compared to other possibilities such as closed circulation

2. Blatt zum Schreiben vom 17.7.64 an Dr. B.L.Shapiro, Chicago, U.S.A.

of destilled water. The solution-capacity and the stabilization of the A 60 is not interfered with by this equipment. Since we use this purification we noticed no longer a deposit of limestone.

Equipment: Purator \$ 150,--

Manfred Hoh K.G., Stuttgart/Untertürkheim, Germany. Manuf:

Yours sincerely

Johann Sommbichler

CARNEGIE INSTITUTE OF TECHNOLOGY

SCHENLEY PARK

PITTSBURGH 13, PENNSYLVANIA

July 17, 1964

DEPARTMENT OF CHEMISTRY

TELEPHONE: 621-2600 AREA CODE 412

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

Dear Barry:

As partial recompense for errors we made in an earlier MELLONMR letter (Kurland, Rubin and Wise, "Inversion Barrier in Singly Bridged Biphenyls", MELLONMR No. 59)(these errors are discussed — i.e. swept under the rug — in footnote 1, below) and as a subscription payment for IITNMR letters, we're passing along some tables which, we hope, will be useful to those readers who, without computer facilities, are interested in analyzing spectra of exchanging AB systems.

These tables yield (1) the separation of the inner lines of the AB pattern (before complete coalescence) and (2) the line-width (after coalescence) for ranges of values of the chemical shift, coupling constant, mean exchange lifetime and relaxation time. The tables are expressed in terms of variables scaled to the coupling constant, J. Thus one can apply these tables to the analysis of a particular AB exchange by means of rescaling and interpolation.

The scaled variables are defined as follows:

i. β is a measure of the relative chemical shift between A and B spins as given by $\beta^2-1=\left(\delta/J\right)^2$

where δ is the chemical shift (in c.p.s) and J is the coupling constant (in c.p.s.);

ii. γ is a measure of the exchange rate as given by

$$\gamma = (1/2\pi \tau) (2/J)$$

where \mathcal{T} is the mean lifetime between exchange (in seconds)

iii. α is a measure of the position of the innermost peak of the AB pattern (before complete coalescence) as given by

$$\alpha = \Delta (2/J)$$

where Δ is the position (in c.p.s.) of the innermost line relative to the center of the AB pattern;

iv. α is a measure of the line-width (after complete coalescence)

We have set $\alpha' = \Delta'(2/J)$ where Δ' is the position (in c.p.s.) of the maximum of the coalesced pattern in the dispersion mode (again, measured relative to the center of the AB pattern);

v. \in is a measure of the line-width in the absence of exchange as defined by $\epsilon = 1/2\pi T_2$ (2/J), where T_2 is transverse relaxation time (in seconds).

In the tables we have taken values of β from 1.1 to 4.0 in intervals of 0.1. Values of γ have been chosen to cover the range, in logarithmic intervals about γ (corresponding to coalescence), from no exchange to rapid exchange. Two values of \leq , corresponding roughly to line-widths (in the absence of exchange and for J = 10 c.p.s.) of 0.03 c.p.s. and 0.5 c.p.s., were used.

The line-shape formulae used to obtain the values of α and α were derived from Alexander's density matrix-treatment of exchanging AB spin systems². A computer program (written in ALGOL-20) was used to determine α from the absorption mode line-shape formula and to get α from the dispersion mode formula. Since the AB pattern is symmetric about its center, only positive values of α and α were considered. Corresponding to the range of the scaled frequency variable and the grid used for determining, via the computer, the maxima for α and α , an approximate precision in α and α of 0.02 to 0.05 may be assigned.

One should note the following in using the tables: (1) $\gamma_{\rm Q}$, the value of γ at coalescence (for the case of zero line-width in the absence of exchange) is given by

$$\gamma_{0} = \sqrt{\frac{1}{2}} (\beta^{2} + 5)^{1/2}$$
;

- (2) the logarithm of the exchange rate (-ln $\tilde{\iota}$) is given by -ln $\tilde{\iota}$ = ln γ + ln(π J);
- (3) δV , the separation between the innermost lines, is given by $\delta V = \alpha J$;
- (4) 8'V, the line-width, (i.e. the separation of the maximum and minimum of the coalesced line in the dispersion mode) is given by

(One last note: we've found that line-width measurements are apt to be deceiving unless care is taken to extrapolate them to zero RF field) A sample page of the tables follows; complete copies (they run about 9 pages) of the tables and/or the computer program are available on request.

Sincerely,

William Wise

William Wise

Systems and Communication Sciences

bert Kurland

Department of Chemistry

1. The errors in our letter were the following: (i) in footnote 1 we stated that Alexander, in his treatment of exchanging AB systems (see footnote 2), had either changed the definition of " \uparrow " or dropped a factor of two; these statements were incorrect; no factor of two had been dropped and " \uparrow " is used consistently as the mean exchange lifetime; (ii) we gave an expression for \uparrow the lifetime at coalescence (for zero line-width in absence of exchange), which was incorrect; the correct expression is given by \uparrow $\frac{\sqrt{2}}{\pi} \frac{\sqrt{2}}{(\delta^2 + 6J^2)^{1/2}}$

where δ and J are in c.p.s.; (iii) the parameter y for thiepin in Table I should be 6.738 (at 294 K) and 6.747 (at 203.5 K) rather than 3.262 and 3.253, respectively. We're grateful to Dr. Alexander and R. Newmark for correspondence which led us to correct these errors.

2. S. Alexander, J. Chem. Phys., 37, 97 (1962).

β = 1.90			$\beta = 2.00$					
	$ \leq = 3 \times 10^{-3} $	5x10 ⁻²		<= 3x10 ^{−3}	5x10 ⁻²			
ln γ	α	α	ln γ	α	α			
-1.573 -1.342 -1.112 -0.882 -0.652 -0.421 -0.191 +0.039 +0.269 +0.500 +0.730	0.884 0.884 0.850 0.850 0.782 0.743 0.646 0.510 0.340 0.000	0.884 0.884 0.850 0.816 0.782 0.714 0.646 0.476 0.272 0.000	-1.551 -1.320 -1.090 -0.860 -0.630 -0.399 -0.169 +0.061 +0.292 +0.522 +0.752	0.980 0.980 0.980 0.945 0.945 0.875 0.840 0.735 0.595 0.385 0.000	0.980 0.980 0.980 0.945 0.910 0.875 0.805 0.700 0.560 0.350 0.000			
$\beta = 1$. 90		$\beta = 2$	2.00				
	$\leq = 3 \times 10^{-3}$	5x10 ⁻²		<= 3xl0 ⁻³	5x10 ⁻²			
$\ln \gamma$	α¹	α¹	$\ln\gamma$	α •	α 1			
+0.730 +0.960 +1.190 +1.421 +1.651 +1.881 +2.111 +2.342 +2.572 +2.802 +3.032	0.680 0.595 0.425 0.340 0.255 0.170 0.170 0.170 0.085 0.085	0.765 0.595 0.510 0.425 0.340 0.255 0.255 0.170 0.170 0.170	+0.752 +0.982 +1.213 +1.443 +1.673 +1.903 +2.134 +2.364 +2.594 +2.824 +3.055	0.788 0.613 0.525 0.350 0.263 0.175 0.175 0.088 0.088 0.088	0.875 0.700 0.525 0.438 0.350 0.263 0.263 0.175 0.175 0.175			
$\beta = 2$.10		β = 2	2.20				
	€= 3xl0 ⁻³	5x10 ⁻²		€= 3xl0 ⁻³	5x10 ⁻²			
ln γ	α	α	ln γ	α	α			
-1.528 -1.298 -1.068 -0.838 -0.607 -0.377 -0.147 +0.084 +0.314 +0.544 +0.774	1.080 1.080 1.080 1.044 1.044 0.972 0.900 0.828 0.648 0.432 0.000	1.080 1.080 1.080 1.044 1.008 0.972 0.900 0.792 0.648 0.396 0.000	-1.506 -1.276 -1.045 -0.815 -0.585 -0.355 -0.124 +0.106 +0.336 +0.566 +0.797	1.184 1.184 1.147 1.110 1.073 0.999 0.888 0.740 0.481	1.184 1.184 1.147 1.110 1.073 0.999 0.888 0.703 0.444			



RICHLAND, WASHINGTON 99352 AREA CODE 509, TELEPHONE 942-11111

HANFORD LABORATORIES

July 9, 1964

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

Dear Barry,

Organophosphorus-Uranyl Complexes

Thank you for adding us to your mailing list for the IIT N-M-R Newsletter. Here is a contribution in "payment" for the back issues which you have supplied.

The metal-extracting ability of organophosphorus compounds has been investigated previously by many workers. Nuclear magnetic resonance studies of organophosphorus compounds may be found elsewhere 2-7. With the neutral organophosphorus compounds solvation complexes are formed with many salts. Uranyl compounds form very strong complexes having the structure $\text{UO}_2\text{X}_2(\text{OP})_2$, where P represents the phosphorus compound. The present study has involved the effect on the proton and phosphorus NMR spectra of saturation with uranyl nitrate in dilute carbon tetrachloride solutions.

A series of compounds has been investigated, including phosphates(1,2)*, phosphonates(3,4), phosphinates(5), and phosphine oxides(6) which are listed in the table in the order of increasing extracting ability. The organophosphorus complexes show proton and phosphorus resonance peaks occurring at lower applied magnetic fields than the uncomplexed form. Representative shifts of the complex relative to the non-complexed compound are shown in the table.

In any given compound it will be noted that the change in chemical shift on complexing is greatest for protons closest to the phosphorus atom, i.e. closest to the active site of complexation with uranyl. This was suggested by earlier work with tributylphosphatel. Further, for the series of compounds the largest low-field chemical shift results for those compounds which have the greatest complexing ability, the phosphinate(5) and phosphine oxide(6). Ferraro has reported a downfield shift for the (-CH₂O-)

^{*}Numbers refer to those in the table.



GENERAL (ELECTRIC

Dr. Bernard L. Shapiro

-2-

July 9, 1964

Change in Chemical Shift for Several Organophosphorus Compounds
Complexing with Uranyl Nitrate*

No.	Compound	OCH ₂	Alkoxy CH ₃	Oth	e r	Phosphorus (cps)
1	(CH ₃ CH ₂ O)P=O	+38	+7	= 1	-	-22
2	[сн ₃ (сн ₂) ₃ о] ₂ Р(о)(осн ₃)	58	3	FOCH +35	СН ₃ (С <u>Н</u> 2)2 ~+15	+29
3	(СН ₃ 0) ₂ Р(О)Н	-	23	Р <u>н</u> 30	o n	172
4	(сн ₃ сн ₂ о) ₂ Р(о)сн ₂ сн ₃	28	9	P-CH ₂ 38	P-CH ₂ C <u>H</u> 3	1,77
5	(сн ₃ о)Р(о)[(сн ₂) ₃ сн ₃]2	æ	21	(СН ₂) ₂ С <u>Н</u> 3 -3	(CH2)2CH3 0,+26**	340
6	[CH3(CH2)7]3PO	•	餐	æ	4 9 2	830

^{*}Positive value for change in chemical shift indicates resonance at lower applied magnetic field ($\Delta \delta = \delta_{\rm UO2} \frac{++}{2}$, CCl_h - $\delta_{\rm CCl_h}$). Proton measurements have been made at 60 Mc and phosphorus at 24.3 Mc on the Varian DP-60 spectrometer at 33 ± 2° C. Chemical shift measurements are reported within ± 0.5 ppm for phosphorus and ± 0.1 ppm for proton shifts.

protons in complexes of the noyltrifluoroacetone with tributylphosphate and dibutyl butylphosphonate. 7

Measurements involving coupling constants and at variable temperatures are presently under way.

Simcerely yours,

Jane L. Burdett

L. L. Burger

^{**}Separated into two peaks on addition of UO2 ++.

Dr. Bernard L. Shapiro

-3-

July 9, 1964

1_{L. L. Burger, Nuclear Science} and Engineering 16 428 (1963).

 $2_{\rm N.}$ Muller, P. C. Lauterbur, and J. Goldenson, J. Am. Chem. Soc. 78 3557 (1956).

3_{J. R.} Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, <u>J. Am.</u> Chem. Soc. <u>78</u> 5715 (1956).

¹⁴C.F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, J. Am. Chem. Soc. 79 2719 (1957).

5Harold Finegold, Ann. N.Y. Acad. Sci. 70 875 (1958).

6Nuclear Magnetic Resonance Spectral Data, Manufacturing Chemists Association Research Project, Agricultural and Mechanical College of Texas, College Station, Texas, 1962.

7J. R. Ferraro, J. Inorg. Nucl. Chem. 26 225 (1964).



Imperial Chemical Industries Limited

DYESTUFFS DIVISION

P.O. Box 42, Hexagon House, Blackley, Manchester, 9, England

Telephone: CHEBTHAM HILL 1411 Telex: 66152/3/4 MANCHESTER
Telegrams: BRIDYCOR, MANCHESTER

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

Your Ref:

Our Ref: PL/PHY-5 Research Department

15th July, 1964

Dear Dr.Shapiro,

A further contribution from this laboratory to I.I.T.N.M.R. Newsletter is due, and we are offering notes on three topics from our recent work.

Proton C13 Double Resonance

equipped our Varian HR-100 spectrometer with facilities for proton-C¹³ double resonance. A frequency of 25 Mc/s is obtained by frequency division and multiplication (÷ 2, x 3) from the 16% Mc/s crystal which controls the V-4311 100 Mc/s r.f. unit. This is then used in a suppressed-carrier (balanced) modulator to generate side-bands at about 25.14 Mc/s and 24.86 Mc/s; the upper side-band is in the region of the C¹³ resonance. The nominal 140 Kc/s modulation frequency is adjusted until the upper side-band excites a C¹³ resonance, as shown by the collapse or splitting of a C¹³ satellite in the proton spectrum. The probe circuit has been modified so as to get effective power transfer to the transmitter coil at 100 Mc/s and 25.14 Mc/s simultaneously. The probe is otherwise unmodified, and uses standard 5 mm o.d. spinning sample tubes. The normal use of the spectrometer for proton spectra is unaffected, and whenever C¹³ satellites are observed the chemical shifts of the corresponding C¹³ nuclei can be measured in a few minutes with a reproducibility of ± 2c/s (± 0.08 ppm).

We have used this technique to investigate C¹³ solvent dilution shifts, which are usually much greater than the corresponding proton shifts. Highly polar solutes undergo much larger shifts than non-polar, and we believe the predominating effect in the former to be that of the electric "reaction field" generated by local polarisation of the solvent. Magnetic anisotropy effects, on the other hand, may be expected to be negligible compared with other solvent effects for C¹³.

A.60 Sensitivity Increase using "Mouse"

Following A.V. Robertson's recent communication (I.I.T.Newsletter 67, 16) we have attached Mouse timing circuits to our A.60 spectrometer. Our choice of circuit was different in that we used trigger tubes and also have a range of stationary times up to $3\frac{1}{2}$ min. This is useful since we can only afford time for Mouse Techniques by leaving the spectrometer working overnight.

(continued)

2

FROM I.C.I. Ltd., Research Department, Dyestuffs Division, Hexagon House, Blackley, Manchester,9.

15th July, 1964 Date

CONTINUATION: Sheet No.

TO Dr.B. Shapiro, Illinois Institute of Technology, Chicago, Illinois, 60616.

In practice Mouse B (the small filter band width mode) is usable overnight, but we can confirm that the gains are not up to theoretical predictions. Mouse A does yield increases almost as calculated (i.e. proportional to the square root of the integration time), but we find that drifts in the integration zero level are an annoying drawback when spectra are left running unattended overnight. We feel that obviously the method is potentially very useful and we would be most interested to hear of the results of any other laboratories trying it out.

Primary and Secondary Hydroxyl Groups

In the usual 10% analytical solutions of compounds or mixtures containing primary and secondary hydroxyl groups, owing to exchange processes only one combined OH peak is observed. Also the -CH2OH and >CH-OH resonances generally overlap between 3 and 46 . However, esterification separates these resonances, as -COOCH2 at about 45 and -COOCH < at about 56, and a comparison of these separated resonances gives directly the proportions of primary and secondary OH. Acetylation is one of the few quantitative organic reactions and we have shown that specimens can be acetylated using any of the standard methods (e.g. acetic anhydride and sodium acetate or acetic anhydride-pyridine mixtures) and the crude reaction mixture examined directly by N.M.R., since none of the acetylation procedures introduces resonances between 4 and 55.

The primary to secondary hydroxyl group ratios can be determined with an accuracy limited only by the A.60 integrator, and amounts of hydroxyl in polymers down to 1% by weight have been dealt with. The method is unaffected by any water in the sample. Full details are to be published shortly in Anal. Chim. Acta.

We continue to find the Newsletter very useful and stimulating; literature index is a particularly valuable feature.

Yours sincerely,

J.K. Berconsall Q. Nathias. P. Mampsons.

J.K.Becconsall

A. Mathias P. Hampson.

JKB/AYK.

CIBA Ltd.
Physical Laboratories
Basle, Switzerland

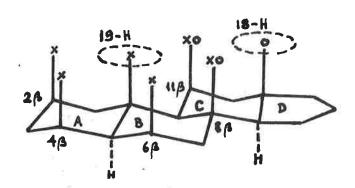
July 20, 1964

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

Dear Professor Shapiro:

I should like to report on a special case of Conformational Analysis with Chemical Shifts.

Steroids display a high degree of internal symmetry. There are, for example, quite a number of equivalent 1,3-diaxial positions relative to one of the two tertiary methyl groups (18-H and 19-H), namely



The 1,3-diaxial positions which are equivalent relative to the C-19-methyl group (x) or to the C-18-methyl group (o).

the 2β , 4β , 6β , 8β and 11β positions in 5α -steroids. These positions are all equivalent relative to the C-19-methyl group, and the last two $(8\beta$, $11\beta)$ relative to the C-18-methyl group as well. Therefore substituents in these positions should cause the same additional chemical shift of the tertiary methyl group. This is approximately true for -OH groups which shift the methyl signals by 11-16 c.p.s. (at 60 mc.p.s.). The same should hold for acetoxy groups. This, however, is not the case; the 2β , 4β , 6β -OAc groups

behave normally (9-13.5 c.p.s.) wherease llβ-OAc shifts the 19-H signal by only 4 c.p.s. and the 18-H signal by 7 c.p.s.

The 11β -acetoxy group is a special case compared with the equivalent 2β -, 4β - and 6β -acetoxy groups in that it experiences a two-fold 1,3-diaxial repulsion (by the C-19- and C-18-methyl groups). Thus a deformation of ring C would be conceivable as the cause for this behavior. We have therefore measured the spectra of several 11β -OAc steroids. The 11α -H signal is invariably a quartet. 11β -acetoxy-12-oxo-steroids give rise to a doublet with approximately the same coupling constant. With the help of modified Karplus equations [K.L.Williamson & W.S.Johnson, J.Amer.Chem.Soc. 83, 4623 (1961); K.Kuriyama, E.Kondo & K.Tori, Tetrahedron Letters 1963, 1485; and our results] one always arrives at the result that ring C cannot be deformed appreciably. This also holds for 11β -bromo-12-oxo-steroids with the bulkier bromine atom.

How then, may the odd behavior of the $ll\beta$ -acetoxy group be explained? The only reasonable explanation seems to be that the $ll\beta$ -acetoxy group is differently hindered compared with the 2β -, 4β - and 6β -acetoxy groups i.e. the movement of the $ll\beta$ -acyl group is confined to a narrower sector than that of another acyl group in an equivalent position. The effects of its magnetic anisotropy and electric dipole moment are therefore averaged out in a different way, giving rise to different chemical shifts of the tertiary methyl groups. The smaller additional chemical shifts of the two tertiary methyl groups due to a $ll\beta$ -acetoxy group are therefore a direct consequence of its different conformation or steric hindrance.

Sincerely yours,

R. F. Zürcher

Jurcher

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