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Newsletter

No. 80
MAY, 1965

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Deadline Dates:	No. 81:	18 June 1965
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A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication".

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.

April 20, 1965

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

Re: Chemical Shifts of Certain Methyl and Methylene Groups
Bonded to Silicon

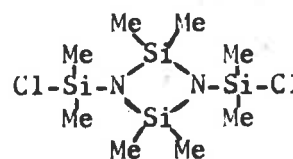
Dear Professor Shapiro:

We would like to describe briefly some observations which might be of interest to some other readers of IIT NMR Newsletter.

We measured the series of chloromethylsilanes (prepared by Dr. Chvalovský and Mr. Svoboda) of the structure $(\text{CH}_3)_{3-n}\text{Cl}_n\text{SiCH}_2\text{Cl}$ and found the results which are summarized in the table below.

n	Chemical shifts in cps, upfield to CHCl_3 at 60 Mc.	
	CH_2 protons	CH_3 protons
0	269.4	426.2
1	261.4	405.9
2	249.2	381.0
3	240.0	--

A compound which is believed to have the structure: was prepared in this laboratory and an interesting solvent effect has been found, which is now being studied. The NMR spectrum of the compound consists, as expected, of a closely spaced doublet centered at $\tau = 9.6$ ppm. with spacing 0.8 cps., when the spectrum is taken in cyclohexane or benzene, but in carbon tetrachloride signals of both groups collapse into one sharp signal. Taking spectra in a series of mixed solvents (cyclohexane- CCl_4) gradual collapsing of the doublet could be observed.



Sincerely yours,

J. Schraml

P. Geymayer

E. G. Rochow

J. Schraml

Peter Geymayer

EG Rochow

UNIVERSITY OF SOUTH FLORIDA

TAMPA, FLORIDA 33620

AREA CODE 813: 988-4131

April 21, 1965

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

Dear Barry:

DEPENDENCE OF 2J ON THE ORIENTATION OF ELECTRONEGATIVE SUBSTITUENTS

The "indirect" coupling contributions, which are associated with electron pairs in the vicinity of coupled protons have been investigated by perturbation theory (1) in the VB formalism of spin-spin coupling (2, 3). It can be shown in this approximation that the "indirect" contribution is given by

$$^2I_{J\alpha\alpha} = [K(C_1, \gamma_1) - K(C_1, \gamma_2)] [K(C_2, \gamma_1) - K(C_2, \gamma_2)], \quad (1)$$

where $\gamma_1 - \gamma_2$ is an electron pair having non-negligible exchange interactions, $K(A, B)$, with the two bonds ($C_1 - H_1$ and $C_2 - H_2$) which contain the coupled nuclei.

If γ_1 and γ_2 denote the $2p$ electrons of a double bond, $K(C_1, \gamma_2)$ and $K(C_2, \gamma_2)$ are negligible, and the resulting angular dependence corresponds to that discussed by Barfield and Grant (4). If two electrons of opposite spin are constrained without correlation to the same atomic orbital, then $\gamma_1 = \gamma_2$ and 2I_J vanishes. Vertical correlation can be introduced, however, by constraining the different spins to opposite lobes of the spherical harmonics. (5,6) The dependence of the resulting interactions of the vicinal type on dihedral angle, ϕ , can be written, $K(C_i, P_j) = A \cos^2 \phi + B \cos \phi + C$. Specializing these to tetrahedral orbitals, and substituting into Eq. (1), leads to

$$^2I_J = -K \cos \phi \cos (\phi + 120^\circ), \quad (2)$$

where K is a positive constant, which is independent of ϕ . It is interesting to note that Eq. (2) provides the same sign and angular dependence as that obtained by Pople and Bothner-By (7) from considerations of ionic effects in MO theory.

Entered in Table I are reported geminal coupling constants, $^2J(H_A H_B)$, for representative acyclic and cyclic compounds having one or two adjacent oxygens. Also included are the "indirect" contributions, 2I_J , which are defined by $^2J = ^2D_J + ^2I_J$, where the "direct" contribution, 2D_J , is equal to the experimental methane value of -12.4 cps and β -substituent effects have been neglected.

If the equilibrium conformation of methanol is assumed to be that in which one of the methyl protons is trans to the O-H bond, then the average value, $\langle ^2I_J \rangle_{av}$ for the three methylene pairs is approximated by,

$$\langle ^2I_J \rangle_{av} = (1/3) [^2I_J(30^\circ, 150^\circ)] = (1/4)K.$$

From the value $\langle ^2I_J \rangle_{av} = +1.6$ cps for methanol, $K \approx 7$ cps and the upper limit on the effect (for a single, adjacent oxygen) is about 5 cps in planar cyclic compounds. Equilibria between puckered ring conformations should give smaller 2I_J . For the case of two adjacent oxygens in a planar fragment, indirect contributions might be as large as +10 cps. The data in Table I are

- 2 -

qualitatively in agreement with these observations.

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^a All geminal coupling constants are assumed to be negative. It should be noted, however, that the small magnitude for item 10 does not preclude the possibility of a sign inversion. ^b Indirect contributions, $2I_J$, are defined by eq. (4). ^c H. J. Bernstein and N. Sheppard, J. Chem. Phys., 37, 3012 (1962); F.A.L. Anet, J. Am. Chem. Soc., 84, 3767 (1962). ^d K. G. R. Pachler, Spectrochimica Acta, 19, 2085 (1963). ^e N. V. Riggs and J. D. Stevens, Tetrahedron Letters, No. 24, 1615 (1963). ^f J. B. Lowry and N. V. Riggs, Tetrahedron Letters, No. 39, 2911 (1964). ^g R. J. Abraham, L. D. Hall, L. Hough, and K. A. McLaughlan, J. Chem. Soc., (London), 275 (1963). ^h U. Scheidegger, K. Schaffner, and O. Jeger, Helv. Chim. Acta, 45, 400 (1962). ⁱ C. Barbier, J. Delmau, and J. Ranft, Tetrahedron Letters, No. 45, 3339 (1964). ^j J. Delmau and C. Barbier, J. Chem. Phys., 41, 1106 (1964). ^k R. U. Lemieux and K. Nagarajan, Can. J. Chem., 42, 1270 (1964). ^l T. A. Crabb and R. C. Cookson, Tetrahedron Letters, No. 12, 629 (1964).

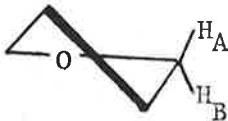
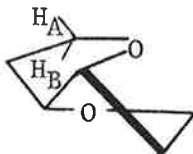
Sincerely yours,

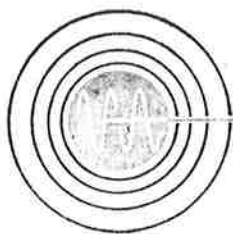
Mike

Michael Barfield
Assistant Professor
Department of Chemistry

MB:af

TABLE I
Representative Geminal Coupling Constants, $^2J(H_A H_B)$, for Cyclic and Acyclic
Compounds Containing the Groups, $-C-CH_A H_B-O-$ and $-O-CH_A H_B-O-$.

Compound	$^2J(H_A H_B)^a$	$2I_J^b$
1. CH_3OH	-10.8^c c.p.s.	$+1.6$ c.p.s.
2. Serine		
(a) alkaline	-11.33^d	$+1.1$
(b) acidic	-12.71^d	-0.3
<u>Cyclic Five-Ring</u> ($-C-CH_A H_B-O-$)		
3. Furanose,	-10.6^e	$+1.8$
		
4. Substituted γ -lactones	-8.7 to 9.1^f	$+3.3$ to $+3.7$
5. 3,6-anhydro-derivatives of 1,2-O-isopropylidene- α -D-xylohexofuranose	-8.1 to -8.7^g	$+3.7$ to $+4.3$
		
6. Two manöol derivatives	-7^h	$+5.4$
<u>Cyclic Six-Ring</u> ($-C-CH_A H_B-O-$)		
7. 1,3-dioxane	-11.0^i	$+1.4$
8. 1,6-anhydro- α -D-galactofuranose triacetate	-11.4^j	$+1.0$
9. β -D-xylopyranose tetracetate	-12^k	$+0.4$
<u>Cyclic Five-Ring</u> ($-O-CH_A H_B-O-$)		
10. Eleven Compounds	0 to 2^l	$+10$ to $+12$
<u>Cyclic Six-Ring</u> ($-O-CH_A H_B-O-$)		
11. Fourteen Compounds	-5.8 to -6.6^1	$+5.8$ to $+6.6$



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Zürich, April 20, 1965

Prof. Bernard L. Shapiro
Illinois Institute of Technology
Department of Chemistry

C h i c a g o 60616

U.S.A.

Re. The Varian VF-16 Spectrometer as a Pure Quadrupole Spectrometer, and the Varian Workshop in Zürich, 1965

Dear Dr. Shapiro,

Your letter to Attilio Melera arrived just as we were planning to tell you and the Newsletter readers about using the Varian VF-16 wide-line spectrometer as a pure quadrupole spectrometer. For a short time we thought we had discovered something new, only to find that it has been previously reported in the literature. However, we believe that it is not generally known that a magnetic resonance spectrometer whose probe is built on the crossed-coil principle can be used as a pure quadrupole spectrometer. It is true, in zero field, one cannot use the crossed coil geometry because there would be no induction into a receiver coil whose axis is oriented in space 90 degrees from that from the transmitter coil. However, the usual small modulation used in wide-line work is sufficient to remove the energy level degeneracy responsible for this lack of induction.

The first mention of the use of the crossed coil geometry in zero polarizing field was made by Haering and Volkoff in 1956 (Can. Journ. Phys. 34, 577) using a home-made spectrometer; they were studying the pure quadrupole transitions of Na^{23} and B^{11} , near 1.5 and 1.3 mc respectively, in the mineral Kernite. Recently Hartmann, Fleissner and Silescu (Naturwiss. 18, 591 (1963)) have studied the pure quadrupole interactions of chlorine and cobalt in a cobalt complex where a number of resonances between 2 and 16 mc were observed with their VF-16. Silescu has written me that they did their pure quadrupole work by turning the fine frequency control by hand, which means that the VF-16 can be used as a pure quadrupole spectrometer as it stands. It was our interest in the pure quadrupole transitions of La^{139} in LaF_3 , (which we found near 2.2, 2.6

-- 2 --

and 3.2 mc) which led us to this idea.

We are here (of course) using the Varian VF-16 spectrometer, so all that one needs to do in order to search for resonances automatically is to mount a small clock motor, by means of a flexible coupling, to the fine frequency control drive of the V-4210A RF-Unit. A motor speed of one revolution per hour, for example, gives a search rate of about 1 kc per minute in the 2 - 4 mc range. One must also remember to pull the probe entirely out of the gap of the magnet because the residual field may broaden the resonance excessively. Attached are the observed absorption and dispersion curves of N^{14} in polycrystalline hexamethylene tetramine at room temperature at 3.3 mc.

Persons working in pure quadrupole resonance know that quadrupole coupling constants may become very high indeed, in some cases reaching several 1000 mc, so that the 2 - 16 mc range of the VF-16 spectrometer represents a certain limitation. However, at looking at expressions for the energy levels (and, for simplicity, taking the asymmetry parameter equal to 0) an upper frequency of 16 mc means that one can measure a quadrupole coupling constant e^2qQ/h up to 224 mc for spin $7/2$. For spin $5/2$ this would be 107 mc, and for spin $3/2$, 32 mc.

So we have thought that, although the Varian wide-line spectrometer cannot be hailed as an universal pure quadrupole spectrometer, those laboratories which happen to have one, or any spectrometer using crossed-coil geometry, may be glad to know the instrument may after all be used as a pure quadrupole spectrometer in the range of its frequencies.

We would like to mention that our Workshop will be held here on September 22 - 29.

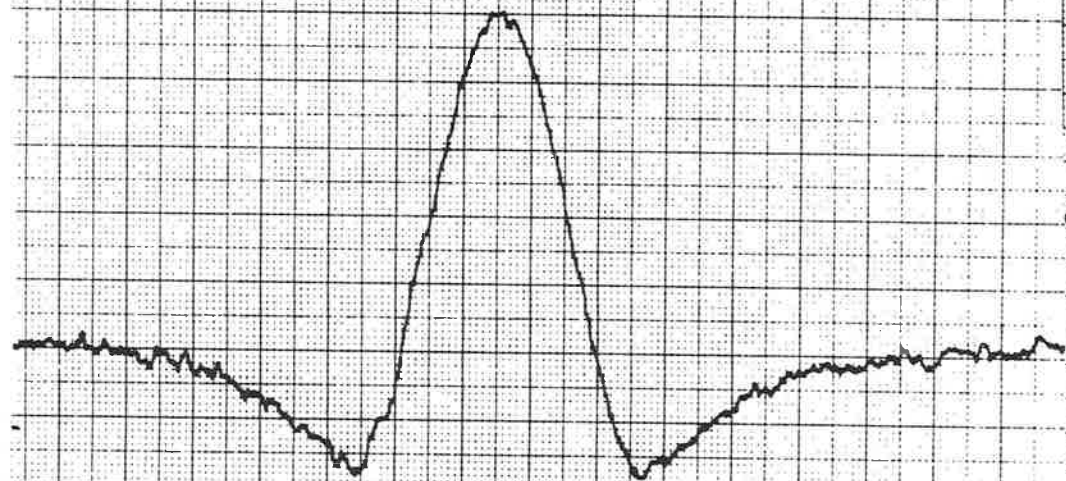
Yours sincerely,

L.O. Andersson

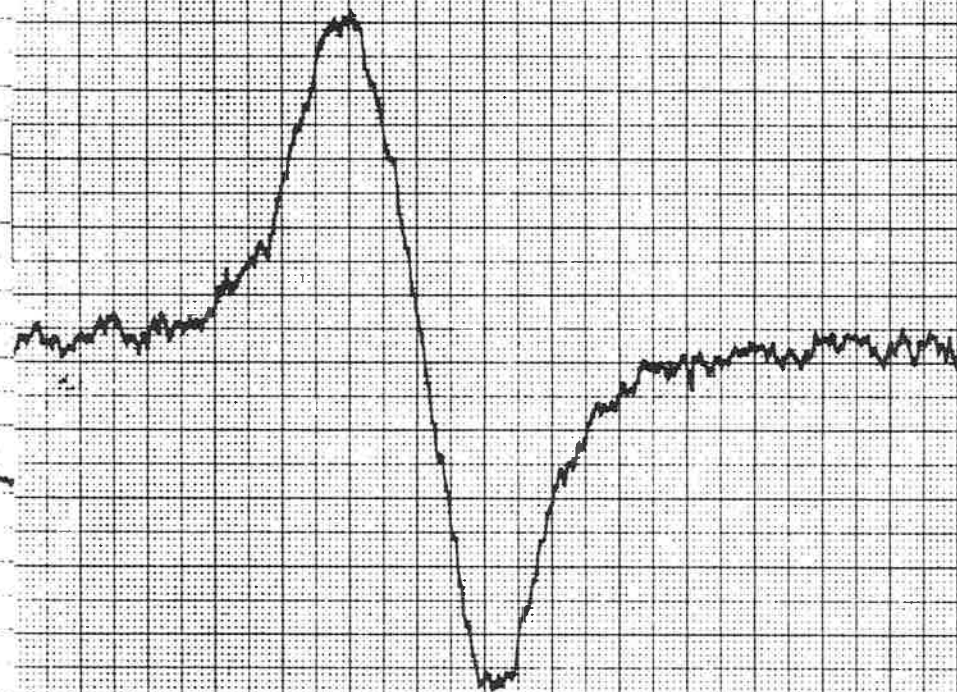
L.O. Andersson
Fellow
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W.G. Proctor
Director of Research
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WGP/ik



U- and V-modes of the 3.30 Mc transition of N^{14} in a powder sample of hexamethylene tetramine at room temperature. Approximate operating conditions were: search rate, 2 Kc/minute; modulation 4 gauss peak-peak, 40 cps; 2 Kc equals 3 cm.



BRYN MAWR COLLEGE
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DEPARTMENT OF CHEMISTRY

26 April 1965

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

Dear Prof. Shapiro:

With apologies for tardiness, we submit the following report on work at Bryn Mawr. for the IITNMR Newsletter.

Chemical Exchange and NMR

During the academic year now almost finished, we have been studying the theoretical treatments of chemical exchange and NMR or NMDR. We were originally motivated by the exciting work of Forsén & Hoffman^{1,2,3} last year, as well as by recent applications^{4,5} of Alexander's^{6,7} density matrix treatment of chemical exchange.

The point of view taken is slightly different from that of Alexander, and much in line with that of the Baldeschwieler group.^{8,9,10} The Hamiltonian for a system of exchanging spins is considered in four parts: (a) Zeeman and spin-spin coupling terms which are time-independent, (b) coupling of spins to lattice, time-dependent through random molecular motion, (c) coupling of spins to one (or two, for NMDR) r.f. fields, time-dependent in an oscillatory sense, and (d) spin-spin coupling of exchanging nuclei, modulated by an exchange frequency. The latter term derives from considering the coupling in time as a step function and using a Fourier synthesis of the step function to introduce the exchange frequency.

A brief examination of the response of the density matrix to such a Hamiltonian reproduces the usual results in slow and fast exchange limits. The novel feature which appears is a "nonlinear" response at frequency $\omega_1 \pm \omega_{\text{exch}}$, which, if experimentally detectable, would provide a very nice way of measuring exchange rates.

B. L. Shapiro
Page 2

In addition, the theory bends over backward to allow for a detailed view of the exchange mechanism, and may provide a method of probing reaction mechanisms in more detail.

There are available (from JMA) a small number of copies of Miss Lichtenstein's B. A. Honors thesis on this subject. We expect this summer to attempt some trial calculations based on the theory. Lack of instrumentation prevents our testing the results experimentally, but we invite test cases from the readers of IITNMR Newsletter.

Sincerely yours,

Rowena K. Lichtenstein

Rowena K. Lichtenstein

Jay Martin Anderson
Jay Martin Anderson

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DER
TECHNISCHEN HOCHSCHULE MÜNCHEN

8 MÜNCHEN 2, den 22.4.1965

Arcisstraße 21
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331

Herrn

Professor Dr. B. L. S h a p i r o

Department of Chemistry,

Illinois Institute of Technology,

C h i c a g o 16, Illinois
USA

NMR-Spektren von Zinn- und Bleialkylen

Sehr geehrter Herr Professor Shapiro !

In Äthyl-metall-verbindungen beobachtet man fast immer eine größere Kopplungskonstante für die Protonen der Methylgruppe mit dem Kernspin des Metalls ($M = \text{Sn}, \text{Pb}$ etc.) als für diejenigen der Methylen-Gruppe. Es gibt verschiedene theoretische Erklärungen dafür. Sie unterscheiden sich in der Vorhersage der Größe der J-Werte für länger-kettige Alkylreste. Wir wollten dies etwas näher untersuchen und haben die Spektren von acht Sn- bzw. Pb-alkylen aufgenommen und in der Tabelle zusammengestellt.

Die Spektren wurden mit einem Varian A-60 bei 33°C gemessen. $\text{Pb}(\text{CH}_3)_4$ und $\text{Pb}(\text{C}_2\text{H}_5)_4$ wurden in 20%-iger Lösung in CHCl_3 , die restlichen Substanzen als reine Substanzen aufgenommen. Sämtliche chemischen Verschiebungen sind bezogen auf internes TMS, positiv nach niedrigeren Feldstärken in Hz angegeben. Für die Signale der CH_2 -Gruppen entsprechen die Zentren der Signalgruppen den Werten der chemischen Verschiebungen.

Es wurde nun weder bei den n-Propyl- noch bei den n-Butyl-Stannanen und -Plumbanen eine Metall-Proton-Wechselwirkung mit den Protonen der endständigen Methylgruppen gefunden. Lediglich ^{13}C -Kopplung machte sich bemerkbar. Offensichtlich trifft also weder die Annahme abwechselnder Größe (bzw. Vorzeichen) der J-Werte, noch die ihres Auftretens in gewissen Gruppen von großen und kleinen Werten eindeutig zu. Wir wären auf diesem Gebiet erfahrenen Lesern der IITNMR-Newsletters für Kommentare oder Hinweise auf ähnliche Messungen dankbar.

Mit besten Grüßen

Ihr

Hans P. Fritz

(H.P. Fritz) und

Karl-E. Schwarzhans

(K.-E. Schwarzhans)

P.S. Wir sind von der Universität München an die Technische Hochschule umgezogen. Bitte, lassen Sie unsere Newsletters nach Möglichkeit an die obestehende Adresse schicken.

Verbindung	Chem. Versch. [Hz]			Kopplungsk. [Hz]		
	CH ₃ a. Metall	CH ₂ - Gruppen	CH ₃ endst.	CH ₃ a. Met.	CH ₂ - Grupp.	CH ₃ endstand.
Sn(CH ₃) ₄	117 4			51,5		
	119			54,0		
Sn(CH ₃) ₃ (C ₂ H ₅)	117 2	54	67	50,5		81,5
	119			52,5		84,5
Sn(CH ₃) ₃ (n-C ₃ H ₇)	117 3,5	93	57,5	50,0		
	119			52,5		
Sn(CH ₃) ₃ (n-C ₄ H ₉)	117 2,5	68	53	50,0		
	119			52,5		
Pb(CH ₃) ₄	44			62		
Pb(C ₂ H ₅) ₄	88	88			41	125
Pb(n-C ₃ H ₇) ₄		102	59,5			
Pb(n-C ₄ H ₉) ₄		88	55			

NMR EVIDENCE FOR $d_{\pi}-p_{\pi}$ BONDING IN SOME PHOSPHORUS COMPOUNDS

By G. S. Reddy and R. Schmutzler *

The P^{31} , F^{19} , and H^1 NMR spectra (Figures 1-3) of $(CH_3)_3C\overset{O}{\overset{||}{P}}F N(CH_3)_2$ showed the presence of two isomers. Elemental analysis as well as gas chromatography studies showed the sample to be pure. The ratio of isomer I to isomer II at room temperature is 3.1:1 as determined from all the three resonances. It is obvious that the two isomers are stereochemical. From the spectra it can be seen that in isomer I (peaks denoted by I) J_{P-NCH_3} is about 8 cps and J_{F-NCH_3} is about 2 cps, whereas in isomer II (peak denoted by II) these coupling constants are almost zero. On the other hand, the $-C(CH_3)_3$ group shows approximately the same couplings in both the isomers. When the sample was heated, the isomer ratios changed as follows:

<u>Temperature</u>	<u>Ratio I:II</u>
35°C	3.1:1
100°C	3.0:1
180°C	2.6:1
200°C	2.4:1
300°C	1.05:1

When the sample was heated to 300°C and cooled to room temperature, the ratio did not change from that at 300°C. These results and the molecular model of the compound clearly suggest that there is steric hindrance for the rotation of the $-N-(CH_3)_2$ group around the P-N bond because of the bulky tertiary butyl group. The complete absence of J_{P-NCH_3} in isomer II strongly suggests that the P-N bonding is different in these isomers. It seems logical to conclude that in isomer I there

* E. I. du Pont de Nemours and Company, Explosives Department, Gibbstown, N. J.

- 2 -

is a considerable amount of double bond due to $d_{\pi}-p_{\pi}$ overlap between phosphorus and nitrogen atoms and that this is broken when the $-N-(CH_3)_2$ group was forced to rotate by 60° by heating as evidenced by lack of P-NCH₃ coupling in isomer II. The fact that the molecule does not return to its initial configuration, which is energetically more stable due to the partial double bond, proves that the bulky tertiary butyl group hinders free rotation.

Rough calculations show that the energy of the barrier is high. These and other observations will be published shortly.

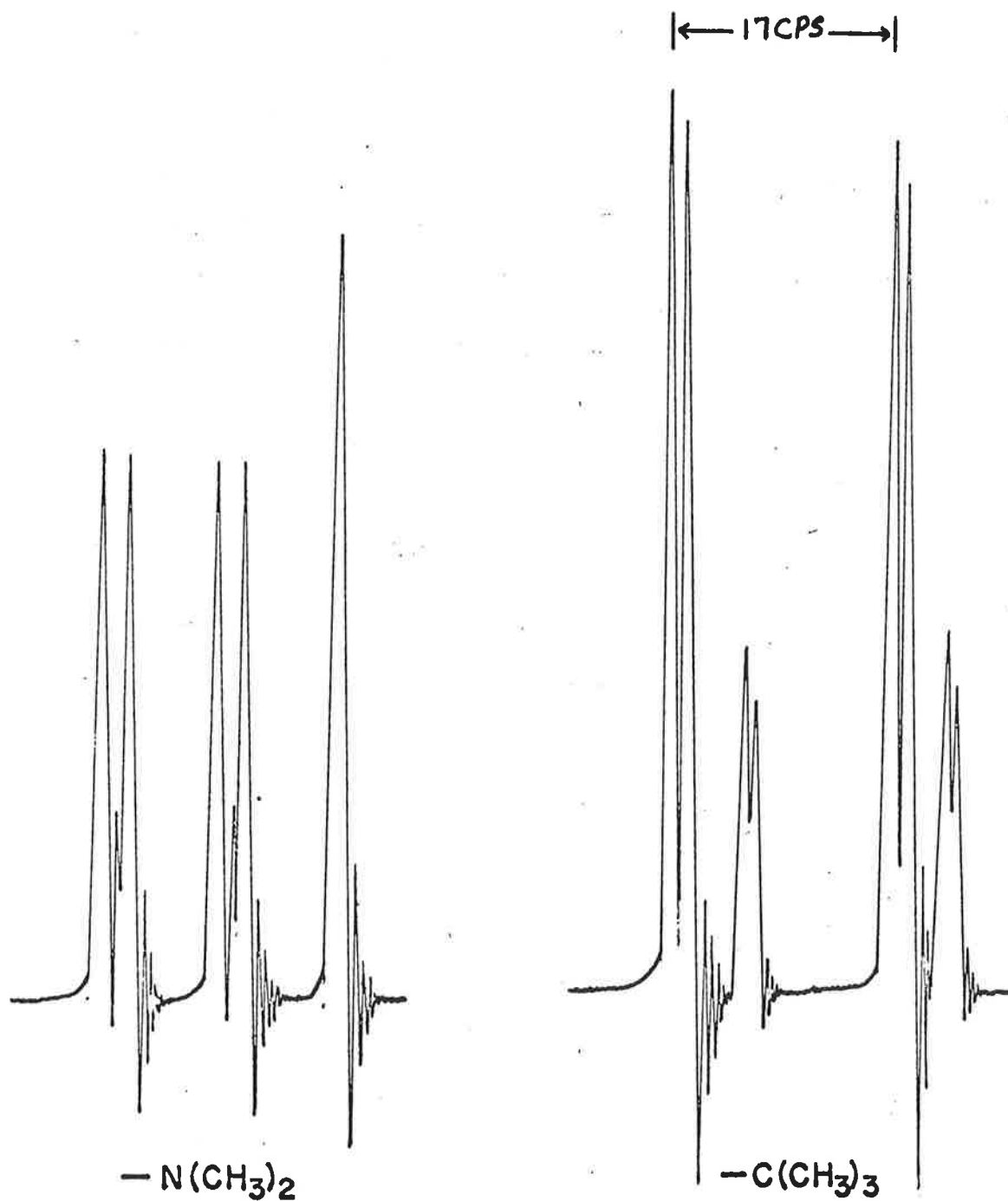


FIG. 1. ^1H SPECTRUM OF $(\text{CH}_3)_3\text{C}-\overset{\text{F}}{\underset{\text{N}(\text{CH}_3)_2}{\text{P}}}=\text{O}$

REF: TMS INTERNAL

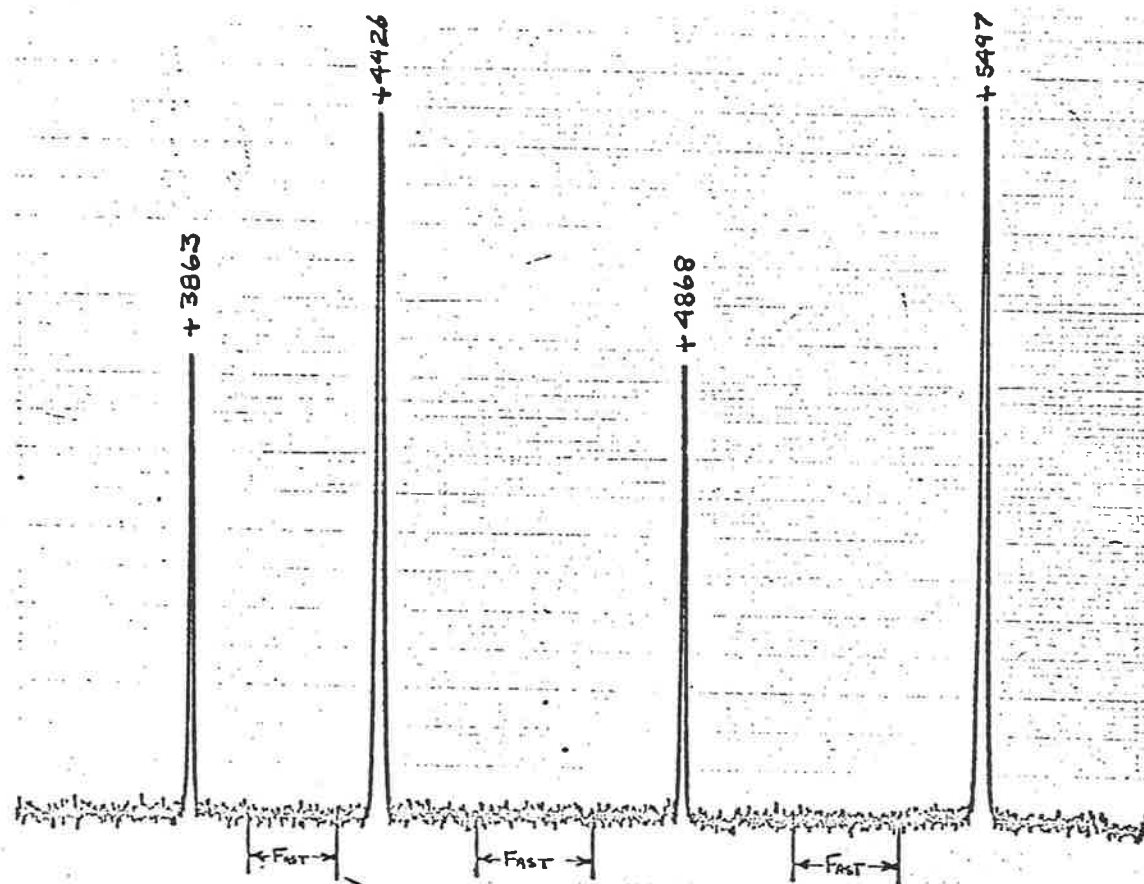


FIG. 2. F^{19} SPECTRUM OF $(CH_3)_3C-P(=O)(F)-N(CH_3)_2$ REF: $CFCl_3$ INTERNAL

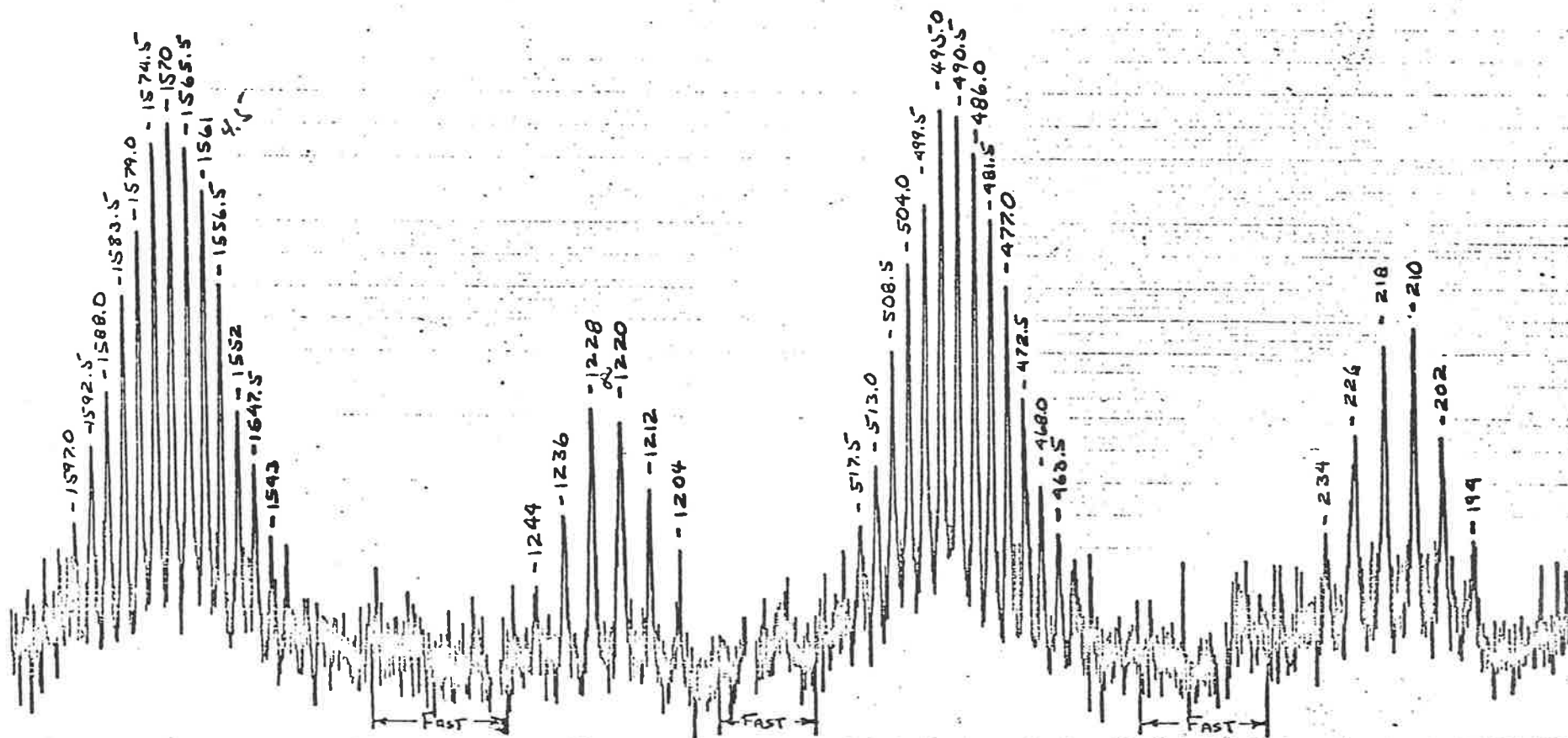


FIG. 3. P^{31} SPECTRUM OF $(CH_3)_3P(=O)F(NH_3)_2$

REF. : H_3PO_4 EXTERNAL



U. S. NAVAL RESEARCH LABORATORY
WASHINGTON 25, D. C. 20390

IN REPLY REFER TO

6110-76:WBM:vmg
29 April 1965

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

Dear Dr. Shapiro:

We hope the following contribution will entitle us to a subscription to IITNMRN.

Variable Autotransformer Replacement in the V2100B Power Supply

The variable autotransformer in our V2100B power supply developed pitted windings in about a year, despite the usual periodic adjustments of brush position. By reversing the polarity of the terminals, which placed the (new) brushes at the other end of the windings, we obtained several more months of use before new pits developed.

Finally, the autotransformer was bypassed, and the regulating range meter kept centered by adjustment of the 208 V input voltage with our external line voltage regulator (at 23 K gauss, a relatively small decrease suffices). While this worked satisfactorily for some time, it shortened the life of the 872A's significantly, probably because of the lowered filament voltage. The 304TL's did not appear to suffer appreciably.

We recently installed a 15 KVA variable autotransformer in place of the defective 9.8 KVA unit. The new transformer is a snug fit, but installation requires only the relocation of the condenser bank and the use of new spacers and mounting plates. We will be happy to supply all details to anyone (including Varian) contemplating this modification.

Sincerely,

A handwritten signature in dark ink, appearing to read "W. B. Moniz".

W. B. MONIZ
C. F. PORANSKI, Jr.
Physical Chemistry Branch
Chemistry Division

THE UNIVERSITY OF BIRMINGHAM

TELEPHONE: SELLY OAK 1301



Department of Chemistry,

BIRMINGHAM, 15.

27th. April 1965.

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

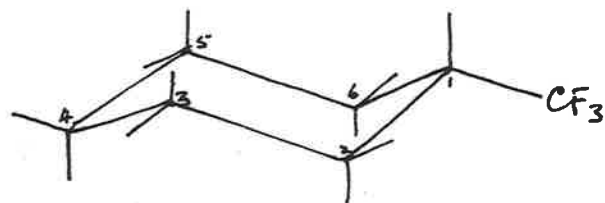
Dear Dr. Shapiro,

Perfluoro(methylcyclohexane) appears to have been a popular subject of study recently and it might be appropriate to add some observations by Mr. Peake and myself to those of Dr. Sutcliffe et al., IITNMRN 75, 6, and Dr. Reeves, 77, 36.

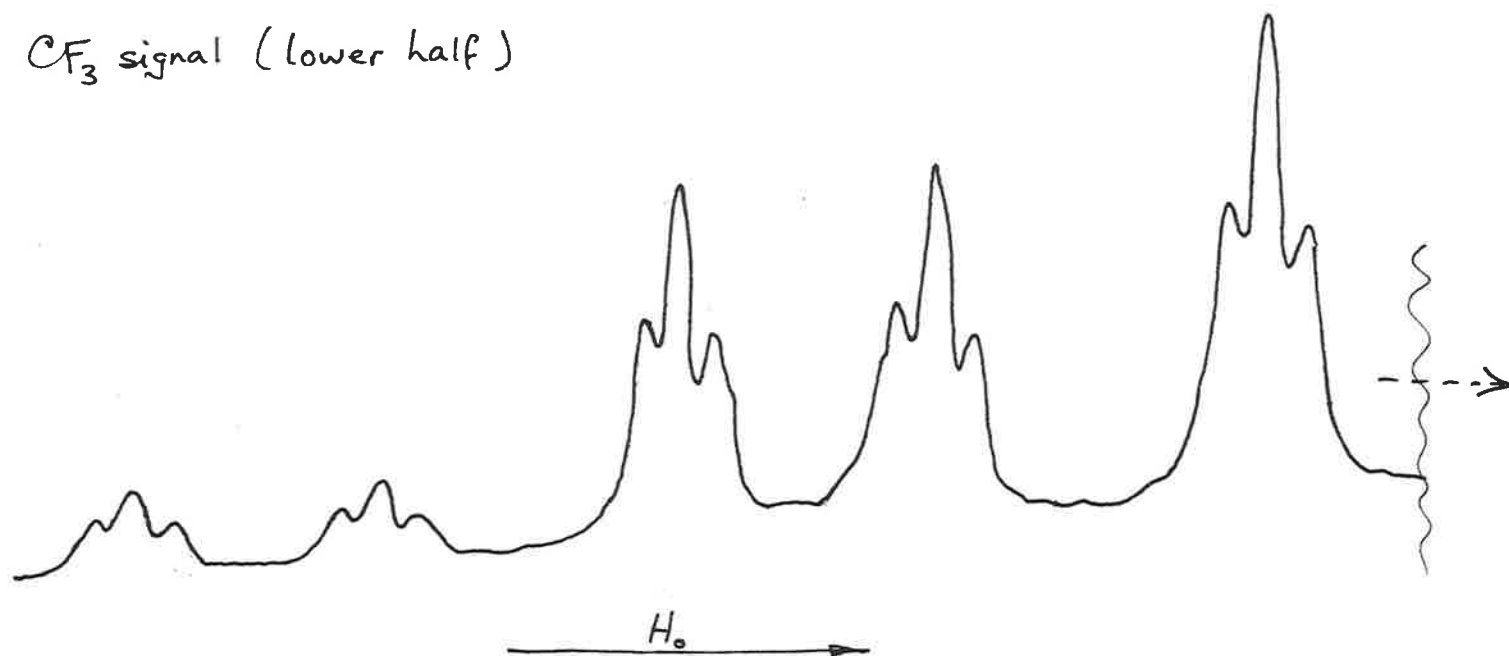
We looked at the spectrum of a concentrated solution in carbon tetrachloride at 94.1 Mc/s and found that the $-CF_3$ multiplet is a quintet (13.8 c/s) of doublets (6.3 c/s) of triplets (0.9³ c/s). Enclosed is a tracing of part of a typical run under slow sweep conditions. There is no resolution of outer weak lines to indicate the quintet suggested by Dr. Reeves and the relative intensities appear to be in the ratio 1:2:1 rather than 4:6:4. Since a molecular conformation with the CF_3 group axially disposed is sterically improbable, and in view of the consistency of chemical shift correlations with the alternative form (CF_3 equatorial) (Homer and Thomas, Trans. Faraday Soc., 59, 2431, 1963), ³ the triplet splitting probably arises from coupling through five bonds to one pair of equivalent nuclei in ring positions 3 and 5. Decoupling experiments indicate that the coupling is to the equatorial nuclei in these positions. It is interesting that the C-C-C-C-F configuration here is the planar zig-zag which is also favourable for long-range proton-proton coupling.

Yours sincerely,

L.F. Thomas



CF_3 signal (lower half)



FACULTÉ DES SCIENCES DE MARSEILLE - SAINT-JÉROME
 TRAVERSE DE LA BARASSE - MARSEILLE (13^e)
 TÉLÉPHONE: 64.31.61

DÉPARTEMENT DE CHIMIE ORGANIQUE

LABORATOIRE DE CHIMIE M. P. C.

J.C. MAIRE: MAITRE DE CONFÉRENCES.

Marseille, 23 th April 1965

Professor B.L. SHAPIRO
 Chemistry Departement
 Illinois Institute of Technology
CHICAGO (Illinois)

Dear Dr. SHAPIRO,

I suppose that you are waiting for my contribution.

In the course of some work on synthesis and chemical properties of dialkyl-dimethoxy stannanes we ran a routine spectrum of $\text{Et}_2\text{Sn}(\text{OMe})_2$. The spectroscopist observed only two peaks and suggested an error in the labelling of the sample. In fact the integrated spectrum shows that the ratio of the areas is correct 10 : 6. Careful examination of the spectrum lead to the conclusion that CH_2 protons and CH_3 protons are equivalent, but the degeneracy is removed by the difference in the coupling of CH_2 and CH_3 protons ^{with} Sn_{117} and Sn_{119} . The splitting differences

$$\pm 1/2 (J_{\text{CH}_3\text{Sn}_{117}} - J_{\text{CH}_2\text{Sn}_{117}}) \text{ and } \pm 1/2 (J_{\text{CH}_3\text{Sn}_{119}} - J_{\text{CH}_2\text{Sn}_{119}})$$

play the part of the absent chemical shift difference.

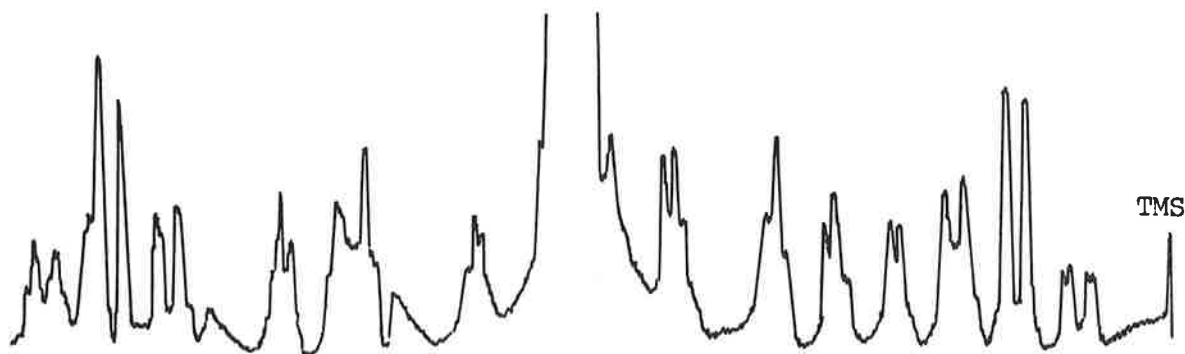
The existence of two tin isotopes with non zero magnetic moments give rise to a somewhat complicated spectrum, shown on the figure below. The methyl part of the spectrum is quite clear and it is possible to deduce from it :

$$J_{\text{Sn}_{117}-\text{CH}_3} = 58 \text{ cps} \quad J_{\text{Sn}_{119}-\text{CH}_3} = 61 \text{ cps} \quad J_{\text{CH}_3-\text{CH}_2} = 8 \text{ cps}$$

The ethyl part is more complicated, as a first approximation we can take :

$$\text{Sn}_{117}-\text{CH}_2 = 30 \text{ cps} \quad \text{Sn}_{119}-\text{CH}_2 = 32 \text{ cps}$$

.../...



VARIAN A 60. solvent: CCl_4 . I cm:10 c.p.s.

One should note that $J_{\text{Sn-CH}_3} > J_{\text{Sn-CH}_2}$ although CH_2 is directly bonded to tin.

Admitting the results of P.T. NARASHIMAN and M.T. ROGERS (J.Chem.Phys. 1955 31 1430) we must conclude that these two coupling constants are of opposite signs.

We are presently looking for the occurrence of similar spectra in other diethyltin compounds.

We are enjoying the IITnewsletter and trust this will pay our subscription on time.

Sincerely yours,

J.C.Maire

R.Karakachian

THE UNIVERSITY OF TEXAS
AUSTIN 78712

THE DEPARTMENT OF BOTANY

April 26, 1965

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

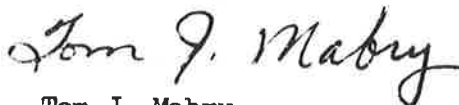
Dear Dr. Shapiro:

We would like to offer to IIT NMR Newsletter readers a collection of some 50 NMR spectra of flavonoids: "Nuclear Magnetic Resonance Analysis of Flavonoids," The University of Texas Publication No. 6418 (1964).

We have found the readily prepared carbon tetrachloride-soluble trimethylsilyl ethers satisfactory for the NMR analysis of all flavonoids thus far examined. Furthermore, the trimethylsilylation is a convenient procedure to obtain carbon tetrachloride-soluble derivatives of other highly hydroxylated natural products.

The collection of spectra of flavonoids is available on request.

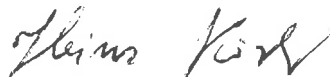
Sincerely yours,



Tom J. Mabry



Jacques Kagan



Heinz Rösler

UNIVERSITY OF COLORADO
BOULDER, COLORADO 80304

April 30, 1965

DEPARTMENT OF CHEMISTRY

Dr. Barry Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois

Dear Barry:

I will have an opening for a postdoctoral fellow in either ESR or NMR spectroscopy beginning September 15, 1965. Anyone interested in applying for this position should write to me directly. Background experience in either ESR or NMR as well as some knowledge of quantum mechanics is required. Will you please put this letter in the IITNMR Newsletter?

Sincerely yours,



Melvin W. Hanna
Associate Professor

MWH:gb



Department of Organic Chemistry,
SCHOOL OF CHEMISTRY,

THE UNIVERSITY,

BRISTOL 2.

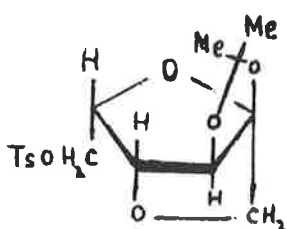
Professor B.L. Shapiro,
Illinois Institute of Technology,
Technology Center,
Chicago,
Illinois,
U. S. A.

4th May, 1965.

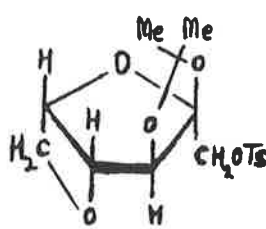
Dear Professor Shapiro,

Thank you for your reminder. We hope to be able to submit a note with a higher n.m.r. content in a few months time; in the meanwhile here is one to keep our subscription alive.

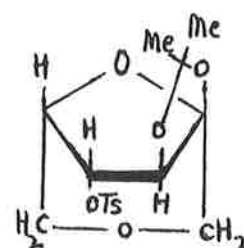
We have recently been looking at the chemistry of some sorbose derivatives, and prepared by several routes a compound which was claimed¹ to have structure (I). Structure (II) seemed more likely to us and (III) was just about possible too.



(I)



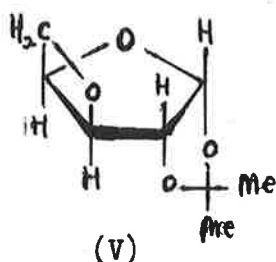
(II)



(III)

The deoxyanalogue of the compound ($-\text{CH}_2\text{OT} \longrightarrow \text{O}-\text{CH}_3$) has a sharp methyl singlet at $\tau = 8.14$ (width at $\frac{1}{2}$ height ≈ 0.8 cps.), as well as the isopropylidene methyl peaks, clearly favouring structure (II). We also have strong chemical evidence for this structure. Furthermore the pattern of ring coupling constants observed is very similar to those we have found for the xylose compound (V) of known structure. The similarity to structure (II) is obvious.

continued.....



Two of us (C.C., L.H.) have a paper in the press (Carbohydrate Research, first issue (1965)) on the conformation of some di-O-isopropylidene arabinose and galactose compounds, previously thought to have a chair conformation, but shown by p.m.r. to have a flexible conformation. As this should appear in the not too distant future we won't enlarge here.

Many thanks for your hard work in keeping the Newsletter going.

Yours sincerely,

C. Cone

C. Cone

L. Hough

L. Hough

B.A. Otter

B.A. Otter

1. Tokuyama, Kiyokawa & Hōki, Bull.Chem.Soc., Japan, 36,1392 (1963).



Imperial Chemical Industries Limited

DYESTUFFS DIVISION

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

BY AIRMAIL

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

Your Ref:

Our Ref: FL/PPT-5.
Research Department.

4th May 1965.

Dear Dr. Shapiro,

C¹³ CHEMICAL SHIFTS FOR THE DIAZINES AND THEIR CATIONS

In the first three issues of the N.M.R. Newsletter for 1965, Lauterbur, Grant and Pugmire communicated C¹³ chemical shift data for various nitrogen heterocyclics obtained by direct observation. In some joint experiments between Sheffield University (V.M.S. Gil and J.R. Turrell) and I.C.I. Ltd. (P. Hampson and A. Mathias) the diazines have also been examined by the indirect method, i.e. spin decoupling the C¹³ satellites in the proton spectrum using our modified HA.100 spectrometer. The indirect method gives the most accurate determination of C¹³ chemical shifts (± 0.02 p.p.m. for details see Allen, Beconsall and Turner, J. Sci. Instr. 41, 673, 1964) but is obviously limited to cases where C¹³ satellites are observable.

The C¹³ chemical shifts we have obtained by the double resonance method for the diazines and their cations (using solutions in trifluoroacetic acid) are as follows. All shifts are given in p.p.m. relative to benzene.

(1) Pyrazine (sat. soln. H ₂ O)	Pyrazine (in T.F.A.)
C _{2,3,5,6} = -16.77	C _{2,3,5,6} = -14.72
(2) Pyridazine (neat)	Pyridazine (in T.F.A.)
C _{3,6} = -24.07	C _{3,6} = -22.57
C _{4,5} = + 1.29	C _{4,5} not measurable
(3) Pyrimidine (neat)	Pyrimidine (in T.F.A.)
C ₂ = -31.34	C ₂ = -23.57
C _{4,6} = -28.91	C _{4,6} = -29.21
C ₅ not measurable	C ₅ not measurable

For the diazines themselves there is good agreement between our results above and those of Lauterbur (N.M.R. Newsletter 76, 30, 1965). As this author has shown good agreement between experimental and calculated C¹³ chemical shifts is obtained if the quantity $\langle r^{-3} \rangle_{2p}$ in the Karplus-Pople Theory is made dependent not only on the π -electron density but on the polarity of the CN σ -bonds as well.

Since protonation of the azines leads to increased positive charge at the C atoms, low field shifts would be expected. However, Grant and Pugmire (N.M.R. Newsletter 78, 30, 1965) found that the α -C¹³ in pyridinium

Continued...

- 2 -

ion (PyH^+) are more shielded by 8.5 p.p.m. than in pyridine (Py). Our results also show this interesting behaviour for the diazines. In fact, the C^{13} shifts of the diazines on protonation can be calculated to within ± 1.3 p.p.m. by taking the average of the corresponding shifts for Py. For example, the shift for pyrazine on protonation, +2.1 p.p.m., is to be compared to the average of the α - and β - C^{13} shifts of Py on protonation, i.e. $\frac{1}{2}(8.5-4.2) = +2.15$ p.p.m. Grant and Pugmire suggest that the high-field shifts in PyH^+ point to the importance of σ -bond effects. However, since the decrease in the total electron density at the α -C atoms is much more important in the Karplus-Pople Theory than any other effect due to the polarity of the σ -bonds, a normal low-field shift should occur.

Here we propose two possible reasons for the observed high-field shifts:

(a) Calculations (Aust. J. Chem. 12, 554 (1959); Z. Physik. Chemie 19, 231 (1959)) show that the free valence index of the α -C in PyH^+ is ca. 0.1 larger than in Py. (The N-C π -bond order in PyH^+ is appreciably smaller than in Py). This change corresponds in the Karplus-Pople equation to a shielding effect of ca. 6 p.p.m.

(b) It is interesting that the α - C^{13} and the N^{14} shifts observed on protonating Py have the same direction. The N^{14} screening constant is known to increase by +120 p.p.m. on protonation, although the total electron density at the N atom decreases. This is mainly due to the low-lying $n \rightarrow \pi^*$ state of Py (absent in PyH^+) which is responsible for a larger paramagnetic term in the case of Py. It is conceivable that due to delocalisation of the σ orbitals, the $n \rightarrow \pi^*$ transition is not entirely localised on the N atom; therefore a smaller value for the mean excitation energy for C^{13} nuclei adjacent to N atoms in the azines might be more appropriate, hence contributing to the large low-field shifts of these nuclei. The absence of the $n \rightarrow \pi^*$ state in the protonated species would therefore partially account for the observed high-field shifts.

Yours sincerely,

V.M.S. Gil.

A. Mathias.

V.M.S. Gil.

A. Mathias.

VMSG/AM/MW.

Dr. W. Brügel i.Fa.
Badische Anilin- & Soda-Fabrik AG · Ludwigshafen am Rhein
 Hauptlaboratorium



Luftpost

Dr. B.L. Shapiro
 Department of Chemistry
 Illinois Institute of
 Technology

Chicago, Illinois 60616

U S A

Ihre Zeichen	Ihre Nachricht vom	Unsere Zeichen	Fernsprecher-Durchwahl	Telex	67 Ludwigshafen
		Dr. Brügel/Fa	(06 21) 600 ...	464 ...	30. April 1965

Betreff Solvent dependence of coupling constants

Dear Dr. Shapiro,

There are many publications dealing with the influence of solvents upon the chemical shift, but there are only a few papers about the influence of solvents on the coupling constants. I only know your own work, that of WATTS et al. (J.Mol.Spectr. 22, 525, 1955) and quite recently that of BATES et al. (J.Chem.Phys. 40, 2415, 1954). I believe solvent effects on coupling constants will be an important field for our work in the future. At this moment I like to inform you about some measurements concerning the variation of the vinyl coupling constants of acrylates in different solvents. The problem is a little more complicated than the already discussed ones because there are three spins coupled together and the coupling constants can not be gathered immediately from the spectrum. Vinyl acrylate seems to be a good example bearing two vinyl groups of different kind. The NMR parameters were computed by our own ABC program and by Dr. Swalen's MIMIT, too (its help for this and other work is gratefully acknowledged). You find the figures at the separate leaf. I don't claim a special accuracy of these measurements, because only one to three spectra are used to get the figures. A deviation of about $\pm 0,15$ cps or so should be a realistic value. Then you see the marked variation of the coupling parameters of the acryl group while those of the vinyl group are really constant. Obviously the acryl group is more polarizable but I do not have any precise idea

- 2 -

how the coupling parameters depend on the properties of the solvent. I think more measurements are needed to obtain real and proper connections. But perhaps these figures will be interesting for other NMR spectroscopists working at a similar field. There are some other curious features in the spectra of the acrylates, e.g. the variation of the geminal coupling constant of the acryl group in a given solvent (CDCl_3) with the length of the alcohol component showing a maximum for ethyl or propyl.

Thank you very much for your kindness during the 5. ENC in Pittsburgh. I enjoyed my attendance of this meeting hearing the problems of the american colleagues.

Sincerely yours,



(Dr. W. Brügel)

	acryl group			vinyl group		
solvent	J _{ab}	J _{ac}	J _{bc}	J _{ab}	J _{ac}	J _{bc}
none	2,27	10,21	16,72	1,48	6,35	13,97
CCl ₄	2,45	10,37	16,58	1,43	6,35	13,87
dioxane	2,49	10,23	16,56	1,48	6,32	13,95
dimethylsulfoxide	1,31	10,80	17,09	1,60	6,30	13,90
cyclo hexane	1,57	10,77	17,35	1,41	6,35	14,05
benzene	1,28	10,54	17,51	1,53	6,37	14,04
dimethylformamide	1,57	10,56	17,21	1,63	6,37	14,04
acetonitrile	1,78	10,73	17,03	1,63	6,37	13,95
acetone	1,35	10,60	17,40	1,63	6,27	13,85
pyridine-d ₅	1,34	10,65	17,16	1,63	6,37	13,95

STATE UNIVERSITY OF NEW YORK AT BUFFALO

Formerly The University of Buffalo, Founded 1846

Department of Chemistry

College of Arts and Sciences

Acheson Hall

Chemistry Road

Buffalo, New York 14214

Telephone 831 - 3014

Area Code 716

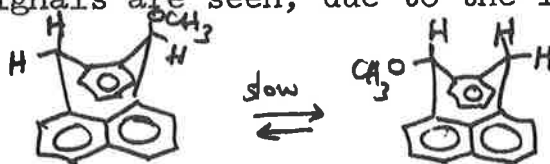
May 5, 1965

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

Dear Dr. Shapiro:

Origin of Magnetic Non-Equivalence of
Diastereomeric Methylene Protons in 7,12-Dihydropleiadenes

In the low temperature spectra of 7-substituted-7,12-dihydropleiadenes, e.g. 7-methoxy (below), two methoxy and two methine signals are seen, due to the individual conformers



but the $-CH_2-$ signal is a single quartet, due to the coincidence of the two expected AB spectra. Thus, the neighboring asymmetric carbon has little effect on the chemical shifts and δ_{AB} must result mainly from the different magnetic environments of axial and equatorial protons. One predicts therefore that during fast exchange, when the conformer populations approach 1:1 as temperature approaches ∞ , that δ_{AB} should approach zero if intrinsic asymmetry doesn't contribute substantially to the magnetic non-equivalence. The enclosed graph of δ_{AB} for the $-CH_2-$ group in 7-methyl-7,12-dihydropleiadene versus temperature (up to 200°) in two solvents shows that the large chemical shift at lower temperature is due mainly to differences in conformer populations rather than intrinsic asymmetry. In 7-methoxy-7,12-dihydropleiadene, $K = \frac{[\text{axial OCH}_3]}{[\text{eq. OCH}_3]} \simeq 2$ at -20° and δ_{AB}

is ca. 110 c.p.s. The compound is not sufficiently stable for a high temperature study as with 7-methyl, but we hope to see if δ_{AB} does decrease as much here when the conformer populations approach 1:1, in which case each proton spends similar times in the two different environments.

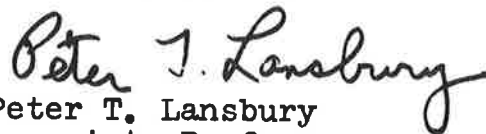
Professor B. L. Shapiro

-2-

May 5, 1965

It turns out that the low field doublet of the AB spectrum is due to the axial protons whereas we had thought that the equatorial protons, lying in the plane of the aromatic rings, would be more deshielded. We welcome any comments on this phenomenon.

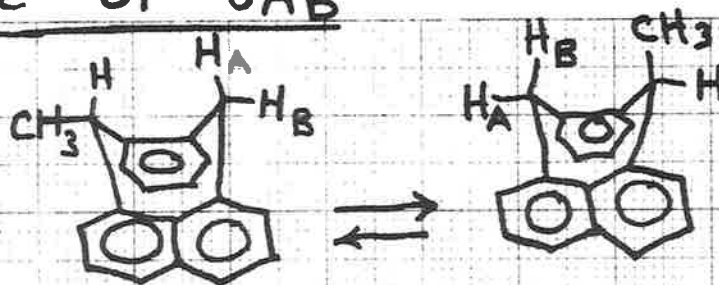
Sincerely yours,



Peter T. Lansbury
Associate Professor

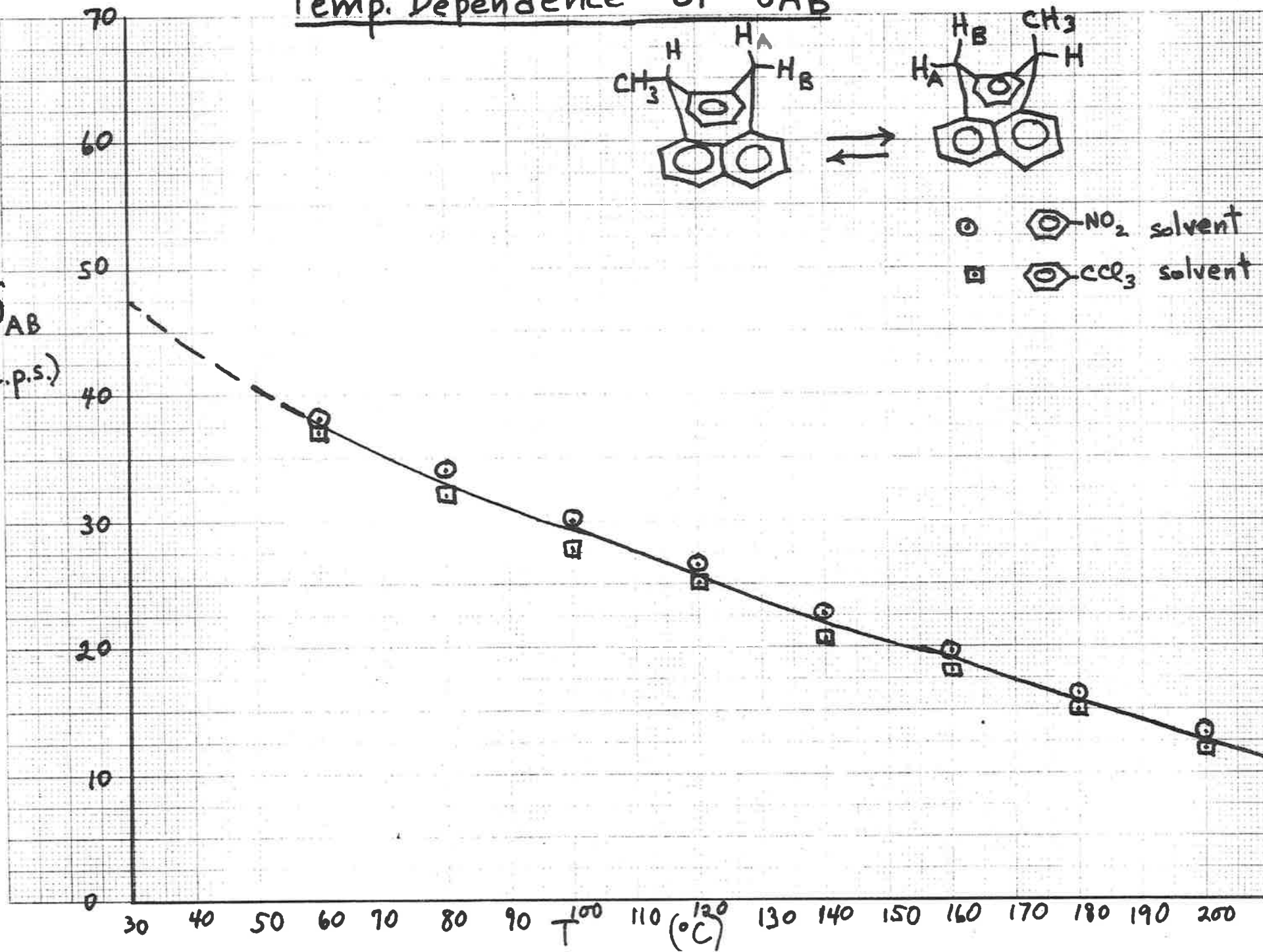
PTL:ck

Temp. Dependence of δ_{AB}



○ c1ccccc1[N+](=O)[O-] solvent
 □ c1ccccc1C(=O)Cl solvent

δ_{AB}
(c.p.s.)





DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
FOOD AND DRUG ADMINISTRATION
WASHINGTON, D.C. 20204

May 5, 1965

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

Dear Barry:

For about two years we have been attaching sample tubes to a vacuum line for degassing, as shown on the enclosed drawing. This gadget is an alternative to that described by Professor J. M. Anderson (cf. ITTNRN 71.43). Although ours looks somewhat complicated, the sealing-off procedure may be less risky.

The following remarks complement the drawing.

1. The T-303.1 and T 304.1 ferrules last only for about ten degassing operations.
2. The hole in the size 300 Swagelok nut must be slightly enlarged for insertion of 5 mm sample tubes.
3. This nut has to be tightened carefully with a wrench, as finger tightening gives a poor seal.
4. The top of the sample tube must be flush with the top end of the front ferrule T 303.1.
5. The vacuum we use is generated only by a forepump. Fifteen microns are attained routinely.

We hope this information may be useful to ITTNRN readers.

Best regards.

Sincerely,

A handwritten signature in cursive script, appearing to read "Ernest".

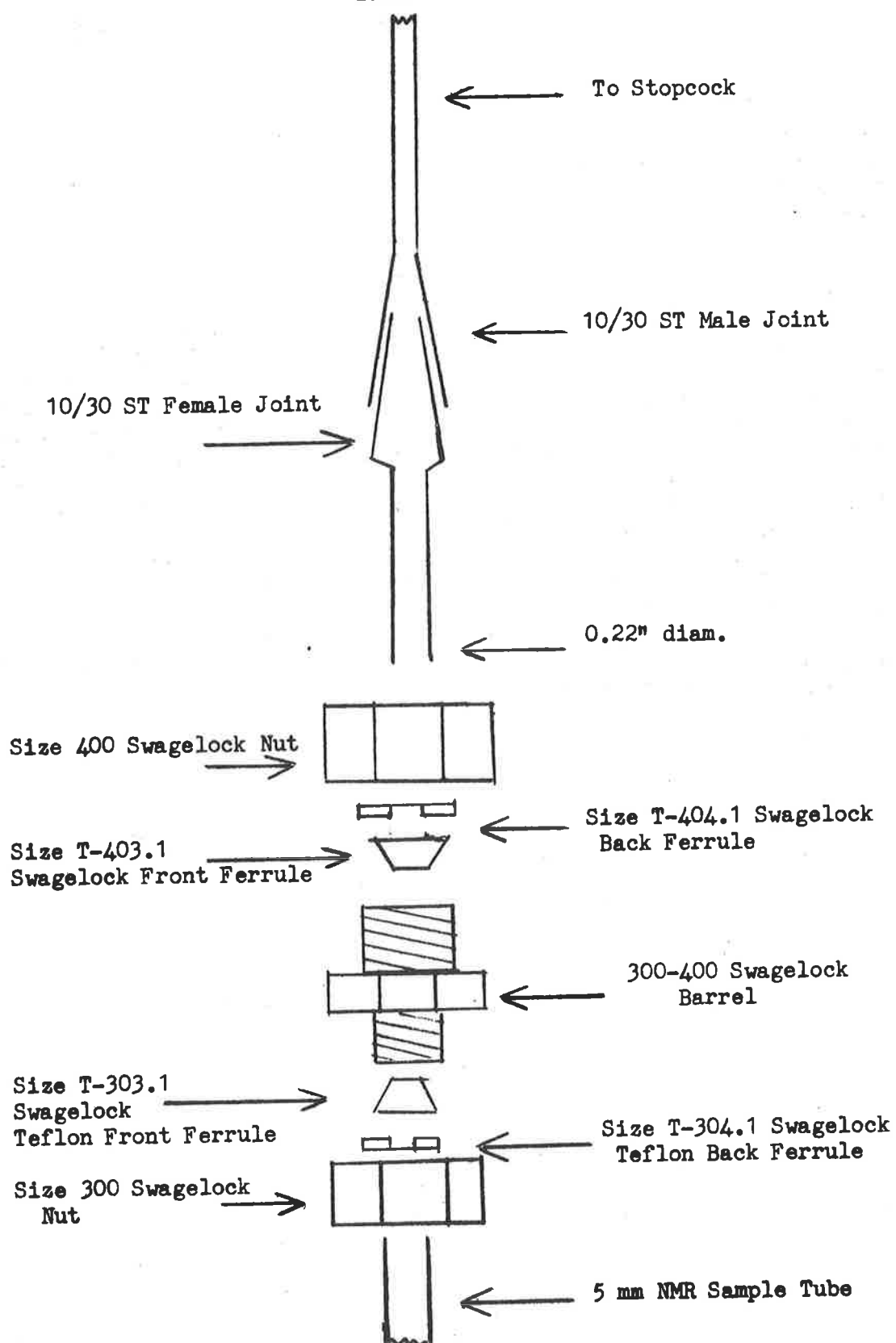
Ernest Lustig
Division of Food Chemistry

A handwritten signature in cursive script, appearing to read "Edward P. Ragelis".

Edward P. Ragelis
Division of Food Chemistry

Enclosure.

Swagelock-to-Glass System for Securing
5 mm Sample Tubes to Vacuum
Line



BELL TELEPHONE LABORATORIES

INCORPORATED

MURRAY HILL, NEW JERSEY 07971

TELEPHONE

AREA CODE 201

582-3000

May 6, 1965

PROFESSOR B. L. SHAPIRO
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

I am enclosing a preprint of our latest contribution to the study of relaxation in polymers by means of N.M.R. techniques. Briefly the results may be described as follows: Nuclear magnetic relaxation in "the rotating frame" has been applied to study of low frequency molecular motions in a linear polyethylene. Measurements were made in the α -transition region. The experiments can be interpreted by means of the theories of Slichter and Ailion, and Look and Lowe. The derived correlation frequencies agree well with corresponding dielectric results. It seems clear that the processes under study occur in the crystalline regions of the polymer. Molecular rotation about the chain axis, perhaps by a dislocation mechanism, is proposed as a model capable of accounting for the various relaxation experiments.

Preprints are available from me upon request.

Sincerely yours,

David W. McCall

David W. McCall

MH-1123-DWM-MC

The Standard Oil Company

(An Ohio Corporation)

Research Department

4440 Warrensville Center Road

Cleveland 28, Ohio

E. C. HUGHES
VICE PRESIDENT

May 10, 1965

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

Methoxy and α -Methyl
Proton Resonance in Styrene
Methyl Methacrylate
Copolymers

Dear Barry:

In extension of previous work done in sequence distribution in polystyrene-methyl methacrylate via NMR¹ in conjunction with Professor H. James Harwood of Akron University, we have correlated the methoxy resonance positions observed in aromatic solvents with calculated methyl methacrylate centered pentad distributions. The complete paper should appear shortly in Polymer Letters. By examining the spectrum of copolymers containing more than 60% methyl methacrylate, the methoxy resonance of six of the ten possible pentads could be assigned to specific resonance areas. The highest field methoxy resonance areas (2.6 p.p.m.), for example, agree remarkably well with the proportion of methoxy protons calculated to be centered in MSMSM type pentads. The spectra of high styrene copolymers could be correlated with pentad distributions, however, only when the resonance of methoxy protons centered in SSMSS and SSMSM pentads was considered distributed among all three methoxy resonance areas (possibly due to tacticity effects).

In addition to the methoxy correlation, the resonance of the α -methyl protons was found to be interpretable in terms of triad distributions. A complete discussion of results will be found in the paper to issue.

Other systems now being studied to confirm our method include acrylonitrile-styrene, methacrylonitrile-ethyl acrylate, and styrene-fumaronitrile copolymers.

¹H. J. Harwood and W. M. Ritchey, J. Poly. Sci., **2B**, 601 (1964).

Very truly yours,

Bill

W. M. Ritchey

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

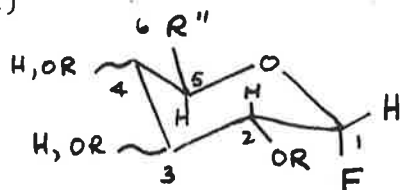
DEPARTMENT OF CHEMISTRY

May 8, 1965

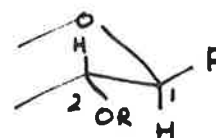
Professor B.L. Shapiro
 Department of Chemistry
 Illinois Institute of Technology
 Technology Centre
 Chicago, ILLINOIS 60616

Dear Barry:

In the last year we have looked at the ^{19}F and ^1H N.M.R. spectra of about 40 specifically fluorinated sugars but in this letter I want to confine comments to 16 glycopyranosyl fluorides having the general formula (I)

(Ia) α -isomers

$\text{R}'' = \text{H or CH}_2\text{OR}$
 $\text{R} = \text{CO.CH}_3$
 or CO.Ph

(Ib) β -isomer

The ^{19}F chemical shifts ($\text{CF}_3\text{CO}_2\text{H}$ in capillary) fall into two distinct ranges

axial ^{19}F (8 α -isomers) + 68.6 to + 72.4 ppm
 equatorial ^{19}F (8 β -isomers) + 52.4 to + 63.3 ppm.

Thus for this class of compounds the ^{19}F chemical shifts are indicative of the fluorine orientation. Moreover, the equatorial fluorine resonance comes to low field of the axial resonance which is analogous to the situation commonly found for protons and supports the many previous suggestions that this might be so.

These compounds also provide data concerning vicinal $^{19}\text{F} - ^1\text{H}$ coupling constants, since for the α -series $J(\text{F}_1 \text{ axial: } \text{H}_2 \text{ axial}) = 23.5 - 25.4$ cps whilst for the β -series $J(\text{F}_1 \text{ equatorial: } \text{H}_2 \text{ axial}) = 4.9$ to 11.7 cps. Thus the stereospecificity of these couplings seems to parallel that of vicinal $^1\text{H} - ^1\text{H}$ couplings, which is once again in agreement with earlier suggestions.

Professor B.L. Shapiro

-2-

May 8, 1965

I shall write a further letter to you about our other fluorinated compounds which demonstrate similar dependences of both coupling constants and chemical shifts - together with a few interesting exceptions.

With best wishes,

Yours sincerely

Lannie Hall *John F. Manville*

LDH/lm

L. D. HALL

J. F. MANVILLE

PHYSIKALISCHES INSTITUT

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

LEIPZIG C1, LINNÉSTR. 5 • TEL. 651 50, 653 42, 653 56

am 5.5.65 Az.: Fri/Hee.

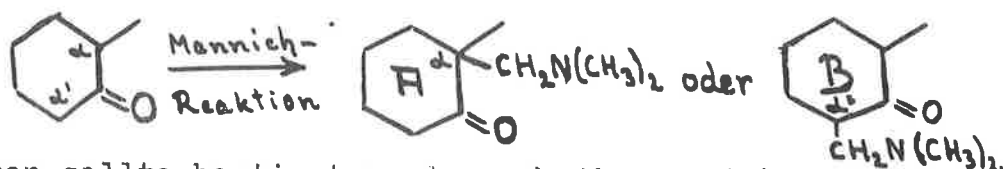
USA

Bestimmung der Mannichprodukte von α -Methyl-cycloketonen

Sehr geehrter Herr Professor Shapiro!

Im Chemischen Institut der Karl-Marx-Universität Leipzig wurden von einer Reihe von α -Methyl-cycloketonen die $-\text{CH}_2\text{N}(\text{CH}_3)_2$ -Mannichbasen hergestellt:

zum Beispiel



Aus den NMR-Spektren sollte bestimmt werden, ob die Mannich-Reaktion am α -C (A) oder am β -C (B) ansetzt - oder ob ein Gemisch beider Reaktionsprodukte vorliegt. /1/

Bei der α -Mannichbase (B) liefern die Protonen der CH_3 -Gruppe infolge ihrer Kopplung mit dem tertiären H am α -C ein Dublett (etwa 7 Hz Aufspaltung) - bei der β -Mannichbase (A) dagegen erscheint die CH_3 -Protonen-Resonanzlinie als Singulett. Liegt ein Gemisch zwischen den Reaktionsprodukten A und B vor, so muß die Überlagerung eines Dubletts mit einem Singulett erscheinen, aus der man auch das Verhältnis beider Reaktionsprodukte bestimmen kann.

Die nebenstehende Tafel enthält einige der erhaltenen Ergebnisse. Die Spektren wurden mit einem Japanischen 60-MHz-Spektrometer (JEOL) bei der DAW, Berlin aufgenommen.

Es drängt sich die Frage auf: Worin liegen die Ursachen für das verschiedene Reaktionsverhalten der einzelnen Methyl-cycloketone?


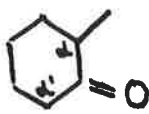


Einige Autoren (siehe /1/) erklären es aus der Enoliesierung der Methyl-cycloketone. Wir wollen versuchen, die Veränderung der Elektronendichte an den α -C und β -C in den Vorstufen zur Mannich-

- 2 -

Reaktion bei den verschiedenen Methyl-cycloketonen zu bestimmen. In welcher Weise verlagert sich die Doppelbindung bei der Enolisierung und wodurch ist dieses Verhalten bedingt?

/1/ House, Trost

J. org. Chem. 29 (1964) 1339

	τ CH_3			%	
	α -Mannichbase	α' -Mannichbase	α -methyl-cycloketon	α -Mannichbase	α' -Mannichbase
	9,15	9,12	8,97	91 \pm 2	9 \mp 2
	8,98	9,07	9,07	80 \pm 6	20 \mp 6
	9,04	9,00	9,01	62 \pm 5	38 \mp 5
	9,10	9,02	9,03	26 \pm 6	74 \mp 6

H. Frischleder

(Horst Frischleder)



QUEEN MARY COLLEGE

(UNIVERSITY OF LONDON)

MILE END ROAD · E.1

TELEPHONE · ADVANCE 4811

6th May, 1965.

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

Position Available. Contact and N¹⁵ Shifts.

Dear Barry,

For the benefit of any itinerant American, wandering Britisher, or any other suitable qualified spectroscopist with a taste for double resonance and missionary work in the East End of London, I announce a vacancy for a post doctoral fellow.

On behalf of Derek Shaw, I should like to claim the world record for the largest chemical shift between inequivalent methylene protons, viz: - 4.97ppm subject to ratification and further H-(H) double resonance! The case in question is the meridial form of the compound (PEt₂Ph)₃ReCl₃. The large shifts are produced by a contact shift mechanism as in (PMe₂Ph)₃ReCl₃ (1). An even larger inequivalence amounting to 11.2 ppm in (PEt₂Ph)₃ReCl₄ is a possibility.

Other interesting features of these spectra are:

(i) the sharp lines produced (<2 c/s wide) (ii) the absence of P³¹-H¹ coupling and hence of the 'virtual' coupling involving the trans oriented phosphine groups, which might otherwise have been (and was initially) expected. We have noted this "decoupling" in other cases also, (iii) the unpaired spin densities both in the aryl and alkyl substituents.

Duncan Gillies, now at N.R.C. Ottawa, finished his thesis in style with some H-(N¹⁵) 'tickling' on formamide N¹⁵ which gave the line position in the N¹⁵ region to within a fraction of a cycle. We believe the accuracy of the determination of the nitrogen shift by this method to be better than in the single resonance experiment either for N¹⁴ or N¹⁵. Of course we require a favourable case, viz:- a compound showing H-N¹⁵ coupling.

Yours sincerely,

Ed Randall

Edward W. Randall.

(1) Chemical Communications, 1965, 82.

UNIVERSITY OF CALIFORNIA

LAWRENCE RADIATION LABORATORY
BERKELEY 4, CALIFORNIA

Inorganic Materials Research Division
Latimer Hall

May 3, 1965

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

Dear Barry:

Here are our latest doings. Thanks again for IITNMRN. They're great!

In order to determine thermodynamic data by nuclear magnetic resonance it is highly desirable to measure the temperature of the sample to within a few tenths of a centigrade degree. A technique for this has been developed which gives consistent results to within $\pm 0.2^\circ\text{C}$.

A capillary filled with a mixture of water, methanol, and hydrochloric acid exhibits two sharp resonance signals. The chemical shift between these two signals is strongly, and approximately linearly dependent upon the temperature of the sample. It can therefore be used as an excellent indication of the sample temperature. In order to calibrate this chemical shift as a function of temperature a capillary, one millimeter in diameter, was fastened to the inside of an NMR tube filled with toluene. In addition, a previously calibrated thermocouple in a second capillary was placed in the NMR tube. The capillary containing the thermocouple was supported at the top by a stationary arm, and hence did not rotate with the sample tube.

Large vertical temperature gradients inside the NMR tube often exist when the sample is being heated or cooled. In an A-60 variable temperature probe operating at 60°C this may be as much as 0.1°C per millimeter. Therefore it was of the utmost importance that the sample temperature be measured at the center of the receiver coil. This position was determined to within ± 0.25 millimeters by integrating spectra of a spherical water sample at various positions in the probe.

The chemical shifts between the two resonance signals in the mixture were determined by the standard sideband technique. As stated above, an approximate linear relationship was found to exist between the chemical shift and the temperature. For a mixture of 51.8% water, 48.1% methanol, and 0.1% hydrochloric acid by weight the observed approximate relationship is:

$$T = 160.00 - 90.50x S$$

(1)

Professor Bernard L. Shapiro

-2-

May 3, 1965

where T is given in degrees Centigrade, and S is given in ppm. In Fig. 1 the deviation between the observed temperature and the temperature calculated using equation 1 is plotted as a function of the observed chemical shift. The figure covers the range between -40°C and 80°C . As can be seen the scatter of points is less than $\pm 0.2^{\circ}\text{C}$.

Since the temperature dependence of the chemical shift is a sensitive function of the concentration of the sample, care must be taken during the sealing of the capillary to avoid alteration of the concentration. The reproducibility of the results from several capillaries made from a single solution was checked by measuring the NMR signal from two capillaries enclosed in one sample tube. Line widths from such a sample were less than 0.3 cps which is similar to the line width of a single capillary, thus indicating that the sample concentrations were not substantially altered.

An accuracy limit is imposed on the calibration of the capillary solution by the broadening of the spectral lines caused by the introduction of the thermocouple in the region of the receiver coil. When a temperature calibrated capillary is in turn used for consequent temperature measurements the precision is increased to $\pm 0.1^{\circ}\text{C}$ because of the improved line resolution. The method allows one to measure the sample temperature at that region in the sample which is being investigated by the NMR technique. It is also independent of the bulk susceptibility of the sample, of the spinning rate, and of the flow rate of the nitrogen used to control the sample temperature.

The above mentioned mixture gives satisfactory results over the range -25°C to 90°C . Below -25°C the lines become too broad for accurate shift measurements. However, mixtures could surely be found applicable to other temperature regions.

We are indebted to Dr. Otto Redlich for his interest in this problem. This research was supported by the U.S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory.

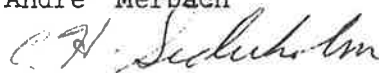
Sincerely,



Richard Duerst



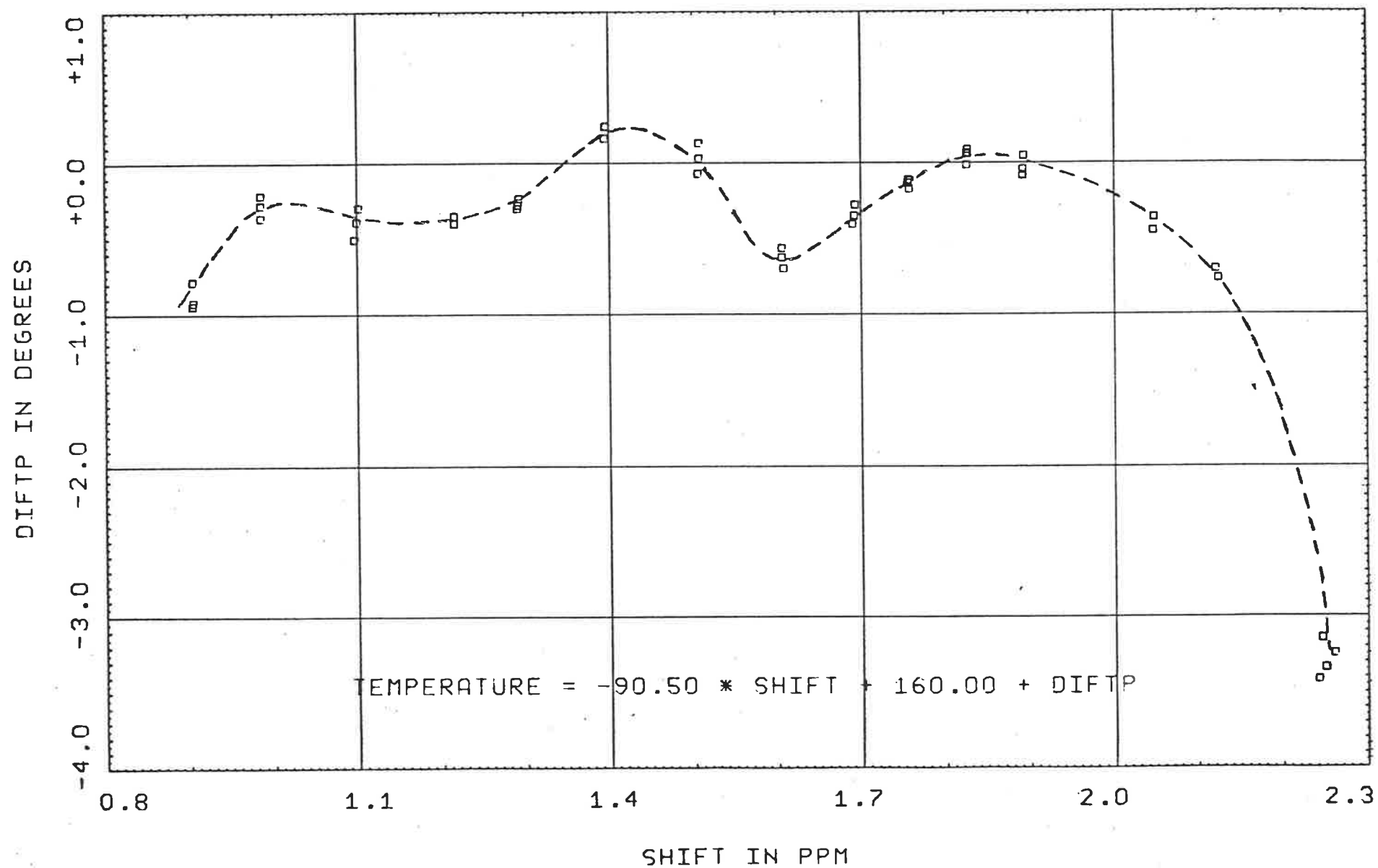
Andre Merbach



C. H. Sederholm

RD:AM:CS/gb

DETERMINATION OF THE TEMPERATURE BY NMR





Eidg. Technische Hochschule
Laboratorium für Organische Chemie
Zürich

8006 Zürich,
Universitätstr. 6
Tel. 051 / 927330

May 11, 1965

Dr. Doris Meuche

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

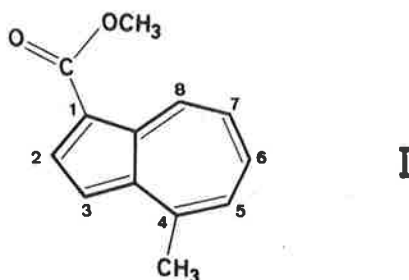
Structure determination by nmr of two azulenes isolated from the liver-moss, Calypogeia trichomanis.

Dear Professor Shapiro:

Thank you for sending us regularly the IIT N-M-R Newsletters. We would not be without them in our institute and although you may have to give us a push sometimes to write our contribution, we are happy to do so. Here it is:

S. Huneck^{1,2} isolated from the liver-moss, Calypogeia trichomanis, a few mgs of two azulenes, one violet and one blue; we have been successful in deducing their structures mainly using nmr.

The nmr spectrum of the violet azulene (fig. a)³ shows that it has the structure I:



The AB-system with $J = 4.4$ cps indicates the presence of the two adjacent protons in the 5-ring on C-2 and C-3. The unusual resonance frequencies of the protons on C-8 and on C-2 are obviously due to the anisotropy of the carbomethoxy group on C-1⁴. The protons of the 7-ring form an ABCXY₃-system: X → proton on C-8, ABC → protons on C-5, C-6 and C-7 respectively with the coupling constants $J_{7,8} = 9.5$ cps, $J_{6,8} = 1.5 - 2.0$ cps.

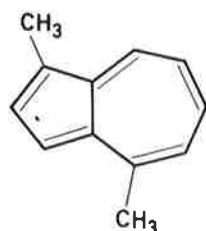
Prof. B.L. Shapiro

- 2 -

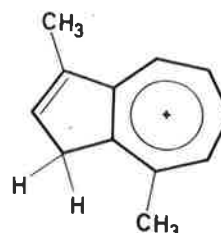
May 11, 1965

The protons Y_3 of the singlet at 2.80 ppm indicate that the methyl group is located at C-4. In the meantime, S. Huneck has proven the structure I of the violet azulene by an unambiguous synthesis ⁵.

The nmr spectra of the blue azulene in CCl_4 (fig. b) and of its conjugate acid in F_3CCOOH (fig. c) show that they have the constitution II and III respectively:



II



III

In the spectrum in CCl_4 (fig. b) there are two singlets at 2.78 and 2.62 ppm, each corresponding to three protons. In the overlapping multiplets of the ring protons the characteristic AB-system with $J_{2,3} = 3.9 - 4.0$ cps for two adjacent 5-ring protons can be nicely resolved on large scale. This type of ABX_3 -system is in agreement with the rules which hold for numerous alkyl-azulenes ^{6,7} and establishes that one of the methyls is on the 5-ring. The protons of the 7-ring and those of the second methyl group form an $ABCXY_3$ -system with A,B,C \longrightarrow protons on C-5, C-6, C-7, X \longrightarrow proton on C-4 or C-8, $J_{7,8}$ or $J_{4,5} = 9.6$ cps, $J_{4,6}$ or $J_{6,8} = 1.5 - 2.0$ cps (compare ring current and π -electron density distribution around the C-atoms of the azulene) and $Y_3 \longrightarrow$ methyl protons of a substituted 4- or 8-methylazulene.

The nmr spectrum of the blue azulene in F_3CCOOH shows that II is in equilibrium only with one conjugate acid III. It follows from previous experience that due to release of steric strain azulenes with methyls in positions 1 and 8 form the two conjugate acids produced by adding a proton in position 1 or 3 ⁷. Since the blue azulene gives only one conjugate acid its

Prof. B.L. Shapiro

- 3 -

May 11, 1965

methylys must be in positions 1 and 4. In agreement with structure II is also the infrared spectrum of the naturally occurring compound which is identical with the spectrum of the synthetic 1,4-dimethyl-azulene determined by H.H. Günthard⁸ many years ago.

Once more we see that nmr is very useful for the rapid determination of constitution with small amounts of material provided that some experience in the investigated group of compounds is available.

Sincerely yours,

Doris Meuche

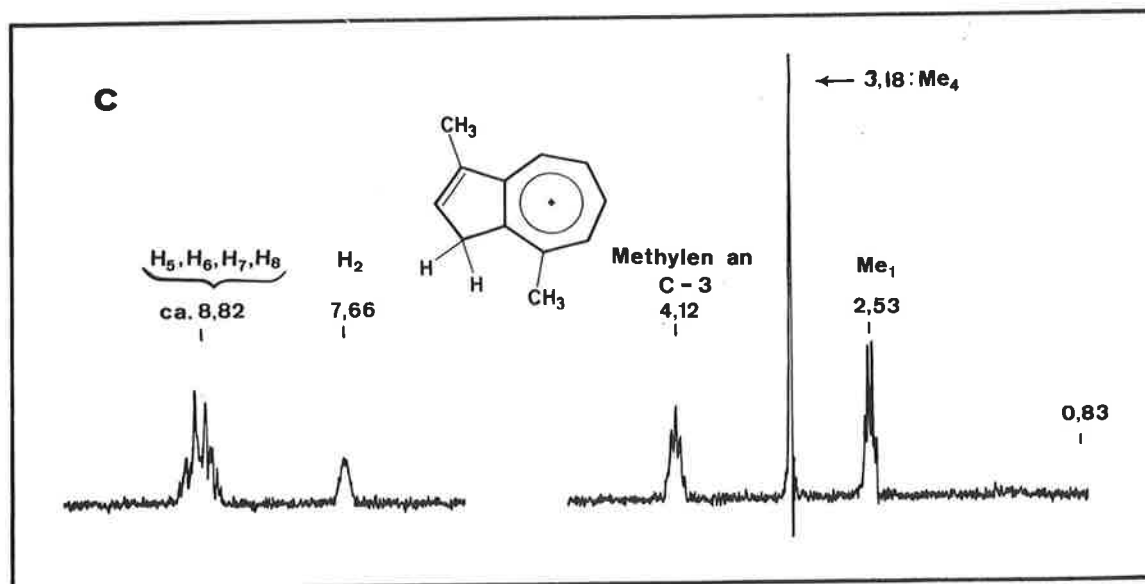
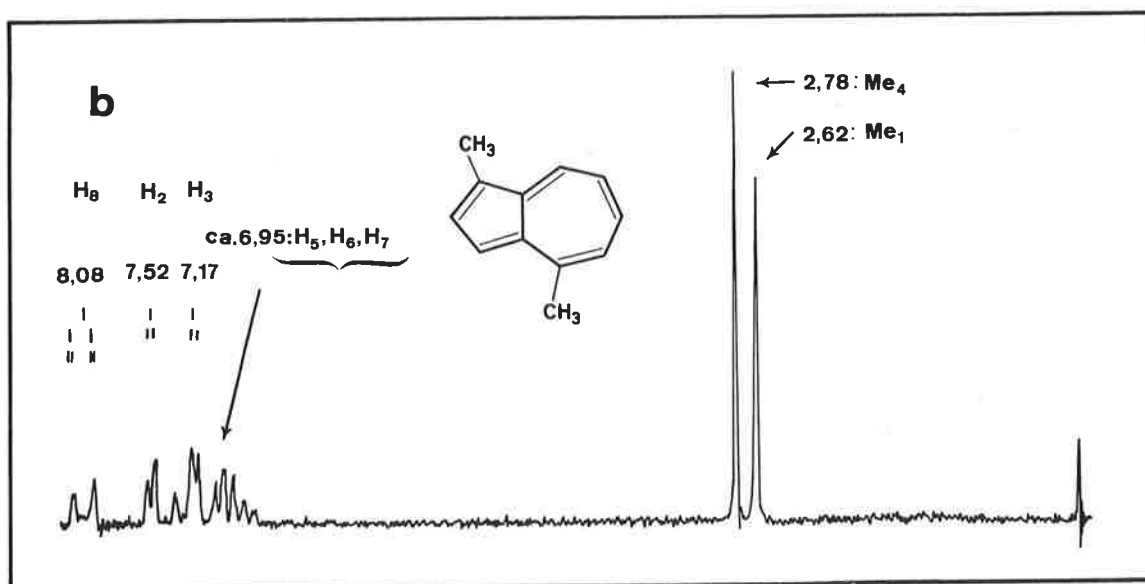
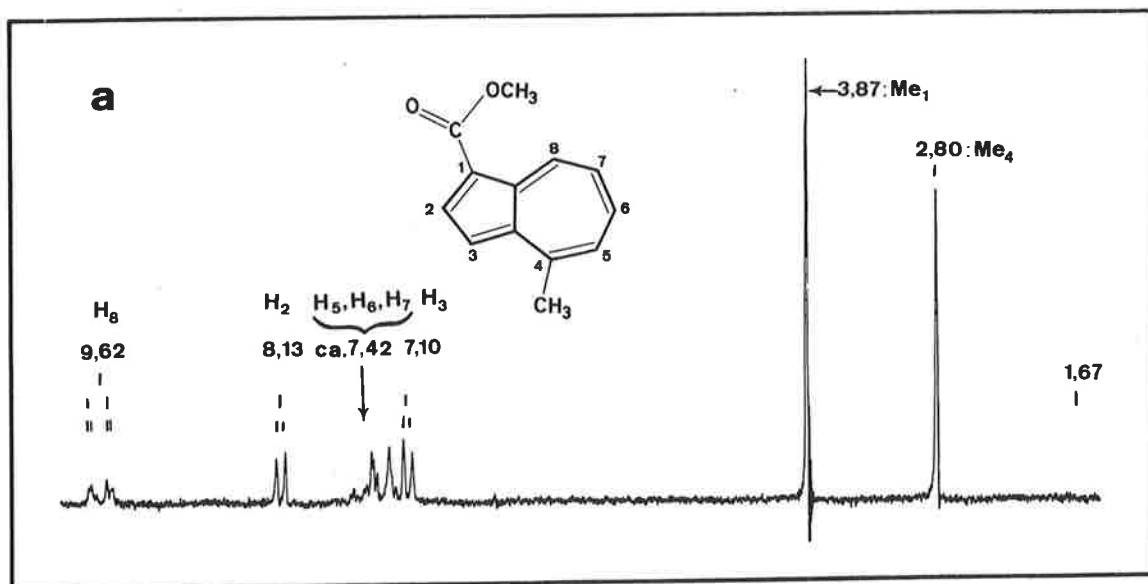
Doris Meuche

1. S. Huneck, Zeitschrift für Naturforschung 18b, 12, 1126 (1963).
2. We thank Dr. S. Huneck, Tharandt, Institut für Pflanzenchemie der Technischen Universität Dresden, for the permission to mention his unpublished results.
3. The nmr spectra have been recorded on a Varian-A-60 Spectrometer, using TMS as an internal standard. The accuracy in δ -values is ± 0.02 ppm and those in J-values ± 0.02 cps.
4. Doris Meuche and E. Heilbronner, Helv. 45, 1965 (1962); Mellon-Letter 48, 18; Doris Meuche, IITNNR-Newsletters 70, 12.
5. We thank Professor K. Hafner, Darmstadt, for his advice in the synthetical work.
6. Doris Meuche, B.B. Molloy, D.H. Reid and E. Heilbronner, Helv. 46, 2483 (1963); Doris Meuche, W. Meier and E. Heilbronner, *ibid.* 46, 1929 (1963); A. Melera and Doris Meuche, Mellon-Letter 51, 16.
7. Doris Meuche, Mellon-Letter 48, 18.
8. H.H. Günthard, Thesis ETH, Zurich (1949).

Prof. B.L. Shapiro

- 4 -

May 11, 1965



MELLON INSTITUTE

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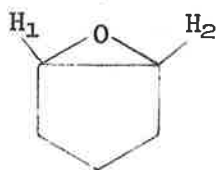
PITTSBURGH, PA. 15213

May 13, 1965

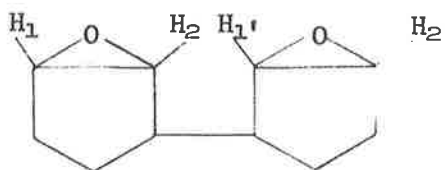
Dr. Bernard L. Shapiro
Associate Professor
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

Since my return to Mellon, Dr. Klaus Meyersen and I have been investigating several polymer systems and their low molecular weight model compounds to test NMR for structure determination. In the course of this work we had occasion to look at the NMR spectra of 1,2-epoxycyclopentane and the closely related di(1,2-epoxycyclopentyl)(II).



I



II

We have observed in I that H_1 and H_2 are represented by a singlet and that no coupling occurs between H_1 and H_2 and other ring protons. This observation is consistent with the spectra reported by Sable, Ritchey and Nordlander (IITNMRN 70-5), and Hall (IITNMRN 70-4) for similar epoxide compounds.

In the spectrum of di(1,2-epoxycyclopentyl), however, H_1 and H_2 and H_1' and H_2' appeared to be represented by a rather complicated multiplet of at least 7 or 8 lines. Further examination revealed that our original sample consisted of a mixture of isomers, presumably stereoisomers. The NMR spectrum of the most abundant isomer revealed that H_1 and H_2 and H_1' and H_2' were represented by a simple quartet (Fig. 1) with $J_{12} = J_{1'2'} \cong 2.5$ cps. No additional coupling to other ring protons could be observed. To confirm our observed $J_{12} \cong 2.5$ cps we looked at the C^{13} satellite spectrum of the H_1H_2 singlet in the 1,2-epoxycyclopentane and found a doublet of $J_{12} \cong 2.5$ cps.

We are now in the process of separating the other isomers which appear to have the $H_1H_2-H_1'H_2'$ quartet separated only by a small chemical shift difference. Our hope is that we might be in a position to assign each spectrum to a specific isomer.

MELLON INSTITUTE

Dr. Bernard L. Shapiro

Page 2

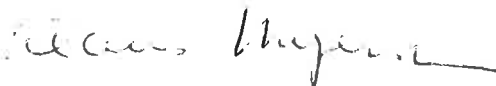
May 12, 1965

I trust that this brief contribution might serve to reestablish my subscription which was relinquished when I left the Institute two years ago. Dr. Meyersen and I will be most happy to share the copy.

Sincerely,



Frank E. Dickson
Fellow, Polymer Science



Klaus Meyersen
Fellow, Polymer Science

FED:il

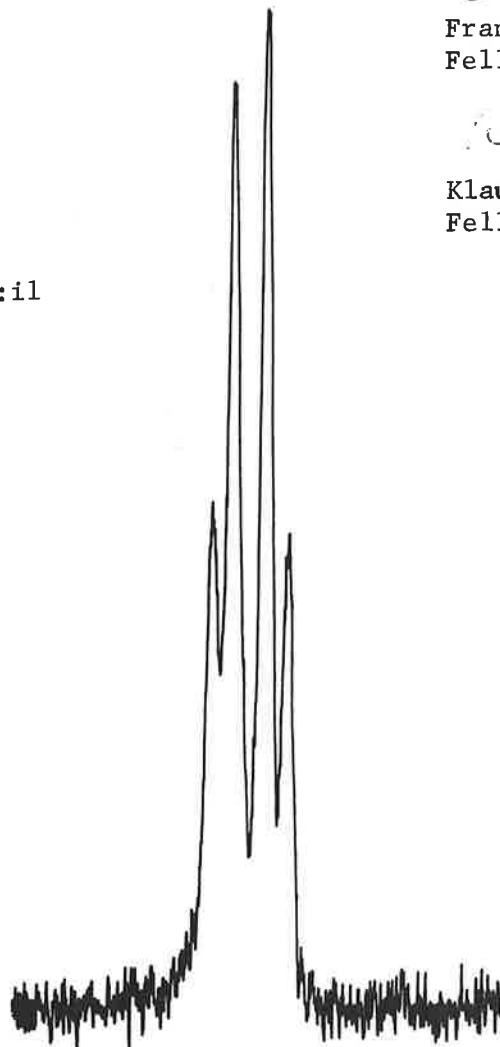


Figure 1

POLITECNICO DI MILANO
 ISTITUTO DI CHIMICA
 Piazza Leonardo da Vinci, 32 - MILANO
 TEL. 292.109-292.110

Milan, May 7th, 1965

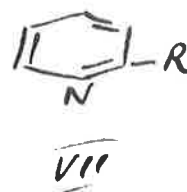
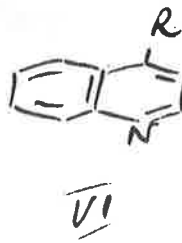
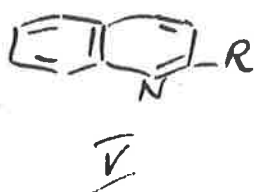
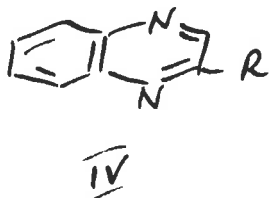
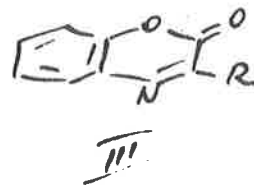
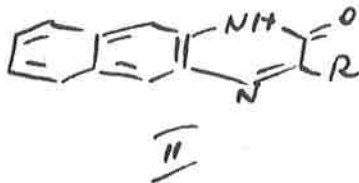
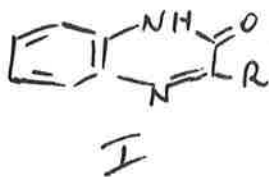
Prof. B.L. Shapiro
 Department of Chemistry
 Illinois Institute of Technology
 Technology Center
 Chicago 16, Illinois

Dear Professor Shapiro,

we have installed in our laboratory an A-60 since one year and an half, and I regret to have not sent before our contribution, because I see the importance to receive the Newsletter.

In the last months, in connection with the structure determination of a natural product, daunomycin (1), we detected in one of its derivatives a long-range coupling across four σ -bonds ($J_{A'B} \sim 1$ cps, fig. 1,2) It is interesting to note that no homoallylic interaction is observed between H_X and $H_{A'}$. This can be explained by the presence of the quinone, which localizes the double bonds in ring B, and decreases the bond order of the 5,6 bond. Unfortunately, we can not decide unambiguously which one of the protons on C-1 and C-3 are coupled each other, even if a diequatorial relationship (2) is more probable, because of the lower field shift of the equatorial protons with respect to the axial ones.

Another topic we are investigating is tautomerism in N-heterocycles. A first note was presented in part at the symposium "NMR in Chemistry", Cagliari, 1964(3). Spectra of some cyano-, carbethoxy-, and acylmethyl derivatives of the following rings



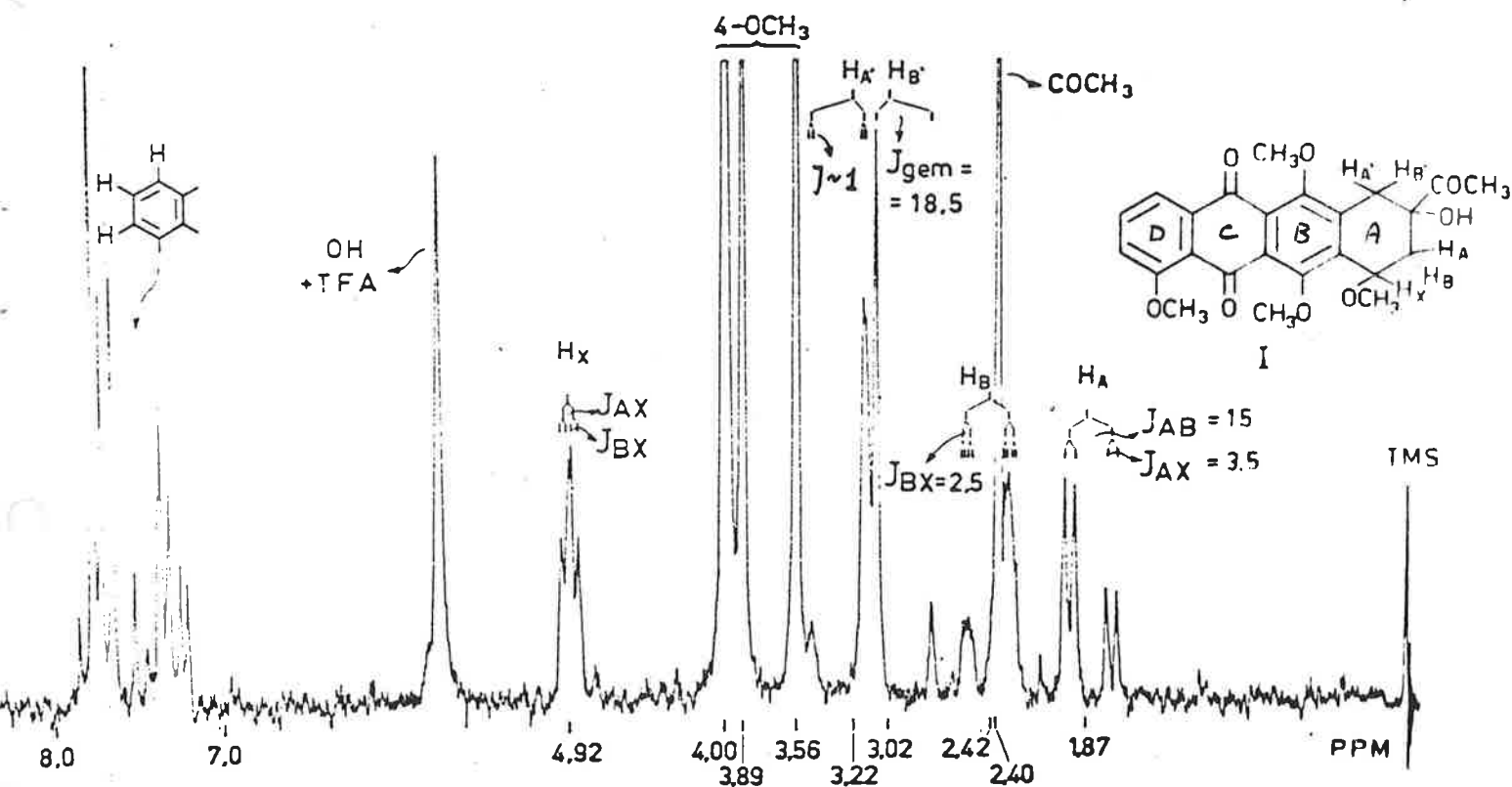
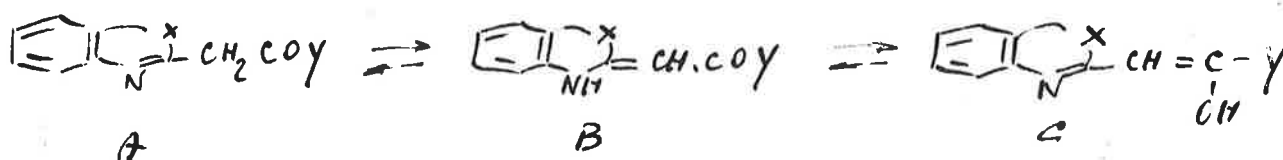
SPETTRO DI R.N.M. DEL DAUNOMICINONE TRIMETILETERE (I) IN CDCl_3 

fig 1

recorded in CDCl_3 , DMSO, and TFA, indicate the existence of tautomeric equilibria with noticeable contribution of enaminic structure B, depending



on the solvent and the aromaticity of the heterocycle. Only in the case of pyridine derivatives the enol tautomer C is preferred. This is proved, together with UV evidence, by the presence in 2-acetylpyridine of an allylic coupling (1 ± 0.1 cps) between CH_3 - and $\text{CH}=\text{C}$ groups. Such a coupling has not been yet observed in enols, as far as we know. Relationships between some NMR parameters and tautomeric structures A and B were observed: i) $J_{2,3}$ and $J_{3,4}$ in the quinoline ring increase from the normal values 8.0-8.2 and 4.0-4.5 (in A) to 9.0-9.2 and resp. 6.5-7.0 cps (in B). ii) enough constant upfield shift (ca. 0.5 ppm) for aromatic protons of the heteroring in tautomer B with respect to tautomer A in IV, V, VI, could be attributed to the loss of ring-current contribution.

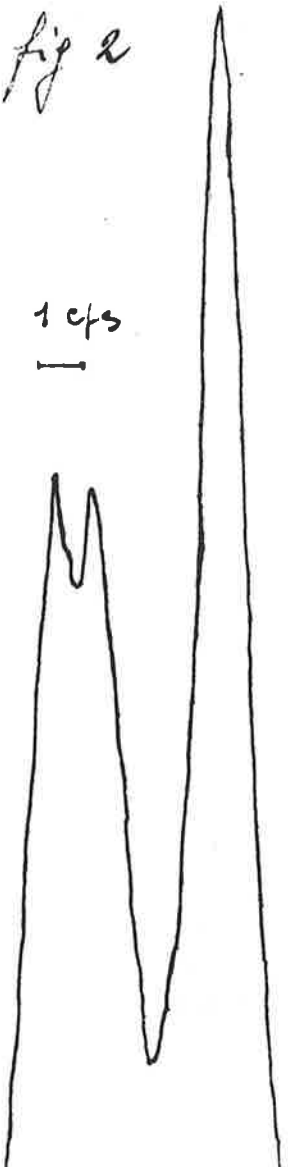
iii) protonation occurs at nitrogen atom of quinoline derivatives (form A) in TFA solution. NH^+ absorptions lie at about 13.5-14.2 δ and are separated from TFA peak. The triplet structure, with $J = 55-60$ cps, is detected in quinoline itself (100 mg/cc) and in some of its derivatives.
iv) coupling between NH^+ and C-2 proton in VI appears in TFA ($J = 5.5-7.0$ cps)
v) protonation probably occurs also in I, II, III, IV, but separate signals of COOH and NH^+ were not detected in the same conditions as for quinoline, probably due to the more rapid exchange because of the weaker basic character of these compounds.

P.S. As well as Dr. Green (ITTNR 74-1) we too succeeded in eliminating water-flow troubles by omitting the small rubber valve intended to control water pressure in A-60. We did not observe any microorganism in our home-made deionized water circulating system. We believe that copper from tubes is sufficient to inhibit their growth.

Sincerely yours,

R. Mondelli

R. Mondelli

- Fig 2*
- 1 cps
—
- 
- (1) F. Arcamone and al. J.A.C.S. 86, 5334 (1964)
 - (2) A. Rassat, C.W. Jefford, J.M. Lehn, B. Waegell, Tetrahedron Letters 1964, 233.
P. Laszlo, J.I. Musher, Bull. Soc. Chim. France 1964, 2558.
 - (3) R. Mondelli, L. Merlini, sent to Tetrahedron.

UNIVERSITÉ DE LYON

FACULTÉ DES SCIENCES

PHYSIQUE PROPEDEUTIQUE

V Réf.:

N Réf.: J. DELMAU

Villeurbanne, le 12 mai 1965

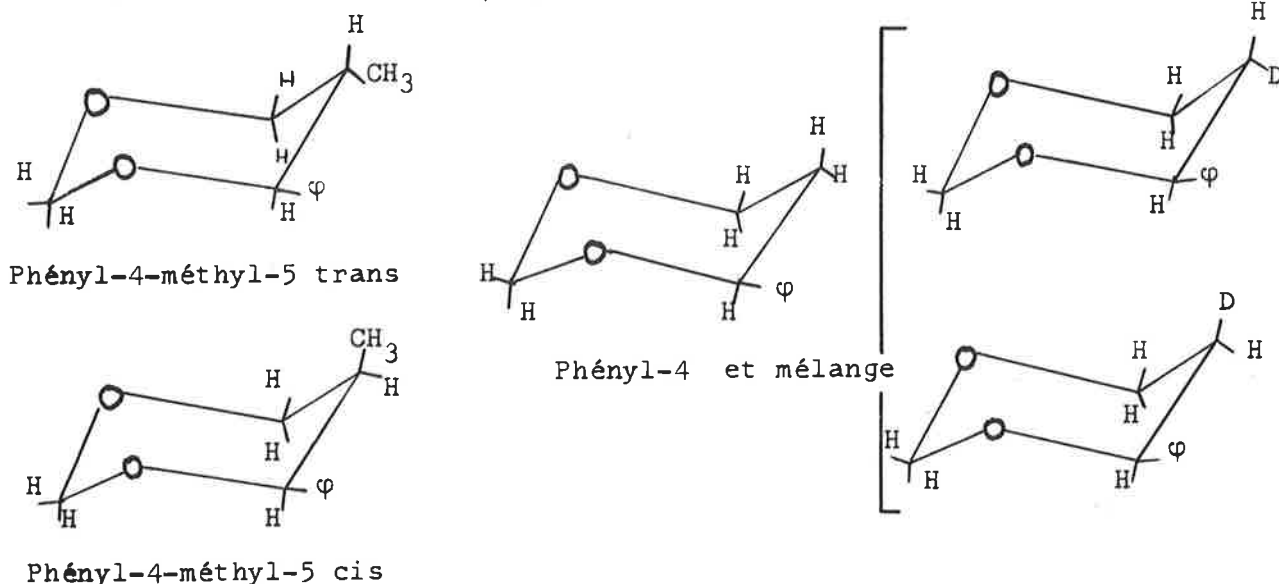
Couplage dans les métadioxannes.

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

Cher Professeur Shapiro,

Nous aimerions, par ces quelques résultats concernant les dioxannes 1.3, nous faire pardonner notre long mutisme. Nous en sommes à notre deuxième rappel à l'ordre !

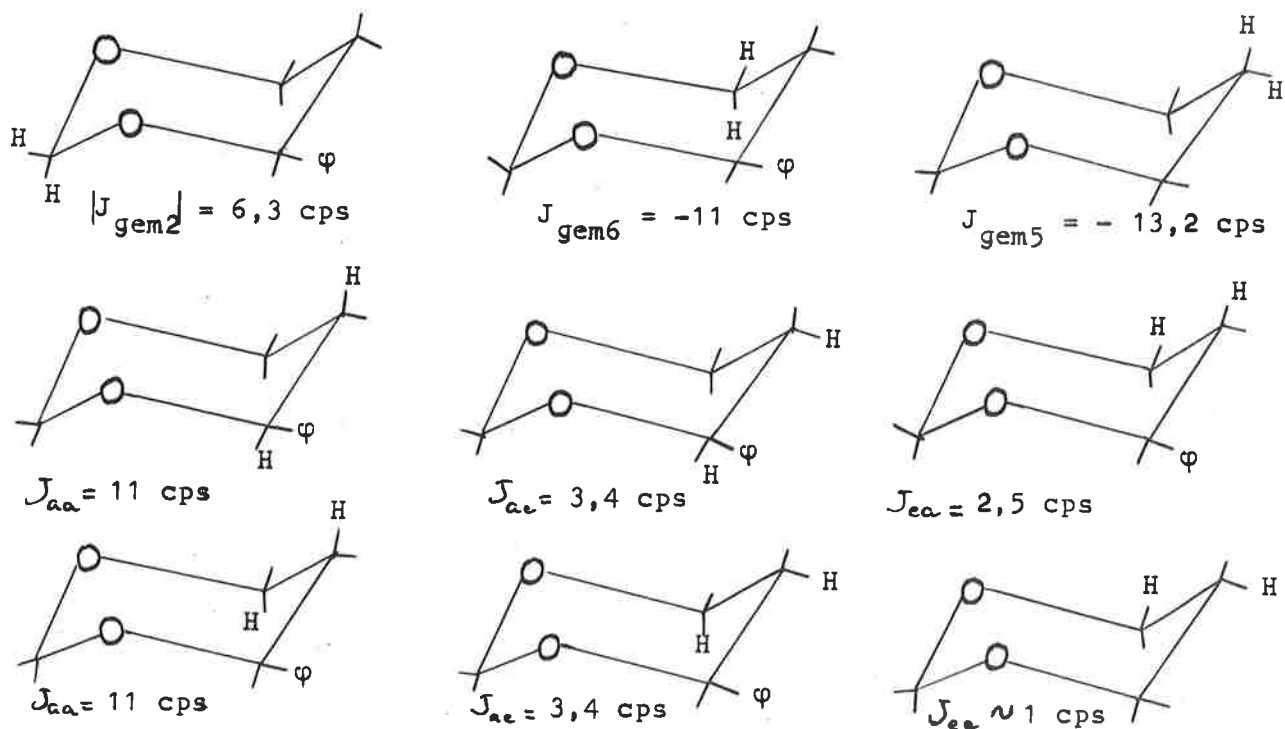
Le substituant phényle fixe les dioxannes envisagés dans une conformation chaise avec φ équatorial. C'est le cas pour :

1. Déplacement chimique des protons en 4 et 6.

δ en ppm	$\delta(H_4)_{\text{axial}}$	$\delta(H_6)_{\text{équatorial}}$	$\delta(H_6)_{\text{axial}}$
Phényl-4-méthyl-5 cis	4,80	3,92	3,92
Phényl-4-méthyl-5 trans	4,00	3,96	3,25
Phényl-4 (confirmé par dérivés deutérés en 5)	4,46	4,00	3,63

Adresse : 43, boulevard de l'Hippodrome - Villeurbanne. Rhône

Téléphone : 52-07-04 . 52-07-05 . 52-07-20 . 52-07-49 . 52-07-52 . 52-07-55 . 52-07-73 . 52-07-80 . 52-07-92

2. Constantes de couplage.3. Couplages à distance.

Signalons, pour terminer, un exemple curieux de couplage à distance :

Dans tous les conformères dioxanniques stables, H_{2a} et H_{2e} , par suite de leur déplacement chimique $\sim 20 \text{ cps}$ et de leur couplage $|J_{gem2}^{2a,2e}| = 6,3 \text{ cps}$, présentent un spectre du type AB.

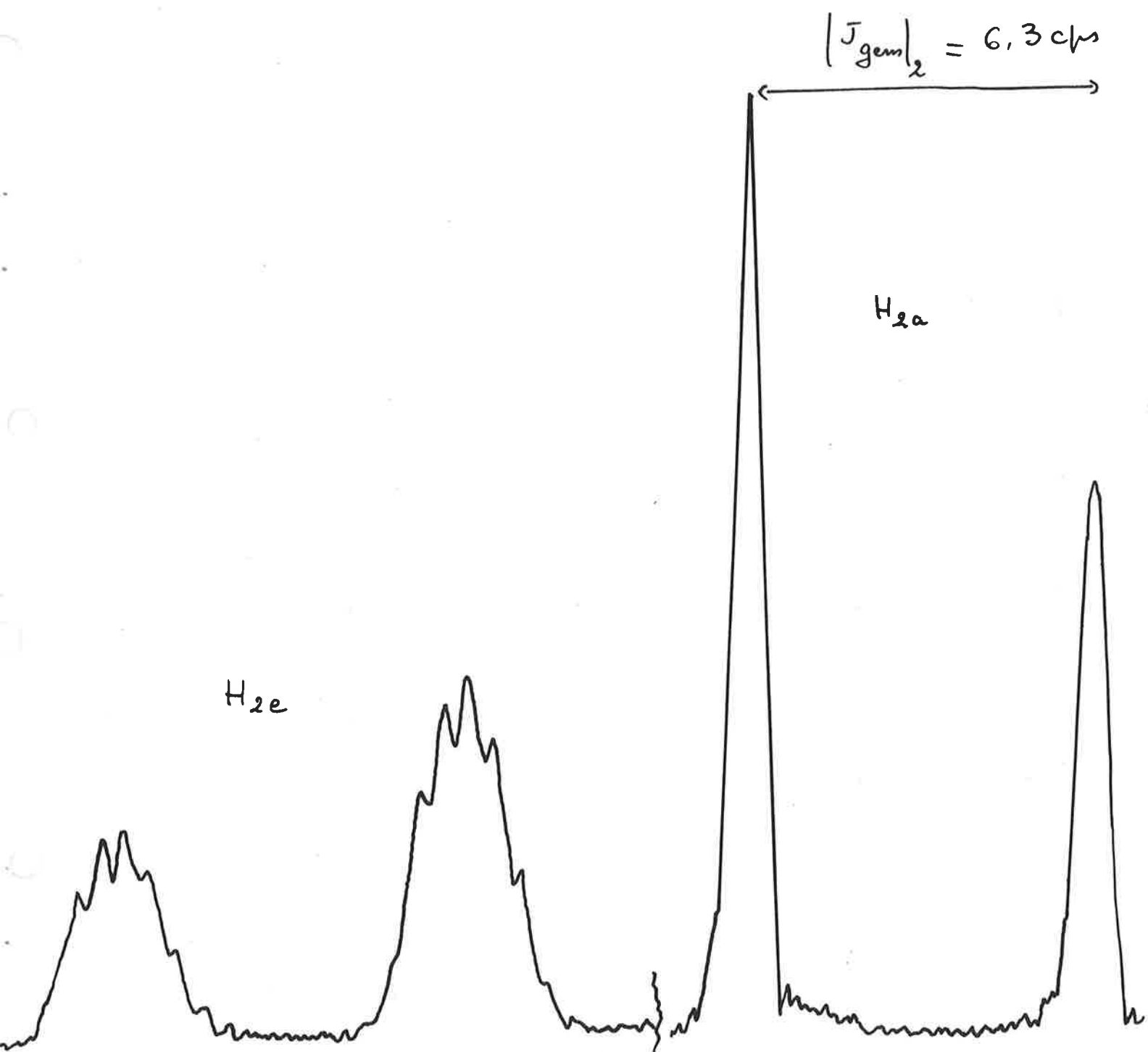
Toutefois, les raies du doublet de H_{2a} (champ fort) sont très fines (largeur instrumentale soit $0,6 \text{ cps}$), tandis que dans tous les dioxannes mono et disubstitués le doublet de $H_{2\text{équatorial}}$ est considérablement élargi par couplage à distance.

Le phénomène est particulièrement important pour le phényl-4-dioxanne mais il est à remarquer que la structure de ce doublet est beaucoup plus apparente -avec même résolution- dans le mélange des phényl-4-deutéro-5-dioxannes que dans le dérivé non deutéré. La résonance de $-O-CH_2-O-$ du mélange des isomères deutérés présente l'aspect suivant. (figuré).

Croyez, cher Monsieur, à nos sentiments les meilleurs.

J. DELMAU

Delmau



STATE UNIVERSITY OF NEW YORK

AT STONY BROOK

STONY BROOK, LONG ISLAND, NEW YORK

Zip Code 11790

DEPARTMENT OF CHEMISTRY

May 13, 1965

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

Dear Barry:

The following is a contribution to IITNMRN.

C^{13} NMR Spectra of Transition Metal Cyclopentadienyl
 and Carbonyl Derivatives

We have begun a study of the carbon NMR spectra of transition metal complexes, and some preliminary results are noted below. As shown in the figure, there is a reasonable good linear relationship between carbon and proton shieldings of the cyclopentadienyl groups in π -cyclopentadienyl compounds, both being anomalously high. We have concocted no convincing explanation of these results in terms of currently fashionable theories.

The table below summarizes all available data on carbonyl carbon resonances in complexes.

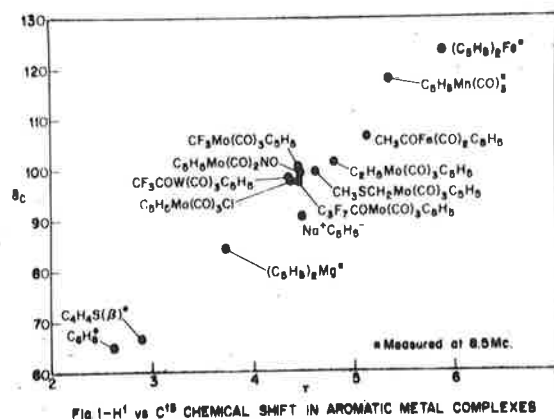
Carbonyl Resonances^a

Compound	C^{13} Shielding (p.p.m.)
CO	11.5 ^{c,d} (gas)
Ni(CO) ₄	1.2 ^{d,e} (neat liquid)
C ₃ F ₇ Fe(CO) ₄ I	-6 ^d (CHCl ₃)
Fe(CO) ₂ (NO) ₂	-14 ^f (neat liquid)
[Fe(CO) ₃ SCH ₃] ₂	-16.6 ^d (CHCl ₃)
Fe(CO) ₅	-16.8 ^d (neat liquid)
C ₅ H ₅ Fe(CO) ₂ I	-20.9 ^d (CHCl ₃)
C ₇ H ₈ Mo(CO) ₄ ^g	-22.4, -26.0 ^d (CHCl ₃)
C ₇ H ₈ Mo(CO) ₄ ^g	-22.0, -25.4 (CH ₂ Cl ₂)
C ₅ H ₅ Mo(CO) ₃ Cl	-32.6 (CH ₂ Cl ₂)
C ₅ H ₅ Mo(CO) ₂ NO	-34.5 (CH ₂ Cl ₂)

-2-

- a Solvent given in parentheses.
 b To high field from CS_2 .
 c R. Ettinger, P. Blume, A. Patterson, Jr., and P.C. Lauterbur, J. Chem. Phys. 33, 1547 (1960).
 d Spectrum measured at 8.5 Mc.; other spectra measured at 25.143 Mc.
 e J.B. Stothers and P.C. Lauterbur, Can. J. Chem 42, 1563 (1964).
 f R. Bramley, B.N. Figgis and R.S. Nyholm, Trans. Faraday Soc. 58, 1893 (1962). Measured at 12.069 Mc.
 g C_7H_8 is bicyclo-[2,2,1]-heptadiene (norbornadiene).

Several features of the results are worthy of comment. Resonances of carbonyl groups bonded to cobalt and manganese are difficult or impossible to find because they are broadened by partially collapsed coupling with the quadrupolar nuclei. In symmetrical species such couplings have been found in the spectra of the metal, as in $\text{Co}(\text{CN})_6^{3-}$ and $\text{V}(\text{CO})_6^-$. In at least one compound, norbornadiene molybdenum tetracarbonyl, non-equivalent carbonyl groups have been distinguished. The data are limited enough that any of several interpretations in terms of the bonding might be proposed, but we plan to obtain more spectra on several series of compounds before venturing into such a discussion.



Yours truly,

Paul C. Lauterbur
 State University of New York
 at Stony Brook

R. B. King
 Mellon Institute
 Pittsburgh, Pa.

PCL:aw

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De Commissie
GEMEENSCHAPPELIJK CENTRUM
VOOR ONDERZOEK

Ispra, May 11, 1965
HS/mg

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

The C-H Hydrogen bond in Liquid HCN and Exchange Phenomena in HCN.

Dear Barry:

Recently I started to look at liquid hydrogen cyanide, a non-aqueous solvent with aqueous properties.

For pure liquid HCN at about 33°C one finds $\delta_{1H} = 4.08$ ppm down-field from TMS and $\delta_{13C} = 120.1$ ppm down-field from $^{13}CH_4$. $J_{CH} = 268$ cps from ^{13}C measurements.

With non polar solvents HCN is not miscible thus one has difficulties to get $\delta_{C=O}$. In chloroform and methylene chloride one gets for $\delta_{C=O}$ 3.85 ppm and 3.74 ppm respectively, values which are still far above the one for gaseous HCN (3.06 ppm).

Contrary to the situation in water solvents such as dioxane, dimethylsulfoxide, and dimethylformamide cause a shift of the proton in HCN towards lower applied field indicating an increase in hydrogen bonding due to interaction with the solvent.

Most interesting is the behavior of acids in HCN. A 3 molar solution of 100 % H_2SO_4 in HCN with 2 mol % TMS as reference does not show any exchange with the hydrogen cyanide as can be seen from linewidth measurements and the existence of ^{13}C satellites with J_{CH} 267 cps. The shift for H_2SO_4 against TMS is 8.14 ppm. Even liquid HF does not exchange rapidly at a concentration of approx. 1 m. $\delta_{HF} = 7.47$ ppm, $J_{CH} = 247$ cps. So far I was not able to observe J_{HF} but it is quite probable that the experimental conditions were not anhydrous enough.

A more quantitative description will be published soon.

Sincerely yours,

H. Spiesscke



מכון ויצמן למדע
THE WEIZMANN INSTITUTE OF SCIENCE

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ISOTOPE DEPARTMENT

May 13, 1965

מחלקת האיזוטופים

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

Dear Professor Shapiro:

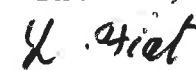
We wish to report in this letter some recent results obtained in the NMR studies of adsorbed molecules [for preliminary reports see: D. Fiat, Bull. Res. Council Israel, 10A, 41 (1961); J. Reuben, D. Fiat and M. Folman, Israel J. Chem. 1, 276 (1963)].

The line widths (Δ) of NH_3 adsorbed on porous Vycor glass were measured at 56.4 Mc and 24.3 Mc as a function of coverage below a monolayer. It was found that $\Delta_{56.4} > \Delta_{24.3}$. The largest difference ($\Delta_{56.4} - \Delta_{24.3}$) were observed in the region $\theta = 0.5 - \theta = 0.6$. The line widths at $\theta = 0.6$ were: $\Delta_{56.4} = 580$ cps, $\Delta_{24.3} = 285$ cps. It was possible, by taking the derivative of the absorption made to resolve the line at 56.4 Mc into a doublet.

The particular dependence on frequency leads to the suggestion that two adsorbed phases with a chemical shift between them are present in the system. A low limit of 5.2 ppm for this shift can be estimated. One possibility for such a phenomenon is the presence of adsorbed NH_3 molecules and NH_4^+ ions formed by adsorption of ammonia on the acidic OH groups of the surface.


J. Reuben

Sincerely yours,


D. Fiat

The University of Strathclyde

Formerly the Royal College of Science and Technology



GLASGOW, C.1. TEL: BELL 4400

Organic Chemistry Section

10th May, 1965.

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

Dear Barry,

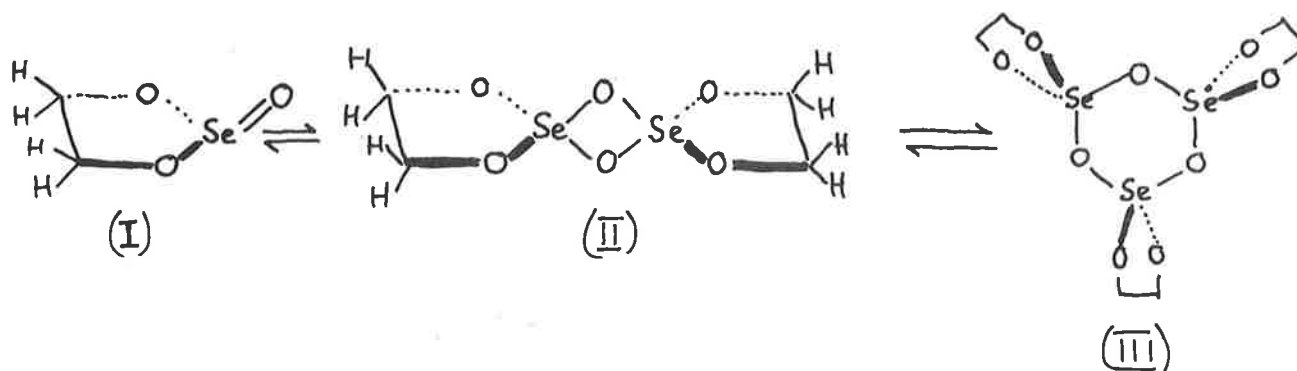
Herewith our contribution which I hope will keep us
in funds for a little longer.

Spectra of ethylene sulphite and ethylene selenite

Abraham (J.Chem.Soc., 1965, 256) has recently reported
on the particular cases of AA'BB' spectra in which $\underline{J}_{AA'} = \underline{J}_{BB'}$
and has shown how the difficult calculation of parameters
can be achieved. We can agree with the difficulty and comment
here on the spectrum and parameters of ethylene sulphite which
he mentioned en passant. We have examined spectra of ethylene
sulphite at 40 Mc/sec and 60 Mc/sec. obtained in a variety of
solvents. (The 60 Mc/sec spectra were kindly run by Colin Fyfe
at Dundee). The parameters obtained for 30% solution in CDCl_3 at
60 Mc/sec are $\delta = 17.93 \text{ c/sec}$, $\underline{J}_{AA'}/\underline{J}_{BB'} = 6.84 \text{ c/sec}$,
 $\underline{J}_{AB} = -8.47 \text{ c/sec}$, $\underline{J}_{AB'} = +6.42 \text{ c/sec}$. These values are
somewhat different from the values quoted by Abraham for the
pure substance since both the chemical shift and coupling

constants are sensitive to solvent changes. Agreement between calculated and experimental spectra was only obtained after three complete rounds of the computation process:- energy level assignment \rightarrow energy level and parameter iteration (15 iterations!) \rightarrow theoretical spectrum.

Ethylene selenite (I) in CDCl_3 gives a similar spectrum to the sulphite $\delta = 10.8$ c/sec, $/J_{AA'}/ = /J_{BB'}/ = 7.0$ c/sec, $J_{AB} = -9.2$ c/sec., $J_{AB'} = +6.2$ c/sec (40 Mc/sec. parameters obtained from algebraical calculation). The $AA'BB'$ spectrum in CDCl_3 is confused by an additional sharp single line which decreases in relative intensity and moves to lower field on dilution. In other solvents (e.g. pyridine) and in the molten state ($> 64^\circ$) the spectrum is a fairly broad line, the shift to lower field on dilution again being noticed. We attribute these results to the reversible formation of a dimer (II) and higher polymers e.g. (III) in which the hydrogen atoms are equivalent. The rates in the monomer - dimer equilibrium must be low (separate spectrum of monomer) but the dimer-polymer equilibrium must be fairly mobile. We are still investigating this phenomena.



A similar dimerisation has been suggested in sulphoxides (cf. R. F. Watson and J. F. Eastman, J. Amer. Chem. Soc., 1965, 87, 664).

Miscellaneous long range couplings

We have found an unexpected long range coupling (4 bonds) between S-H and the H's in the tertiary butyl group in tert-butylmercaptan. ($J = 0.6$ c/sec), and a not unexpected one (5 bonds) in 2,2,2-trifluorethyl formate between the fluorines and the formyl hydrogen ($J = 1.0$ c/sec.). We think these are new. Collectors please note!

1-Bromo-1-chloro-2,2,2-trifluoroethane as a test substance in fluorine resonance.

When operating our Perkin-Elmer R10 spectrometer on fluorine frequency, we have for some time felt the need for a test substance suitable for trimming and testing the field

homogeneity by the wiggle beat method, analogous to acetaldehyde in proton work. We would like to suggest CF_3CHClBr to fill this gap. It is readily available as the anaesthetic "fluothane" or "halothane". The H-F coupling constant is 5.3 c/sec. so that the wiggle-beats are about twice as frequent as in acetaldehyde.

Yours sincerely,

Peter Bladon.

P. Bladon

Norman M. D. Brown.

N. M. D. Brown.

LABORATOIRE DE SPECTROSCOPIE HERTZIENNE

ANNEXE DU

LABORATOIRE DE RECHERCHES PHYSIQUES A LA SORBONNE
1, RUE VICTOR-COUSIN, PARIS-V^e

2276/RF/JM

PARIS, le 3 mai 1965

ODÉ : 24-13 POSTES 484, 483 et 263

M. le Professeur B. L. SHAPIRO
ILLINOIS INSTITUTE OF
TECHNOLOGY
Technology CenterCHICAGO 60616
U. S. A.

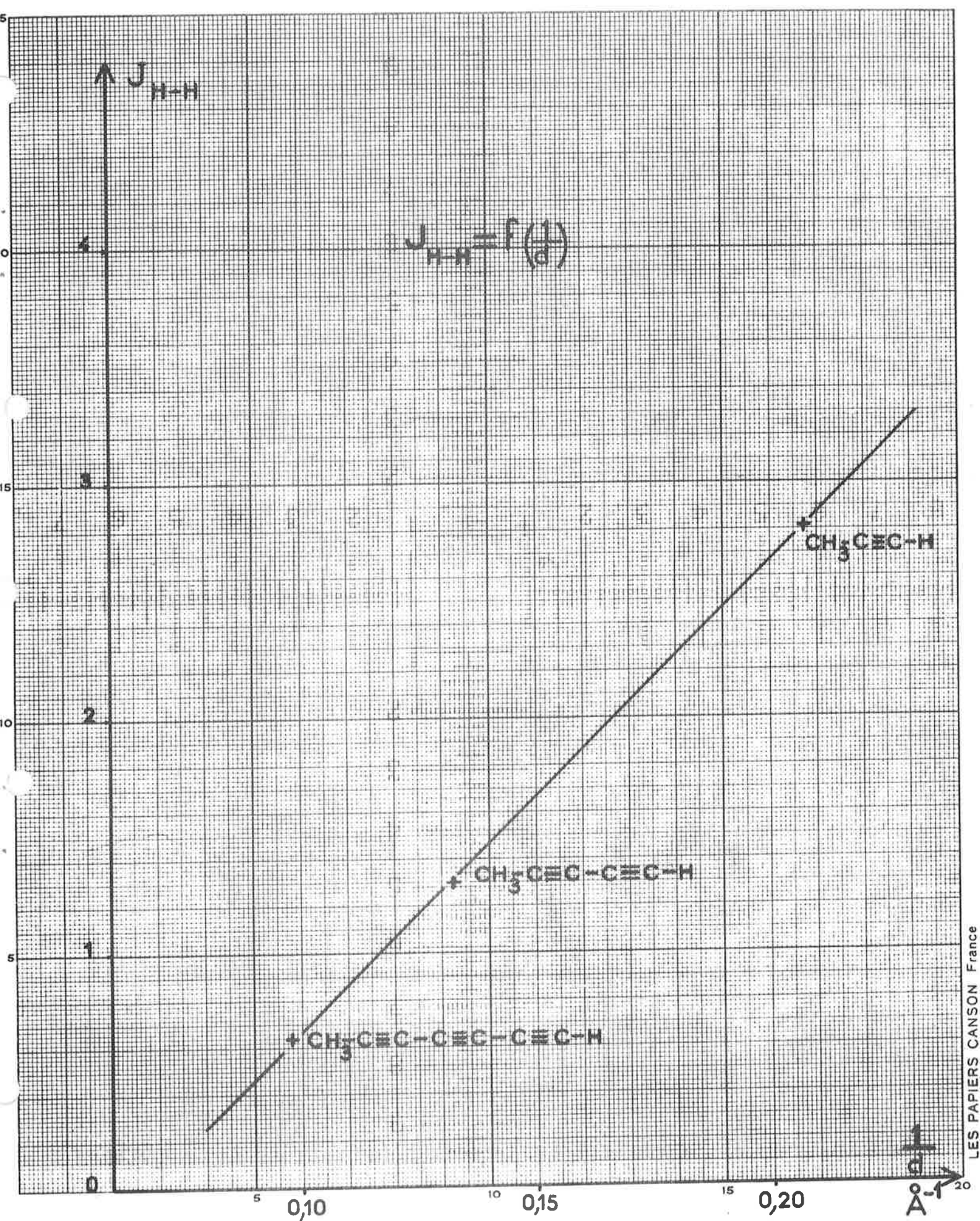
Cher Docteur Shapiro,

Dans une étude générale des composés acétyléniques que nous avons entreprise au Laboratoire, nous avons été amenés à mesurer les couplages à longue distance entre protons. La série $\text{CH}_3 - (\text{C}\equiv\text{C})_n - \text{H}$ est particulièrement intéressante car les couplages entre le proton acétylénique et les protons du groupement méthyl peuvent s'effectuer à longue distance. Nous avons obtenu les résultats suivants :

	J(Hz)	d(Å)	1/d (Å ⁻¹)
$\text{CH}_3 - \text{C}\equiv\text{C} - \text{H}$	2,80	4,82	0,207
$\text{CH}_3 - \text{C}\equiv\text{C} - \text{C}\equiv\text{C} - \text{H}$	1,30	7,49	0,133
$\text{CH}_3 - \text{C}\equiv\text{C} - \text{C}\equiv\text{C} - \text{C}\equiv\text{C} - \text{H}$	0,65	10,16	0,098

Snyder, Altmann et Roberts ⁽¹⁾ avaient déjà mesuré les couplages dans les deux premiers composés. Le couplage à travers 8 liaisons dans le méthyltriacétylène a été mesuré pour la première fois ⁽²⁾ dans notre laboratoire grâce à un composé synthétisé par M. Chodkiewicz ⁽³⁾ du laboratoire du Professeur Cadiot. Cette valeur du couplage 0,65 Hz est la plus élevée qui ait été observée à travers 8 liaisons.

.../...



Les carbones de $\text{C}\equiv\text{C}$ étant parfaitement alignés, on peut tenter de comparer J et l'inverse de la distance qui sépare les protons.

Comme le montre la figure il y a une relation sensiblement linéaire entre $1/d$ et J.

Ces résultats montrent que les triples liaisons conjuguées transmettent bien les couplages et que cette transmission semble diminuer comme l'inverse de la distance entre protons.

Veuillez agréer, Cher Docteur Shapiro, l'expression de nos sentiments cordiaux.



R. FREYMANN



P. JOUVE

-
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M. Anteunis and F. Alderweireldt
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"¹³C N.M.R. Studies. Pt. III. Carbon-13 N.M.R. Spectra of Substituted Acetophenones"

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V. J. Shiner, Jr. and D. Whittaker
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"Nuclear Magnetic Resonance Spectroscopy. Analysis of the Proton Spectrum of Cyclobutene"

S. Borcić and J. D. Roberts
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G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts
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"Analysis of Proton Magnetic Resonance Spectra of Cysteine and Histidine and Derivatives. Conformational Equilibria"

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G. A. Olah
J. Am. Chem. Soc. 87, 1103 (1965)

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"Halogen Complexes. I. An Investigation by Nuclear Magnetic Resonance of Complexes Formed by Iodine and some para-Substituted Phenyl Methyl Sulfides"

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R. Breslow, L. J. Altman, A. Krebs, E. Mohacs, I. Murata, R. A. Peterson, and J. Posner
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