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Illinois
Institute of
Technology
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Newsletter

No. 88
JANUARY, 1966

OVER

Deadline Dates: No. 89: 18 February 1966
No. 90: 18 March 1966

MONASH UNIVERSITY
DEPARTMENT OF CHEMISTRY

P.O. BOX 92, CLAYTON, VICTORIA, AUSTRALIA

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

13th December, 1965.

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

Title: Spectral Parameters for isoquinoline.

Dear Barry,

I have now become accustomed again to standing on my head; many of us here in Australia would like to see more people from the Northern Hemisphere trying this ~~excuse~~ exercise ! Seriously however, I found my recent visit to the States very enjoyable and rewarding in a number of ways.

One of the problems that we tried some time ago, and put aside for a rainy day, was that of unravelling the closely coupled system, isoquinoline. We only required chemical shift data for our own particular purposes but we were also interested in the patterns of coupling values in these sorts of systems. We were able to make a bit more progress on the problem when we had a second look at it. The spectra of the pure liquid, the solution in CCl_4 and also acetone were examined and the parameters were extracted using an iterative computer programme of the Reilly-Swalen type. The acetone results were not too satisfactory, mainly because we could not assign enough transitions. However we were able to get moderately accurate estimates of the chemical shifts. We used field-sweep spin decoupling in order to determine the approximate chemical shifts of protons 4, 5, 7 and 8. The results obtained are set out below:

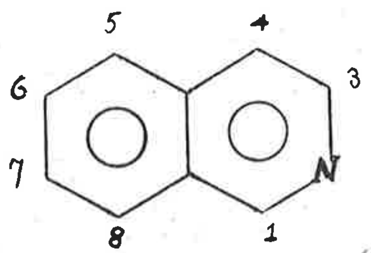


Table: Chemical Shifts and coupling constants (c/s) for isoquinoline.

	Isoquinoline pure liquid	Isoquinoline 0.063g/ml in CCl_4	Isoquinoline 0.050 g/ml in acetone
τ_1	0.553	0.856	0.71
τ_3	1.233	1.550	1.49
τ_4	2.515	2.501	2.26
τ_5	2.427	2.295	2.08
τ_6	2.542	2.433	2.26
τ_7	2.632	2.508	2.34
τ_8	2.264	2.137	1.92
J_{13}	~ 0	~ 0	
J_{15}	<0.5	<0.5	
J_{34}	5.8	6.0	
J_{48}	~ 0.8	~ 0.8	
J_{56}	8.62	8.68	
J_{57}	0.88	1.07	
J_{58}	0.82	0.90	
J_{67}	7.02	6.99	
J_{68}	1.09	1.29	
J_{78}	8.39	8.21	

The spectra and those calculated with the above parameters are shown in Figures 1 and 2. We have also compared in Figure 3, the proton shifts in the pure liquid and acetone with those obtained in CCl_4. An effect rather similar to that found in quinoline (P.J. Black and M. L. Heffernan, Aust. J. Chem., 17, 558, (1964)) was noticed wherein a specific influence seems to be operating at the protons closest to the heteroatom, particularly in the case of the pure liquid. The protons more distant from the hetero-atom seem to undergo only a more general shift, presumably arising from reaction field effects. However, like a lot of "effects" in NMR, they may proceed from a multiplicity of causes!

Best wishes,

Michael L. Heffernan

Peter J. Black*

Michael L. Heffernan

* Present address:
Department of Chemistry,
University of British Columbia,
Vancouver 8,
B.C., Canada.

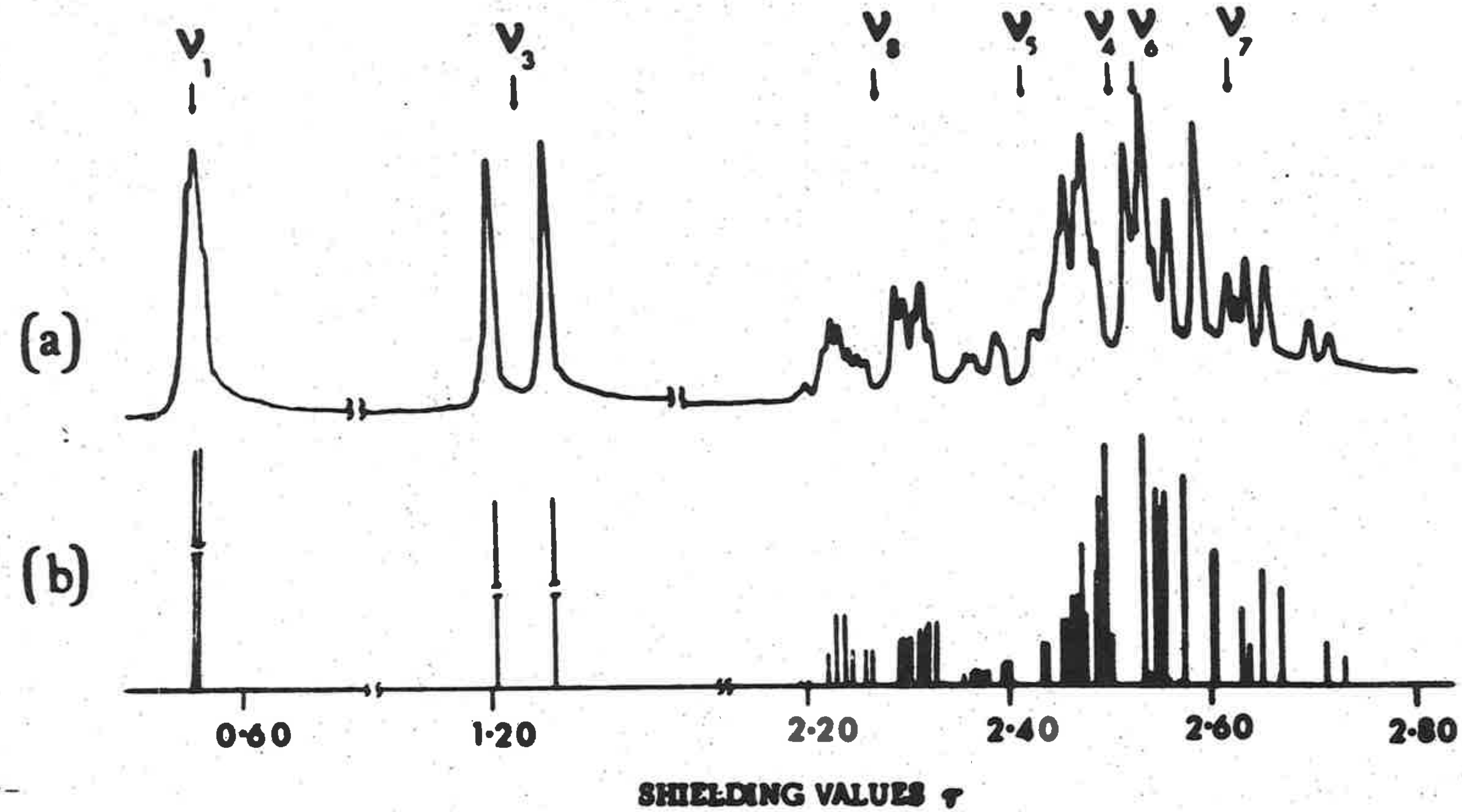


Figure 1 (a) Experimental and (b) Calculated spectrum of isoquinoline as pure liquid at 100 Mc/S

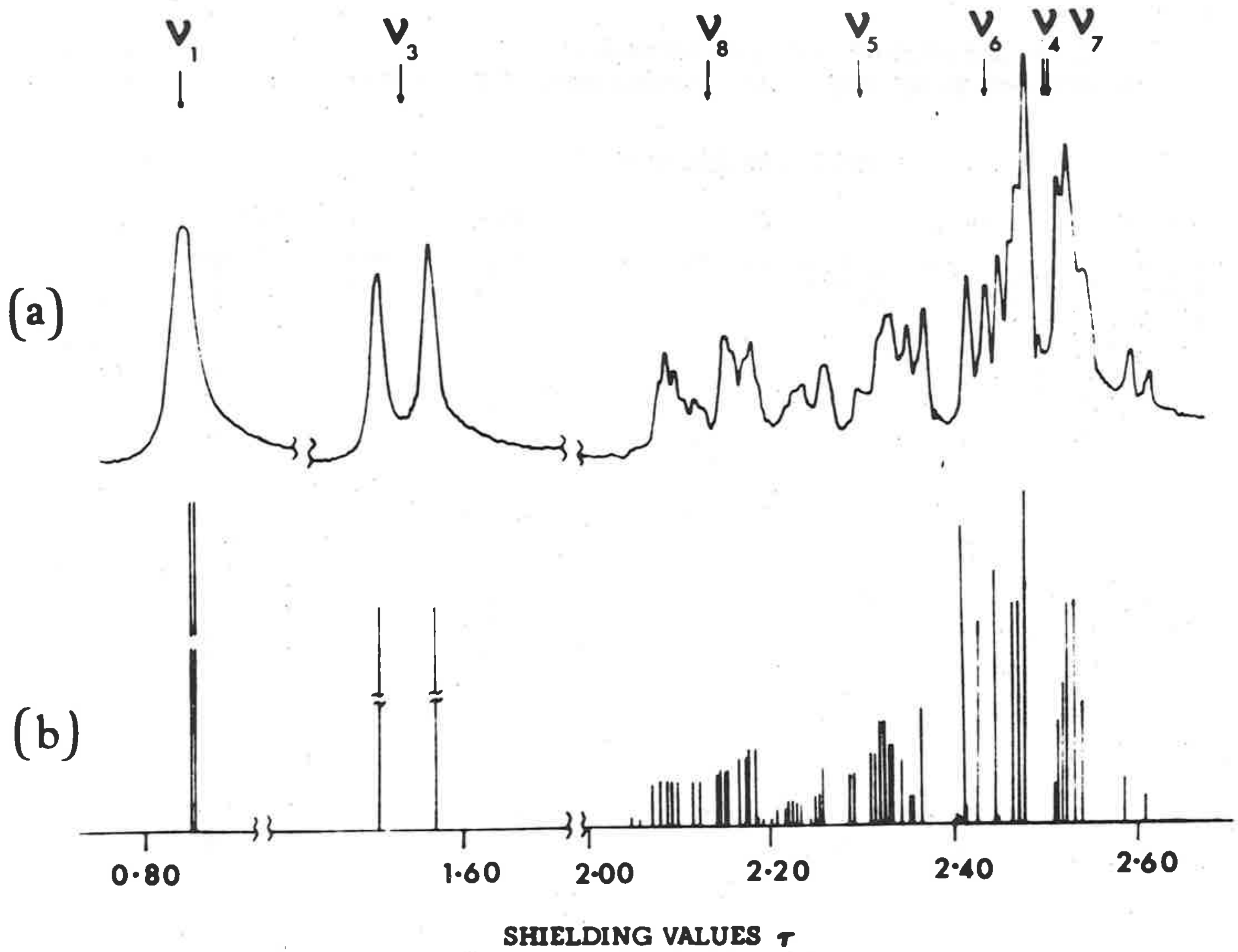


Figure 2 (a) Experimental and (b) Calculated spectrum of isoquinoline (0.063 g/ml in CCl_4) at 100 Mc/s

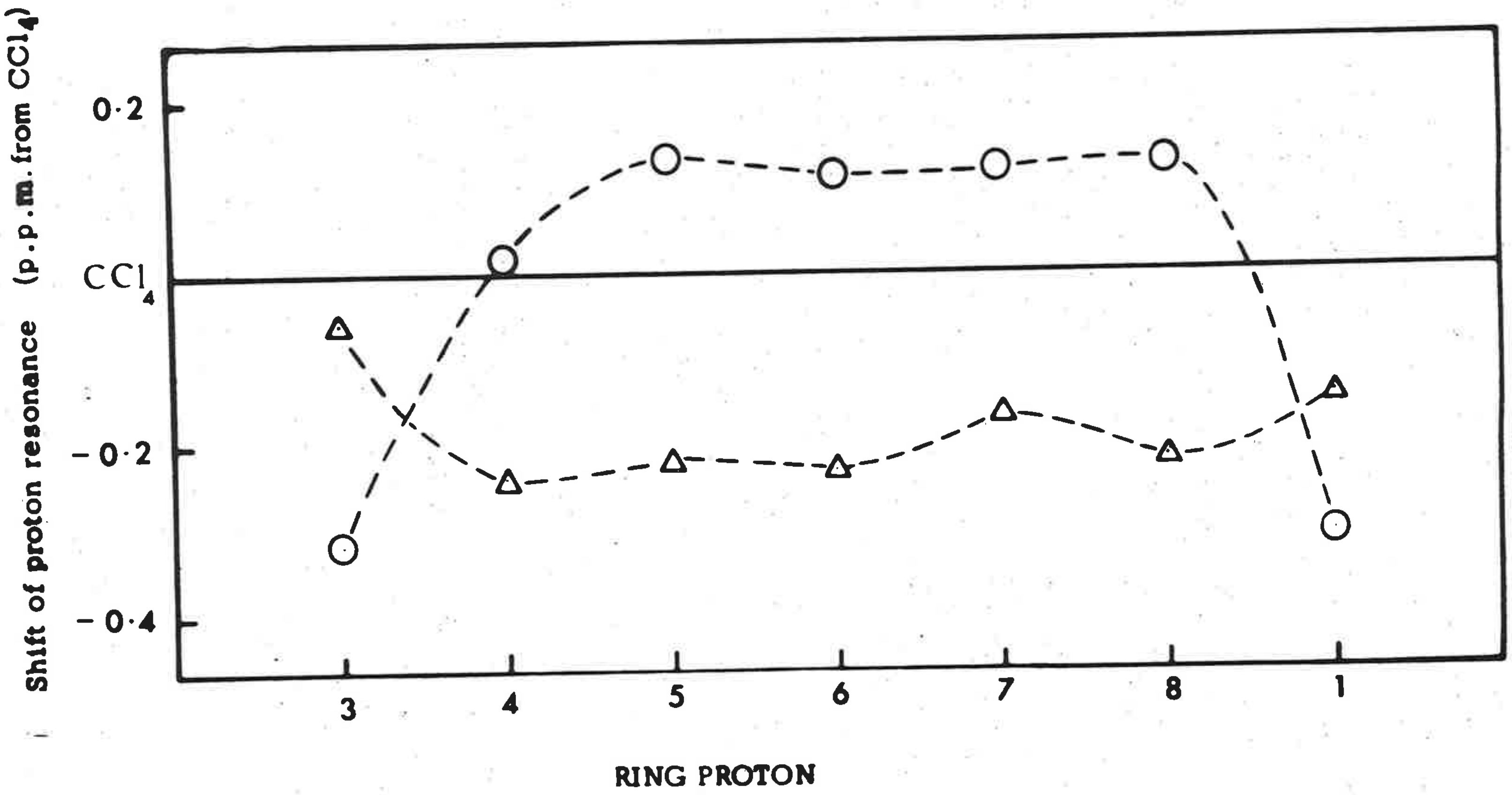


Figure 3. Shifts of ring protons in isoquinoline relative to their positions in CCl_4 solution; △ acetone solution; ⊙ pure liquid

POLAROID CORPORATION
CAMBRIDGE 39, MASSACHUSETTS

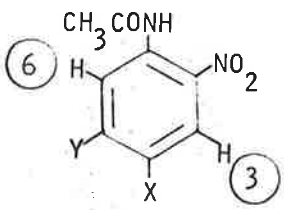
November 29, 1965

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

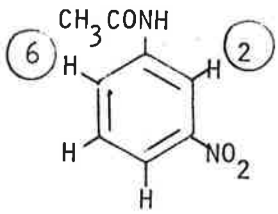
Selective Deshielding of Aromatic Protons in some Nitro Acetanilides

Dear Barry:

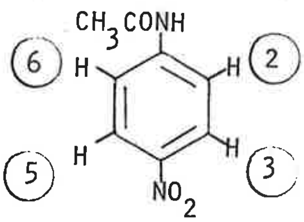
We have examined several nitro acetanilides on our A-60 spectrometer and find that certain o-nitroacetanilides exhibit signals at unusually low field for the aromatic proton adjacent to the acetamido group and for the amido proton itself. Our results are summarized in the Table.



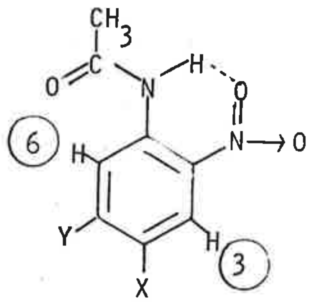
I a $X=Y=H$
b $X=CH_3\ Y=H$
c $X=H,\ Y=OCH_3$



II



III



IV

TABLE

		τ Values					
		$CDCl_3$, 30°			CH_3CN, 70°		
		H-3	H-6	NH	H-3	H-6	NH
Ia	2-nitroacetanilide	1.80	1.23	-0.29	1.82	1.51	0.18
Ib	4-methyl-2-nitroacetanilide	1.95	1.31	-0.25	2.03	1.69	0.31
Ic	5-methoxy-2-nitroacetanilide	1.83	1.58	-0.75	1.75	1.68	-0.45
II	3-nitroacetanilide		*		H-2: 1.36	~2.2	1.19
III	4-nitroacetanilide		*		H-3,H-5: 1.75	H-2,H-6: 2.16	1.13

* insufficient solubility in deuteriochloroform

The splitting patterns in the substituted nitroacetanilides Ib and Ic permit unambiguous assignment of the aromatic proton signals[1]. In both compounds the H-6 proton resonance appears consistently at lower field than the H-3, in acetonitrile as well as in chloroform-d. For o-nitroacetanilide itself (Ia) the assignment of the pair of doublets at lower field to the H-6 proton and the pair of doublets at 1.8τ to the H-3 proton follows logically.

We believe that the resonance of H-6 at low field results from intramolecular hydrogen-bonding in o-nitroacetanilides, already demonstrated by infra-red[2] and ultra-violet[3] spectral studies. Such hydrogen-bonding might be expected to favor the conformation (IV), in which the N-H and C=O groups have the trans relation typical of acyclic amides. In this conformation the H-6 proton should experience the strong deshielding effect resulting from the particular proximity of the carbonyl group. This conclusion is supported by the following evidence:

1. The appearance of the broad N-H signal in compounds Ia, b and c at lower field than is normal for simple anilides, confirming the existence of intramolecular hydrogen-bonding.
2. The entirely normal behavior of 3-nitroacetanilide (II) and 4-nitroacetanilide (III) which exhibit N-H and aromatic proton resonances at positions expected in the absence of intramolecular hydrogen-bonding.
3. The unusual solvent sensitivity of the H-6 resonance in the o-nitroacetanilides (Ia-c), which is reasonable if the polar solvent acetonitrile at 70° is effective in breaking down some of the intramolecular hydrogen-bonding present in chloroform solution. The reduction in population of molecules having conformation (IV) would diminish the net deshielding effect of the carbonyl group on the H-6 proton and also lead to the observed upfield solvent shift of the N-H proton.
4. The resonance of the amido proton in Ic appears at lower field than the equivalent protons in Ia and Ib by about 0.5-0.7 ppm. The solvent dependence of this amido proton as well as of H-6 is less in Ic than in Ia and Ib, all of which can be explained by stronger intramolecular hydrogen-bonding in Ic owing to increased electron density of the nitro-oxygens under the influence of the para methoxy group.

Further systems in which related intramolecular hydrogen-bonding is likely are currently under study.

We wish to thank Mrs. Patricia Morrison and Mr. Martin Mach for valuable assistance in the determination of the spectra.

Sincerely,

James R. Bartels-Keith
Ronald F. W. Cieciuch

James R. Bartels-Keith
Ronald F. W. Cieciuch

1. Relevant coupling constants lay within the ranges 7.5-10.0 c./sec. for $J_{HH(ortho)}$ and 1.5-3.0 c./sec. for $J_{HH(meta)}$.

2. e.g. a) E. J. Forbes, K. J. Morton, and J. Newton, J. Chem. Soc. 835 (1963),
b) L. Skulski, J. Org. Chem. 28, 3565 (1963).

3. a) H. E. Ungnade, J. Amer. Chem. Soc., 76, 5133 (1954).
b) A. E. Lutskiĭ, V. N. Konel'skaya, and B. P. Kondratenko, Zhur. Obshcheĭ Khim. 30, 3782 (1960), C.A. 55, 19472 (1961).

POLAROID CORPORATION
CAMBRIDGE 39, MASSACHUSETTS

January 6, 1966

Professor Bernard Shapiro
Illinois Institute of Technology
Chicago, Illinois, 60616

Dear Barry:

Since mailing in our communication on "Selective Deshielding of Aromatic Protons in some Nitroacetanilides" we noticed the letter of Dr. Sternhell in the January 1965 issue of IITNMRN, No. 76, page 2. We regret having missed this previously and would like to note at this time Dr. Sternhell's prior reporting of the phenomenon that we came upon independently.

Of some relevance also is the letter of Dr. Anteunis in the March 1965 issue, No. 78, page 31.

With best wishes for the New Year.

Sincerely,

POLAROID CORPORATION

James Bartels-Keith

Ronald F. Cieciuch

James Bartels-Keith
Ronald F. Cieciuch

UNIVERSITY OF SOUTH FLORIDA
TAMPA, FLORIDA 33620
AREA CODE 813: 988-4131
DEPARTMENT OF CHEMISTRY

January 3, 1966

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

Dear Dr. Shapiro:

I hope this brief note will serve as notification of my new address and also to keep my subscription to IITNMR going. I'm finally getting settled and trying to put the A-60 here to good use.

The last few months I was still at Texas we were doing some C^{13} work and were using a NDC-800 Enhancetron which was available to improve S/N. Since several people voiced an interest in the use of such computers, especially on instruments besides the A-60, I've included a circuit diagram of the trigger we used to correlate the magnetic field sweep of our DP-60 with the Enhancetron memory storage. Part (a) of the circuit utilizes the V-4352 linear sweep flyback to trigger the Enhancetron storage while (b) provides a suitable trigger signal if the S/N of a peak in the spectrum exceeds 3/1. A little care is required to adjust memory sweep and field sweep times but both modes have been used to advantage. We also found Jim Shooling's 2000 c.p.s. sideband, direct absorption technique very successfully with 12 mm OD spinning samples that were plugged to prevent a vortex. A number of metal carbonyls, prepared in vacuum, were observed this way.

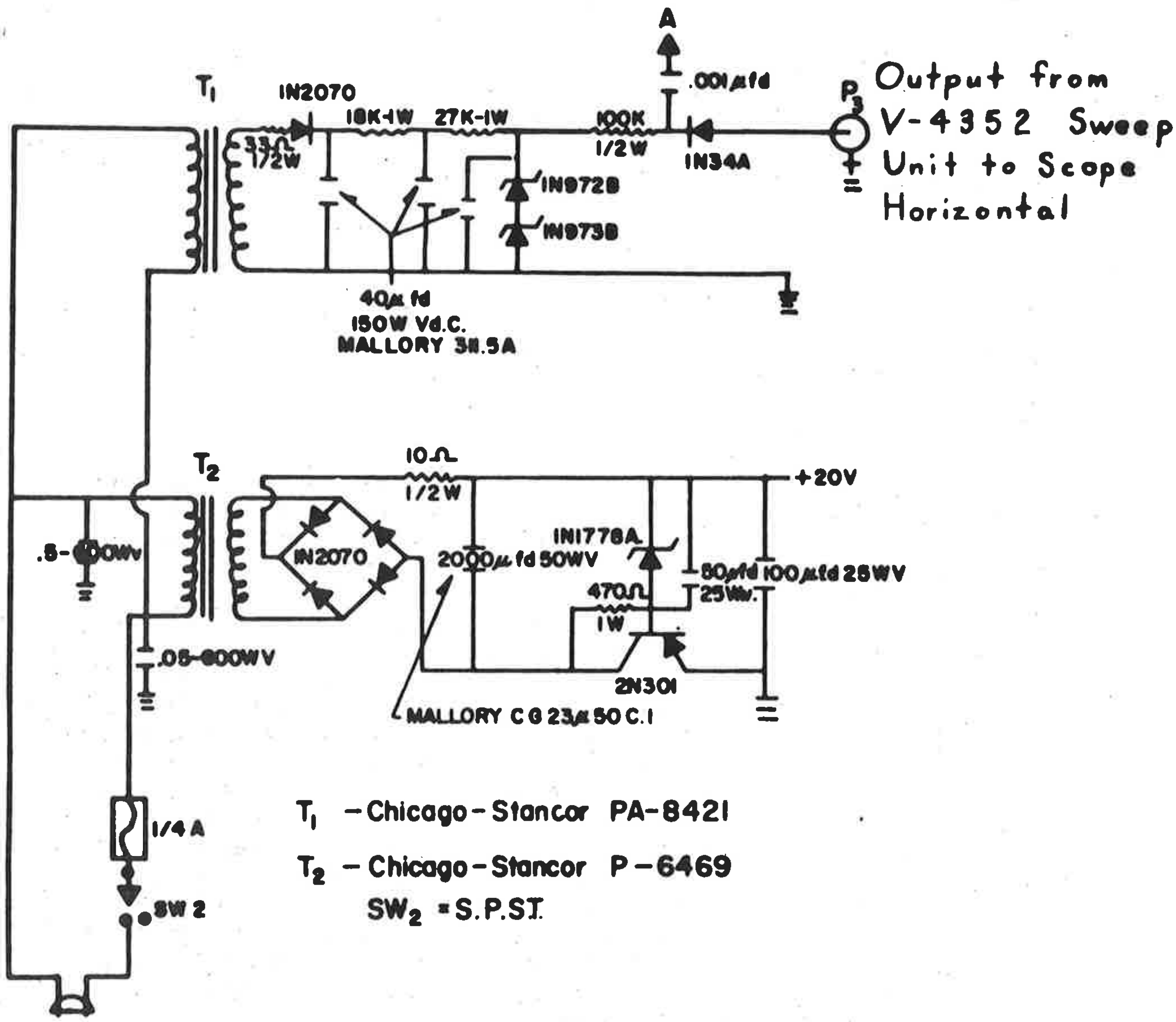
I hope I'll be able to report on some of our other work in the near future.

Sincerely yours,

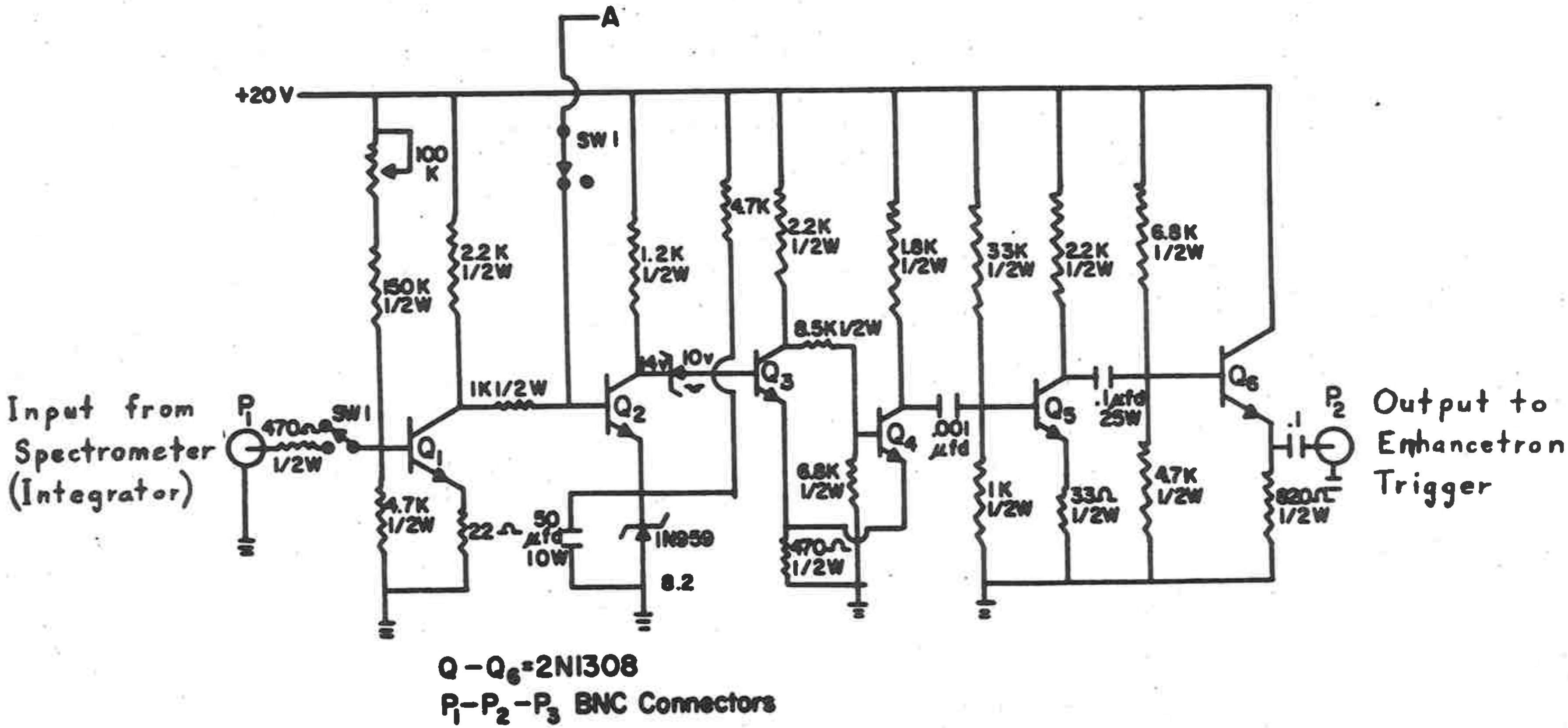
Jeff

Jeff C. Davis, Jr.
Associate Professor

JCD:sdd


A
.001μfd
T1
IN2070
18K-1W
27K-1W
100K
1/2W
IN34A
P3
Output from V-4352 Sweep Unit to Scope Horizontal
33Ω 1/2W
IN972B
IN973B
40μfd
150W Vd.C.
MALLORY 3II.5A
T2
10Ω
1/2W
+20V
IN2070
.5-600WV
IN1778A
2000μfd 50WV
80μfd 25Wv.
100μfd 25WV
470Ω
1W
2N301
.05-600WV
MALLORY CG 23μ 50 C.I
1/4A
SW 2
T1 - Chicago-Stancor PA-8421
T2 - Chicago-Stancor P-6469
SW2 = S.P.S.T.

a


A
+20V
SW1
100 K
150K 1/2W
2.2K 1/2W
1.2K 1/2W
4.7K
2.2K 1/2W
1.8K 1/2W
33K 1/2W
2.2K 1/2W
6.8K 1/2W
8.5K 1/2W
14v
10v
1K 1/2W
Q1
Q2
Q3
Q4
Q5
Q6
Input from Spectrometer (Integrator)
P1
470Ω 1/2W
4.7K 1/2W
22Ω
50 μfd 10W
1N959
8.2
6.8K 1/2W
470Ω 1/2W
.001 μfd
.1μfd 25W
1K 1/2W
33Ω 1/2W
4.7K 1/2W
820Ω 1/2W
.1
P2
Output to Enhancetron Trigger
Q - Q6 = 2N1308
P1-P2-P3 BNC Connectors

b

STERLING-WINTHROP RESEARCH INSTITUTE
A DIVISION OF STERLING DRUG INC.
RENSSELAER, NEW YORK

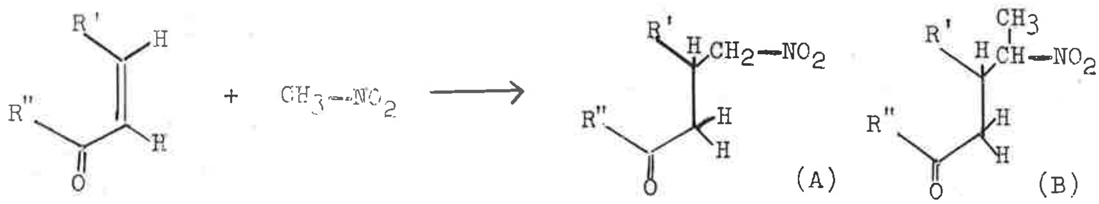
December 10, 1965

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

Dear Professor Shapiro:

May I submit an example of deceiving simplicity in a PMR-spectrum and, by doing so, restore my good standing on the mailing list.

One of our colleagues obtained a product from a Michael-addition of nitromethane to an unsaturated ketone:



He expected this product to have structure A. The observed signals at about 4.6 ppm (Fig. 1) obviously have neither the features expected for an "equivalent methylene group" nor the usual pattern for a "nonequivalent methylene group." Who will blame me for looking for unusual and fancy structures which were compatible with the observed facts.

When the spectrum of the compound which was obtained from the corresponding reaction with nitroethane (B) showed a doublet for the methyl group, I began to calculate. To my surprise I found that this observed pattern could be readily interpreted as an AB(X)-case:

$\nu_0 \delta_{AB} = 4.1$ cps, $J_{AB} = 12.3$; $J_{AC} = -11.65$; $J_{BC} = -3.45$.

Transition[1]	Calculated	Observed	Intensity (Calc.)
1	284.9	286	0.17
2	291.1	--	0
3	272.6	273.2	1.83
4	278.8	278.8	2.0
5	270.0	270.8	1.83
6	278.9	278.8	2.0
7	257.7	258	0.17
8	266.5	--	0

[1] The number of the transitions corresponds to Pople, Schneider, Bernstein "High-resolution NMR" p.134.

The presence of the weak lines 1 and 7 was confirmed by a "mouse-track." (Fig. 2)

Sincerely yours,

R. K. Kullnig

R. K. Kullnig

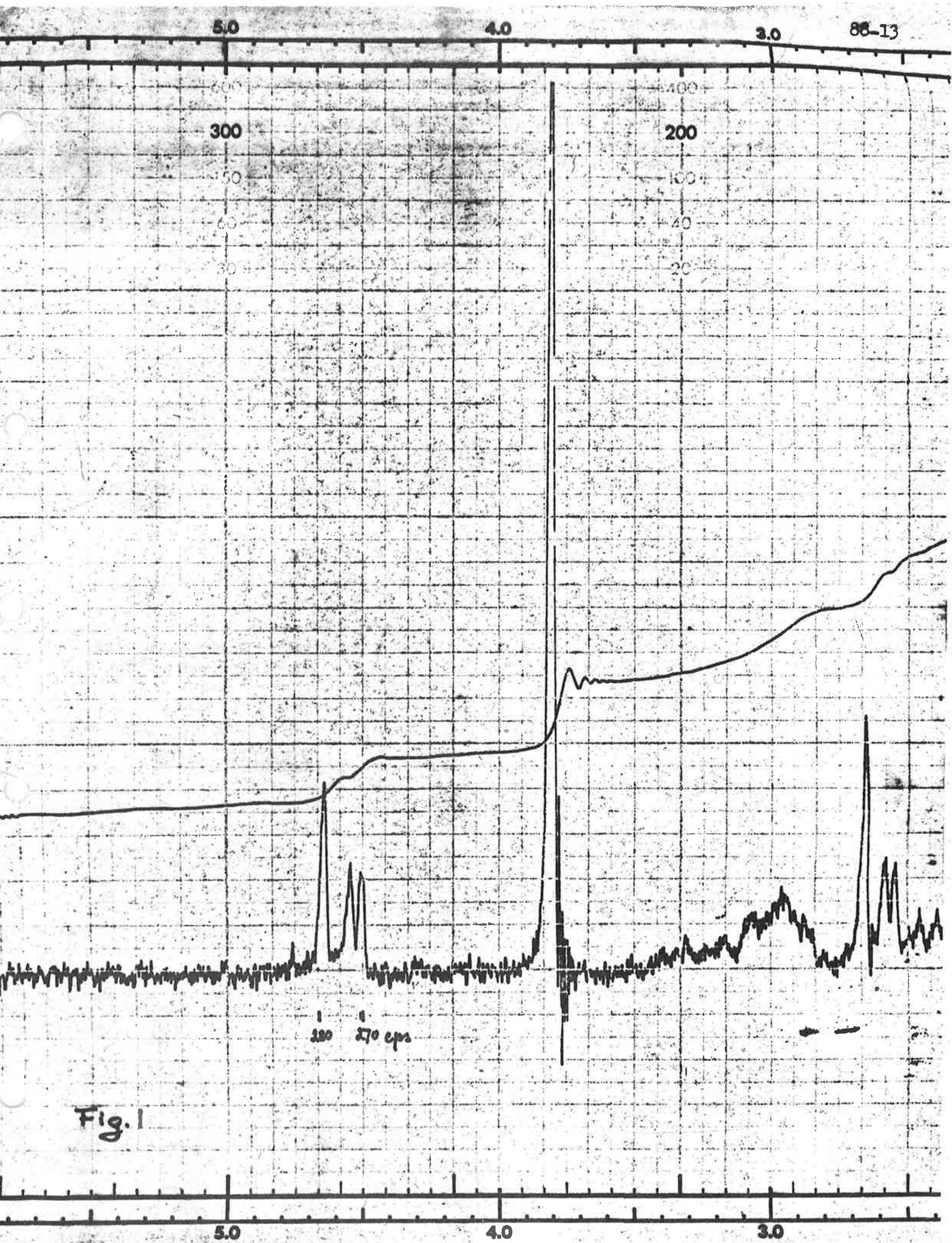


Fig. 1

88-14

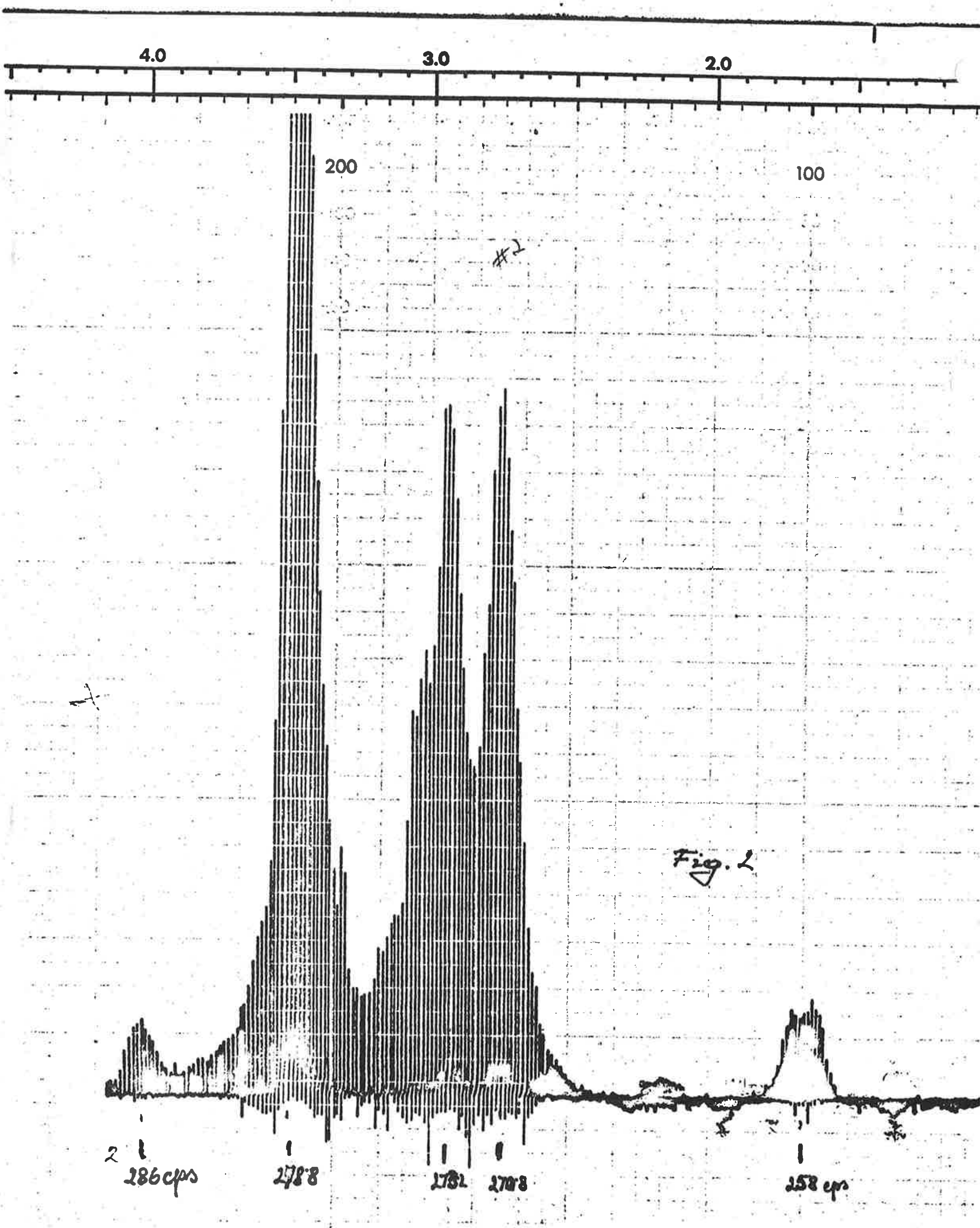


Fig. 2

UNIVERSITY OF CALIFORNIA, LOS ANGELES

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

DEPARTMENT OF CHEMISTRY
LOS ANGELES, CALIFORNIA 90024

December 30, 1965

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

Dear Barry,

N.M.R. of 1,4-dichalcogenocyclohexanes

I won't blame anybody if I hear of complaints about our chosen title; this is simply the result of applying nomenclature rules without regard for phonetics.

We have characterized a series of 1,4-diheterocyclohexanes of the group VI elements (provided to us by Professor J.D.McCullough of these laboratories) in anticipation of their use as ligands in transition metal complexes (of which such an application has already appeared in the literature).[1] The symmetrical derivatives, 1,4-X,X , display a single sharp line (half-intensity band width 0.5 cps). The unsymmetrical derivatives, 1,4-X,O , show two groups of lines for which a typical spectrum is given in Fig. 1; the protons in the unsymmetrical derivative 1,4-S,Se were very nearly equivalent.

Each of the lines on spectra similar to that shown on Fig. 1 is actually a closely spaced doublet (line width at half-intensity, 0.9 cps; TMS at these conditions, 0.3 cps). These spectra were analyzed essentially by the procedure outlined in a recent report of spectra of other 1,4-diheterocyclohexanes.[2] Our calculations were performed on the improved[3] NMRIT-NMREN programs of Reilly and Swalen. The data on the present compounds and some previously determined compounds is presented in Table 1.

Satellites arising from magnetically active hetero-atoms are satisfactorily resolved for coupling to α-protons and less well separated for β-coupling. ^{13}C coupling constant was found to depend mainly on the heteroatom attached to a particular methylene group (α) and very little on the other heteroatom (β) in the molecule, when it was different than α. The chemical shift of the protons, strongly dependent on the α-hetero atom , also show some significant dependence on the β-hetero atom (when different than α).

The spectra show that these compounds are rapidly equilibrating chair forms at temperature of investigation (30^{o}). No change was observed in the spectrum of selenoxane from +170 to -70 ^{o}C , in marked contrast to behavior noted for 4,5-tetra-deutero-1,2-dithiane,[4] and the substituted thioxanes recently reported in IITNMR.[5]

References listed bottom of Table 1

Sincerely yours,

Herb

M.L.Maddox and Herbert Kaesz
Associate Professor

CC: Prof. J.D.McCullough, U.C.L.A.

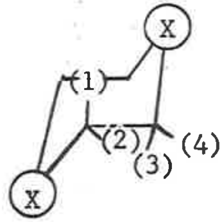


Table 1

Proton Magnetic Resonance Data (Varian A-60) on 1,4-dichalcogenocyclohexanes.

X	X'	tau δ_{CH_2}	tau $\delta_{CH'_2}$	c.p.s. ΔJ_{gem} (2)	c.p.s. $J_{1,3}$	c.p.s. $J_{1,4}$	c.p.s. $J_{^{13}C-H}$
O	O (2)	6.30					
S	S	7.48_7					138.0
Se	Se*	7.28_7					140.0
O	S (2)	6.12	7.43	1.9_7	2.6_5	7.3_5	
O	S	6.13_5	7.43_3				138.0
O	Se‡	6.00_4	7.38_1	1.7_4	2.7_5	7.3_5	142.0 140.0
O	Te§	5.98_7	7.31_2	1.6_3	2.9_5	7.4_9	142.0 139.5
S	Se**	7.28_7					

*) J(Se-C-H) 11.6_0
‡) " " ±14.0 J(Se-C-C-H) ∓ 5.2
**) " " 11.0
§) J(Te-C-H)±29.5 J(Te-C-C-H) ∓ 9.6
cps

References

(1) H.C.E.McFarlane and W. McFarlane, J. Inorg. Nucl. Chem., 27,1059 (1965).
(2) W.B.Smith and B.A.Shoulders, J. Phys. Chem., 69,579 (1965).
(3) R.C.Ferguson and D.W.Marquardt, J. Chem. Phys., 41, 2087 (1964) and IBM SHARE Publication SDA 3165.
(4) G. Claeson, G.M.Androes and M. Calvin, J. Am. Chem. Soc., 82,4428 (1960).
(5) P.W.Henniger, Th.J.Sekuur and N. de Wolf, IITNMR No.86, p. 58 (1965).

Table 1 -- M.L.Maddox and H.D.Kaesz

Fig. 1 M.L.Maddox and H.D.Kaesz

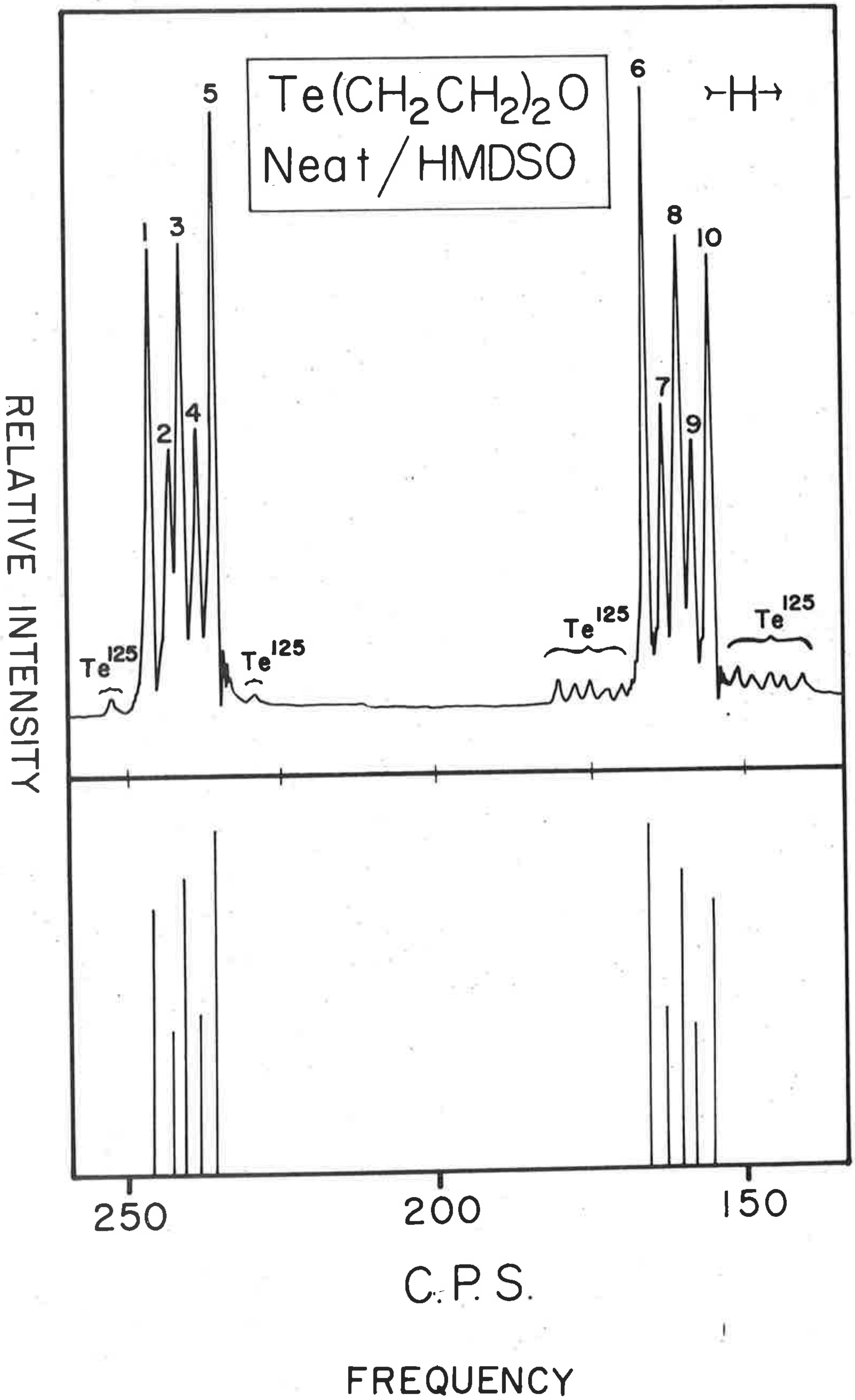


FIGURE 1

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN

Dr. H. Günther

KÖLN, Dec. 15, 1965
ZÜLPICHER STRASSE 47
TELEFON: 2024239

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

U S A

NMR of Cyclic Olefins

Dear Barry,

The enclosed communication summarizes results we have obtained recently for cyclic dienes and trienes. The compounds studied were of interest in connection with our investigations of cyclodecapentaenes and oxepines and the synthetic work of Prof. E. Vogel and his group.

The complete analysis of the spectra clearly shows, that the different appearance of diene- and triene-system, mentioned earlier (IIT-NMR-Newsletter 76-20) is due mainly to the different size of the parameter N in diene- and triene-type AA'BB'-spectra and speculations about the influence of the double bond anisotropy on chemical shifts are not necessary in this case.

Sincerely yours,

H. Günther H.-H. Hinrichs

^{1}H-NMR-SPEKTREN CYCLISCHER DIENE UND TRIENE [1]

Von Dr. H. Günther und Dipl.-Chem. H. H. Hinrichs
Institut für Organische Chemie der Universität Köln

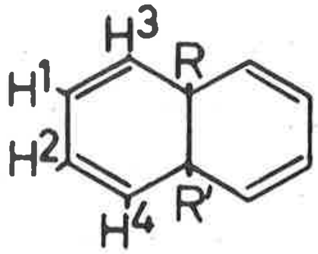
NMR-spektroskopische Untersuchungen an überbrückten Cyclodecapentaenen [2] und am Oxepin [3] veranlaßten uns zum Studium cyclischer Olefine mit verwandten Strukturen. In Tabelle 1 sind die bisher an cyclischen Hexadien-(1.3)- und Heptatrien-(1.3.5)-Systemen erhaltenen Ergebnisse zusammengestellt [4]. Die angegebenen Parameter wurden für (1) - (6) durch komplette Analyse der Spektren vom A_2B_2-Typ [5], für (7) und (8) durch partielle Analyse für ß- und γ-Protonen und für (9) durch komplette Analyse des $A_2B_2C_2$-Systems bestimmt [6].

Die Gegenüberstellung läßt charakteristische Unterschiede zwischen den Kopplungskonstanten beider Systeme erkennen: $J_{12}^{Dien} < J_{12}^{Trien}$; $J_{13}^{Dien} > J_{13}^{Trien}$; $J_{34}^{Dien} > J_{34}^{Trien}$. Die Analyse des Spektrums erlaubt danach in fraglichen Fällen (z.B. bei Norcaradien-Cycloheptatrien Valenztautomeren) eine eindeutige Strukturzuordnung. Der Parameter N (= $J_{13} + J_{14}$) beträgt für die untersuchten Diene ca. 10 Hz, für die Triene dagegen nur ca. 6 Hz. Da N in vielen Fällen dem Spektrum direkt entnommen werden kann [10], ist ein Hinweis auf das Vorliegen der einen oder anderen Struktur auch auf einfache Weise erhältlich.

Beim Oxepin findet man bei Raumtemperatur die aufgrund des nachgewiesenen Gleichgewichts mit dem Benzoloxyd [3] zu fordernden Mittelwerte der Kopplungskonstanten. Die Temperaturabhängigkeit [11] dieser Parameter bestätigt den prinzipiell möglichen Nachweis einer schnellen Valenztautomerie zwischen Verbindungen vom Norcaradien- und Cycloheptatrientyp durch Analyse des Spektrums bei verschiedenen Temperaturen (vergl. hierzu auch Ref. [8]).

T A B E L L E 1 [7]

A) Parameter im Cyclohexadien-(1,3)-System

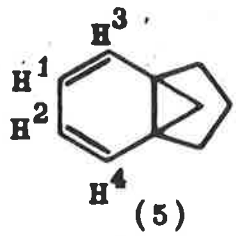


(1) R = R' = $COOCH_3$

(2) R-R' = -CO-O-CO-

(3) R-R' = $-CH_2OCH_2-$

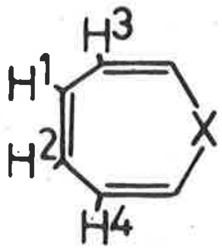
(4) R-R' = $-CH_2-CH_2-$



(5)

	$\nu_0\delta$	J_{12}	$J_{13}=J_{24}$	$J_{14}=J_{23}$	J_{34}
(1)	11.78	5.41	9.59	0.90	0.88
(2)	22.78	5.88	9.51	0.75	0.96
(3)	19.65	5.35	9.55	0.89	0.88
(4)	25.51	5.48	9.71	0.72	1.09
(5)	21.65	5.94	9.25	0.58	1.31

B) Parameter im Cycloheptatrien-(1,3,5)-System



(6) X = CH_2; α,α'-Dimethyl-

(7) X = CH_2

(8) X = $N-COOC_2H_5$

(9) X = O

	$\nu_0\delta$	J_{12}	$J_{13}=J_{24}$	$J_{14}=J_{23}$	J_{34}	
(6)	27.54	11.20	5.39	0.73	-0.20	
(7)	24.42	11.04	5.58	0.68	-0.12	[2],[8]
(8)	35.74	11.44	5.43	0.65	-0.03	
(9)	27.62	9.68	6.80	0.73	-0.16	[9]

[7] Alle Werte in Hz; Spektren wurden, wenn nicht anders vermerkt, in CCl_4 (1 molar bzw. 20 Vol%) mit einem Varian A 60 Spektrometer bei 60 MHz aufgenommen.

[1] III. Mitteilung der Reihe "PMR-Spektroskopie ungesättigter Ringsysteme"; II. Mitteilung siehe Ref. [3]. Teil der geplanten Dissertation von H. H. Hinrichs. Herrn Prof. Dr. E. Vogel danken wir für sein förderndes Interesse.

[2] H. Günther, Z. Naturforschg. 20 b, 948 [1965].

[3] H. Günther, Tetrahedron Letters 1965, 4085.

[4] Eine ausführliche Diskussion der Ergebnisse folgt an anderer Stelle. Zur Synthese der untersuchten Verbindungen siehe: E. Vogel, W. Meckel und W. Grimme, Angew. Chem. 76, 786 [1964], (1) - (3); E. Vogel, W. Maier und J. Eimer, Tetrahedron Letters, im Druck, (4); E. Vogel, W. Wiedemann, H. Kiefer und W. F. Harrison, ebenda 1963, 673 (5); E. Vogel und H. D. Roth, unveröffentlicht, (6); K. Hafner und C. König, Angew. Chem. 75, 89 [1963], (8); E. Vogel, W. A. Böll und H. Günther, Tetrahedron Letters 1965, 609, (9). Den Herren Prof. Dr. K. Hafner, Dipl.-Chem. W. Meckel, Dipl.-Chem. W. Maier, Dr. H. D. Roth und Dr. W. A. Böll danken wir für die Überlassung von Substanzproben.

[5] Die Wechselwirkung zwischen den Protonen auf verschiedenen Seiten der 9.10-Bindung in den Dihydronaphthalinen liegt unterhalb der Nachweisgrenze.

[6] Alle Parameter wurden durch iterativen Angleich der berechneten an die experimentellen Spektren mit Hilfe des Rechenprogrammes LAOCOON II (S. Castellano und A. A. Bothner-By, J. chem. Phys. 41, 3863 [1964]) erhalten. Die wahrscheinlichen Fehler sind kleiner als 0.1 Hz. Die Spektren von (6) - (9) sind gegenüber Änderungen von J_{34} wenig empfindlich. Der Fehler dieses Parameters dürfte deshalb größer sein (ca. 0.2 Hz). Die Rechnungen wurden am Rheinisch-Westfälischen Institut für Instrumentelle Mathematik, Bonn, ausgeführt.

[8] Diese Verbindung wurde inzwischen auch von anderer Seite analysiert: J. B. Lambert, L. J. Durham, P. Lepoutere und J. D. Roberts, J. Amer. chem. Soc. 87, 3896 [1965].

[9] In CS_2 aufgenommen.

[10] J. A. Pople, W. G. Schneider und H. J. Bernstein, "Highresolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc. New York 1959, S. 147; B. Dischler und G. Englert, Z. Naturforschg. 16 a, 1180 [1961].

[11] Über die Analyse des Oxepin-Spektrums und die Temperaturabhängigkeit der Parameter wird an anderer Stelle ausführlich berichtet.

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF ALBERTA
QUAECUMQUE VERA

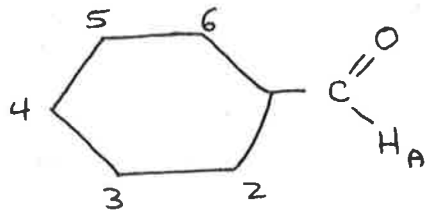
EDMONTON, ALBERTA
CANADA

December 17, 1965.

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

Dear Barry:

I've noticed that I seem to be in disagreement with the Kowalewskis on the values of couplings to the aldehyde proton in some p-substituted benzaldehydes (compare Kowalewski and Kowalewski, J. Chem. Phys. 37, 1009, to Martin and Dailey, ibid., 37, 2594). Bob Green, a student of mine, has been studying some unsaturated aldehydes on the HA100 with the idea of getting some conformational energy barriers, etc., and we hereby present our best values:



Substituents & positions	Observable couplings, c.p.s. at 32°C.
4 - Cl	$J_{A3} = J_{A5} = 0.42 \pm .02$
4 - Br	$J_{A3} = J_{A5} = 0.31 \pm .03$
3 - Cl, 4 - Cl	$J_{A5} = 0.35 \pm .03$
2 - Cl, 4 - Cl	$J_{A3} = J_{A5} = 0.78 \pm .05$
(these become unequal at low temperature)	
4 - $N(CH_3)_2$	$J_{A2} = 0.2 \pm 0.1$
	$J_{A3} = 0.42 \pm 0.05$

This last molecule shows evidence of an eight-bond aldehyde to N-methyl coupling, as shown in the accompanying spectra of the CHO proton. The increase in sharpness when the N-methyls are irradiated is evidence of a coupling of perhaps 0.01 or 0.02 c.p.s. It's reproducible; we've checked the possibility of its being second-order splitting via the ring protons, or an obscure dynamic effect; we think it is a real coupling.

We've been breaking off the locking piece of the pressure caps for the V4333 variable-temperature probe with alarming ease, and have replaced the bottom section with aluminum, as shown in the accompanying diagram.

We have found the reports of the experience of other laboratories with the HA100 and its associated equipment to be immensely valuable.

Many thanks.

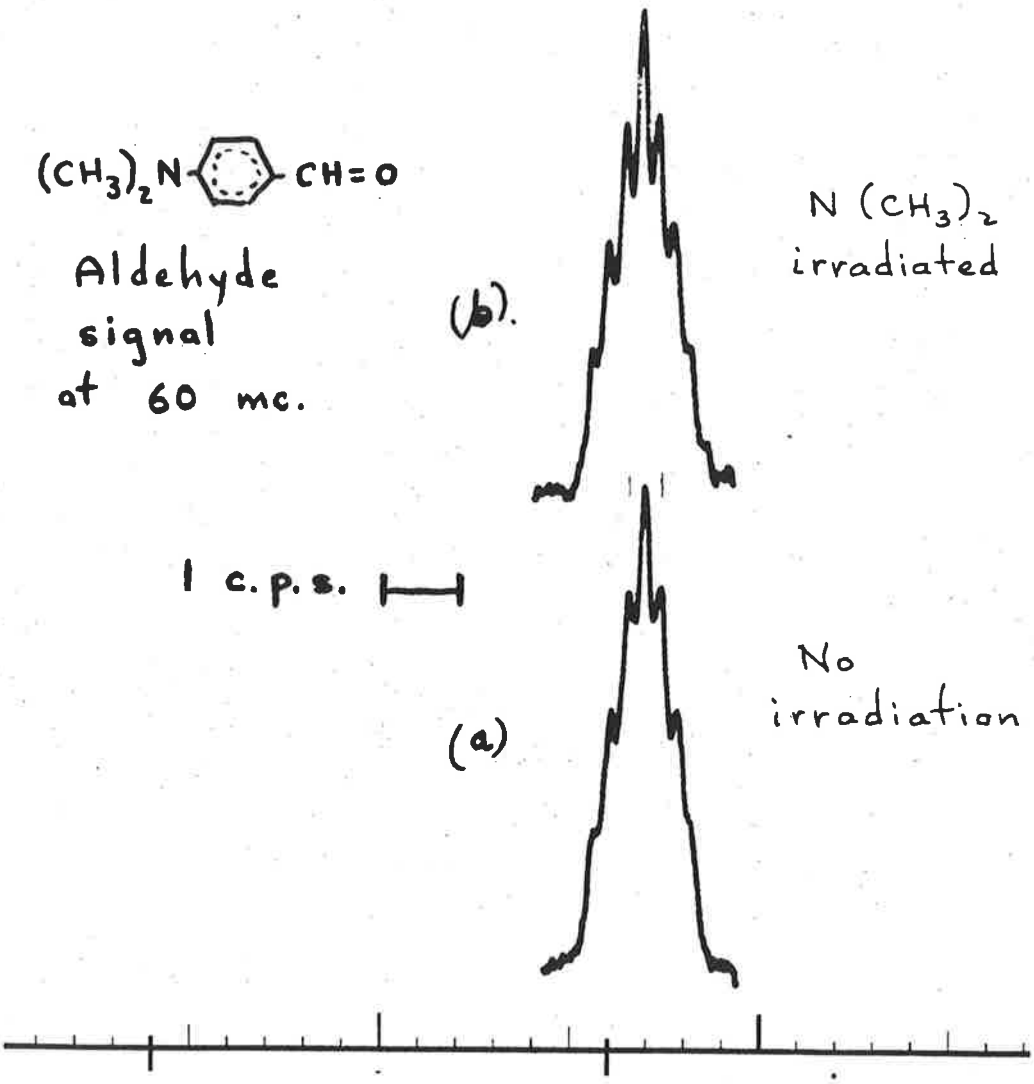
Sincerely,

John Martin

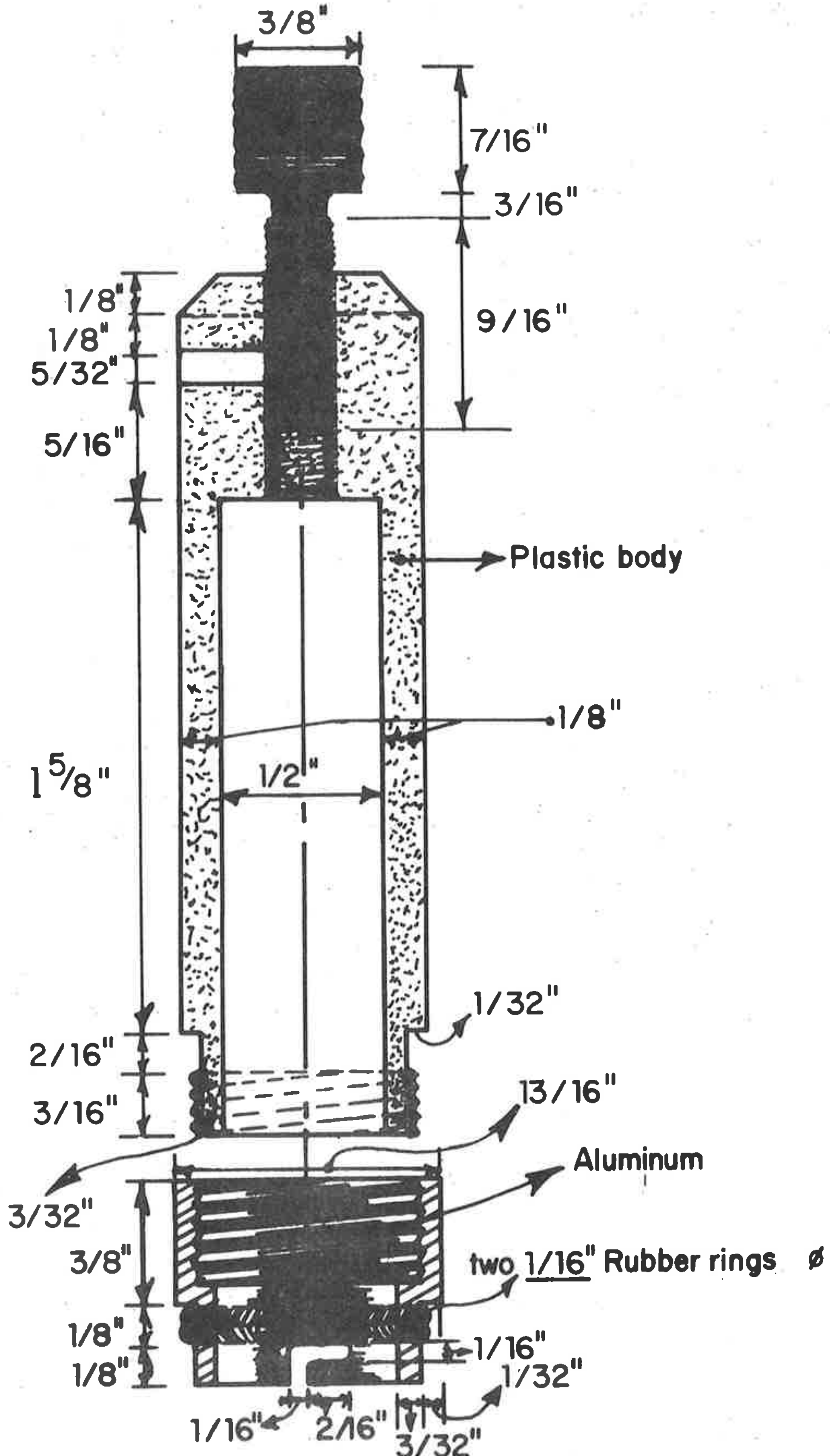
J.S. Martin

Suggested Titles: Benzaldehyde couplings; another long one; V4333 pressure cap modification.

Enclosures: 2 diagrams


$(CH_3)_2N-C_6H_4-CH=O$
Aldehyde
signal
at 60 mc.
(b).
$N(CH_3)_2$
irradiated
1 c.p.s.
(a)
No
irradiation

PRESSURE CAP MODIFICATION FOR VARIAN V 4333 Variable Temperature Probe



Dr. H. Fritz
c/o J.R. Geigy S.A.
Basle 21 (Switzerland)

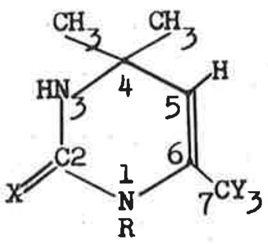
20th December, 1965

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

Long-range couplings with protons on Nitrogen

Dear Professor Shapiro,

We have observed rather unusual long-range couplings between protons on Nitrogen 3 and on Carbon 5 in compounds I a - d. 1)



I a - d

Comp.	X	R	Y
I a	O	H	H
I b	O	H	Br
I c	S	H	H
I d	S	CH_3	H

These couplings (J_{35}) are of the same magnitude as the allylic couplings J_{15} in I a - c and somewhat larger than J_{75} in I a, I c, and I d. The coupling constants are listed together with τ-values of the olefinic protons in the following table. 2)

Comp.	τ_5	J_{35} cps	J_{15} cps	J_{75} cps
I a	5.66	1.6	1.6	1.3
I b	5.13	1.5	1.5	-
I c	5.50	2.0	2.0	1.3
I d	5.28	2.6	-	1.3

In I b and I d the J-values can directly be read from the line spacings of the olefinic proton signals and verified by decoupling experiments.

In I a and I c the olefinic proton resonances are unresolved multiplets which upon irradiation at the position of the allylic CH_3 signal become triplets with splittings of 1.6 and 2.0 cps respectively.

After shaking the solutionswith a drop of aqueous 1 n NaOD all couplings with NH vanish, resulting in a quartet for the olefinic proton in I a, I c and I d and a singulet in I b.

Yours sincerely,

Hans Friz

---

1) The compounds were synthesized by Prof. Zigeuner, University of Graz, Austria. We are grateful to him for permission to report the above results prior to publication of his synthetic work.

2) The NMR-spectra were recorded on a HA-100 Spectrometer in approximately 5 % (w/v) solutions in $CDCl_3$. Spin-decoupling experiments were performed in the frequency-sweep mode.

UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA 15213
DEPARTMENT OF CHEMISTRY

22 December, 1965

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

Dear Barry:

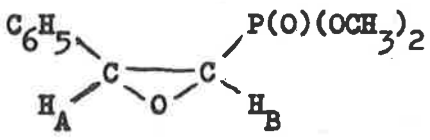
Asymmetry Effects in α,ß-Epoxyphosphonates

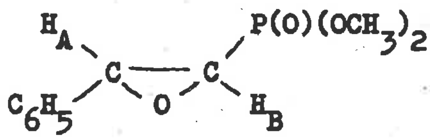
In a number of cases, the observed doubling of proton resonances in -P(O)(OR)$_2$ groups has been attributed to the presence of an asymmetric center in the molecule. A chemical shift difference of ca. 4 c.p.s. between the pairs of O-methyl doublets has been reported in a phosphonate [RR'C*HP(O)(OCH$_3$)$_2$] by Ramirez. A similar chemical shift difference has been reported by Bentrude for a phosphate system [RR'R"C*OP(O)(OCH$_3$)$_2$]. The methyl protons and the interacting asymmetric centers are separated by four and five bonds, respectively, in these examples.

We have recently examined the spectra of a number of α,ß-epoxyphosphonates and have observed similar asymmetry effects. In both the cis- (I) and trans- (II) epoxides, the O-methyl proton signals appear as pairs of doublets. The chemical shift difference between the doublets reflects the stereochemistry of the particular isomer, 7.2 c.p.s. in I and 1.6 c.p.s. in II. The doubling is not a result of restricted rotation since the spectra of I and II are unchanged over the range -30 to 125°. The same asymmetry effects are apparent in the methylene resonances of the ethyl analogs of I and II, although the assignment of chemical shift differences is difficult because of the complexity of the methylene multiplets.

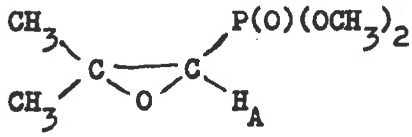
Compounds I and II possess two asymmetric centers, four and five bonds removed from the methyl protons. In order to determine which of these centers is responsible for the doubling phenomenon, the spectrum of III was examined. Two doublets with a 1.0 c.p.s. separation were observed for the O-methyl protons of III indicating, for this system at least, that the longer range five bond interaction is the more important. A similar lack of attenuation with distance of asymmetry induced nonequivalence has been observed by Roberts in alkyl benzenes.

The spectra of these compounds are also solvent sensitive. While I, II and III showed doubled O-methyl resonances in CCl_4 solution, nonequivalence is not observed in the spectra of neat samples. A study of these nonequivalence and solvent effects is continuing in this and other rigid systems.





	I	II
τ_B	6.72	6.97
τ_{CH_3}	6.70, 6.58	6.25, 6.22
J_{AB}	4.5	2.3
J_{PB}	27.4	30.2
J_{PCH_3}	10.5, 10.5	10.3, 10.3



III

τ_{OCH_3}	6.27, 6.25
τ_A	7.67
τ_{CCH_3}	8.57, 8.55
J_{POCH_3}	10.3, 10.3
J_{PA}	25.8
J_{PCCCH_3}	10.2, 7.7

Best regards,

C. E. Griffin   W. E. Byrne

R. H. Churi   M. P. Williamson

88-30

TELEPHONE : MW 0522.

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

The University of Sydney
Department of Organic Chemistry
SYDNEY, N.S.W.

IN REPLY PLEASE QUOTE :

30.12.65.

ALLYLIC COUPLING TO EXOCYCLIC VINYLIC PROTONS

Dear Barry,

We have noted previously on the basis of some scattered data[1] that in systems of type (I) the transoid allylic coupling constants (i.e. J_{AX}) appear to be larger than the cisoid allylic coupling constants (i.e. J_{BX}) which is the opposite of what is generally, but not always [2,3], found in acyclic systems. We have now examined compounds (II)-(V) and find the trend confirmed. Numbers are δ in c/s ex TMS for a 2% solution in CCl_4. While we intend to look at many more structures before considering this rule established, a tentative explanation can already be proposed:

The trend towards larger cisoid allylic coupling constants has been rationalised[2] on the basis of a contribution by a positive interaction carried through the sigma framework[4,5] which is at a maximum for the W-configuration, i.e. in the allylic cases for the transoid configuration with the allylic angle = 0° (c.f. VI). In systems with vinylic protons exocyclic (i.e. I), the allylic angle cannot approach 0° and hence this contribution is suppressed.

With best regards,

Yours sincerely,

G. P. Newsoroff

S. Sternhell.

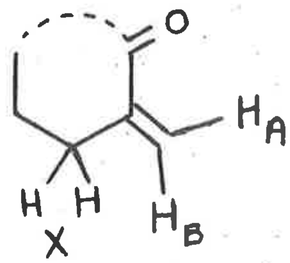
1. Brookes, Sternhell, Tidd and Turner, Aust. J. Chem., 18, 373 (1965)

2. Rottendorf, Sternhell and Wilmshurst, ibid., 18, 1759 (1965)

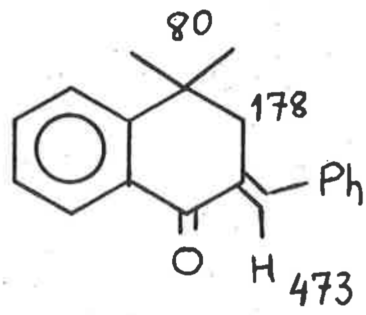
3. Sternhell, Rev. Pure Appl. Chem., 14, 15 (1964)

4. Barfield, J. Chem. Phys., 41, 3825 (1964)

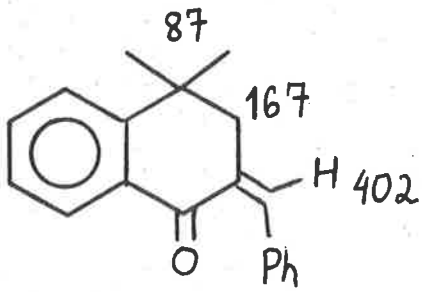
5. Garbisch, J. Am. Chem. Soc., 86, 5561 (1964).



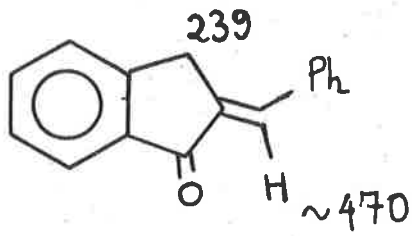
(I)



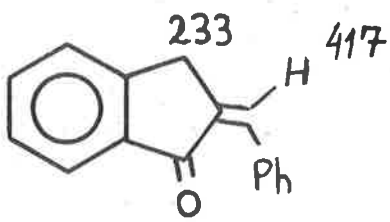
(II) $J_{allylic}$ = 1.78 c/s



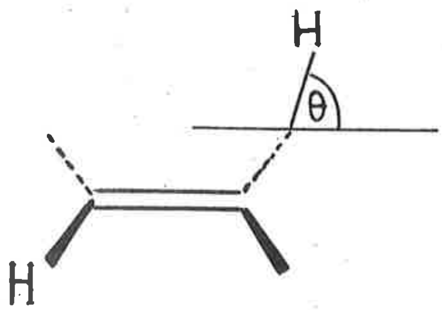
(III) $J_{allylic}$ = 1.35 c/s



(IV) $J_{allylic}$ = 1.95 c/s



(V) $J_{allylic}$ = 1.7 c/s



(VI)

88-32

HARVARD MEDICAL SCHOOL
THE DEPARTMENT OF PHARMACOLOGY
25 SHATTUCK ST., BOSTON, MASS. 02115

January 6, 1966

Professor Barry Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois

Dear Dr. Shapiro:

In a series of investigations of NMR spectra of peptides containing a glycine residue, we have observed in several cases magnetic non-equivalence of the two protons of glycine. Thus the signal of the Ch_2 protons shows an AB-type pattern with a gem-coupling constant of 16~17 c.p.s. Among glycylamino acids so far investigated, only glycyl-L-phenylalanine and glycyl-L-tryptophan show this splitting. On the other hand, among aminoacylglycines, the zwitterion forms of almost all peptides which have an α-asymmetric carbon atom in the aminoacyl group show the splitting. An aromatic group or a bulky alkyl group attached to the β-carbon increases the splitting. Although L-alanylglycine and L-leucylglycine show the splitting, L-alanylglycylglycine and L-leucylglycyl-L-leucine do not. The chemical shift difference between the two CH_2 protons is dependent on temperature and ionic strength. As temperature or concentration of LiCl increases, the chemical shift difference decreases by up to 30%.

Sincerely yours,

Oleg Jardetzky (AN) Asao Nakamura
Oleg Jardetzky Asao Nakamura

Enclosure

Table. Chemical shifts of glycine-CH_2 protons in peptides containing a glycine residue. c.p.s. from DSS as an internal reference (60 Mc., conc. 0.05M/1)

peptide	cation	zwitterion	anion
glycyl-L-alanine	231.4	228.8	199.3
glycyl-L-valine	233.7	232.6	201.3
glycyl-L-leucine	232.3	229.9	199.4
glycyl-L-isoleucine	233.5	231.7	200.8
glycyl-L-methionine	232.9	230.7	201.2
glycyl-L-serine	234.8	233.8	202.1
glycyl-L-proline	239.8	236.8	206.2
glycyl-L-aspartic acid	232.5	230.9[1], 228.9[2]	199.4
glycyl-L-glutamic acid	233.2	230.7[3], 230.2[4]	200.1
glycyl-L-lysine	233.0	233.5[5]	206.9[6], 200.3
glycyl-L-histidine	231.9	230.1[7], 220.4[8]	196.3
glycyl-L-tryptophan	{227.4, 221.2	-*	189.0
glycyl-L-phenylalanine	226.5	{227.1, 220.3	192.9
glycyl-β-alanine	226.9	226.4	196.6
L-alanylglycine	243.8	{231.2, 224.8	226.1
L-valylglycine	244.8	{235.2, 222.4	226.7
L-leucylglycine	244.0	{233.5, 221.5	225.5
L-serylglycine	245.5	{235.2, 226.4	227.4
L-prolylglycine	244.8	{230.5, 225.5	225.8
L-hydroxyprolylglycine	244.8	228.3	225.8
L-lysylglycine	243.8	228.2[9], 226.3[10]	225.9
L-histidylglycine	{245.8, 240.2	{235.1, 221.7[11], 226.3[12]	223.1
L-tryptophylglycine	{239.2, 232.6	{239.7, 215.4	216.3
L-phenylalanylglycine	239.0	{231.6, 213.3	{223.4, 217.3
L-tyrosylglycine	239.9	{232.0, 214.2	{225.6, 219.4
β-alanylglycine	241.0	226.0	225.2

1) pD 3.61, 2) pD 6.94, 3) pD 3.79, 4) pD 6.85, 5) pD 3.59, 6) pD 8.47, 7) pD 4.80, 8) pD 7.60, 9) pD 5.88, 10) pD 9.58, 11) pD 4.11, 12) pD 6.61.

* Solubility is not enough for the measurement.

88-34

THE UNIVERSITY OF MANCHESTER

MANCHESTER, 13.

FROM

PROFESSOR GEOFFREY ALLEN
PROFESSOR OF CHEMICAL PHYSICS
TELEPHONE: ARDWICK 3333

4th January 1965

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

Dear Professor Shapiro,

We report a study of coupling constants and chemical shifts in a series of mono-substituted pentachloro triphosphonitrile rings $N_3P_3Cl_5Y$, where Y = F, OMe, OEt, OPr^i, OCH_2CF_3, NMe_2. The spectra belong to the class AB_2R_p or $AB_2R_pX_q$ where A and B represent the ^{31}P nuclei and R and X are the magnetic nuclei in the substituent Y. A program written in Atlas Autocode was used to compute trial spectra. The results are sumarised below.

Y	$-F^a$	$-OCH_2CF_3$	$-OCH_3$	$-OCH_2CH_3$	$-OCH(CH_3)_2$	-Cl	$-N(CH_3)_2$
δ_A^* p.p.m.	14.4	16.5	16.7	13.6	12.6	19.6	22.7
δ_B^* p.p.m.	23.0	22.7	22.5	21.3	21.7	19.6	20.6
J_{AB} c/s	$\pm$ 78.3	66.2	63.3	63.3	62.7	-	49.7
J_{AR} c/s	$\mp$ 1012	10.5	16.5	10.2	11.3	-	18.3
δ_α^+ p.p.m.	-	4.58	3.84		4.76	-	2.68
δ_β^+ p.p.m.	-	-	-	1.42	1.42	-	-

* downfield from H_3PO_4

+ downfield from T.M.S. δ_α - α protons, δ_β - β protons in Y

a For $N_3P_3Cl_5F$ $J_{BR} = \mp 11$ c/s

The line-widths of the ^{31}P spectra were too great to allow the ^{31}P - β proton coupling constants to be measured ($J_{Ax} < 1$ c/s and $J_{Bx} \simeq 0$ c/s).

In the fluoroderivative J_{AB} and J_{BR} have opposite signs to J_{AR}. The relative signs could not be determined with confidence for the other compounds. This may be due in part to a variation in line-width in the observed spectra causing poor agreement with the calculated spectra (which assume a constant line-width) for the contours of overlapping multiplets. There is a variation in line-width in the spectra of the monofluoro compound also but it is not troublesome because each line is discrete. The variation is consistent with a relaxation mechanism in which the efficiency of relaxation depends on the F_z value for the transition.

Broadly speaking the magnitudes of $\delta_A - \delta_B$ and J_{AB} increase with increasing electron withdrawing power of the group Y.

We are extremely grateful to Dr. H. Verenkamp of the University of Munich for providing us with excellent ^{31}P spectra at 40 mc/s.

Yours sincerely,

Geoff. Allen, F. Heatley, R.F. Warren.

G. Allen,
F. Heatley,
R. F. Warren.

Short title: N.M.R. spectra of monosubstituted chloro triphosphonitriles.

ROCHE PRODUCTS LIMITED
WELWYN GARDEN CITY, HERTS, ENGLAND
TELEPHONE: WELWYN GARDEN 28128 TELEGRAMS: ROCHE, WELWYN GARDEN CITY

AAW/GS

4th January, 1966

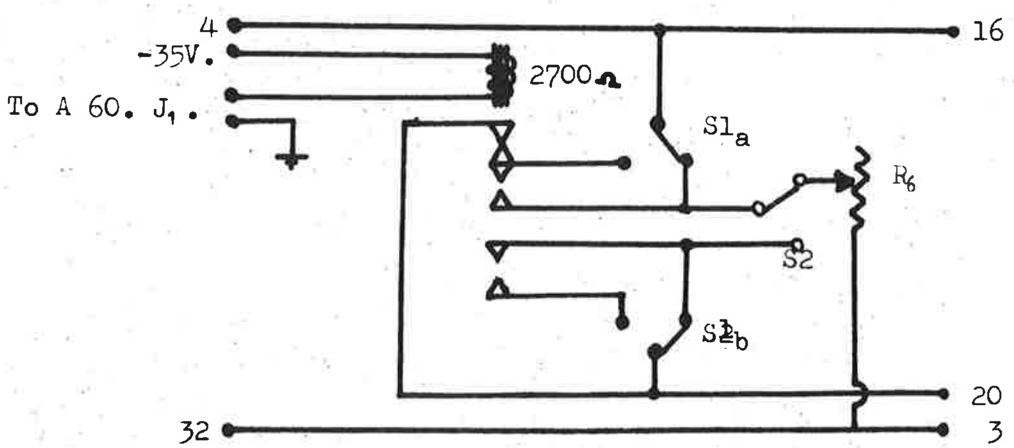
Professor B.L.Shapiro,
Department of Chemistry.
Illinois Institute of Technology,
Technology Centre.
CHICAGO, Illinois 60616

Dear Professor Shapiro,

I enclose the following communication, which will, I hope, serve as my first subscription to the Newsletter:

We have been using a Hewlett Packard 3440.A digital voltmeter with our A.60 for the measurement of integrals and have developed a method of operating the voltmeter from the A.60.

The conversion of the voltmeter is simple. A switch is fitted on the front panel above the sample rate knob and a miniature jack plug on the rear panel to carry the switch leads to the A.60. A double pole single throw relay is mounted inside the case close to the sample rate potentiometer, the circuit being modified as follows:



Ramp Generator Circuit Fig. 5/14.

The -35V used to switch the relay is obtained from the power supply of the voltmeter. The A.60 is connected via the external equipment switch of the spectrometer. The switch S_1 is used to switch the digital voltemter back to its normal operation when required.

When S_1 is connected to the relay, the voltmeter is on 'hold' until the normal sweep switch of the A60 is operated. On releasing the sweep switch, the voltmeter holds the integral voltage enabling this to be easily read.

Yours faithfully,

A. Alan Wagland.

A.A.Wagland.

ESSO RESEARCH AND ENGINEERING COMPANY
BAYTOWN RESEARCH AND DEVELOPMENT DIVISION P. O. BOX 4255, BAYTOWN, TEXAS 77520

CHEMICALS DEPARTMENT
A. T. WATSON, DEPT. HEAD

December 13, 1965

Corrosion Inhibitors in A-60 Cooling Systems

The pump troubles which accompanied the use of chromate corrosion inhibitor in the recirculated water cooling system of an A-60 spectrometer, as outlined by C. A. Hirt in IITNMR Newsletter 86-34, are very similar to problems we have encountered. We have found the use of corrosion inhibitors necessary to the satisfactory operation of our A-60 magnet, however, and have studied the problem enough to find a workable solution.

The direct cause of the pump failures appears to be a gelatinous deposit which forms under the seals and behind the carbon vanes. This deposit first opens the seals to permit leakage, and finally restricts the sliding action of the vanes so as to cause excessive wear and rapid loss of pressure. This deposit is slightly water soluble and can be washed away by running fresh, unhibited distilled water through the system for a few hours. It is detectable in the water by its dark cloudy appearance, so that washing should be repeated until the circulated water stays sparkling clear.

Changing to a gear pump which uses glass-filled teflon and metal gears reduces the rate of pump wear, but does not stop the leakage past the seals. Control of the problem requires elimination of the deposit.

Composition of the deposit has not been determined, but it was thought to be produced by attack of the basic (pH about 8) inhibitor solution on the rubber hoses used in the system. Accordingly, the long hoses were replaced with 1/2-inch copper tubing and a new chromate inhibitor solution which is buffered to a pH of about 6 and has a lower concentration of chromate was used. The short pieces of rubber tubing used inside the heat exchanger housing were not changed.

These modifications have eliminated the pump problems while still controlling magnet cooling system fouling. The circulating water stays sparkling clear, and inhibitor concentration can be estimated from the intensity of the yellow color. Our cooling system has operated without difficulty for 5 months since these changes were made.

The inhibitor recommended by our Mr. R. V. Comeaux is prepared as a concentrate with the following composition:

33% $CrO_4^{=}$, added as $Na_2Cr_2O_7$
5% Zn^{++}, added as $ZnSO_4$
5% $PO_4^{\equiv}$, added as Na_3PO_4

Buffered if necessary by adding $NaHCO_3$. We have not found this necessary.

One cc of this concentrate is added to each 5 gallons of circulating distilled water in the system initially. The yellow color fades slowly due to reduction of six-valent chromium, making it necessary to withdraw about one gallon/week and replenish with the fresh inhibitor solution (1cc/5 gal). This replacement procedure replenishes the inhibitor while removing the undesirable reduced products.

N. F. Chamberlain

NFC:osa

VARIAN associates

UNIVERSITÀ DI NAPOLI
ISTITUTO CHIMICO

8 December 1965

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

Dear Barry,

'Transient Nutations in Nuclear Magnetic Double Resonance'

If a strong radiofrequency field, adjusted to resonance for a given nmr line, is suddenly switched to a high level H_1 well above saturation, a transient oscillation of the kind described by Torrey[1] may be observed. This corresponds to a nutational motion of the magnetization vector, that is to say a precession about H_1 in the rotating frame of reference. For exact resonance, and if $\gamma H_1\lambda \gg \frac{1}{T_1}, \frac{1}{T_2}, \frac{1}{T_2}*$, the detected v mode signal oscillates with a frequency $\Omega = \gamma H_1\lambda$ where λ is the matrix element of the line in question, and decays through spin-spin and spin-lattice relaxation with a time constant

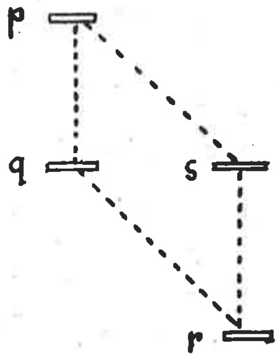
$$\frac{1}{T} = \frac{1}{2}\left[\frac{1}{T_1} + \frac{1}{T_2}\right]$$

The strong field H_1 overrides the dephasing effects of spatial inhomogeneity in H_o.

Among other applications, we have been exploiting this phenomenon in double resonance. In an internally locked proton spectrometer[2], a saturating rf field ω_1 is held at exact resonance for a chosen line ω_{pq} of a complex spectrum while a second rf field ω_2 of about the same strength is swept through the entire spectrum at such a rate that the adiabatic fast passage conditions are approximated:

$$\gamma H_2\lambda \gg \frac{1}{H_2\lambda}\frac{dH_o}{dt} \gg \frac{1}{T_1}, \frac{1}{T_2}$$

(Note that the matrix element λ may vary considerably from line to line.)



As ω_2 sweeps through a typical line and inverts the spin populations of the two energy levels, one observes one of three possible effects:

(a) If the line does not terminate on the levels p or q (for example, ω_{sr}), there is no appreciable change in the signal carried at ω_1.

VARIAN associates

J. A. Ferretti and R. Freeman

(b) If ω_2 sweeps through a connected transition that bears a 'progressive' relation to ω_{pq} (for example, ω_{qr}), excess population is pumped into the lower level q (or out of the upper level p) and excites a transient 'Torrey oscillation' at the spectrometer frequency ω_1, very similar to that observed when H_1 is suddenly switched on.

(c) If ω_2 sweeps through a regressive connected transition (for example, ω_{ps}), excess population is transferred into the upper level p (or out of the lower level q) leaving the net magnetization vector aligned temproarily along the negative Z axis. Precession about H_1 therefore carries it first into the negative Y direction; that is to say, the transient oscillation starts out in the negative sense.

We believe that this technique draws such a clear distinction between progressive and regressive connected transitions that it may be preferred over 'spin tickling' for the assignment of transitions of complex spectra to the appropriate energy level diagram. An illustrative example is provided by the ABC spectrum of 2-chlorothiophene where line 3 has been monitored by ω_1 and transient nutations detected as ω_2 is swept through the connected transitions 5 and 14 (progressive) and 1, 7, 8, and 12 (regressive). Note that the weak matrix element of the 'combination' line 1 can be compensated by increasing H_2 as in inset (d).

A more detailed discussion may be found in preprints of an article submitted to J.C.P. (obtainable by writing to R. F.). Would you please add Jim Ferretti to your mailing list and credit this letter as his first subscription?

Yours sincerely,

James A. Ferretti

Ray

James A. Ferretti
Istituto Chimico
Università di Napoli
Via Mezzocannone 4
Naples, Italy

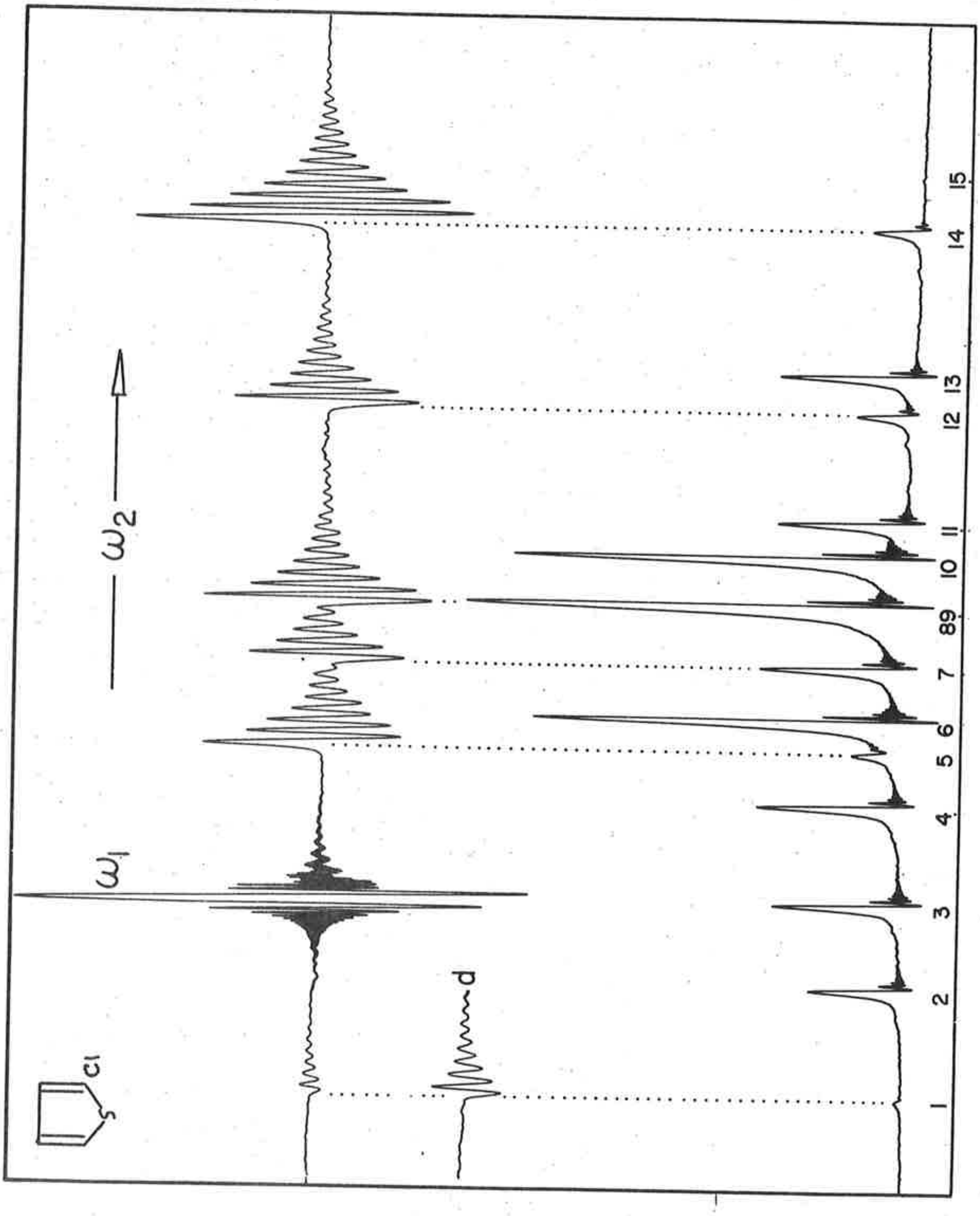
Ray Freeman
Analytical Instrument Research
Varian Associates
Palo Alto, California 94303

[1] H. C. Torrey, Phys. Rev. 76, 1059 (1949).

[2] Home-made conversion of HR 60.

VARIAN
associates

J. A. Ferretti and R. Freeman



LABORATORIUM FÜR PHYSIKALISCHE CHEMIE UND ELEKTROCHEMIE DER TECHNISCHEN HOCHSCHULE STUTTGART

H. Dreeskamp

E. Sackmann
(Now at the M.P.I. für Spektroskopie in Göttingen)

7 STUTTGART N, Germany
Wiederholdstraße 15
Telefon 29978393

January 9, 1966

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

Dear Doctor Shapiro:

Quadrupole - versus Hexadecapole - relaxation in GeH_4

When we first measured the proton nmr spectrum of GeH_4 [Zeitschrift f. Naturf. 19a 139 (1964)] we noticed that the satellite lines due to a coupling with the germanium isotope Ge^{73} (Spin $^9/_2$; 7,6 % abundance) were not of equal width. See Fig. 1. This we explain as due to a different life-time of the Ge in its spin-states. We now remeasured these satellite-lines very carefully and the spectra at -60°C are given in Fig. 2. For a strict tetraeder the relaxation due to the quadrupole-moment of the Ge^{73} would be exactly zero.

In case of a lorentzian shaped line the line width is given by:

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{T_{m'}} \qquad \text{where} \quad \frac{1}{T_2'}$$

is due to the dipole-dipole relaxation of the protons which in case of negligible slow relaxation of the Ge^{73} dominates the line width. In case of any higher multipole-interaction with components Q_i the other term $\frac{1}{T_{m'}}$, might become dominant and may be evaluated for the state m' considered by summing the transition probabilities $P_{m',m''}$ over all other states m''.

$$\frac{1}{T_{m'}} = \sum_{i,m''} Q_i \left\langle m' \middle| f_i\,(I_{Ge}) \middle| m'' \right\rangle$$

There seem to us two ways to explain our findings:

1. The actual instantaneous symmetry of the GeH_4 molecule departs slightly from tetraedal symmetry due to nuclear motion. Depending on the resulting symmetry, different line width pattern may result. As examples Fig. 4, a deformation to C_{3v} and D_{2h} has been assumed - that is $\Delta m = \pm 2$ transition become allowed - or Fig. 3 greater symmetry distortion is assumed - where also $\Delta m = \pm 1$ are allowed.

2. The next higher electric moment of a nucleus beyond the quadrupole-moment, i.e. the electric hexadecapole-moment, though it is smaller by many orders of magnitude than the octopole-moment, gives even for strict tetraedal symmetry a relaxation due to an interaction of this moment with the molecular electric field. This makes $\Delta m = \pm 4$ transition allowed and an example is given in Fig. 5.
In Fig. 4 and 5 a reasonable amount of proton relaxation was included to give similarity with experiment.

We do not feel like making a final statement on these effects. However, we are studying these things further and would very much like if anyone who comes across related effects would let us know.

Sincerely yours

H. Dreeskamp
E. Sackmann

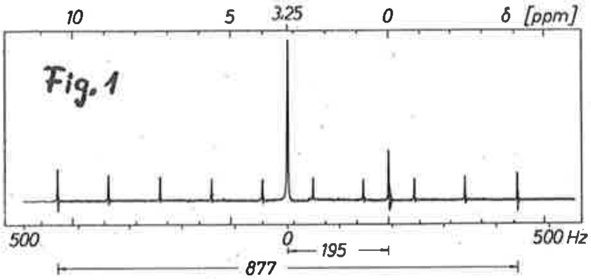


Fig. 1

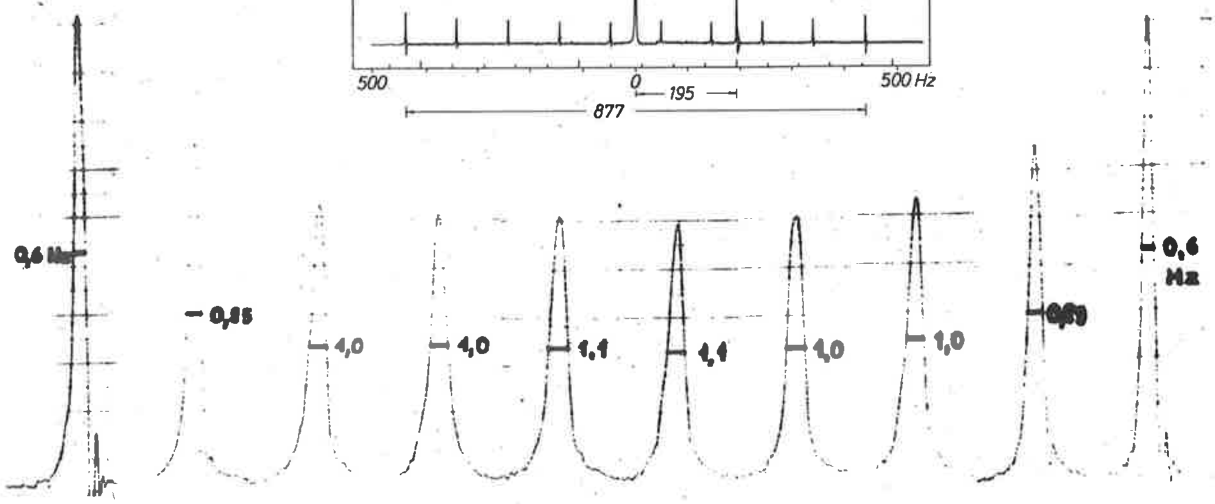


Fig. 2

Fig. 3

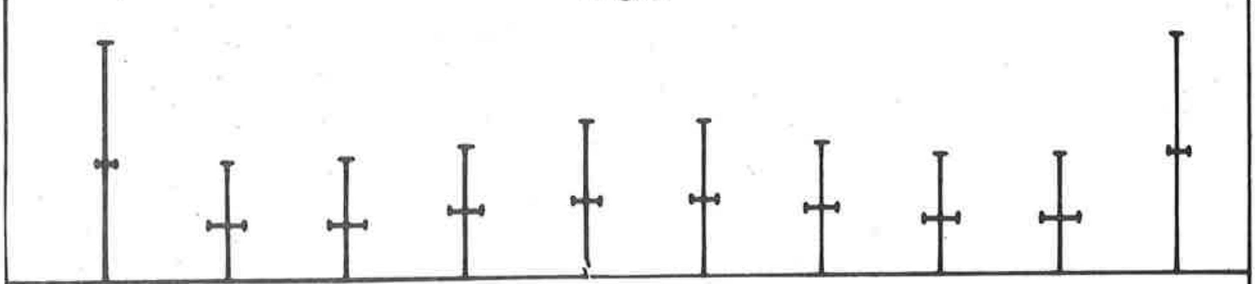


Fig. 4

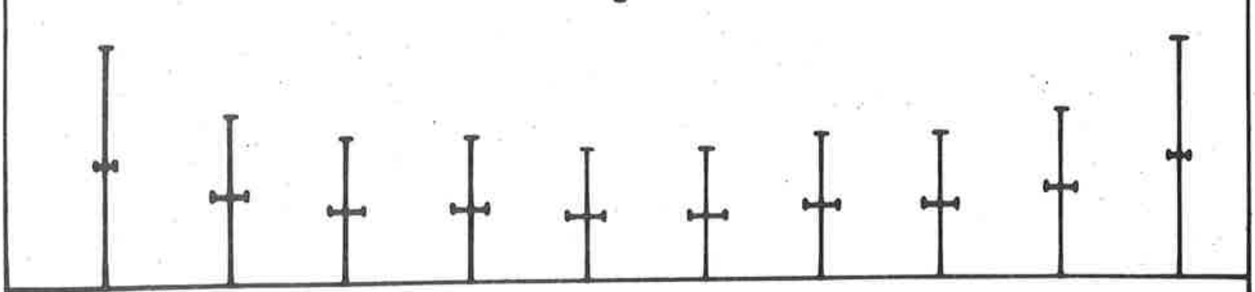
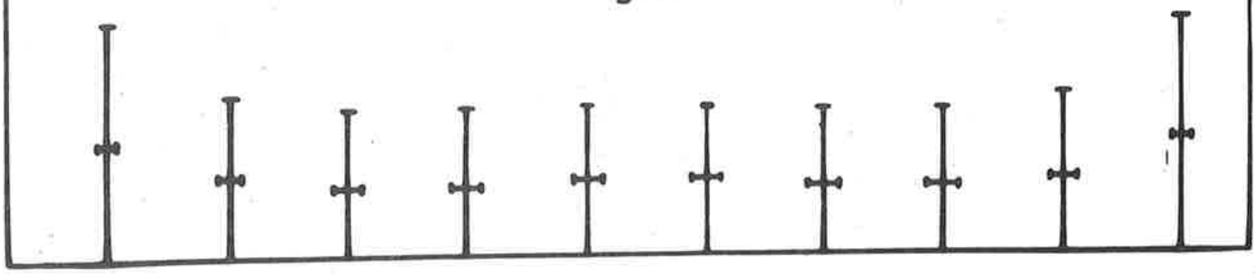


Fig. 5



NORTH CAROLINA STATE UNIVERSITY | AT RALEIGH

SCHOOL OF PHYSICAL SCIENCES AND APPLIED MATHEMATICS

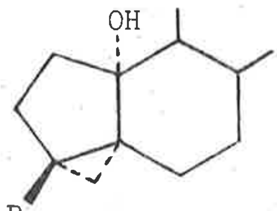
DEPARTMENT OF CHEMISTRY
BOX 5247 ZIP 27607

January 10, 1966

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

Dear Barry:

Some time ago we assigned [Tetrahedron Letters 1517 (1963)] structures Ia and IIa, respectively, to the solvolysis products obtained from the 3α-



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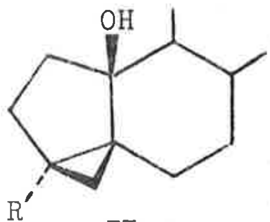
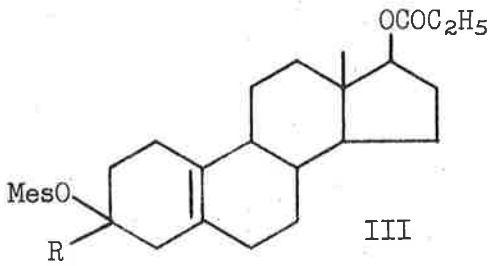


II

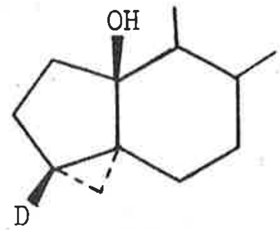


III

a: R = H b: R = D

and 3β- mesylates IIIa. Based on NMR evidence, we have now concluded that structure I is incorrect.

These solvolysis reactions have been repeated using epimeric 3-mesylates(IIIb) in which deuterium is present at C-3 instead of hydrogen. The resulting 3,5-cyclosteroids "Ib" and IIb produce strikingly different patterns for the (now isolated) cyclopropane methylene protons. The α-mesylate product "Ib" shows these protons as an AB quartet: $\delta_A = 0.16$ ppm, $\delta_B = 0.27$ ppm, $J_{AB} = 5$ c/s. The β-mesylate product IIb exhibits the C-4 methylene protons as an AX pattern: $\delta_A = 0.125$ ppm, $\delta_X = 0.675$ ppm, $J_{AX} = 5$ c/s. The latter result is easily explained since models show a close proximity of the angular hydroxyl group and 4β-H of II, leading to deshielding. The absence of this effect in the α-mesylate solvolysis product is best explained by formulating it not as I but as IV in which the hydroxyl and methylene are trans to the 5-ring. This



IV

new structure also avoids the boat form of ring B which is required by I.

The low field half of the AB pattern in IV is further split by long range coupling (J ~ 1 c/s) which is removed by irradiation at 2.32 ppm. This effect may involve the 2β and 4β protons which, along with the connecting bonds, form the arrangement known to produce small couplings such as this. The rather low field position of the 2β-proton may result not only from its being "allylic" to the cyclopropane ring but possibly also from deshielding by the angular hydroxyl.

Charlie Moreland performed (or directed) all of the NMR work described here and I hope you will credit this letter to his "account."

Best personal regards.

Sincerely yours,

Sam

Samuel G. Levine
Associate Professor

SGL:mg

88-48

Dr. G. ENGLERT

c/o **F. HOFFMANN-LA ROCHE & CO.**

LIMITED COMPANY

ADDRESS: P.O. BOX 20 710, BASLE 2, SWITZERLAND — TELEPHONE: 32 38 20 — TELEGRAMS: ROCHE BASLE — TELEX: 62292

DEPARTMENT Phy.A.
Eng/to

Basel, January 11th, 1966

Professor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
CHICAGO, Ill., 60616
--USA--

Dear Professor Shapiro,

At the Liquid Crystal Conference at Kent/Ohio (August 1965), Dr. Saupe and I reported on the

PMR Spectra of Some Acetylenic Compounds and of Acetonitrile

oriented in the nematic phase of 4,4-di-n-hexyloxy-azoxybenzene (I). Since our preliminary results will be published in "Molecular Crystals" not before April 1966, I should like to give here a short abstract.

The following compounds have been studied:

$H\text{-}C{\equiv}C\text{-}CH_2X$ X=Cl (1) and Br (2)

(3) $H\text{-}C{\equiv}C\text{-}CH_3$ (4) $H\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_3$

(5) $H_3C\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_3$ (6a) $N{\equiv}C\text{-}CH_3$ (6b) $N{\equiv}C\text{-}{}^{13}CH_3$

Chemical shift anisotropies:

From the chemical shift difference of the acetylenic proton in the isotropic and nematic phase and from the known molecular geometry (Microwave data) we obtained for compounds 1) to 4)

$$\underline{\Delta\sigma} = \sigma_{\parallel} - \sigma_{\perp} \approx (10.8 - 13.0)\cdot 10^{-6}$$

$\sigma_{\parallel}, \sigma_{\perp}$ = screening for parallel and perpendicular orientation of the carbon triple bond with respect to the magnetic field direction. It can be concluded that the C≡C-axis are preferably parallel to H_o and the optical axis of the nematic liquid.

The absolute sign of the indirect spin-spin coupling J (^{13}C-H) in compound 6b) has been found to be positive.

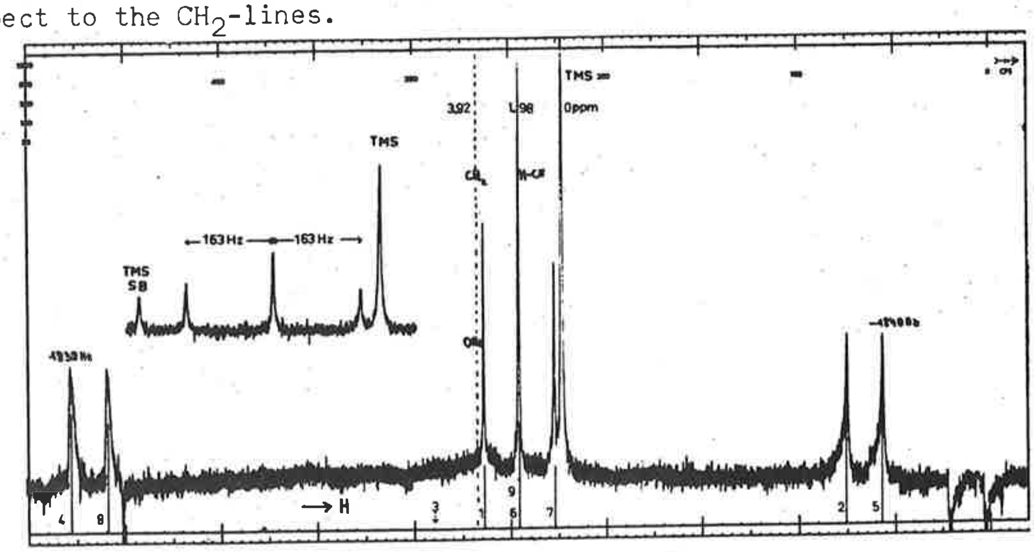
From the ratio of the direct spin-spin couplings D (H-H) and D (^{13}C-H) of compound 6b) the H-C-H bond angle of the methyl group has been found to be 108° 58' ±6' in two different nematic solvents (I and 4-n-octyloxy-benzoic acid). Similar measurements with Methanol-^{13}C, other ^{13}C-species of acetonitrile and with $^{13}CH_3J$ have also been successful in the mean-time.

These experiments show that not only aromatic compounds can be oriented in nematic liquids but all other molecules - even gases - provided their molecular structure deviates sufficiently from a "spherical" shape (tetramethylsilane TMS cannot be oriented!).

As an example we present the 100 Mcps spectrum of oriented (2) plus TMS at 70°C in I. The theoretical spectrum has been calculated with the parameters:

A	=	79,5 cps	(direct coupling H, CH_2)
B	=	-1169 cps	(direct coupling CH_2)
$\Delta\nu$	=	193 cps	(chemical shift difference)

All parameters are defined in ref.[1]. First order explanation of the spectrum: the strongly coupled CH_2-protons give rise to a doublet, splitted by a smaller coupling with the acetylenic proton. The latter gives rise to a triplet (coupling with the CH_2-protons) in the central part of the spectrum shifted by $\Delta\nu$, the chemical shift difference, with respect to the CH_2-lines.



Yours sincerely,

G. Englert

ref.[1]: G. Englert and A. Saupe;
Z. f. Naturforschung 20a, 1401 (1965).

GENERAL CHEMICAL DIVISION

Allied Chemical Corporation

RESEARCH LABORATORY • P. O. BOX 405 • MORRISTOWN, NEW JERSEY
JEFFERSON 8-8000

January 12, 1966

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

Dear Dr. Shapiro:

In response to inquiries, I would like to make a progress report on the analysis of NMR spectra using computer techniques which was mentioned in IITNMR 71 31 and reported at the 6th Experimental NMR Conference last February. The program for decomposition of overlapping spectral peaks (DECOMP) provides very accurate frequency values and moderately good intensities for peaks which are completely unresolved in a spectrum. These values are sufficiently good such that we have written a program (ASSIGN) which will find all possible sets of energy levels using the peaks resolved from the experimental spectrum by DECOMP. ASSIGN utilizes both frequency and intensity sum rules as constraints for the assignments, but is general for all systems of spins in that an input algorithm, which can be varied according to the system involved, is used to guide the computation.

A description of the method applied to the analysis 3-chlorothietane, is scheduled for publication in the Jan. 15,1966 issue of J. Chem. Phys. FORTRAN IV listings of the programs for use with an IBM 7094 and descriptions of their use are contained in appendices of reference 1; these appendices will be available as a separate report in the near future. Requests for these listings, when available, and questions regarding their use should be addressed to T. R. Lusebrink.

The present version of ASSIGN contains an option to take advantage of information from double resonance experiments, but only utilizes the information that certain lines have energy levels in common. This modification significantly reduces the computer time required to solve a five spin system[1]. The program is currently being rewritten so that it can take full advantage of the information identifying regressive and progressive lines from the Nuclear Overhauser Effect obtained by observing one line and frequency sweeping the rest of the spectrum[1,2]. This modification is expected to further reduce the computer time by a significant amount, but it is not anticipated that the program will be completed and tested for several weeks.

It is hoped that this will be considered as a subscription to the IITNMR; please send the IITNMR to T. R. Lusebrink.

Very truly yours,

CH Sederholm TRL

C. H. Sederholm
IBM Systems Res. & Devel.
2670 Hanover Street
Palo Alto, Calif.

T R Lusebrink

T. R. Lusebrink
Gen. Chem. Res. Lab.
P. O. Box 405
Morristown, N. J.

TRL/pl

1. T. R. Lusebrink, "Improved Techniques for the Analysis of NMR Spectroscopic Data: Analysis of Four-membered Ring Compounds", Ph.D. Thesis, Univ. of Calif., Berkeley (1965)

2. R. Kaiser, J. Chem. Phys. 39 2435 (1963)

88-52

UNIVERSITY OF ILLINOIS
Department of
CHEMISTRY AND CHEMICAL ENGINEERING
URBANA
61803

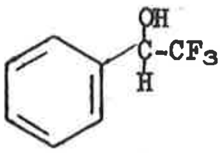
The William Albert Noyes Laboratory

January 13, 1966

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

Dear Dr. Shapiro:

We have observed a difference in the F^{19} n.m.r. spectra of enantiomers when a suitable optically active solvent is used. The racemic fluoroalcohol I shows a doublet, $|J|_{HF}$ 6.7 c.p.s. in carbon tetrachloride but exhibits two sets of doublets $|J|_{HF}$ 7.2 c.p.s. when in l-α-phenethylamine, II. The shift of one set relative to the other is 2.0 c.p.s. Only one set of doublets is observed in racemic amine.



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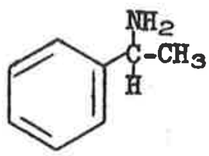


II

By using this technique and measuring the intensities of the two sets of doublets, we have determined the optical purity of a sample of I $(\alpha]_D + 1.6^\circ$ neat) produced by an asymmetric induction to be 52%. The specific rotation of the dextro enantiomer is calculated to be $40 \pm 10^\circ$. To our knowledge, this is the first example of nonequivalence of n.m.r. spectra of enantiomers in an optically active solvent.

Respectfully,

Wm H. Pirkle

W. H. Pirkle
Assistant Professor
of Organic Chemistry

WHP:sgm

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

INSTITUT DE CHIMIE DES SUBSTANCES NATURELLES
GIF-SUR-YVETTE (S.-&-O.)

TÉL. : 928.46-76

January 10,1966.

Dear Barry:

Benzene Shifts for Methyl Substituted Cyclohexanones.

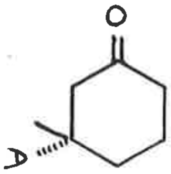
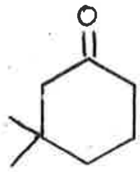
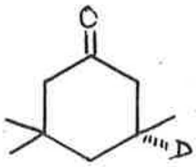
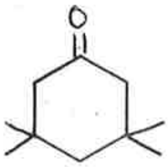
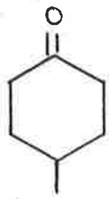
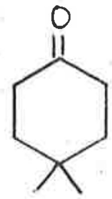
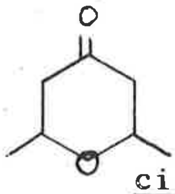
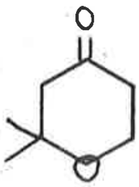
By looking at cyclohexanones and tetrahydropyranones, methyl-substituted in the β and γ positions,we could enlarge the scope of the previous observations (S.Bory,M.Fétizon,P.Laszlo,and D.H.Williams,Bull.Soc.Chim. France, 2541 (1965)).The data presented here are less liable to precise interpretation in terms of conformational changes,since the experimental shifts for the β position are now of the order of 22 cps (equatorial CH_3) and 12 cps (axial CH_3),differing much less than the corresponding values at the α position : 16 cps (axial CH_3) and - 5 cps (equatorial CH_3).Nevertheless,the present results are consistent with strong deformations (into a flattened or twist chair conformation) for both tetramethyl- cyclohexanone and tetrahydropyranone,as well as for the trimethyltetrahydropyranone.Precise control of the concentrations, for such studies to be significant,is to be obeyed.This work was performed in collaboration with M.Fétizon,J. Goré,and B.Waegell,and is presently submitted for publication.

Sincerely,

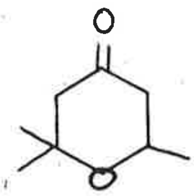
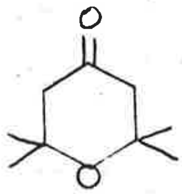
Pierre

Pierre Laszlo

88-54 (cps,at 60 Mc)

		chem.shift (CCl_4)	$\Delta^{CCl_4}_{C_6H_6}$	$\Delta^{CDCl_3}_{CCl_4}$
	CH_3 (t):e	60.7	21.7	- 0.5
	CH_3(s)	58.5	16.7	- 0.8
	CH_3 (t):e CH_3 (s):e CH_3 (s):a	62.7 60.0 52.3	18.4 19.3 11.6	0.1 0.1 0.2
	CH_3 (s)	62.3	13.6	- 0.3
	CH_3 (d):e	60.8	21.4	0.0
	CH_3 (s)	65.5	23.0	0.1
 cis	CH_3 (d)	75.5	21.1	4.0
	CH_3 (s)	73.0	15.8	3.2

/...

	CH_3 (s) CH_3 (d) CH_3 (s)	66.0 73.7 77.5	13.0 15.1 12.7	4.5 2.3 3.5
	CH_3 (s)	75.5	14.4	0.9

s = singlet;d = doublet;t = triplet.

<u>e</u> = equatorial;<u>a</u> = axial.

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

January 13, 1966

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 63616

Dear Barry,

The time has come ... (I think), and so here is a brief report on some work done in collaboration with Peter Diehl of the University of Basel.

In the table below are shown all n.m.r. parameters involving H and F, of 1,2,3,5-tetrafluorobenzene, ("m-$C_6H_2F_4$"), and AA'XX'MR system with A = A' = H and all others F's. In the subspectral treatment of this system all chemical shifts were ignored.

This cannot be done in a similar system, that of pentafluorobenzene, where M = H and all others are F's. At ω_o = 56.4 MHz, δ_{RX} is about 475 Hz. In this case second order perturbation theory accounts for the observed splittings of the order of J^2_{RX}/δ_{RX} and predicts small shifts of lines in the R band, as seen in the figure (the diagram is not drawn to scale).

We should like to acknowledge the help of Bill Moniz (NRL), of Tom Farrar and Rolf Johannsen (NBS), and of Harlan Foster (Dupont), who supplied us with carefully recorded spectra.

Best regards and wishes.

Ernest

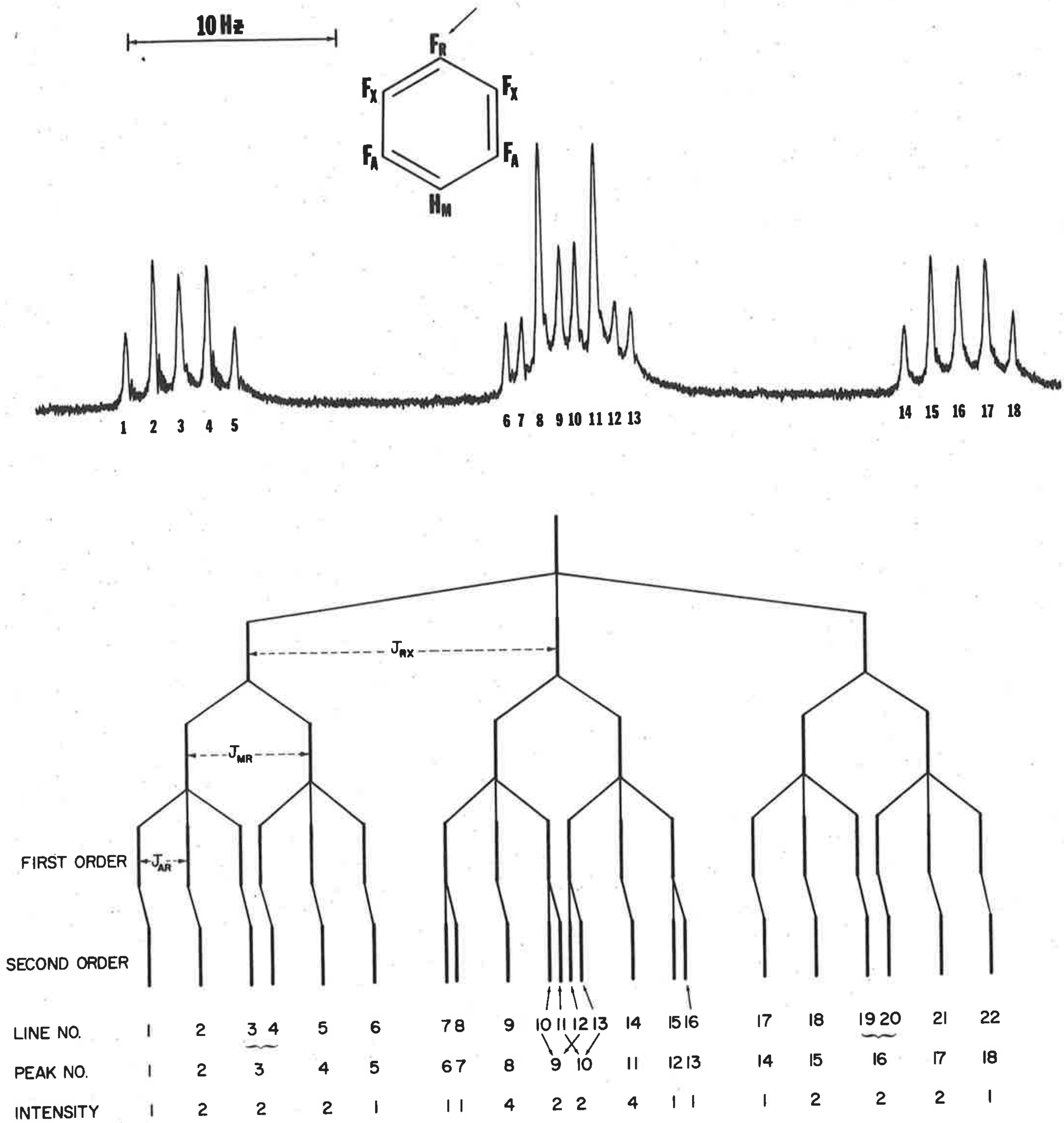
Ernest Lustig
Additives & Instrumentation Branch
Division of Food Chemistry

δ's and J's for m-$C_6H_2F_4$

i	A	X	M	R
δ_i	3.26 τ	131.2 φ	112.8 φ	165.8 φ

ij	AX	AM	AR	AX'	AA'	RX	XX'	MX	MR
J_{ij}	±10.43	8.61	5.60	∓2.46	3.11	19.77	5.74	1.73	11.02 Hz

Refinement of J_{ij}'s was done by the application of LAOCOON II to the entire 116-line spectrum. R.m.s. error in fitting: 0.055 Hz. Values for neat, degassed liquid.


10 Hz
F_R
F_X
F_X
F_A
F_A
H_M
1 2 3 4 5
6 7 8 9 10 11 12 13
14 15 16 17 18
J_{RX}
J_{MR}
J_{AR}
FIRST ORDER
SECOND ORDER
LINE NO. 1 2 3 4 5 6 78 9 10 11 12 13 14 15 16 17 18 19 20 21 22
PEAK NO. 1 2 3 4 5 67 8 9 10 11 12 13 14 15 16 17 18
INTENSITY 1 2 2 2 1 1 1 4 2 2 4 1 1 1 2 2 2 1

88-58

National Chemical Research Laboratory

of the South African Council for Scientific & Industrial Research

NCRL
OF THE CSIR

Telegrams NAVORSCHEM   Telephone 74-6011

Our file   Your file   **P.O. Box 395, Pretoria**

15. JAN 1966

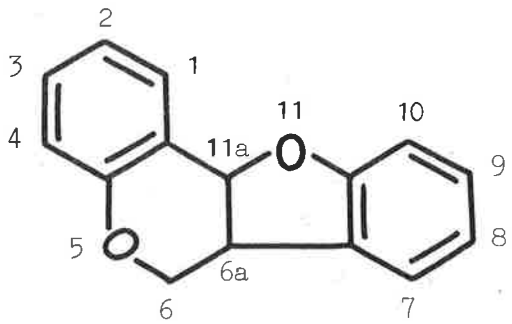
Prof. B.L. Shapiro,
Illinois Institute of Technology,
CHICAGO, Ill. 60616,
U. S. A.

Dear Prof. Shapiro,

The Conformation of the Pterocarpan Ring System

Pterocarpin (I: 3-OMe; 8,9-OCH_2O-), a constituent of the heartwood of Swartzia madagascariensis, contains a coumarochromane ring system common to a variety of naturally occurring compounds. The name pterocarpan has recently been proposed for this system.[1] (Fig. 1).

Figure 1



I

A cis-fusion of the two heterocyclic rings has been suggested for homopterocarpin (I: 3-OMe, 8-OMe) on the basis of models (ring-strain) and n.m.r. evidence,[2] but there are still two conformers possible. We have determined the conformation by analysing the complex four-spin system of the 6, 6a, and 11a protons for a few compounds related to pterocarpin and homopterocarpin using an iterative computer programme.[3] The average coupling constants for four closely related compounds are given below:

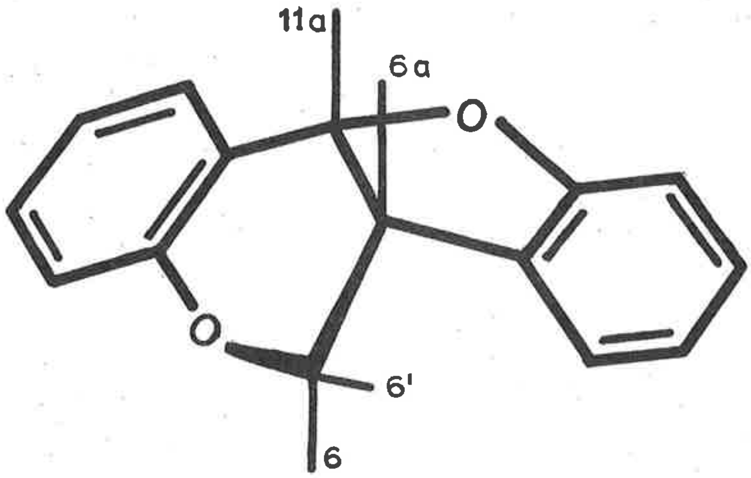
Average Coupling Constants (c.p.s.)

$J_{6a,11a}$	$J_{6a,6}$	$J_{6a,6'}$	$J_{6,6'}$	$J_{6,11a}$	$J_{6',11a}$
7.2	10.6	5.2	-11.0	-0.8	0.6

These values support the conformation given in Fig. 2 with protons 6 and 6a in an axial/axial relationship to each other. A high degree of conformational purity seems probable from the data above.

Figure 2 / ...

Figure 2



It is also interesting to note that the two four-bonded couplings are of opposite sign. Their relative magnitudes are in qualitative agreement with the calculations of Barfield.[4]

Yours sincerely,

K Pachler

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

References

1 S.H. Harper, A.D. Kemp, W.G.E. Underwood, Chem. Comm., 1965, 309.

2 H. Suginome, T. Iwadare, Experientia, XVIII, 164 [1962].

3 J.D. Swalen, C.A. Reilly, J. Chem.Phys., 37, 21 [1962].
We are grateful to the authors for a listing of their programme.

4 M. Barfield, J. Chem. Phys., 41, 3825 [1964].

KP/ED

88-60

UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

January 14, 1966

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

Re: Carbon-13 Chemical Shifts in Some Methylcyclohexanes

Dear Barry,

We have recently recorded the carbon-13 chemical shift values for the ring carbons in 15 selected methylcyclohexanes of known structure. A numerical factor analysis of these 60 different chemical shift values has indicated that a limited set of structural parameters can be used to predict the experimental values with a considerable degree of accuracy. These parameters are given in Fig. 1 for the several conformational features which they represent, and they predict the chemical shift relative to the 101.44 ppm chemical shift of cyclohexane. Five of the significant parameters are methyl substituent terms, while an additional four parameters are required to account for important methyl-methyl pair interactions. All of these parameters reflect important conformational features in this molecular system and form a basis for conformational studies on such compounds. The success of the correlation by these seven significant parameters is exhibited in Fig. 2.

The factor analysis was originally carried out for the data taken on only 12 of the 15 available compounds. These compounds were those (4 compounds) in which the two possible chair conformations were equally populated because of their equivalence in energy and those (8 compounds) for which only one conformation makes a significant contribution to the ground state description of the molecule. Using the parameters obtained in this manner, the spectral data for methylcyclohexane, 1,<u>trans</u>-2,<u>cis</u>-4-trimethylcyclohexane and 1,1,2-trimethylcyclohexane were analyzed. The spectrum of methylcyclohexane was fit best if a conformational energy of + 2.1 Kcal/mole (range in exp. error 1.4-3.0) for the axial and equatorial forms was used to predict the relative populations. Likewise, a ΔE value of 1.2 Kcal/mole (range in exp. error 0.9-1.6) gave a good fit of the spectral features in the 1,<u>trans</u>-2, <u>cis</u>-4 compound. All attempts to interpret the spectrum of 1,1,2-trimethylcyclohexane in terms of a mixture of the two chair conformations failed, as the spectral peaks fell outside of the range predicted for the two extreme chair conformers. When considered with the information from the PMR data on this compound that the axial and equatorial protons are averaged through interconverting structures, one may conclude that the skewed boat form may well contribute to a description of this rather sterically hindered molecule.

We hope to have a preprint on this work available for distribution by early spring, and we will be happy at that time to provide further details upon request.

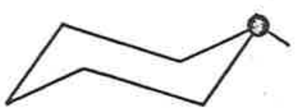
Sincerely yours,

David M. Grant

Don K. Dalling
Don K. Dalling

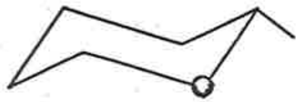
DMG:fjc

SUBSTITUENT PARAMETERS OBTAINED FROM FACTOR ANALYSIS
(GIVEN IN PPM)

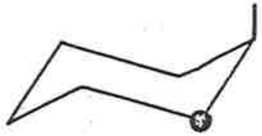


-5.71 ± .22

-1.09 ± .44

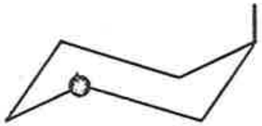


-8.89 ± .12

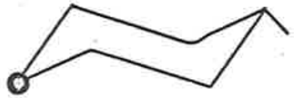


-5.24 ± .33

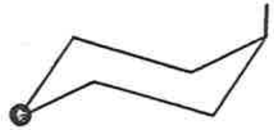
neg.



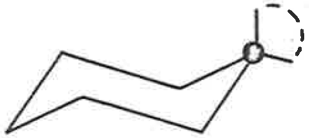
+5.37 ± .25



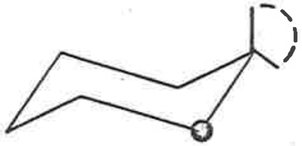
neg.



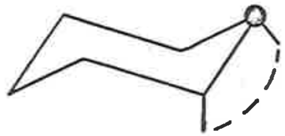
neg.



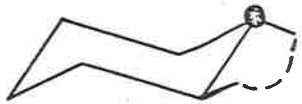
+3.51 ± .59



+1.22 ± .42



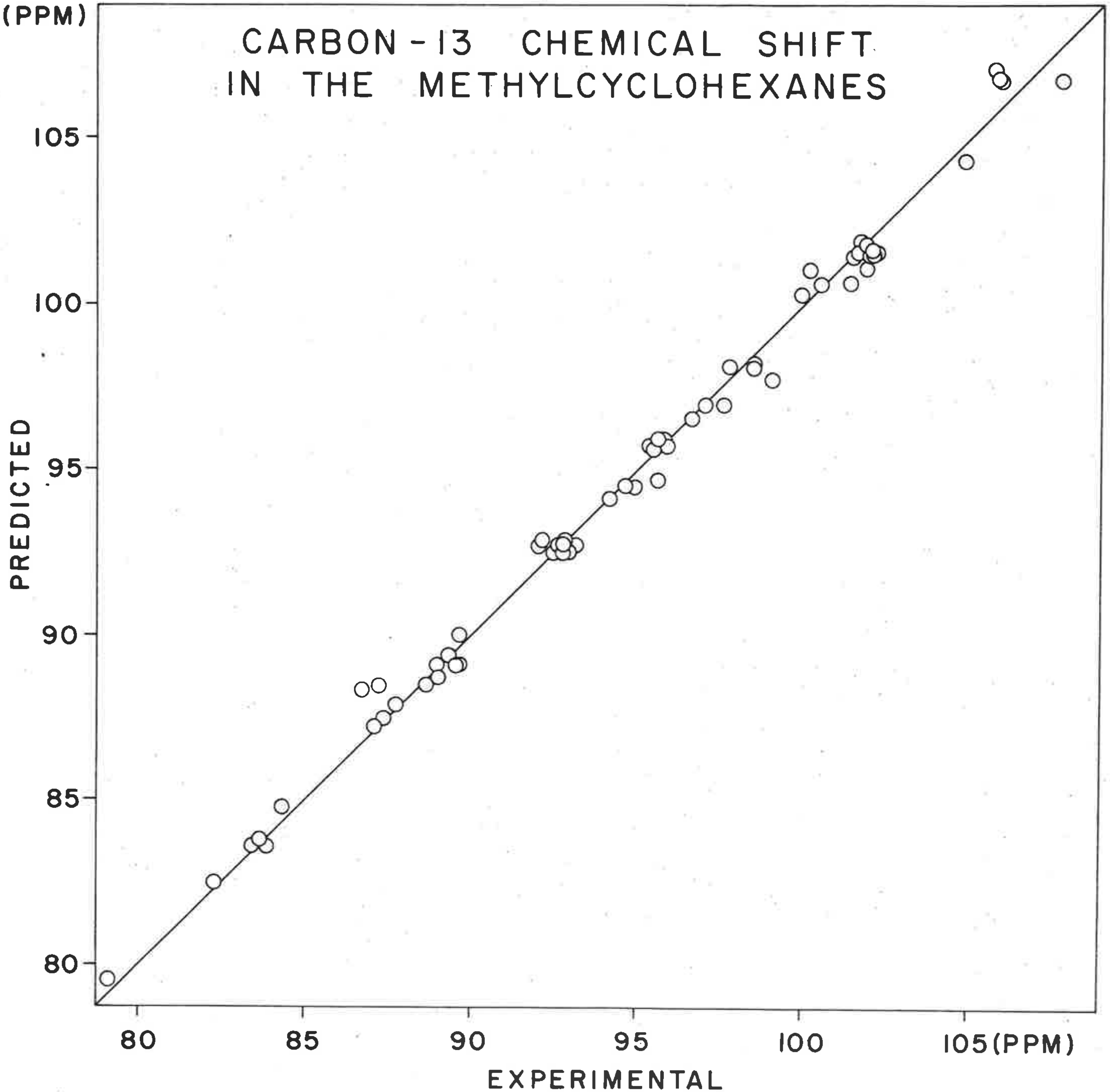
+3.22 ± 0.59



+2.33 ± 0.27

STANDARD ERROR OF FIT 0.51 PPM

MULTIPLE CORRELATION COEF. 0.9990


CARBON-13 CHEMICAL SHIFT
IN THE METHYLCYCLOHEXANES
(PPM)
105
100
95
90
85
80
PREDICTED
80
85
90
95
100
105(PPM)
EXPERIMENTAL

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

Milan, january, 13th, 1966

Prof. Bernard L. Shapiro
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Professor Shapiro,

sometimes strange natural molecules allow the discovery of strange long-range couplings. In the course of the structure determination of a rare natural product " pederin " (1), we met an unusual long-range coupling, which may be of interest to readers of IITNMR.

The hydroxylic proton at C-6 (Fig.1) is coupled to H-5ax across oxygen with $^4J=2.0$ cps, but not with the geminal H-5eq.

Although examples of long-range interactions across oxygen are known (2), this is, I suppose, the first case of such a coupling involving an hydroxylic proton in a saturated fragment. Freeman, Bhacca and Reilly (3) have reported the unique example of splitting of a phenolic proton by a $^5J=0.4$ cps.

The preferred chair conformation of the ring is deduced from the values of allylic coupling constants : $J_{=CH_2,H5ax} = 2.0$ cps, $\vartheta \cong 100°$; $J_{=CH_2,H5eq} = 0$ cps, $\vartheta \simeq 15-18°$;
if the orientation of the chain at C-6 is equatorial (this seems probable, but it is not yet proved), the partial chelation of OH-6 with the carbonyl could induce the molecular fragment $H-C_5-C_6-O-H$ to adopt a "zig-zag" configuration, with the coupled protons in the C-C-O plane ($\phi_5 = \phi_{ox} = 180°$)(4). This may be an explanation of the relatively high magnitude (absolute value) of the ^4J. The influence of substituents and the contribution of the oxygen, of course, has to be considered, the orbitals of which seem directly involved. These factors may be more important than stereochemistry, especially because the shift of 6.07 δ of OH-6 does not suggest a strong H-bonding.
It should be very interesting to get the sign of this ^4J (Gagnaire, Payo-Subiza and Rousseau have reported a positive ^4J across oxygen)(5), because without knowing it, no discussion is possible.

The long-range coupling is visible from the doublet of OH-6 at 6.07 δ, and the doublet ($J_{gem}=13.5$ cps) of quartets ($J_{allyl} = {}^4J = 2.0$) of H-5ax at 2.93 δ partially overlapped by H_2O .
These assignements are justified by decoupling experiments (Fig.1 and 2) and by the spectrum with a trace of D_2O (Fig.1a) : the OH signal desappears and the doublet of quartets is reduced to a doublet of triplets.

The signal at 6,07 δ cannot be due to OH-12 because the same H-5ax interacting with OH-6, is coupled to $CH_2=$ protons (triplets at 4.82 and 4.66 δ ; $J_{gem}=J_{allyl}=$ 2.0 cps). Furthermore in the similar natural product with OCH_3 at C-6, the signal at 6.07 δ and the long-range coupling lack.[3]

In the structure determination of this biologically interesting substance, we have been successful using nmr, especially because of the small amount of material available.

We thank you very much for sending us the IITNMR News Letters and for all the trouble you have in doing it

yours sincerely R. Mondelli

R.Mondelli

-An unusual long-range coupling across oxygen-

Fig.1- Spectrum at 100 Mc in acetone-d_6 : a) with D_2O; b) decoup. of H-5ax $\Delta\omega$ = +306 cps ; c) decoup. of H-5ax $\Delta\omega$ = +189 and +176 cps ; d) decoup. of OH-6 $\Delta\omega$ = -300 cps ; e) signal of H-5ax at higher amplitude.

Fig.2- Signal of H-5ax at 2.93 δ : without decoup. a) in acetone, b) in acetone + D_2O ;
with decoup. of H-5eq at 2.05 δ : a') in acetone, b') in acetone + D_2O $\Delta\omega$ = +88 cps
b") decoup. of $CH_2=$ at 4.82 and 4.66 δ in acetone + D_2O $\Delta\omega$ = -184 and - 177 cps .

I thank very much Dr. Wolfgang von Philipsborn for the kindly permission to use his nice Hr-100 instrument.

(1) C.Cardani, D.Ghiringhelli, R.Mondelli and A.Quilico, Gazz.Chim.Ital. in press.
(2) S.Sternhell, Rev.Pure and Appl.Chem., 14, 15 (1964).
(3) R.Freeman, N.S.Bhacca and C.A.Reilly, J.Chem.Phys, 38, 293 (1963).
(4) M. Barfield, J.Chem.Phys., 41, 3825 (1964).
(5) D.Gagnaire, E.Payo-Subiza and A.Rousseau, J.Chim.Phys., 42 (1965).

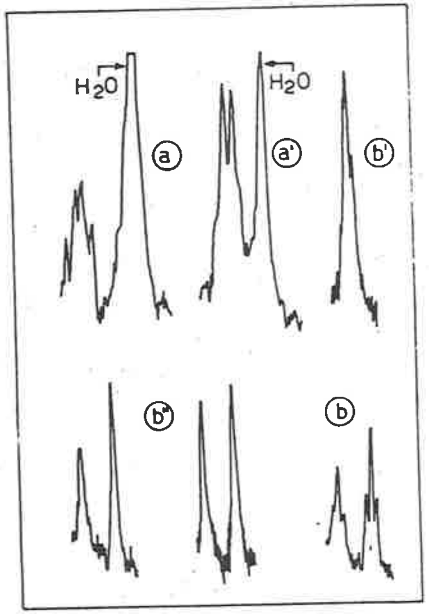


fig 2

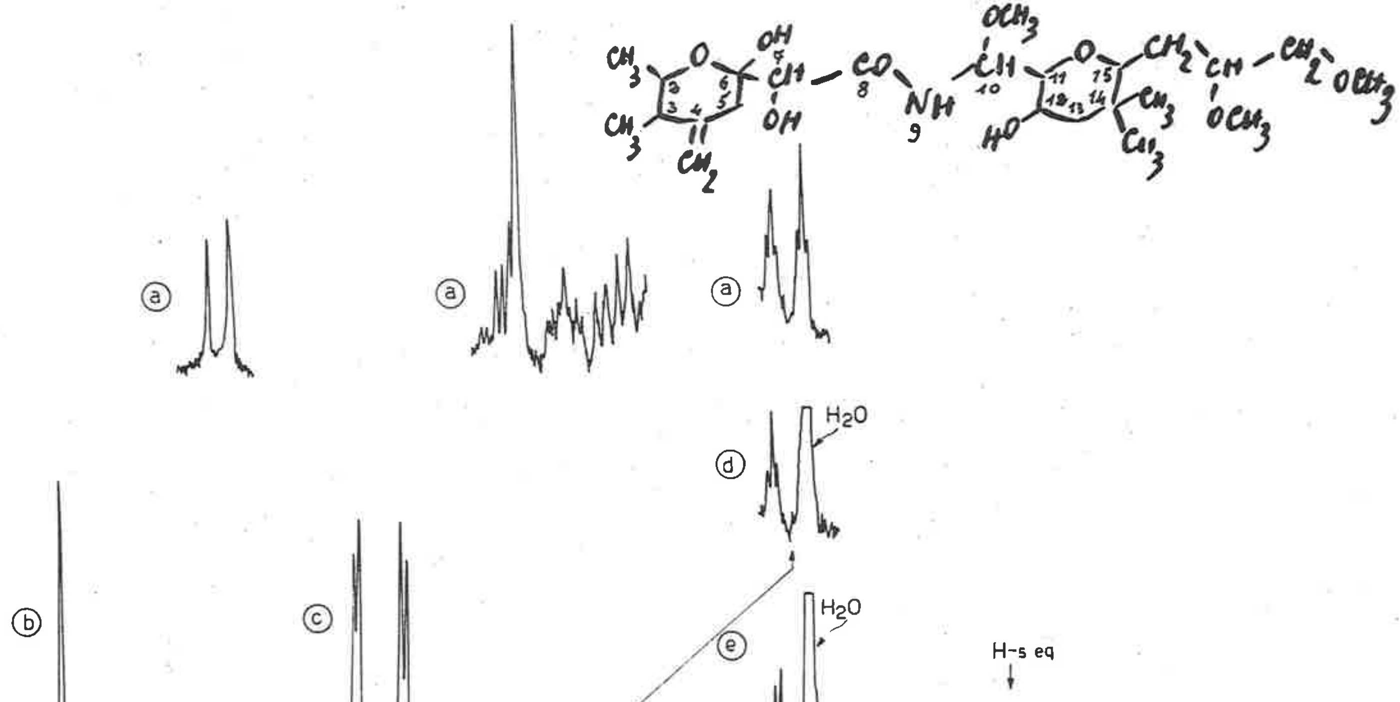
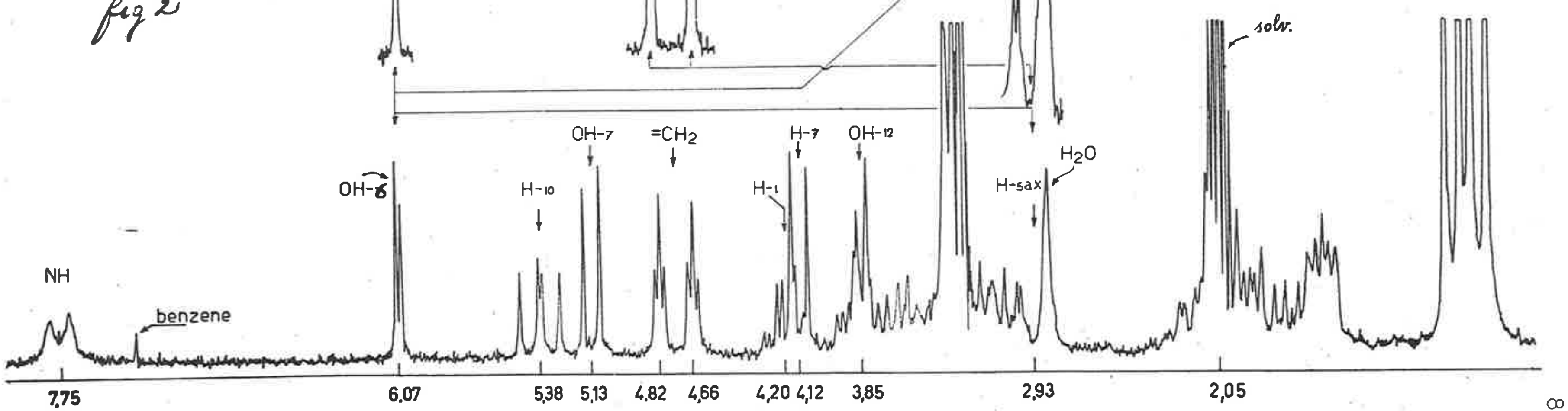



fig 1

88-65

88-66

VARIAN associates

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

13 January 1966

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

Dear Barry: "The Rich Get Richer and the Poor Get Poorer"

Reinhold Kaiser's recent description of a 'Feedback Spectrometer' (I.I.T. Newsletter 87, 38) brings up some interesting new concepts. Clearly a lot depends on the outcome of the promised theoretical analysis, but there are also some questions that might be answered experimentally. We would like to inject a note of caution on two points:

Although in the conventional linear systems one usually thinks of certain quantities as almost synonymous

Signal-to-noise $\equiv$ Sensitivity

Line-width $\equiv$ Resolution

this is not necessarily carried over into non-linear systems such as a feedback spectrometer, which favors strong signals over weak signals. Sensitivity should be examined in terms of the weakest detectable line, and resolution in terms of the smallest resolvable splitting.

The ^{13}C spectrum of neat benzene (or dioxane) is not a very good test of the new spectrometer's sensitivity, since the signal is stronger than the noise on a single scan without feedback. Operating at 14 Kgauss but with a sample in a 9mm inner diameter tube (we feel that 23 Kgauss and 4mm i.d. tubes should give about comparable sensitivity) we obtained quite respectable signal-to-noise in a single scan (at 5 cps/sec) through the absorption mode in a conventional ^{13}C spectrometer (Fig. 1). We were then able to 'improve' signal-to-noise by introducing a non-linear element into the circuit (the square-law portion of a diode characteristic). See Fig. 2. Enhancement through non-linearity does not of course improve sensitivity.

One would also like to establish to what extent the attainable resolution is degraded by the tendency to 'pull in' to the center of an nmr signal, particularly in the case of a weak line close to a very strong one (compare for example the AFC circuit in a radio).

It remains unclear whether the properly defined sensitivity and resolution of the feedback spectrometer are significantly better than in adiabatic fast passage.

Yours sincerely,

Richard Ray

R. R. Ernst R. Freeman
Analytical Instrument Research

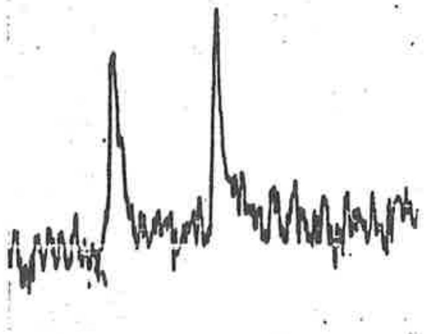


Fig. 1

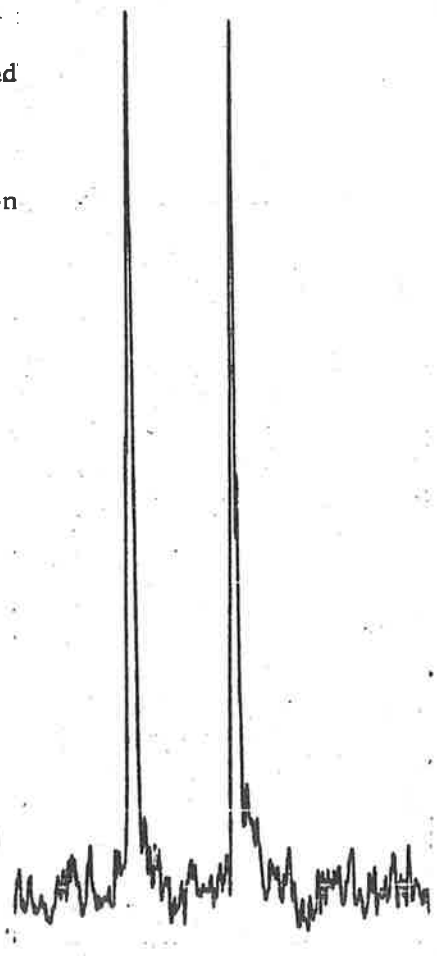


Fig. 2

THE UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

January 17, 1966

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

Dear Barry:

"C_6 - Fluorinated Sugars"

We took delivery of our HA-100 just before Christmas and so we hope to get down to some new projects in the near future.

As a somewhat stop-gap contribution I mention the chemical shift data which we have for hexose sugars having a single fluorine at the terminal position, (C_6). The compounds we have made so far, give a resonance somewhere in the range +230 to +232 p.p.m. ($CHCl_3$ solutions with CCl_3F as internal reference). We are now preparing a further selection of these derivatives for other reasons and hope that they will enable us to decide whether there is any regular steric dependence for these resonances - I suspect not. Anyway, these shifts are of use to identify such compounds.

With very best regards for 1966.

Yours,

Laurie Hall.

L. D. HALL
Assistant Professor
of Chemistry

LDH/ds

"NMR Studies of Multiple Relaxations in Polymers"
W. P. Slichter
ACS Polymer Preprints 6, 632 (1965)

"Nuclear Magnetic Resonance and X-Ray Determination of the Structure of Polyvinylidene Fluoride"
J. B. Lando, H. G. Olf, and A. Peterlin
ACS Polymer Preprints 6, 632 (1965)

"Favorsky Rearrangements. VIII. The Rearrangement of 1,3-Dibromo-3-methyl-2-ones"
C. Rappe and R. Adeström
Acta Chem. Scand. 19, 273 (1965)

"Ozonation of Compounds of the type Ar-CH=CH-G. Cis-trans Isomeric Ozonides from Methyl p-Methoxy Cinnamates. I. Structure of the Ozonides"
P. Kolsaker
Acta Chem. Scand. 19, 223 (1965)

"The Bromination of 3-Bromocyclopentane-1,2-dione"
C. Rappe
Acta Chem. Scand. 19, 274 (1965)

"Near Infrared and Nuclear Magnetic Resonance Spectrometry in Analysis of Butadiene Polymers"
A. J. Durbetaki and C. M. Miles
Anal. Chem. 37, 1231 (1965)

"NMR-Spektroskopische Konformationsanalyse an Menthyl- und Carvomenthylaminen"
H. Feltkamp
Angew. Chem. 77, 723 (1965)

"Zum aromatischen Charakter von Systemen mit 10 π-Elektronen: Die H-NMR-Spektren von 1.6-Methano- und 1.6-Oxydocyclo-decapentaen"
H. Günther
Angew. Chem. 77, 726 (1965)

"11-Deoxojervine, A New Alkaloid from Veratrum Species"
T. Masamune, Y. Mori, M. Takasugi, A. Murai, S. Ohuchi, N. Sato and N. Katsui
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