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Illinois
Institute of
Technology
N - M - R
Newsletter

No. 78
MARCH, 1965

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Isomérisation d'Ethers Acétyléniques

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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".

UNIVERSITÉ DE NANTES
FACULTÉ DES SCIENCES
B. P. 1044 NANTES

Laboratoire de Chimie Organique-Physique
38, Boulevard Michelet - Nantes

Nantes, le 25 février 1965

Mr. le Professeur B.L.SHAPIRO
Illinois Institute of Technology
Technology Center
CHICAGO 60616

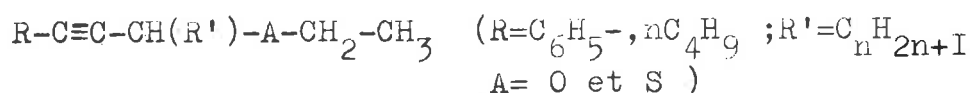
Isomérisation d'éthers acétyléniques

Cher Professeur Shapiro,

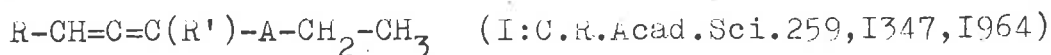
Nous vous prions d'excuser le retard apporté à l'envoi de notre contribution aux IITNERN newsletters.

Celle-ci se rapporte à une étude de l'isomérisation d'éthers α -acétyléniques et aux problèmes de non équivalence magnétique rencontrés dans ces composés.

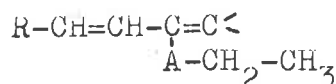
Les dérivés acétyléniques du type



ont été isomérisés en allènes(I) de formule

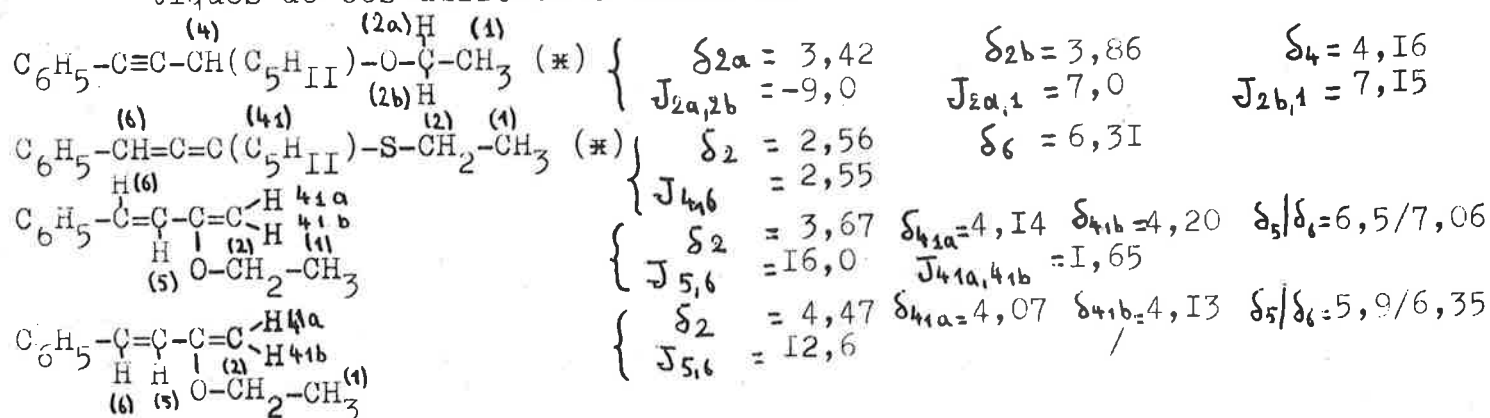


La R.M.N. est dans ce cas un excellent moyen d'étude des conditions et des pourcentages d'isomérisation. Elle permet en outre de mettre en évidence l'évolution ultérieure de l'allène en diène conjugué



et de déterminer la configuration des systèmes éthyléniques formés.

Le tableau suivant donne quelques exemples de paramètres caractéristiques de ces différents isomères:



(δ exprimés en ppm par rapport au TMS; J exprimés en hertz; * dans CCl_4)

Les éthers acétyléniques envisagés présentent une asymétrie moléculaire; ils permettent donc la détermination de différents couplages geminaux. Nous étudions l'influence de la nature de A et R sur les différences de δ entre groupements magnétiquement non équivalents.

Bien cordialement: *M. Martin* M. MARTIN

G. J. MARTIN

UNIVERSITY OF COLORADO
BOULDER, COLORADO 80304

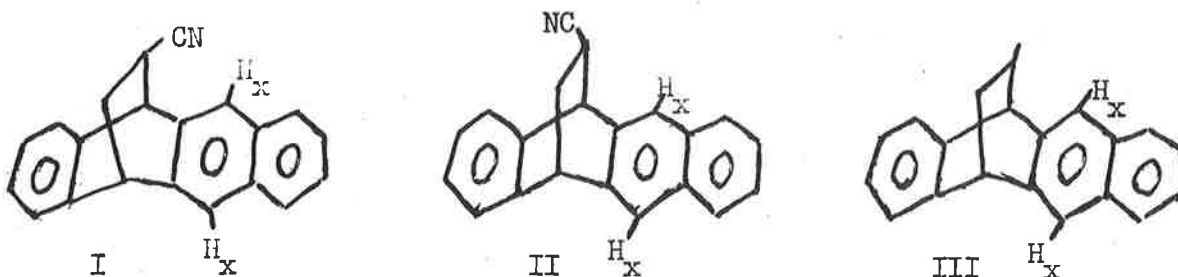
DEPARTMENT OF CHEMISTRY

February 23, 1965

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

Dear Barry:

I thought that the readers of IITNMR might be interested in an example of how magnetic anisotropy effects can be used in structure proof. The Diels-Alder reaction between tetracene and acrylonitrile has recently been carried out by Mr. Fred Dewey of our department. He isolated two isomers, A, m.p. 187° and B, m.p. 205° . These must have structures I or II



The problem is to tell which is which. The aromatic region of the n.m.r. spectrum of ethanotetracene (III) consists of a pair of overlapping A_2B_2 spectra plus a single fairly sharp line which must be due to the two protons marked H_x in structure III. In isomer A, this single line is unchanged from the ethanotetracene spectrum. In isomer B, however, the intensity of this single line is reduced to one half of its original value, and a new line appears with equal intensity 0.140 ppm downfield from the original. This result conclusively shows that isomer B must be structure I. The center of the $C \equiv N$ bond lies over one of the H_x protons in structure I shifting it downfield. A calculation of the expected downfield shift on the basis of a mag-

Professor Barry Shapiro

February 23, 1965

Page 2

netic anisotropy of $16.5 \times 10^{-6} \text{ cm}^3/\text{mole}^1$ and a geometric factor calculated from Dreiding models ($R = 3.88 \text{ \AA}$, $\theta = 78^\circ$) gives a value of 0.136 ppm, in excellent agreement with experiment.

Other Diels-Alder chemists, using acrylonitrile in rigid systems, may be benefited by the above considerations.

Sincerely yours,

M. W. Hanna

Melvin W. Hanna
Associate Professor

MWH:gb

¹G. S. Reddy and J. H. Goldstein, J. Chem. Phys., 39, 3509 (1963).



ESSO RESEARCH AND ENGINEERING COMPANY

BAYTOWN RESEARCH AND DEVELOPMENT DIVISION P.O. BOX 4255, BAYTOWN, TEXAS 77620

February 16, 1965

D. L. BAEDER
MANAGER

NMR Chemical Shifts of Aliphatic Amines and Amides

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

Dear Dr. Shapiro:

Currently we are in the process of revising and extending our NMR Shift Charts. This correspondence reports some of our work on aliphatic amines and amides. The NMR spectra were obtained on our A-60; the liquids were run neat and in 10% solution in D₂O, CDCl₃, or CCl₄. The solids were run in 10% solution in D₂O, CDCl₃, or CCl₄. All data were referenced to tetramethylsilane or to hexamethyldisiloxane. Protonation of amines was accomplished by dissolving the amine in concentrated HCl, H₂SO₄, or HCOOH. About fifteen amines and fifteen amides have been studied thus far. The data on some sixty compounds reported in the literature (1,2,3,4,5) are also included in the ranges given in the charts.

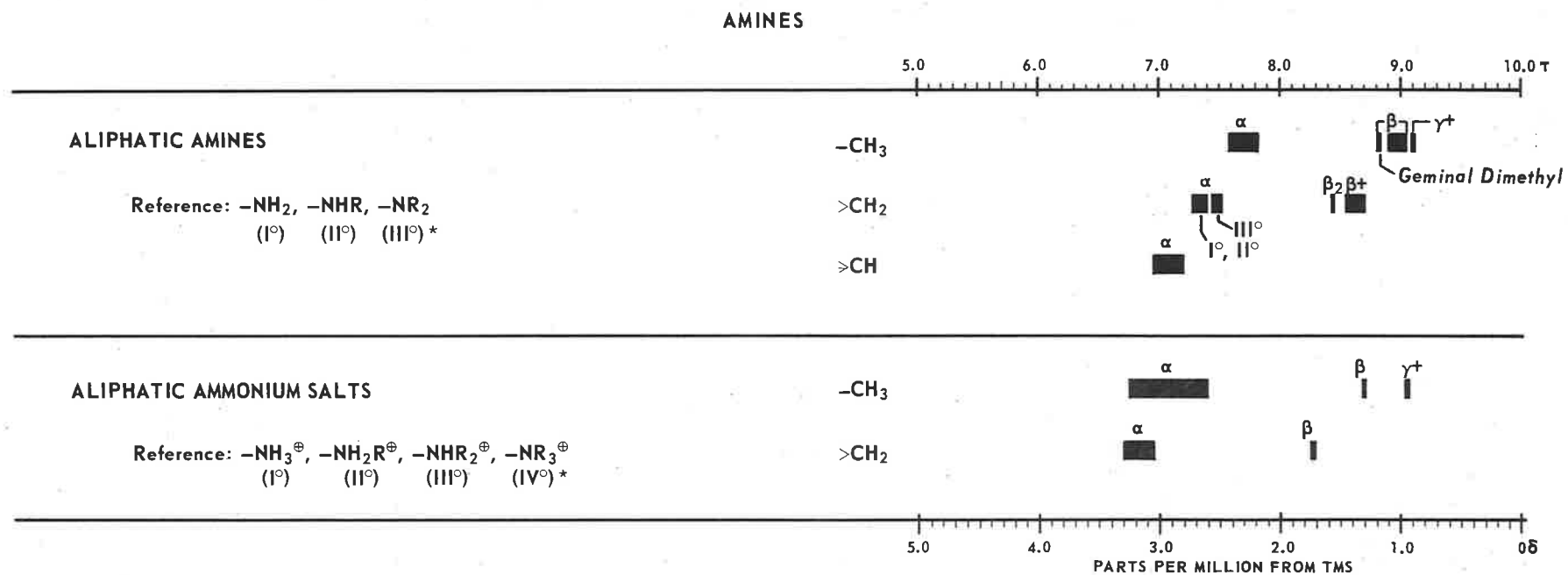
As is evident in figures 1, 2, and 3, the shift data are far from complete. We intend to fill in the gaps in these charts as well as to extend our chemical shift knowledge to aromatic amines and amides.

Very truly yours,

J. J. R. Reed
J. J. R. Reed

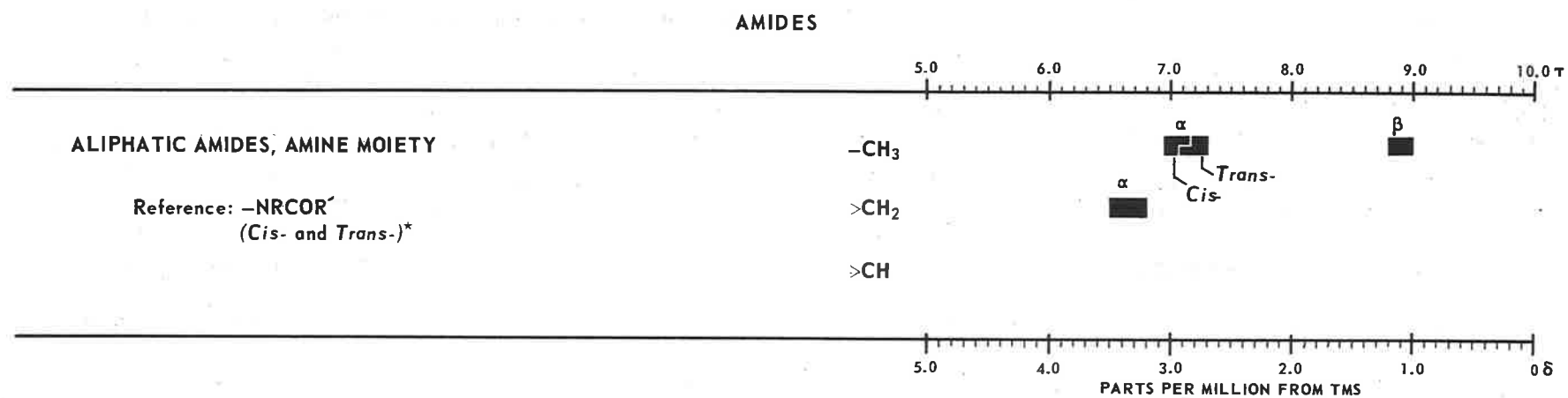
JJRR:osa

- (1) J. L. Sudmeier and C. N. Reilly, "Nuclear Magnetic Resonance Studies of Protonation of Polyamine and Aminocarboxylate Compounds in Aqueous Solution," *Anal. Chem.* 36, 1698 (1964).
- (2) R. M. Moriarty, "The Effect of Solvent upon the NMR Spectra of N-Methylamides. I. Solvent-Solute Complex Formation between Amides and Aromatic Solvents," *J. Org. Chem.* 28, 1296 (1963).
- (3) L. A. LaPlanch and M. T. Rogers, "Cis and Trans Configurations of the Peptide Bond in N-Monosubstituted Amides by Nuclear Magnetic Resonance," *J. A.C.S.* 86, 337 (1964).
- (4) J. V. Hatton and R. E. Richards, "Solvent Effects in NMR Spectra of Amide Solutions," *Mol. Phys.* 5, 139 (1962).
- (5) L. A. LaPlanch and M. T. Rogers, "Configuration in Unsymmetrical N, N-Di-substituted Amides," *J.A.C.S.* 85, 3728 (1963).



*I° = Primary, II° = Secondary, III° = Tertiary, IV° = Quaternary.

Fig. 1. Hydrogen Magnetic Resonance Chemical Shifts.



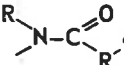
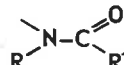
^{*}Reference may be *Cis*-:  or *Trans*-: 

Fig. 2. Hydrogen Magnetic Resonance Chemical Shifts.

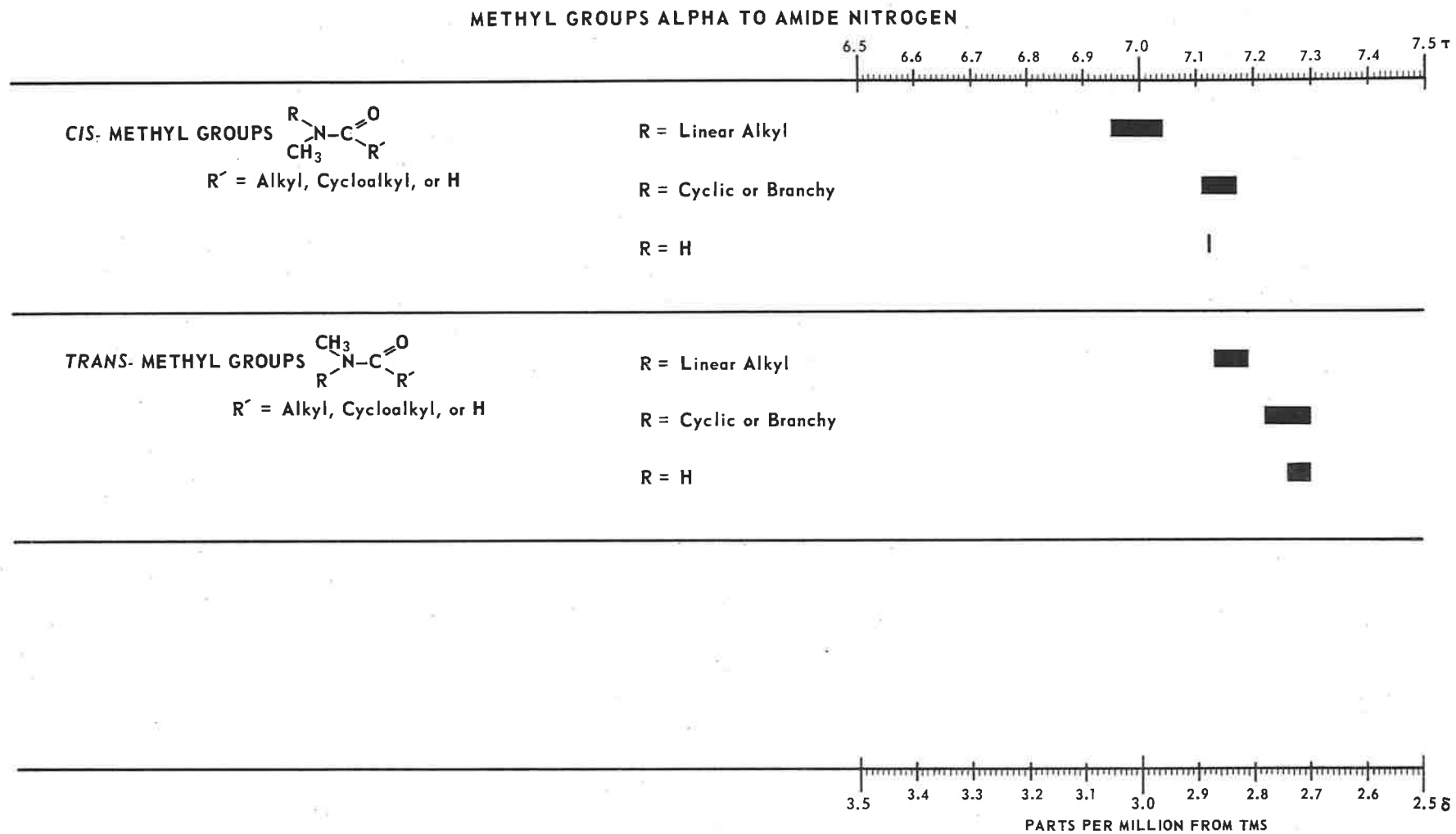


Fig. 3. Hydrogen Magnetic Resonance Chemical Shifts.



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HILLTOP 5-5611

MEDICAL RESEARCH
LABORATORIES

February 26, 1965

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

Dear Dr. Shapiro:

Your pioneering n.m.r. work on the di-O-methyl derivative of the C₁₁-fragment from oleandomycin, referred to here as "C₁₃-compound", certainly played a major role in the overall structural elucidation¹ of oleandomycin. I have continued to build on the details² of this knowledge to gain information regarding the absolute configuration at the asymmetric centers which have been localized in the C₁₃-compound, cf. Chart 1. From your early study² it is obvious that an erythro³ relative configuration must exist between C-5 and C-6; since C-6 has been fixed as (6S)⁴ in oleandomycin via L(-)-methylsuccinic acid (derived from C-5, 6, 7, 8 in the antibiotic, cf. Ref. 1), the coupling specification (5S:6S) must also follow in I. Accordingly, the C₁₃-compound can now be viewed as a 5D-ketopyranoside; cf. Chart 1 where numbering reflects ultimate origin in oleandomycin and theoretically-possible structures are indicated according to remaining epimeric (C-8) and anomeric (C-9) variables.

Since observed² J_{5a}, 6a dictates a C1 conformation⁵, one candidate (β ,D-S) is automatically dismissed as an impossible diaxially-fused

Prof. B. L. Shapiro

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6-5 ring system⁶. Further study considering base lines for chemical shifts of methoxyl groups⁷ in various environments leads to the inescapable conclusion that the observed 6.31 τ and 6.37 τ values can arise from only one remaining possibility (β ,D-R)⁸, hence (8R)⁹ in oleandomycin.

-
1. F. A. Hochstein, H. Els, W. D. Celmer, B. L. Shapiro and R. B. Woodward, J. Am. Chem. Soc., **82**, 3225 (1960).
 2. B. L. Shapiro, "A Summary of Proton Magnetic Resonance Studies on Compounds Related to Oleandomycin", Mellon Institute, Pittsburgh, Penna., April 27, 1960, example No. 20, a privately circulated report. Excerpts from this reference (60 and 40 Mc, MeCO-d₆ data and conclusions summarized in a chair conformation complete except for the nature of the ring junction) are adapted to numbering in Chart 1 as follows: C-5-H, a doubled doublet centering at 6.07 τ , J 5a,6 gauche/5a,6a: 3/10 cps; C-3-OMe, C-9-OMe as singlets at 6.31 and 6.37 τ , cf. CH₃COOCH₃, 6.35 τ . The author expresses appreciation to Dr. Shapiro for permission to reveal this information.
 3. (a) Nomenclature Committee, Division of Carbohydrate Chemistry of the American Chemical Society, J. Org. Chem., **28**, 281 (1963); (b) S. Furberg and B. Pederson, Acta Chem. Scand., **17**, 1160 (1963).
 4. R. S. Cahn, C. K. Ingold, and V. Prelog, Experientia, **12**, 81 (1956). The system outlined in Ref. 4 is used for accounting purposes while the more descriptive carbohydrate system (Ref. 3a) is employed in discussion, a practice condoned in Ref. 4.
 5. R. E. Reeves, "Advances in Carbohydrate Chemistry", Vol. **6**, C. S. Hudson and S. M. Cantor, Ed., Academic Press, New York, N. Y., 1951, pp. 107-134.
 6. E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 112-114.
 7. H. Conroy in "Advances in Organic Chemistry: Methods and Results", Vol. II, R. A. Raphael, E. C. Taylor and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp. 308-311.

Prof. B. L. Shapiro

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8. This argument follows classical lines (Ref. 19) invoking wealth of well known model systems in the field of carbohydrate chemistry. One of the observed 6.31 and 6.37 τ values has already been accommodated (Ref. 2) as due to C-3-OMe, which is understandably low on the shielding scale (models and theory). Because of their similarity, it is immaterial which value actually represents C-3-OMe. The critical point is that only β ,D-R, possessing equatorially-disposed C-9-OMe deshielded by the ring oxygen (this alone accounts for 6.50 τ values in classical models) and further deshielded by oxygen functionality in other planes can account for either value. This is further evident by considering that the remaining possibilities, α ,D-R and α ,D-S, both contain C-9-OMe as axial anomeric groups which are traditionally more shielded than their equatorial counterparts (cf. 6.6-6.7 τ baselines). Inspection of scale models (Metaloglass, Inc., Boston, Mass.) of each axial-methoxyl possibility reveals no exception to expected shielding thus substantiating their exclusion.
9. The (8R) specification in oleandomycin was reached earlier by a different line of correlations involving erythromycin in which 8R has been established [via (+) α -methyllevulinic acid, cf. Djerassi, et al, Tetrahedron, 4, 369, (1958)], cf. W. D. Celmer, Proceedings of the Congress on Antibiotics (June 15-19, 1964) Prague, Czechoslovakia, in press.

I am communicating this aspect in advance of publication announcing the total absolute configuration of I, i.e. 2R:3S:4S:5S:6S:8R:10R:11S:12R:13R:1'R:3'S:4'R:5'S:1"S:2"R:3"S:5"R.

With best personal regards.

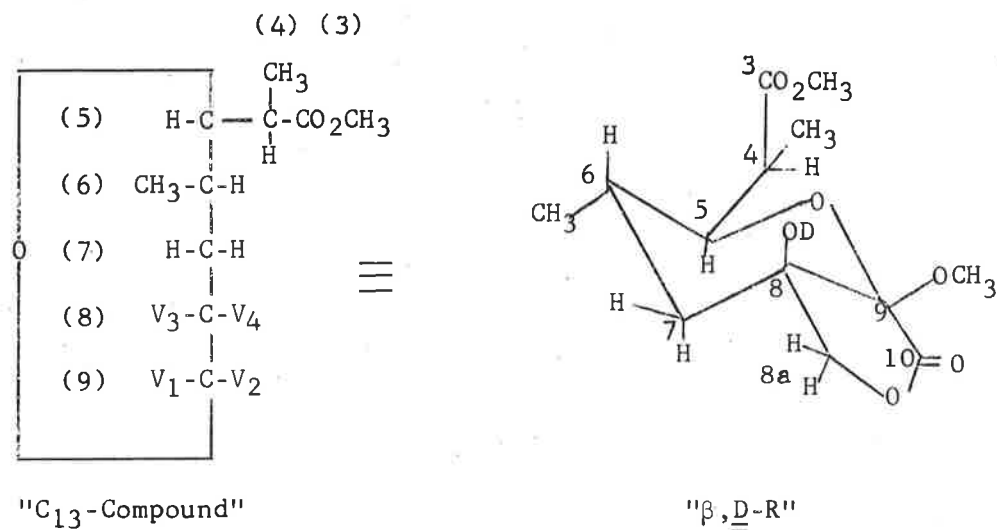
Very sincerely,



W. D. Celmer

/ssc

Chart 1



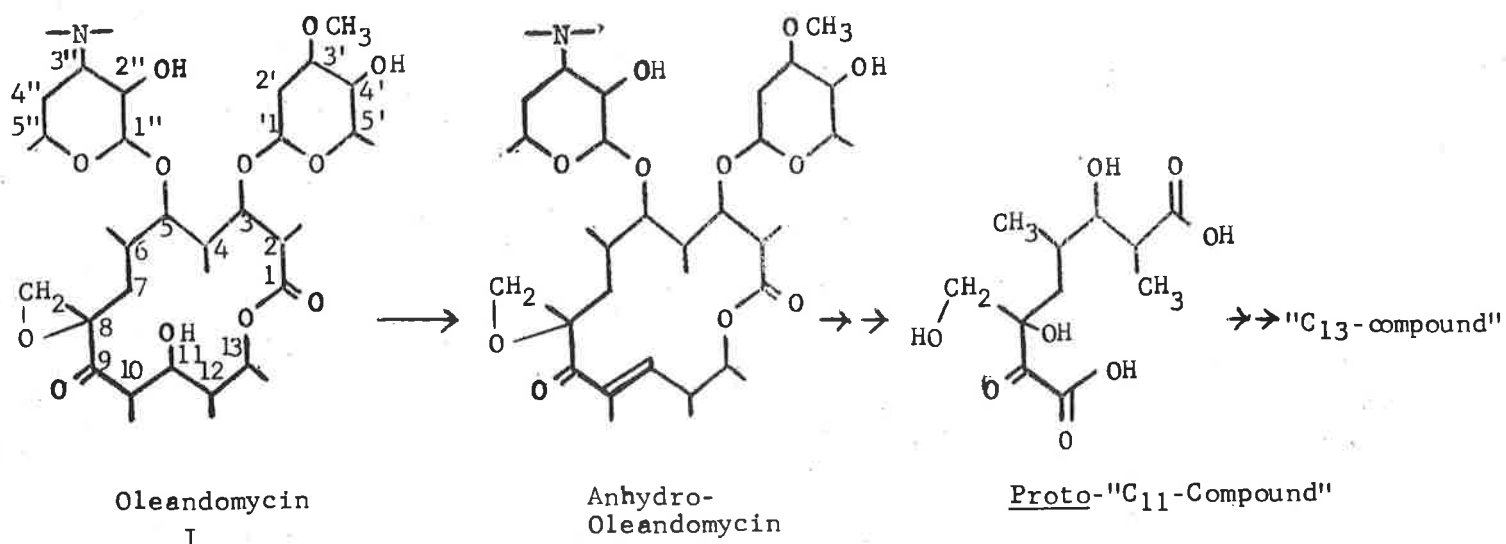
β, D-R : $\text{V}_1-\text{V}_3 = \text{CO}-\text{OCH}_2$; $\text{V}_2 = \text{OCH}_3$; $\text{V}_4 = \text{OD}$

α, D-R : $\text{V}_1 = \text{OCH}_3$; $\text{V}_2-\text{V}_3 = \text{CO}-\text{OCH}_2$; $\text{V}_4 = \text{OD}$

β, D-S : $\text{V}_1-\text{V}_4 = \text{CO}-\text{OCH}_2$; $\text{V}_2 = \text{OCH}_3$; $\text{V}_3 = \text{OD}$

α, D-S : $\text{V}_1 = \text{OCH}_3$; $\text{V}_2-\text{V}_4 = \text{CO}-\text{OCH}_2$; $\text{V}_3 = \text{OD}$

Origin





UNION CARBIDE CORPORATION

P. O. BOX 278, TARRYTOWN, N. Y. 10592

UNION CARBIDE
RESEARCH INSTITUTE

March 3, 1965

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

Dear Barry:

One problem that has occupied us here is the direct measurement of first moments of spectra on the A-60. From these one can obtain the average chemical shift directly (W. A. Anderson and H. M. McConnell, J. Chem. Phys., 26, 1496 (1957)), which may be of interest either in itself or as a starting point for the application of sum rules.

At first we adopted a head-on approach by inserting a linear potentiometer between the spectrometer output and integrator input, and mechanically coupling its wiper arm to the recorder drive. This gave an output proportional to $x G(x)$, which when integrated gave the first moment. We then obtained the integral by fixing the wiper arm (actually by switching to a fixed voltage divider), and obtained the centroid of the spectrum from the quotient of the two.

It later dawned on me that double integration gives a more direct route to the same thing. This follows simply from integrating the definition of G_1 by parts:

$$G_1 = \int_{x_1}^{x > x_2} x G(x) dx = x G_0 - \int_{x_1}^{x > x_2} \int_{x_1}^{x > x_2} G(x) du dx$$

It is assumed, of course that all the spectrum of interest lies between the limits x_1 and x_2 . This equation tells us that the double integral becomes linear once the spectrum is traversed ($x > x_2$) and the horizontal intercept of this line is just G_1/G_0 . Hence all one has to do is extrapolate this linear portion of the double integral back to its intersection with the base line, and the centroid can be displayed right along with the integral on a standard A-60 trace.

We have used either two integrators in series or a double integrator circuit which requires only one operational amplifier. On reasonably concentrated ($\sim 10\%$) solutions an accuracy within 1.0 c.p.s. was not difficult to obtain. In a number of cases we have been able to solve structure problems on the basis of the centroids of spectra.

Professor B. L. Shapiro

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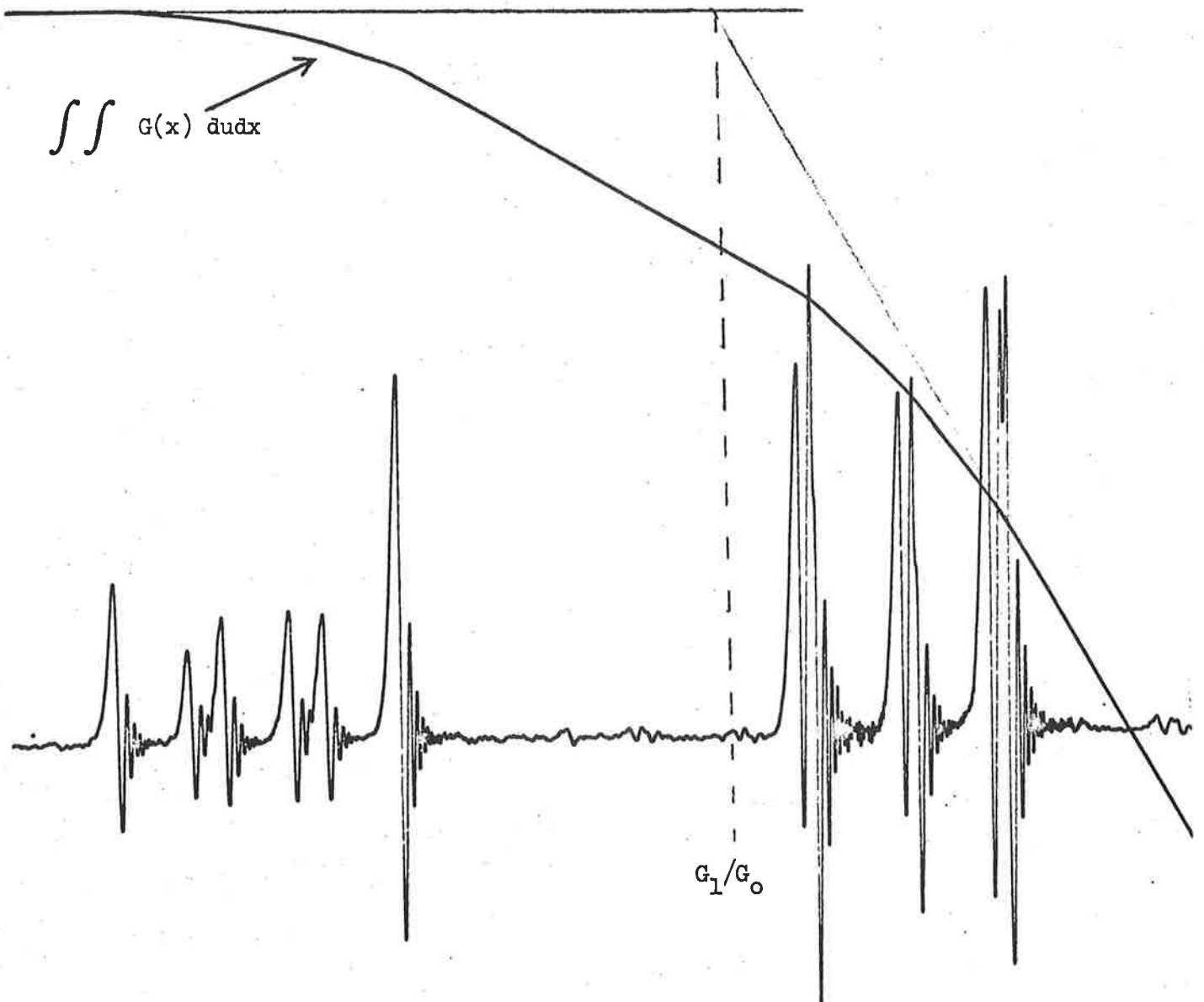
March 3, 1965

I hope to have a limited number of preprints available shortly which go into more detail.

Sincerely yours,

E. B. Whipple
E. B. Whipple

EBW:srb



UNIVERSITY OF WASHINGTON

DEPARTMENT OF CHEMISTRY

SEATTLE, WASHINGTON 98105

March 5, 1965

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

Dear Barry:

Recently I had an occasion to do some work on several B^{11} compounds. In order to check my field I used a pure sample of tetraborane which we had. The resulting spectra looked so interesting I decided to look into it further.

The coupling constants obtained for $H_{1,3}B_{1,3}$ and $H_{2,4}B_{2,4}$ agreed excellently with those found by Williams, Gibbins and Shapiro.¹

$J_{H_{2,4}B_{2,4}} = 129$ c/s. $J_{H_{1,3}B_{1,3}} = 150$ c/s.
 Instead of a value for $J_{HxB_{2,4}}$ of 35-40 c/s. for the bridge protons¹, I found a value of only 29 c/s. This value was readily obtained from the low-field triplet in the B^{11} spectra.

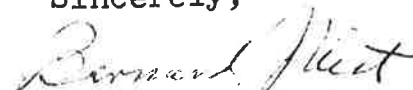
In regards to the up-field doublet, Rigdin, Hopkins and Baldeschwieler² have indicated that $B^{10}-B^{11}$ coupling is small. If this is true, the complexity must originate from a $B_{1,3}^{11}-B_{2,4}^{11}$ or a $B_{1,3}H_{2,4}$ interaction. It is possible to assign a set of peaks to the $J_{HxB_{2,4}}$ coupling in this multiplet but it is difficult at this time to explain the asymmetry present in each group which go to make-up the main doublet.

Maybe with time additional information will help determine this but for the present the complete picture of tetraborane remains not clear.

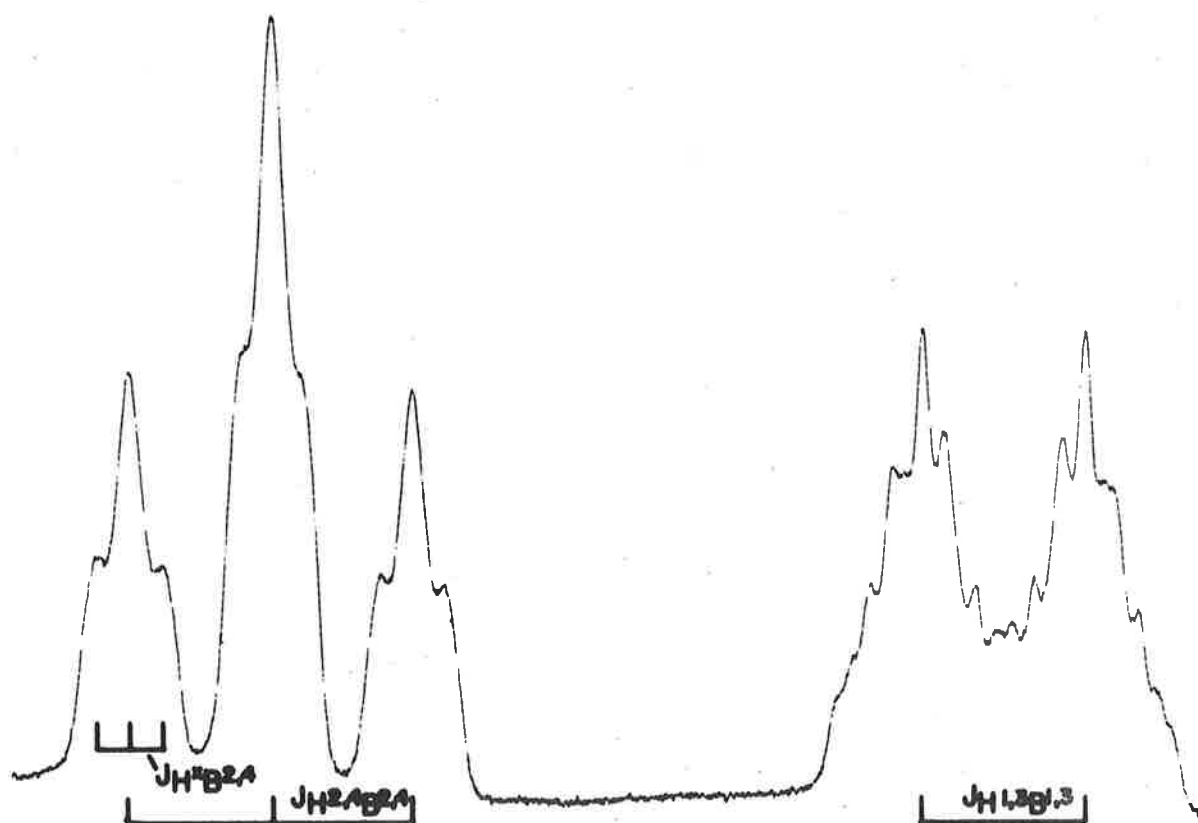
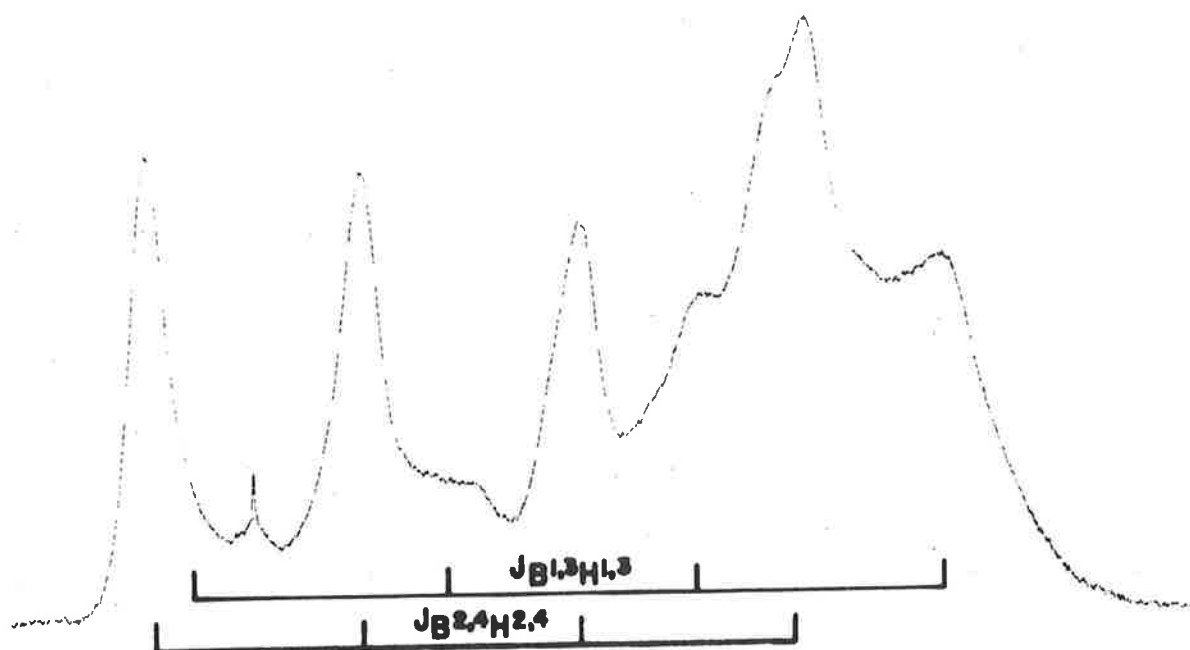
The B^{11} spectra was taken at 19.25mc. and the H^1 spectra at 60mc.

1. R.E.Williams, Sidney G. Gibbins and I.Shapiro, J.A.C.S. 81, 6164 (1959).
2. J.S.Rigdin, R.C.Hopkins and J.D.Baldeschwieler, J.Chem.Phy.35, 1532 (1961).

Sincerely,


 Bernard J. Nist

BJN/lb

Tetraborane B^{11} Spectra (19.25 mc.)Tetraborane H^1 Spectra (60.0 mc.)

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN

Dr. H. Günther

KÖLN, March 7, 1965
ZÜLPICHER STRASSE 47
TELEFON: 2024 239

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

Dear Barry,

On inspection I found a misprint in my recent Newsletter 76-20. The estimated ratio of the equilibrium mixture between oxepin (I) and benzene oxide (II) should read

II : I \sim 0.5 instead of I : II \sim 0.5.

I may add, that in the meantime we have been able to observe the individual spectra of I and II (below -130°C) and I hope to report the complete data soon.

Sincerely yours,



Dr. H. Günther



THE DOW CHEMICAL COMPANY

MIDLAND, MICHIGAN 48641

March 5, 1965

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

Dear Professor Shapiro:

Here is still another "SNAIL - MOUSE - DOG" control circuit for the A-60. It probably doesn't do any better or worse job than anyone else's, but it's fairly cheap and easy to construct. I am enclosing circuit diagrams and a parts list that I used in constructing the device. As shown, accumulation intervals of from about 2 to 80 seconds are available, and "sweep on" times of from about 0.05 to 1.0 sec. are provided. Not shown is a modification consisting of the addition of a switch between the 5 meg pot and the 100K pot which allows an additional 5 or 10 megs to be added to the RC product which determines accumulation times. This increases maximum accumulation time to about $3\frac{1}{2}$ minutes. Since this is a better way of controlling very long accumulation times than the 100K pot shown between B^+ and ground, this 100K pot could easily be omitted in favor of a switch choosing 0, 5 meg, or 10 meg resistance to B^+ .

Another comment I will make is that the expensive metallized paper capacitors may not be necessary. Electrolytics seemed to be as good in the original version with 2-80 seconds range of accumulation time.

Please credit this contribution, if accepted, to the subscription of Dr. J. P. Heeschen, same address as mine.

Yours truly,

A. W. Douglas
Chemical Physics Research Laboratory
6103 Building
Phone - MElrose 5325

Enclosure

abj

FIG. (I.)
WIRING FOR "SNAIL"

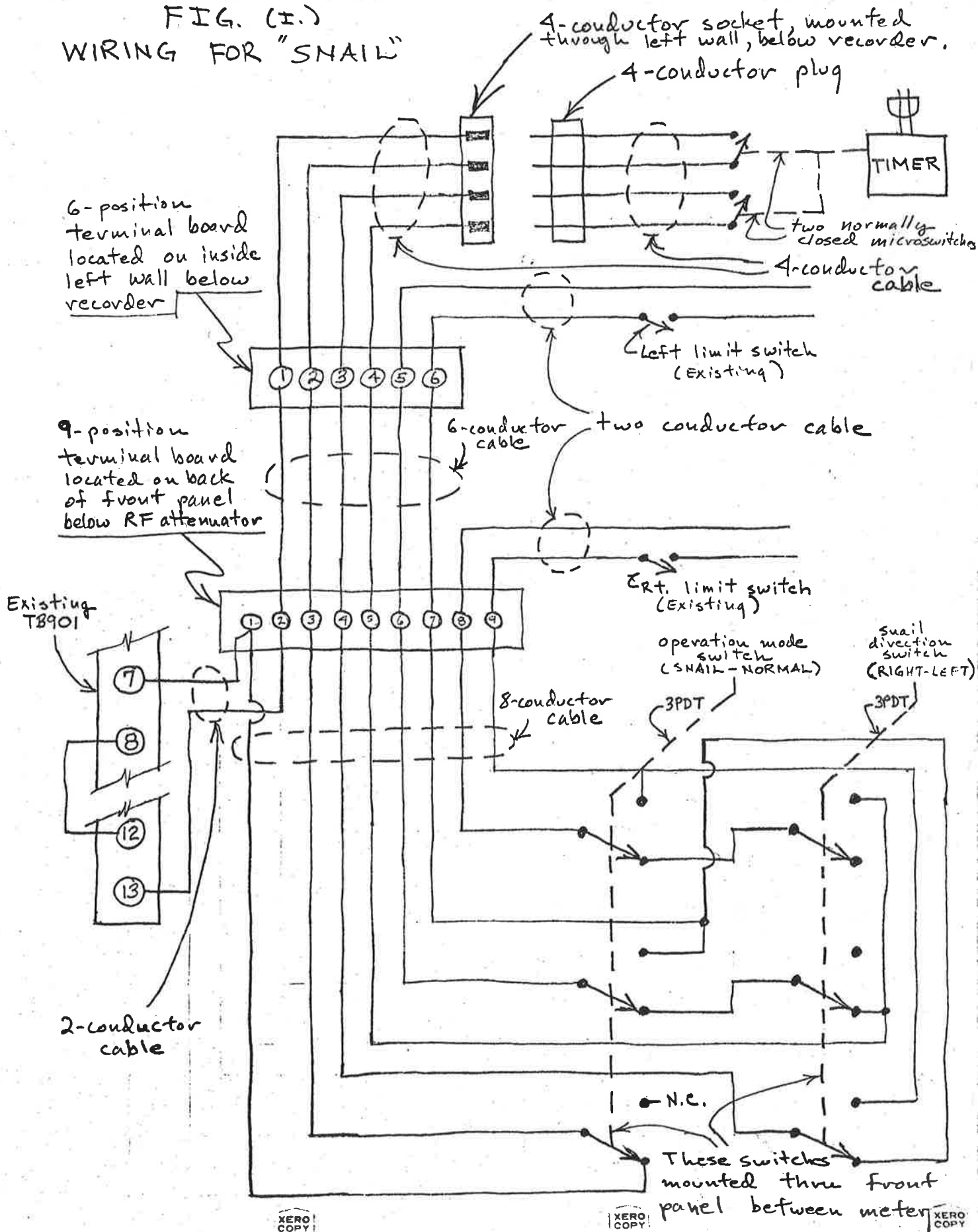
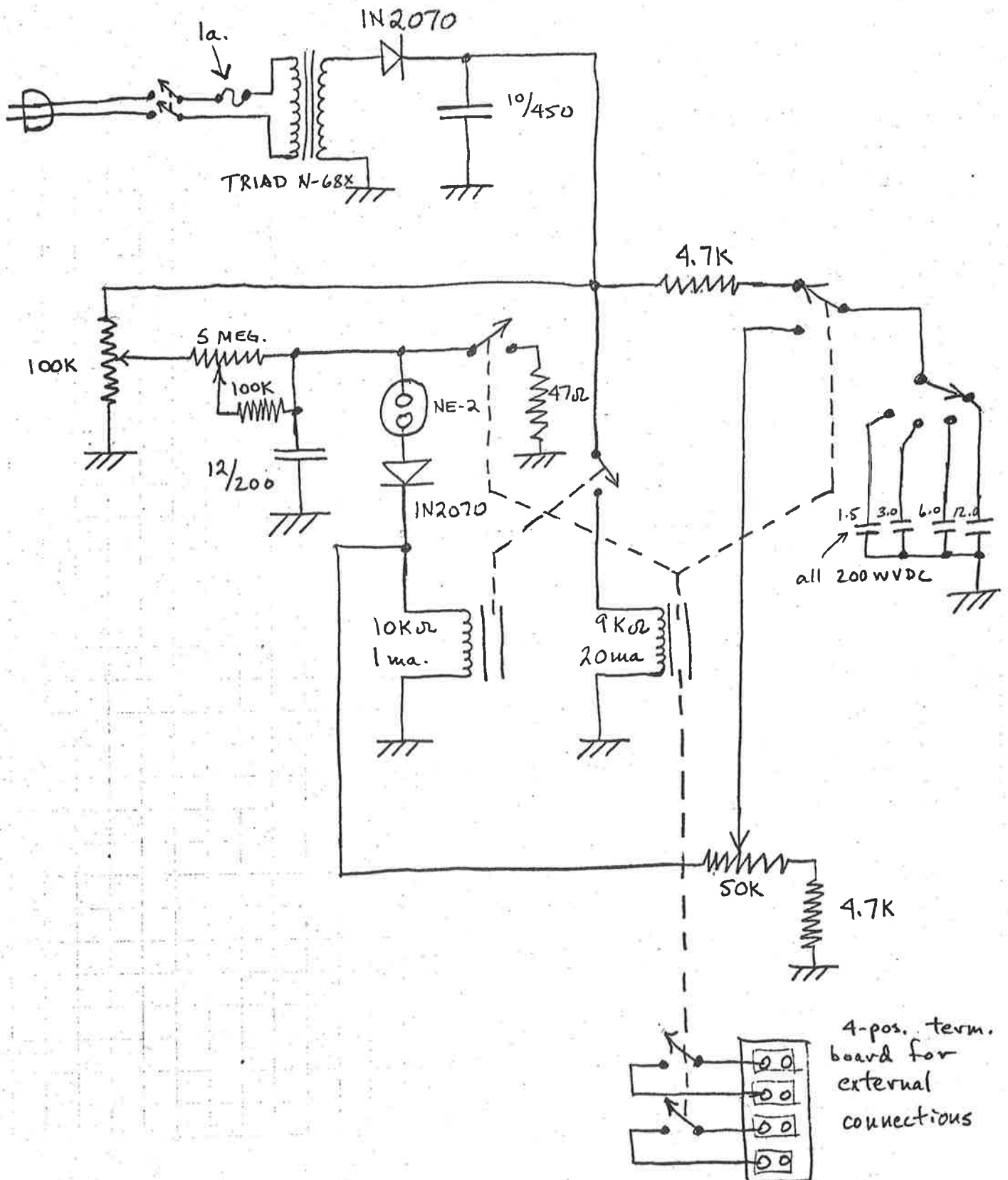


FIG. (II.)

ELECTRONIC TIMER FOR
"SNAIL"

- 6 -

Parts List for sensitivity enhancement device
for the Varian A-60 Spectrometer.

A. For wiring changes:

<u>Quantity required</u>	<u>Manufacturer</u>	<u>Mfr's type</u>	<u>Description</u>
1 ea.	Cinch-Jones	S-304	Four-cond. socket
1 ea.	"	P-304	" " plug
1 ea.	"	6-140	Six-pos. term. strip
1 ea.	"	9-140	Nine- " " "
1 ea.	"	MS-6-140	Six- " marker "
1 ea.	"	MS-9-140	Nine- " " "
2 ea.	any	-	3PDT toggle switch
~7'	"	-	two-cond. cable
8" plus desired external length	"	-	four-cond. cable
~4'	"	-	six- " "
~16"	"	-	eight- " "

(A small piece of hookup wire is used as a jumper from
TB-901-8 to TB-901-12.)

B. For mechanical timer

<u>Quantity required</u>	<u>Manufacturer</u>	<u>Mfr's. type</u>	<u>Description</u>
1 ea.	Industrial Timer Corp.	E-12	40 sec/rev gear assem
1 ea.	" "	RC-4	2-circuit multi-cam timer

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C. For electrical timer

Quantity	Req.	Manufacturer	Mfr's Type	Description
1 ea.		Triad	N-68X	Isolation Transformer
1 ea.		Sigma	5J 010K G	SPDT relay 10K Ω , 1 ma
1 ea.		Potter Brumfield	KHP17D11	4PDT relay 48VDC, 2600 Ω , 20 ma
1 ea.		Grayhill	5001-4	4-pos tap switch
1 ea.		Cutler-Hammer	8370K7	DPST toggle switch
1 ea.		Buss	HKP	$\frac{1}{4}$ " x $1\frac{1}{4}$ " fuse post
1 ea.		Ohmite	CU5031	50K ohm potentiometer
1 ea.		"	CU1041	100K ohm "
1 ea.		"	CU5052	5M ohm "
2 ea.		Sprague	1269252	12 mfd 200V. metallized paper capacitor
1 ea.		"	6059252	6 " " "
1 ea.		"	3059252	3 " " "
1 ea.		"	1559252	1.5" " "
1 ea.		"	TVA1705	10 mfd 450V. electrolytic capacitor
1 ea.		any	-	47 Ω , 1W resistor
2 ea.		any	-	4.7K Ω , 1W resistor
1 ea.		any	-	100K Ω , $\frac{1}{2}$ W resistor
2 ea.		Texas Instruments	IN2070	IN2070 Silicon rectifier
1 ea.		G. E.	NE-2	neon bulb
1 ea.		Cinch-Jones	4-140	4-pos. term. strip
1 ea.		"	MS-4-140	" " marker strip
1 ea.		Bud	AC-429	5"x7"x3" Alum. Chassis
1 ea.		Potter Brumfield	9KH1	Relay Socket

Also needed will be miscellaneous hardware, grounding posts, rubber grommets, power cord, terminal posts, hookup wire, spaghetti, etc.

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

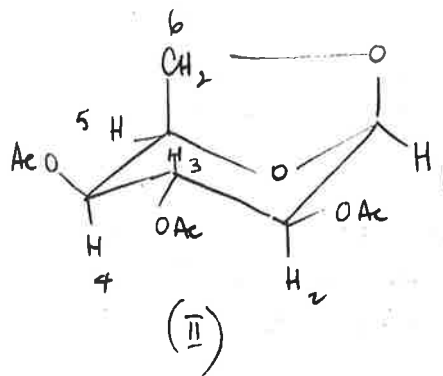
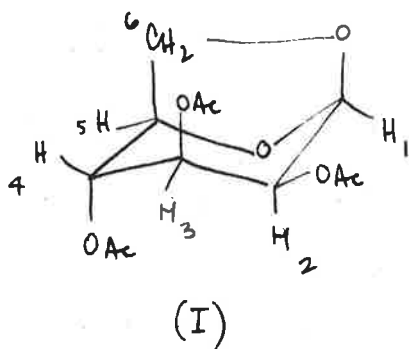
DEPARTMENT OF CHEMISTRY

March 12, 1965

Professor B. L. Shapiro,
 Department of Chemistry,
 Illinois Institute of Technology,
 Technology Centre,
 Chicago, Illinois,
 United States of America.

Dear Barry,

This is just an interim letter and I hope to be able to send you some more interesting data in a few weeks' time. Roy Johnson has recently run some 100 M.c. spectra on the 1,6-anhydro-hexopyranoses which I had previously reported in note form, and these spectra confirmed that the 1,3 - couplings between diequatorial H_1 and H_3 are definitely "long-range" and not "virtual". We also find several additional long-range couplings which can be added to the enormous list already available. These are between H_3 and H_5 of the D-manno-isomer (I) and between H_4 and H_6 of the D-ido-isomer (II).



We shall be giving a full report on these compounds soon.

With best regards,

Lannie Hall

L. D. Hall
 Assistant Professor of Chemistry

SHIFT RANGE AND SUBSTITUTION

Dear Professor Shapiro:

The NMR chemical shift data for the 700 compounds in the two volume Varian NMR Spectra catalog have been compiled and tabulated according to structure and substitution. A few atypical cases are excluded, and strained ring protons are not represented. Chemical shifts are in ppm. downfield from TMS. Data for water are from J. R. Holmes, J. Am. Chem. Soc., 84, 4667 (1962).

PROTONS BONDED TO SATURATED CARBON

ALKANES: METHYL

0.57-2.47	RCH ₃
1.53-2.87	ARCH ₃
1.78-2.68	O=CCH ₃
1.50-3.69	-SCH ₃
1.92-4.30	N-CH ₃
2.15-4.30	XCH ₃
3.22-4.40	-OCH ₃
4.33	O ₂ NCH ₃

ALKANES: METHYLENE

0.35-3.65	RCH ₂ R
2.04-3.52	ARCH ₂ R
2.10-4.28	O=CCH ₂ R
2.21-4.73	-OCH ₂ R
2.23-4.07	XCH ₂ R
2.20-4.47	ARCH ₂ AR
3.13-3.82	O=CCH ₂ AR
3.23-3.57	O=CCH ₂ C=O
3.17-4.67	-OCH ₂ C=O
3.48-4.05	XCH ₂ C=O
3.30-5.03	-OCH ₂ AR
3.93-4.17	XCH ₂ AR
3.10-6.23	-OCH ₂ O-
4.13-5.30	XCH ₂ X
5.57	-OCH ₂ X

ALKANES: METHINYL

1.53-2.40	R ₃ CH
2.14-3.58	O=CCHR ₂
2.46-3.97	ARCHR ₂
2.30-5.02	AR ₂ CHR
3.20-5.33	-OCHR ₂
3.63-3.85	O=CCHRAR
3.59-5.41	-O (O=C) CHR
3.83-5.18	-O (AR) CHR
3.98	(O=C) ₂ CHR
4.10-4.67	XCHR ₂
4.20-5.52	(-O-) ₃ CH
4.20-5.93	O=CCHXR
4.58-6.31	(-O-) ₂ CHR
5.15	ARXCHR
4.73-5.47	AR ₃ CH
4.82-5.50	(-O-) ₂ CHC=O
5.52	-OCH (C=O) ₂
5.63	-OCHRX
5.81-5.82	AR{O=C} CHO-
5.77-6.07	X ₂ CHR
5.93	X ₂ CHC=O
6.12-6.27	(AR) ₂ CHX
5.58-7.75	(-O-) ₂ CHAR
6.85-7.27	X ₃ CH

SHIFT RANGE AND SUBSTITUTION

PROTONS BONDED TO UNSATURATED CARBON

ALKYNES

1.80-2.62	$\text{RC}\equiv\text{CH}$
2.87-3.08	$\text{ARC}\equiv\text{CH}$

ALKENES: UNSUBST.

4.49-5.08	$\text{R}_2\text{C}=\text{CH}_2$
4.77-5.32	$\text{RCH}=\text{CH}_2$
5.12-5.88	$\text{R}_2\text{C}=\text{CHR}$
5.07-6.12	$\text{RCH}=\text{CHR}$ (cis)
5.68-5.93	$\text{RCH}=\text{CHR}$ (trans)
5.72-6.27	$\text{RCH}=\text{CH}_2$

AROMATIC: o-SUBST.

6.03-6.78	$(-\text{O}-)_2$
6.38-7.50	$-\text{O}-$
6.62-7.50	$\text{H}, \text{R}, \text{R}_2$
6.90-7.75	X, X_2
6.83-8.27	AR
7.40-8.36	$\text{C}=\text{O}$
7.77-8.37	$(\text{AR})_2$
8.00-8.61	NO_2
8.70-9.55	$(\text{NO}_2)_2$

ALDEHYDE, FORMYL

7.40-8.30	$-\text{N}=\text{CH}-$
8.02-8.20	$-\text{O}-\text{CH}=\text{O}$
9.47-9.81	$\text{RCH}=\text{O}$
9.48-10.06	$\text{ARCH}=\text{O}$

ALKENES: SUBST.

3.79-4.85	$\text{HC}=\text{CO}-$
5.05-6.99	$(\text{HC}=\text{CH})\text{AR}$
5.73-6.70	$\text{C}=\text{CHC}=\text{O}$
5.38-7.94	$\text{HC}=\text{CC}=\text{O}$ (trans)
6.10-7.83	$\text{HC}=\text{CC}=\text{O}$ (cis)
5.73-8.10	$\text{C}=\text{CHO}-$
6.55-7.33	$(\text{C}=\text{CH})(\text{AR})_2$
7.73	$\text{C}=\text{CHNO}_2$
8.20	$\text{HC}=\text{CNO}_2$

HETEROCYCLIC

5.73-6.30	β } Pyrrole
6.37-6.98	α }
6.13-7.32	β } Furan,
7.03-7.78	α } Thiophene
6.51-7.98	β }
7.20-8.23	γ } Pyridine
8.08-9.04	α }

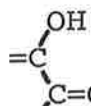
SHIFT RANGE AND SUBSTITUTION

PROTONS BONDED TO OTHER ATOMS:EXCHANGEABLE PROTONS

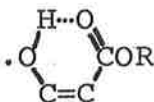
OXYGEN: OH

2.16-4.00	H ₂ O
4.50-5.00	HDO
1.43-4.28	ROH
3.96-5.00	AROH, hindered
5.00-6.00	AROH, common
6.00-8.18	AROH, acidic
10.00-14.22	AROH, chelated

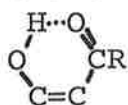
6.77



12.30-12.69



14.17-16.71



7.90

=NOH

8.38-10.30 =NOH

8.86-10.97 α -oxy-COOH

9.63

 α -keto-COOH

10.28-12.14 RCOOH

11.00-13.21 ARCOOH

SULFUR: SH

1.35-2.26	RSH
3.27-3.45	ARSH
4.73	R(C=O)SH

NITROGEN: NH

1.10-2.17	R ₂ NH, RNH ₂
3.30-4.63	AR ₂ NH, ARNH ₂
5.61-6.15	vinyl amine
5.00-13.40	divinyl amine
5.16-7.67	O=CNHR, O=CNH ₂
7.88-9.34	O=CNHAR
8.47	(O=C) ₂ NH
10.95-12.52	C=N-NH

Richard D. Campbell
University of Iowa
Iowa City, Iowa
March 5, 1965

ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, 60616

DEPARTMENT OF CHEMISTRY

15 March 1965

Scale Expansion for the A-60 High Impedance Sweep System.

The following scale expansion system is for the newer high impedance A-60 sweep system. (Cf. Shapiro, Lorenc and Rickert, MELLONMR 54, 14 (1963). The scale expansion circuit is shown in figure 1. It consists of a fixed resistance R1 (47K Ω , 1/2 watt) and a variable resistance R2 (100K Ω , Borg model 205, precision ten turn pot). Switch S1 (SPST) serves to bypass the expansion circuit when normal chart widths are being used.

As in the low impedance sweep circuit, the scale expand resistance is placed in series with the D.C. sweep voltage going to the probe. This point in the high impedance circuit is between the wiper arm of R 918, the chart sweep pot, and R 907. Physically, **this** means disconnecting the lead from the wiper arm terminal of R 918 and connecting the scale expand components between this lead and terminal. These two points were brought out to the mounting position of the scale expander through a two wire shielded cable.

Due to the high impedance of the new sweep system, the value of scale expand resistance has to be much higher for a given scale expansion than that used in the low impedance circuit. Using only the 100K Ω pot in the circuit the maximum scale expansion attainable was about 17 c/s full scale. Seeing that the scale expander would probably be most useful at even greater scale expansions, a 47K Ω fixed resistor was put in series with the 100K Ω pot. This allows the chart to be expanded to about 13 c/s full scale. Using this system, there is an immediate scale expansion of about 25 c/s full scale with the 100K Ω pot at zero resistance. The chart widths between 25 and 13 c/s full scale can then be selected with the 100K Ω pot.

The 100K Ω pot, fixed resistor and, the switch were mounted on a 11"x5¹/₄"x1¹/₈" aluminum plate which was bolted to the under side of the console cabinet on the right side. This location of the controls puts them somewhat out of reach for the casual switch and dial twiddlers. For the potentiometer dial, a Borg Microdial, similar to the Sweep Offset dial, was used.

Finally, a calibration curve was plotted of dial setting versus the scale expansion, full scale, in c/s. The standard used for measuring the chart widths was the separation of the outer peaks in the CH₃CHO quartet, which is 8.55 c/s. The chart widths found in this way were checked by the usual sideband techniques.

Gerald Dagenais

Electronics Technician

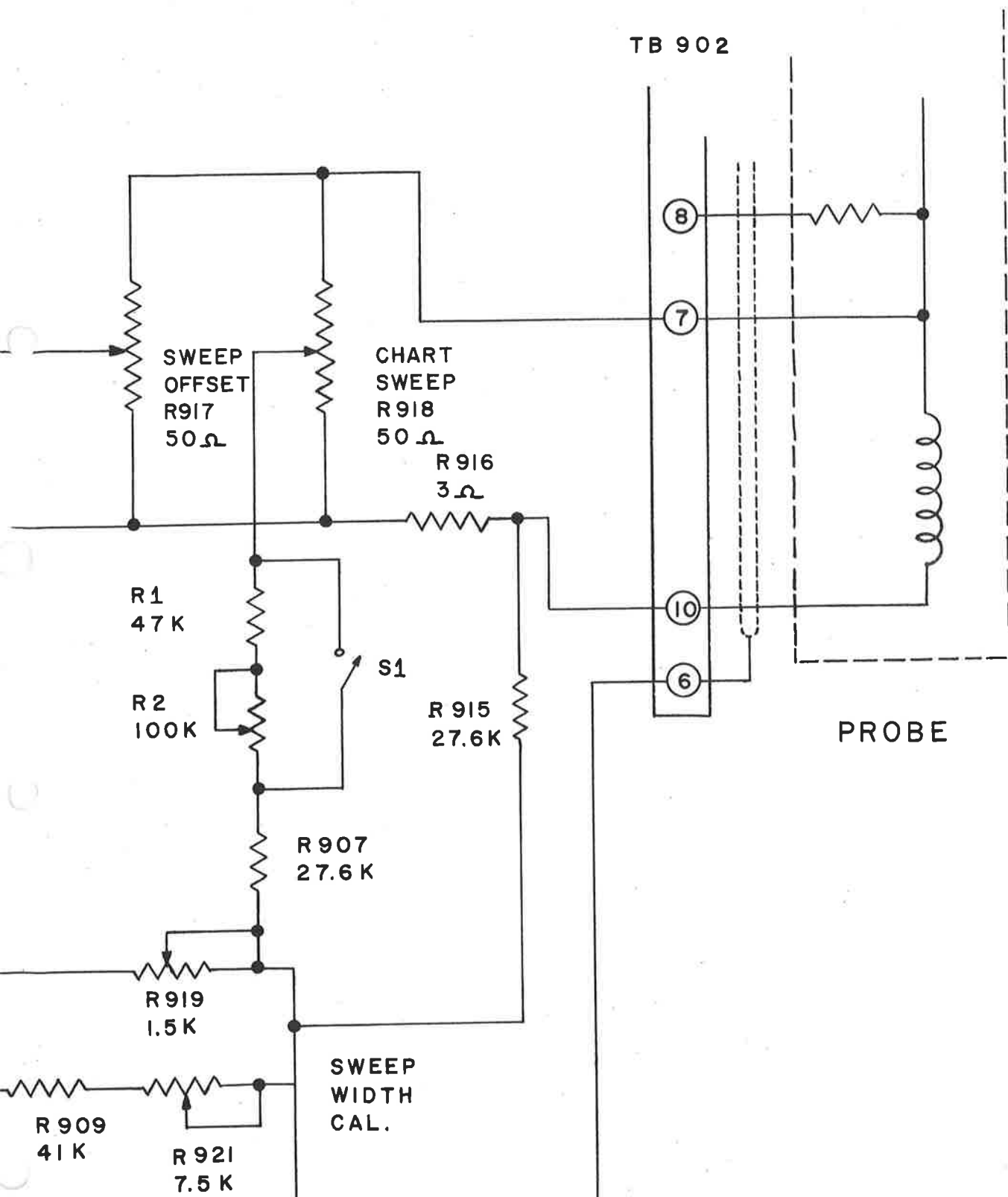


FIGURE 1

UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA 15213
DEPARTMENT OF CHEMISTRY

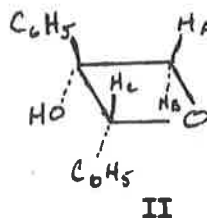
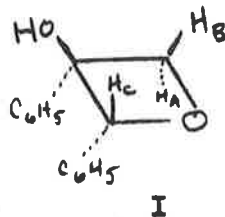
17 March, 1965

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

Dear Barry:

We have recently observed stereospecific long-range (cross-ring) couplings in cis- and trans-2,3-diphenyl-3-oxetanols (obtained by the photocyclization of α -benzyloxyacetophenone). For each compound, cleanly resolved ABC spectra were observed with $J_{AB} \neq J_{BC}$. The p.m.r. parameters are listed below.

	<u>Cis Isomer (I)</u>		<u>Trans Isomer (II)</u>	
Assignment	τ (ppm)		τ (ppm)	
Hydroxyl	6.54		7.58	
H_A	5.17	$J_{AB} = 7.1$ c/s	5.30	$J_{AB} = 7.1$ c/s
H_B	4.94	$J_{BC} = 0.9$ c/s	5.03	
H_C	4.07	$J_{AC} = 0.3$ c/s	4.15	$J_{AC} = 0.9$ c/s
Aromatic	2.95, 2.82		2.63, 2.40	



The isomer assignments were made on the basis of chromatographic behavior and p.m.r. evidence; the hydroxyl proton above the face of the aromatic ring in the trans-isomer (II) is shielded relative to the hydroxyl proton of the cis-isomer (I). A similar behavior is also observed in the analogous cyclobutanols (1).

The assignments of H_A and H_B in both isomers is not unequivocal. The high field shift of the methine proton (H_C) cis to the phenyl ring in II relative to the shift of H_C in I indicates that the methylene proton in I and II cis to the adjacent phenyl group might be observed at higher field; thus H_A is indicated as the proton cis to the phenyl ring and H_B as the proton cis to the hydroxyl group. The difficulty in assigning with certainty the positions of H_A and H_B is

enhanced by the observation that the four methylene protons in 3-phenyl-3-oxetanol give rise to a sharp singlet at $\tau = 5.15$ p.p.m. in CDCl_3 ; however, in dimethylsulfoxide, the geminal protons no longer show magnetic equivalence but exhibit the expected AB pattern, $J_{AB} = 6.5$ c/s (2).

If these assignments are valid, then the large cross-ring coupling (0.9 c/s) occurs between protons in a cis relationship, with a significantly smaller (0.3 c/s) coupling of the trans protons, observable only in I. Johnson *et al.* have reported a trans cross-ring coupling of -1.5 c/s in 3,4-dichlorocyclobutane-1,2-dicarboxylic acid and an undetermined (i.e., cis or trans) cross-ring coupling of 0.5 c/s in the analogous dibromo compound (3). Roberts has observed a cross-ring coupling between a methyl group and a fluorine across a cyclobutane ring (cis-relationship) (4). It is evident in the cases of I and II that the cross-ring coupling is a highly stereospecific one, presumably occurring between two protons in a cis-relationship.

Sincerely,

Clay

C. E. Griffin

Myra

M. Gordon

Bob

R. B. LaCount

- (1) R. B. LaCount and C. E. Griffin, Tetrahedron Letters, submitted.
- (2) P. Yates and A. G. Szabo, Tetrahedron Letters, 485 (1965).
- (3) L. F. Johnson, V. Georgian, L. Georgian and A. V. Robertson, Tetrahedron, 19, 1219 (1963).
- (4) M. Takahashi, D. Davis and J. D. Roberts, J. Am. Chem. Soc., 84, 2935 (1962).

UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

March 17, 1965

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

Re: Carbon-13 Chemical Shifts for Pyridine and
Imidazole and Their Ionic Derivatives.

Dear Barry:

Paul Lauterbur reported carbon-13 chemical shift data for nitrogen heterocyclics two months ago in *IIITNMRN* and exhibited that these values could be rationalized in terms of theoretical π -electron charge densities. Contained in Table I are chemical shift values for pyridine, pyridinium cation, imidazole, imidazolinium cation and the imidazolate anion.

Table I
Position and Carbon-13 Chemical Shift
(in ppm relative to benzene)

Compound	2,6-carbons	3,5-carbons	4-carbon
Pyridine (C_5H_5N)	-21.7(0.952)	+4.6(1.004)	-7.4(0.981)
Pyridinium Ion ($C_5H_5NH^+$)	-13.2(0.899)	+0.4(0.927)	-19.2(0.829)
	2-carbon	4,5-carbons	
Imidazolate ($C_3H_3N_2^-$)	-16.5	+1.8	
Imidazole ($C_3H_3N_2H$)	-7.2	+6.7	
Imidazolinium ($C_3H_3N_2H_2^+$)	-5.6	+8.9	

These data indicate the sensitivity of the carbon-13 chemical shift upon protonation of the nitrogen atom. Furthermore, it is interesting to note that the theoretical estimates [see R. D. Brown and M. L. Heffernan, *Aust. J. Chem.* **12**, 554 (1959)] of the π -electron charge densities given in parentheses in Table I for pyridine and its protonated cation show the same trends as the corresponding chemical shift values. Note that the order in both the chemical shift and the charge densities is different for the two compounds. While this explanation for the scrambled chemical shifts would argue for the validity of π -electron charge density correlations, the plot of chemical shift vs charge density do not coincide for the two compounds, thereby suggesting the additional importance of sigma bond effects. No satisfactory agreement has been found between π -electron charge densities and the experimental shielding values for the three imidazole species.

Sincerely yours,

David M. Grant
David M. Grant

Ronald J. Pugmire
Ronald J. Pugmire

P.S. I still have a few reprints of the NMR section of the 1964 Annual Reviews of Physical Chemistry and would be happy to distribute them so long as the supply lasts.
(DMG)



LABORATORIUM
VOOR
ORGANISCHE CHEMIE

Dir.: Prof. Dr. F. GOVAERT

GENT, March 16th 1965.

J. Plateaustraat, 22
België - Europa

Tel. 23.38.21

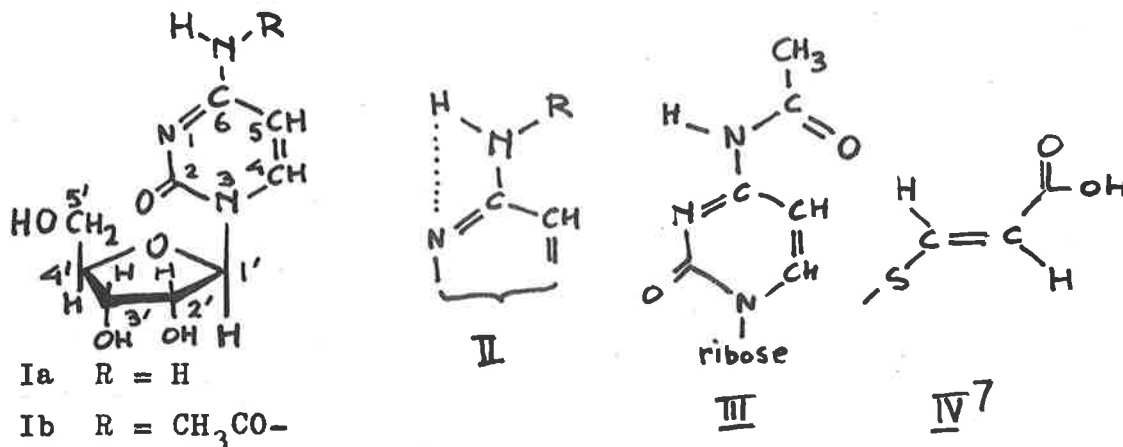
Prof. B. L. SHAPIRO,
Illinois Institute of Technology,
Technology Center,

CHICAGO, ILLINOIS 60616.

Concerning : ortho deshielding by the acetamido group
(cf. Prof. S. Sternhell, IITN MR, 76-2 (1965)).

Dear Professor Shapiro,

In connection with Prof. Sternhell's observation (loc.cit.) of the above mentioned effect, it is interesting to compare with a similar phenomenon found in a nucleoside derivative¹-N₆ acetylcytidine (Ib)-which was prepared² at our University and whose spectrum (fig. 1) was run at our department. That cytidine (Ia) is been acetylated at N₆, rather than at N 1, has been demonstrated unambiguously³. We have now compared the NMR data of cytidine, N₆-acetylcytidine, N 1-methylcytidine⁴ and cytidine sulfate in DMSO at 25 and 70° (table).



Spectra of cytidine and its sulfate have been already published and commented extensively⁵. The table shows that the deshielding effect of the olefinic protons, especially of the ortho C5H, is striking, and this must be attributed for a great part to the preferential orientation as in III, the carbonyl group having a nodal deshielding effect as found in other cis-systems⁶, such as in IV⁷. The temperature dependance is great, in comparison with the other substances recorded, and this illustrates the dislocking of the preferred orientation.

.../...

Table

Chemical Shifts (in δ from internal TMS Signal) and Coupling Constants of
Cytidine and Derivatives (VARIAN 56.4 Mc).

Assignment		4 H	5 H	1' H	2'H/3'H 4'H	5' H	MeCO	N-Me	OH	N(6)H a.o.
Product		δ $J_{c/s}$	δ $J_{c/s}$	δ $J_{c/s}$	δ	δ	δ	δ	δ	δ
N(6)-acetyl cytidine (Ib)	Roomtmpt	8.44 5.5 (1)	7.19 5.5 (1)	5.80 2.5 (1)	3.99 (3)	3.71 (2)	2.12 (3?)		5.50 & 5.10 (1) (2)	10.8 (1)
	70°	7.44 8 (1)	6.52 8 (1)	5.47 2.5 (1)	4.02 (3)	3.71 (2)	2.17 (3)		4.75 (3)	9.2 (1)
Cytidine (Ia)	Roomtmpt	7.96 7.5 (1)	5.88 * (1)	5.81 * (1)	4.00 (3)	3.65 (2)			5.40 & 5.15 (1) (2)	7.36 (2)
	70°	7.85 7.5 (1)	5.88 * (1)	5.76 * (1)	4.01 (3)	3.68 (2)			4.65 (5)	see OH
Cytidine sulfate **	Roomtmpt	8.14 7.5 (1)	6.04 8 (1)	5.74 2.5 (1)	3.99 (3)	3.66 (2)			6.55 (3.5)	8.6 (2)
	70°	8.09 7 (1)	6.08 7.5 (1)	5.79 2.5 (1)	4.02 (3)	3.69 (2)			6.9 (5.5)	see OH
N ¹ Me-cytidine chlorhydrate	Roomtmpt	8.37 8 (1)	6.43 7.5 (1)	5.74 2.5 (1)	3.99 (3)	3.68 (2)		3.40 (3)	5.20 (3)	9.7 (5)
	70°	8.28 8 (1)	6.43 7.5 (1)	5.75 2.5 (1)	4.03 (3)	3.69 (2)		3.44 (3)	5.0 (3)	9.5 (5)

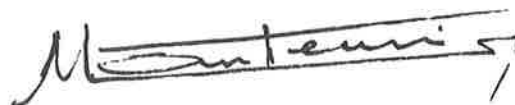
* Could not be evaluated (overlapping)

** This product is protonated at N1 (C.A.Dekker, Ann.Rev.Biochem. 29, 453 (1960);
A.R.Katritzky, A.J.Waring, J.Chem.Soc., 3046 (1963)).

.../...

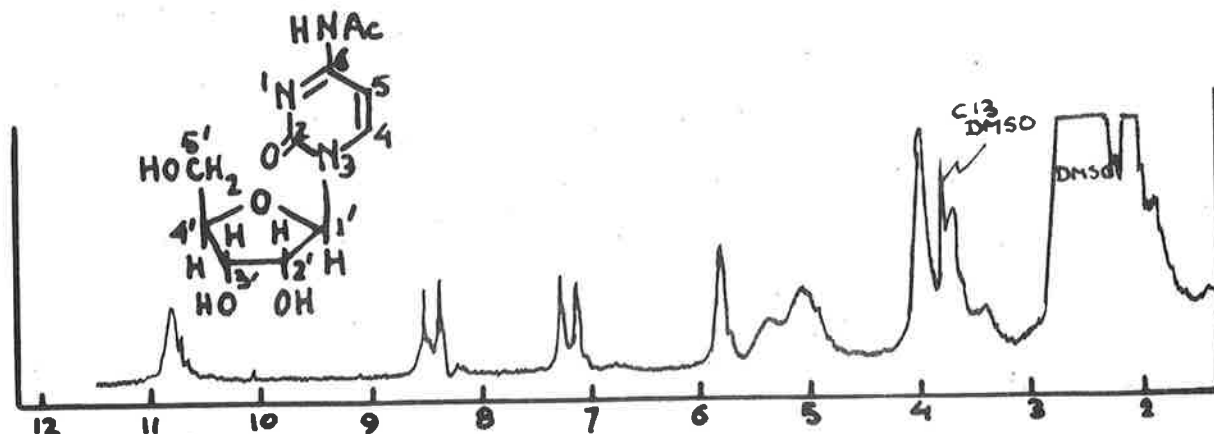
Although possible hydrogen bond formation (as in II) has been advanced⁸, it is even more plausible that the excess of the population of the rotamer III is due to dipolar repulsion. The models investigated by Prof. Sterhell, Brown and Rae (loc.cit.) do not reject this possibility. It can be argued f.i. that some structures, such as 2,5-dimethoxy-, and 2,5-dichloro acetanilide should be less appropriated for a (five membered) H-bond formation than the ortho substituted nitro acetanilides. Perhaps it should be of some interest to examine those acetanilides with meta polar substituents, such as 3,4-dinitro acetanilide ?

With kind regards,



Marc ANTEUNIS.

1. More ample discussion on the NMR spectra will be published (M.Anteunis, M.Van Montagu).
2. M.Van Montagu, Lab. of Physiological Chemistry, University Ghent.
3. M. Van Montagu, to be published.
4. Prepared according P.Brookes, P.D.Lawley, J.Chem.Soc., 1348 (1962).
5. L.Gatlin, J.C.Davis Jr., J.Am.Chem.Soc., 84, 4464 (1962) and references therein.
6. L.M.Jackman "Applications of NMR Spectroscopy in organic Chemistry" Pergamon Press (1959).
7. H.Hogeveen, C.Maccagnani, F.Taddei, Tec.Trav.Chim., 83, 937 (1964).
8. S.F.Mason, J.Chem.Soc., 3619 (1958).



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

March 17, 1965

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

Dear Barry:

We will have a new post-doctoral position available for the academic year 1965-66.

We are looking for a good chemist with a strong physical background and an interest in using NMR for unravelling the tertiary structure of polypeptides and proteins. Thorough prior knowledge of NMR and protein chemistry is most welcome but not essential. Conditions of the appointment, salary etc. can be adjusted to mutual satisfaction; enthusiasm for the project is an absolute prerequisite.

Sincerely,


Oleg Jardetzky

OJ:rrl

"Studies Concerned with the Synthesis of 1-Methyl-2-Phenyl-benzocyclobutadiene"

A. T. Blomquist and C. G. Bottomley
J. Am. Chem. Soc. 87, 86 (1965)

"Vinca Alkaloids. XVII. Chemistry of Catharanthine"

M. Gorman, N. Neuss and N. J. Cone
J. Am. Chem. Soc. 87, 93 (1965)

"Hydrogen Exchange in Chlorophyll and Related Compounds, and Correlation with Molecular Orbital Calculations"

R. C. Dougherty, H. H. Strain and J. J. Katz
J. Am. Chem. Soc. 87, 104 (1965)

"Photoisomerization of trans-15,16-Dimethyldihydropyrene"

H.-R. Blattmann, D. Meuche, E. Heilbronner, R. J. Molyneux and V. Boekelheide
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