Texas A & M University N-M-R Newsletter

No. 126
MARCH, 1969

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Deadline Dates: No. 127: 1 April 1969
No. 128: 5 May 1969

All Newsletter correspondence, etc., should be addressed to:

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

הטכניון - מכון טכנולוגי לישראל
TECHNION - ISRAEL INSTITUTE OF TECHNOLOGY

הפקולטה לכימיה
DEPARTMENT OF CHEMISTRY

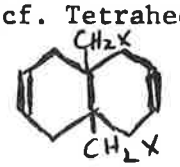
13 February, 1969

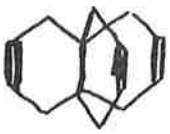
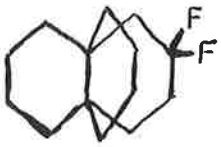
Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Dear Barry,

A. Ring Inversions; B. Relaxation Times. *

Sorry you had to remind me of my contribution. Aren't the subscribers of TAMU NMR NEWSLETTER entitled to a sabbatical (that is omitting one subscription every 54 (6 x 9) months)?

A. Dr. J. Altman and H. Gilboa have continued their work on the kinetics or ring inversion (cf. Tetrahedron Letters 14,1329 (1967)). The systems under study are  where X = Br, CN, CO_2CH_3;

 and  . Arrhenius activation energies were obtained from line shape anylisis of proton or fluorine resonances. The work is presently written for publication.

B. R. Adar and me are busy measuring relaxation times. In a solution of $K_3Co(CN)_6$ the N resonances get narrow with increasing temperature whereas the Co resonances behave in an opposite manner i.e. broaden with increasing temperature. This behavious probably is due to a large spin-rotation contribution to the Co relaxation whereas the N relaxation is predominantly quadrupolar. We try to measure precise values of T_1 for the Co. We have also started with other similar systems which might give information on molecular motions in liquids and solutions.

Yours sincerely
Aharon
A. Loewenstein.

Dear Aharon:

Your idea is not bad, and I will be happy to apply it, although selectively. Requests for such dispensations will be handled on an individual basis, with the answer almost invariably being no, especially in those instances where I have abundant reason to believe the requester has much of interest he really could write. To anticipate your next question, the answer is no.

BLS

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Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station
Texas 77843
United States of America

Your ref:

Our ref: JSG/CG/CAG

Date: 4 February 1969

Dear Professor Shapiro,

Substituted Celluloses

Thank you for your reminder about our contribution to the Newsletter.

One of our present research topics concerns the order of substitution of the hydroxyls in the cellulose molecule during both esterification and etherification reactions, e.g. acetylation, nitration, methylation, etc. Much of this work is being done by infra-red techniques but we have also examined one or two derivatives by N.M.R. using a Perkin-Elmer R10 60-megacycle spectrometer with interesting results.

Infra-red measurements with phenylurethan derivatives of cellulose acetates in dilute solution has indicated that cellulose diacetate, prepared in the usual manner from acetic acid, acetic anhydride and H_2SO_4 has predominantly structure I.

The N.M.R. spectrum as a 20% solution in acetone-D_6 has a sharp absorption at 7.15τ which disappears on deuteration and is clearly due to the remaining hydroxyl. There is some evidence from the spectrum of splitting of this peak which we take to be due to an increase in the lifetime of the protons in the hydroxyl groups due to the high concentration of acetone as found by Boris et al for methanol. There will also be a contribution from hydrogen bonding. The complete assignments we have made are as follows:

Table 1

Protons	τ
a	7.90
b	7.88
c	5.15
d	6.10
e	7.15

FROM: J.S. Glasby/C. Gordon

CONTINUATION SHEET NO.: 1.

TO: Professor B.L. Shapiro

DATE: 4 February 1969

As might be expected, the absorption due to (c) and (d) are very broad and little fine structure is evident.

The phenylurethan of cellulose diacetate, prepared by reacting the latter with phenyl isocyasate in pyridine at 85°C for five days, shows a similar spectrum with the aromatic absorption centered at 2.60τ .

One singular feature we have encountered is that, on deuteration of the cellulose diacetate, the peaks due to protons (a) and (b) are shifted downfield by 0.1τ. So far we can find no explanation for this anomalous behaviour.

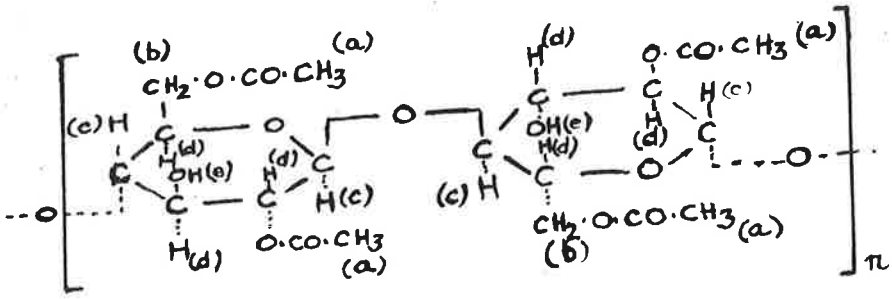
Shortly, we hope to extend these investigations to cover a wide range of cellulose derivatives.

Sincerely yours,

J.S. Glasby

Charles Gordon

C. Gordon



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LABORATORIUM
voor
ORGANISCHE CHEMIE

GENT, February 5th 1969.
KRIJGSLAAN 105
(België - Europa)
Tel. (09) 22.60.95

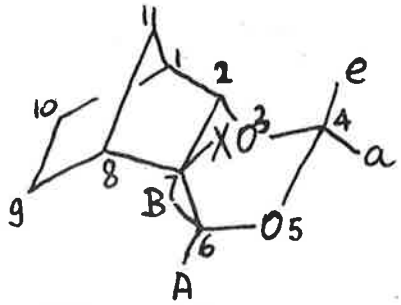
Professor B. L. SHAPIRO,
Department of Chemistry,
Texas A and M University,
College Station,

TEXAS 77843.

A genuine boat 1,3-dioxane derivative.

Dear Prof. Shapiro,

We wish to report some NMR-data on a new 1,3-dioxane derivative, synthesised in order to complete a set of models of a boat-family. From the observed coupling constants and the solvent shifts the compound appeared to be endo-3,5-dioxa-tricyclo-[6.2.1.$0^{2,7}$]-undecane (I).



The 100 Mc NMR-spectrum was run in CS_2 and in benzene. The different proton shifts are listed in the table.

Proton shifts of (I) (10 % solution, TMS internal reference).

	CS_2	ØH
H_2	3.98	3.88
H_{4_e}	4.76	4.87
H_{4_a}	4.52	4.48
H_{6_A}	3.79	3.75
H_{6_B}		3.66

The AB-part of the ABX-spin system formed by the $2H_6$- and by the H_7-proton (ØH-sol.), is analyzed by the subspectral method.

$$J_{AB} = 11.66 \text{ cps}, \quad J_{AX} = 4.61 \text{ cps}, \quad J_{BX} = 7.30 \text{ cps}$$

In CS_2 we observe only a doublet for the AB-protons, J being 6.14 cps (deceptively simple spectrum).

.../...

.../...

The values for $J_{2,1}$ and $J_{2,7}$ are nearly independant of the solvent :

$$J^{\emptyset H}_{2,1} = 4.92 \text{ cps}, \qquad J^{CS_2}_{2,1} = 4.91 \text{ cps}$$

$$J^{\emptyset H}_{2,7} = 9.30 \text{ cps}, \qquad J^{CS_2}_{2,7} = 9.63 \text{ cps}.$$

By multiple irradiation experiments (ØH), H-1 could be located at about δ 2.1-2.4.
The H-6A proton shows a long-range coupling of about 0.8 cps with H2e. This coupling follows a planar zig-zag path if a deformation of the "classical" boat is accepted.
In this compound we observed a $^2J_4$ of 4.73 cps. In another product, the 2,4-dioxa-bicyclo-[3.3.1]-nonane (1), the J_{gem} is only 5.30 cps, where in 1,3-dioxanes in the "ideal" chair conformation a geminal coupling constant of ca 6.0-6.2 cps is normally found. This algebraic decrease of the geminal coupling (O-$\underline{CH}_2$-O) is in accordance with our expectations.

In previous papers it was noticed that an increase of the number of p-orbitals parallel to vicinal C-H bonds increases J_{gem} (2). It seems therefore to be experimentally settled that the value of the geminal coupling constant can be used as a criterium for the evaluation of a chair and/or boat form. A maximal parallelity being expected in the flexible or twist-boat conformation, the expected $^2J_2$ value in twist-forms may be evaluated at ca. -3.5 cps.

G. SWAELENS.

M. ANTEUNIS,
Prof. Organic Chemistry.

References.

(1) G. Swaelens, and Anteunis M.; Bull.Soc.Chim.Belges (1969); in press.

(2) i.e. : Anteunis M.; Bull.Soc.Chim.Belges 75, 413-25 (1966).

CZECHOSLOVAK ACADEMY OF SCIENCE
INSTITUTE OF ORGANIC CHEMISTRY AND BIOCHEMISTRY,
FLEMINGOVO NÁM. 2
PRAHA 6

Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station
Texas 77843 - U.S.A.

February 6th, 1969

Standard steroid model for semi-empirical chemical shift calculations

Dear Professor Shapiro:

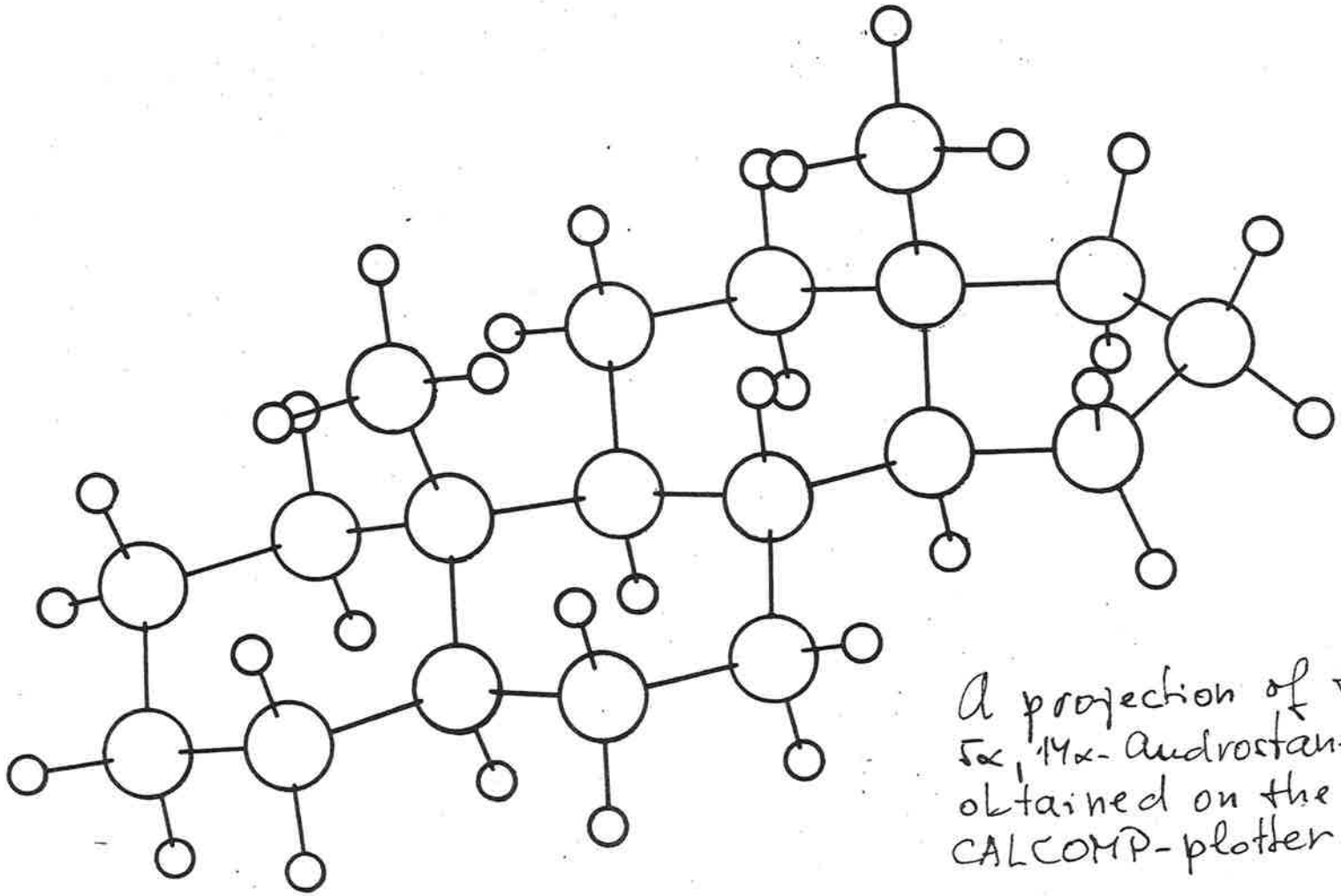
One of our project under way at present is the study of the applicability of various approximative formulas of McConnell type in solving of structural and stereochemical problems of organic compounds. As the comparison and reproducibility of the calculations based on the measurements on Dreiding modles is difficult, we tried to calculate standard mathematical models based on the data from roentgen analysis. At first we calculated a standard steroid skeleton with various types of ring junctions. An ALGOL program was written to calculate the coordinates of all atoms. The input are the bond lengths, valency and torsional angles (obtained from published roentgen data /1/) and topological information. The torsional angles are varied to achieve the ring closure /2/. The agreement between calculated shielding contributions on angular methyl groups using this model and known Zürcher's data is quite good. A projection of 5α, 14α-androstane obtained on the CALCOMP-plotter using the calculated coordinates is shown for illustration.

The ALGOL program is available on request.

Yours sincerely,

Z. Samek P. Sedmera

1. Giese, H.J., Altona C., Romers C.: Tetrahedron 23, 439 (1967)
2. Vítek A.: Coll.Czech.Chem.Commun. 33, 1601 (1968)



A projection of the calculated 5α, 14α-androstane skeleton obtained on the CALCOMP-plotter

National Chemical Research Laboratory

of the South African Council for Scientific & Industrial Research

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Telephone 74-6011

Our file Your file

P.O. Box 395, Pretoria

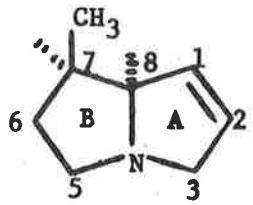
7th February, 1969

Prof. B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
COLLEGE STATION,
Texas 77843,
U.S.A.

Dear Prof. Shapiro,

NMR Study of Heliotridene

We recently analysed the 100 MHz spectrum of heliotridene (I) in $CDCl_3$ which is structurally very similar to heliotridine and retronecine investigated by Culvenor *et al.*[1]



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We obtained all chemical shifts and coupling constants from a first-order analysis. The vicinal and allylic couplings require a planar pyrroline ring A while the other ring exists in two rapidly interconverting exo- and endo-buckled conformers with the 6-carbon out of the plane of the other B-ring atoms (angle of buckle *ca.* 45°).

The homoallylic couplings $J_{3\alpha,8}$ and $J_{3\beta,8}$ (3.65 and 5.05 Hz, respectively) are exceptionally large, but similar to those reported for heliotridine (2.0 and 4.6 Hz) and retronecine (3.5 and 5.4)[1]. We found only one further homoallylic coupling of comparable magnitude in the literature (futronolide: 5.0 Hz)[2]. Decoupling experiments showed the signs of the 3α,8- and 3β,8-couplings in heliotridene to be positive with respect to the assumed negative geminal 3α,3β-coupling constant, which is in accord with theoretical predictions[3]. The planar conformation of the unsaturated ring does, however, not account for the abnormally large values nor can it explain the differences in magnitude between $J_{3\alpha,8}$ and $J_{3\beta,8}$. σ-Bond contributions via two pathways are possible and could be positive to increase the coupling. However, the 5-bond σ-contribution is expected to be small and no couplings between the 3 and 5 or 5 and 8 protons could be observed despite of their steric relationships being very similar to the 3,8-stereochemistry. This renders an appreciable σ-bond

coupling via the nitrogen atom unlikely and excludes the effect of the nitrogen lone-pair electrons as a possible explanation for the difference between the homoallylic couplings. Furthermore direct contributions to the coupling constants are likely to be small and negative.

Any suggestions how to explain these homoallylic couplings satisfactorily, would be very much appreciated.

Yours sincerely,

P.L. Wessels J.P. Tollenaere K.G.R. Pachler

References

(1) C.C.J. Culvenor, M.L. Heffernan, W.G. Woods, *Austr. J. Chem.* **18**, 1605 (1965).

(2) H. Appel, R.P. Bond, K.H. Overton, *Tetrahedron* **19**, 635 (1963).

(3) M. Barfield, *J. Chem. Phys.* **48**, 4458 (1968).

The University of Western Ontario, London, Canada

Faculty of Science
Department of Chemistry

February 12, 1969

Prof. B.L. Shapiro,
Dept. of Chemistry,
Texas A & M University,
College Station Texas 77843
U.S.A.

Dear Barry,

Homoconjugative Interactions in β,γ-Unsaturated Ketones

Faced with your ultimatum on the pink paper, I hereby submit the "price" for a continuing subscription to the TAMU NMR Newsletter. By this time I had hoped to be able to show some ^{13}C spectra from our up-graded instrument but, because of the delays I must postpone this until the next "payment" is due. Instead a brief report of some work done in the old-fashioned way may fulfill my obligation.

One of the first features noted in our initial studies of carbonyl carbon shieldings is their apparent sensitivity to conjugative interactions. Conjugation tends to shield these nuclei appreciably (9-12 ppm) and the degree of shielding can be altered by steric interference with the conjugated system. An extension of this work led us to an examination of the effects of β,γ-olefinic bonds with the idea that a homoconjugative π-π interaction between the double bond and carbonyl group might be detected by ^{13}C NMR. It follows that some fixed systems will have the appropriate geometry for extensive overlap while others, either flexible or rigid will not. Since these interactions affect electronic spectra, it may be possible to devise, by a combination of UV and NMR data, a means for assessing the relative contributions by homoconjugative interaction in the excited and ground states. Some representative data from our ^{13}C work are collected in the Table in which the effects of an α,β-olefinic bond are compared, where possible, with those for a β,γ-olefinic group, $\Delta\delta(\alpha)$ and $\Delta\delta(\beta)$, respectively. One of the first systems examined showed the largest effect yet found. This ketone was included in one of George Savitsky's studies and was published in connection with another aspect of carbonyl shieldings. [J. Phys. Chem. 69 3105 (1965)]. Several pairs of ketones were examined by Dr. Gurudata, as a part of his Ph.D. program, and most of the data in the Table are his. It seems clear that

a relation exists between the orientations of the olefinic and carbonyl bonds and the carbonyl carbon shieldings, especially in the bicyclic systems. It is interesting that the anomeric assistance factors for the corresponding anti or exo-tosylates [Schleyer, JACS 86, 1856 (1964)] roughly correlate with $\Delta\delta(\beta)$ for the 7-norbornenone, bicyclo[3.2.1] oct-2-enone and 2-norbornenone systems, as one would hope if the homoconjugative interaction is indeed reflected by the carbonyl shielding.

I hope that these comments fill the "bill".

Sincerely,

Jake

J. B. Stothers
Professor of Chemistry

JBS:vl

Carbonyl ^{13}C Shieldings of Some β,γ-Unsaturated Ketones
(ppm from CS_2)

Compound	δ_c	$\Delta\delta$*	
		$\Delta\delta(\alpha)$	$\Delta\delta(\beta)$
4-penten-2-one	-11.9	+10.1	+1.9
5-hexen-3-one	-13.9	+ 9.6	+1.9
3-methyl-4-penten-2-one	-13.9	+11.6	+2.5
4-hexen-2-one	-11.4	+11.5	+2.9
3,3,5-trimethyl-4-hexan-2-one	-16.9	-	+1.3
(1-cyclohexenyl)-acetone	-11.6	-	+0.8
3-cyclopentenone	-23.1	+9.1	+1.3
3-cyclohexenone	-15.1	+11.8	+1.0
3,3,5-trimethylcyclohex-3-enone	-14.1	+11.4	+1.1
bicyclo[2.2.2]oct-5-en-2-one	-20.2	-	-0.2
bicyclo[2.2.1]hept-5-en-2-one	-20.4	-	+1.4
bicyclo[3.2.1]oct-2-en-8-one	-22.0	-	+4.0
bicyclo[2.2.1]oct-2-en-7-one	-10.5	-	+10.6

* Shifts relative to the corresponding saturated ketone for the α,β and β,γ-unsaturated systems, denoted (α) and (β) respectively.

DOW THE DOW CHEMICAL COMPANY

MIDLAND DIVISION
MIDLAND, MICHIGAN 48640

February 12, 1969

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry: Improved Pulse Generator for "Time Sharing" Operation of an NMR Spectrometer.

L. W. Burd and I are submitting this for the TAMUNMRN to stanch momentarily the flow of blue letters.

The sketch shows the pulse forming circuit which we now use for switching transmitter and receiver in our spectrometer. The two identical output transistor circuits (three 2N3093 and one 2N440) will drive the r.f. switches we described previously (RSI 36, 1495, 1965). The receiver switch should follow the preamplifier and the transmitter switch should follow the r.f. oscillator as described before (HP 10514A balanced modulators or the equivalent can be used as r.f. switches).

The five 9923 JK flipflops form a shift register divider and with the associated 9914 dual gates divide down the switching oscillator by a factor of ten. A duty cycle of 10% for the transmitter and 80% for the receiver is maintained with a 10% gap following the transmitter pulse to suppress ringing effects.

The use of a shift register divider guarantees a constant pulse pattern even if interrupted. This pattern remains constant as switching frequency is varied, making it unnecessary to readjust pulse widths, delays, etc. This was the principal purpose of the logic circuit design.

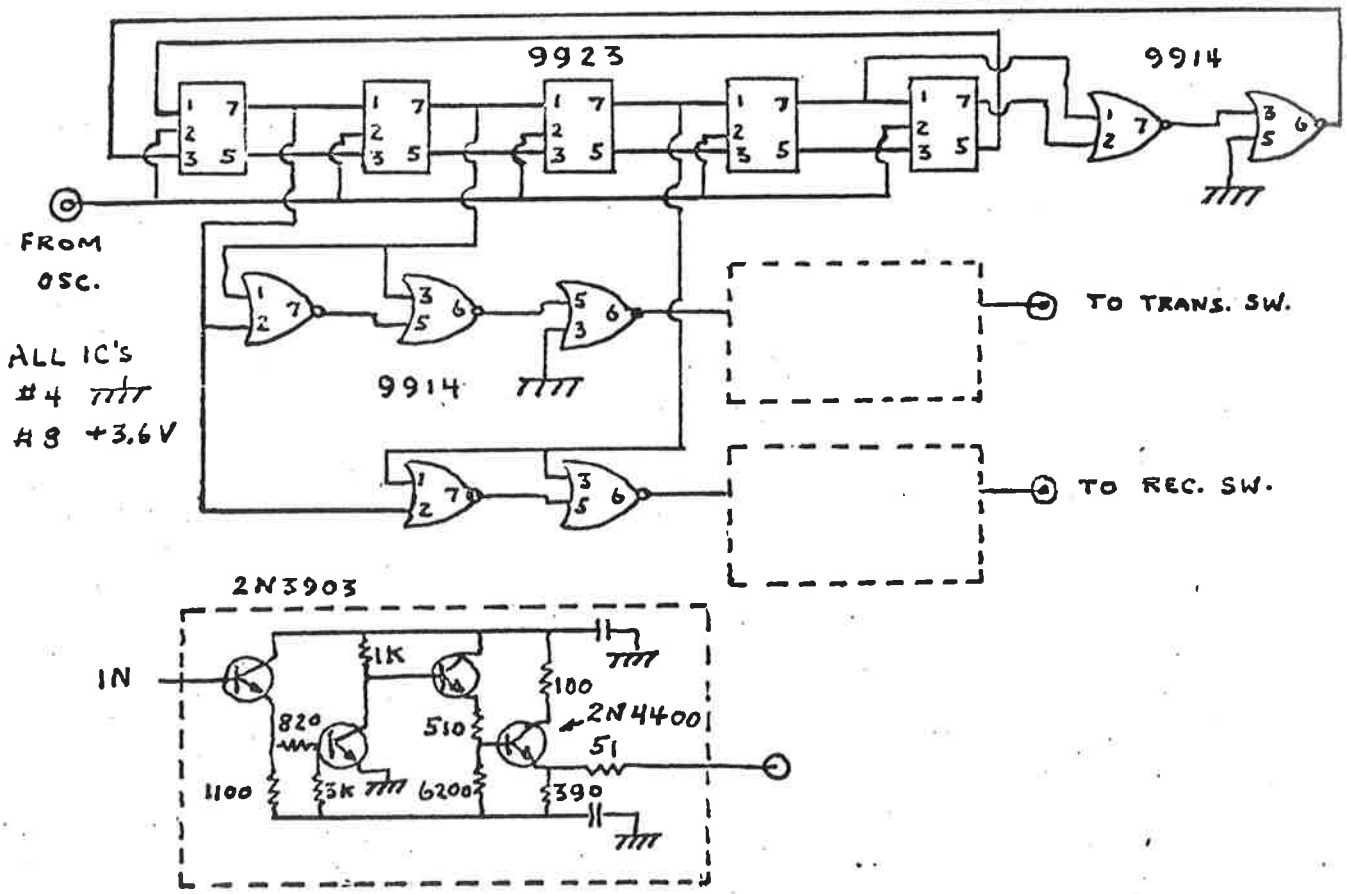
With best regards,

Sincerely yours,

Ned

E. B. Baker
Physical Research Laboratory
1712 Building

bms


9923
9914
FROM OSC.
ALL IC's
#4 ⏚
#8 +3.6V
9914
TO TRANS. SW.
TO REC. SW.

2N3903
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1K
100
820
510
2N4400
51
1100
3K
6200
390

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DEPARTMENT OF CHEMISTRY

February 18, 1969

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

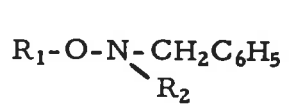
Dear Barry,

Chemical Shift Nonequivalence and Conformational Interchange in Trivalent Nitrogen Compounds

Our group has been continuing our investigations of chemical shift nonequivalence (CSN) and conformational interchange in trivalent nitrogen compounds. Some areas of current interest are described below.

1. We have investigated electronegativity effects on the free energy of activation for torsion about the sulfenyl S-N bond in three series of sulfenamides 1-3 (see Table I). Linear least squares analysis furnished ρ-values of 2.1 ± 0.1 for 1, -3.0 ± 0.1 for 2, and 0.0 ± 0.2 for 3. While the interpretation of these results is difficult, it appears clear that factors in addition to electron repulsion and steric hindrance play a role in determining the torsional barrier. The results can be explained by postulating either overlap or a powerful dipole-dipole interaction between the nitrogen lone pair and the S-C σ-bonding (or σ^*) orbital. We would be grateful for any suggestions concerning the interpretation of this phenomenon.

2. The barriers to conformational interchange in trialkylhydroxyl amines seems formally similar to that in the sulfur analogs, the dialkylsulfenamides. We have measured the free energies for conformational interchange in series 4. The steric effect found in



4a: $R_1 = R_2 = CH_3$; $\Delta G^* = 12.3$ kcal/mole

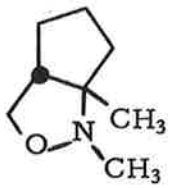
4b: $R_1 = CH_3$, $R_2 = CH(CH_3)_2$; $\Delta G^* = 12.8$ kcal/mole

4c: $R_1 = CH(CH_3)_2$, $R_2 = CH_3$; $\Delta G^* = 12.8$ kcal/mole

this system is in the same direction as that in the sulfenamides

[IITNMRN 115-31, Tetrahedron Letters, 5055 (1968)], suggesting that a torsional barrier is responsible for the CSN observed in series 4 as well as in the sulfur analogs rather than the previously postulated nitrogen inversion. This is in contrast to the steric effect in cyclic hydroxylamines (see next section).

3. The spectrum of the bicyclic oxazolidine 5 exhibits CSN of diastereotopic C-methyl signals at low temperatures. The coalescence temperature (Tc ~ -16°C) is much lower than that observed for simple monocyclic oxazolidines [cf. D. L. Griffith and B. L. Olson, Chem. Commun., 1682 (1968); F. G. Riddell, J. M. Lehn, and J. Wagner, ibid., 1403 (1968).] A considerable steric effect on the nitrogen inversion barrier is operative. Thus, the presence of a bulky t-alkyl group in 5 attached to the nitrogen atom lowers the barrier from about 15 kcal/mole to about 13 kcal/mole rather than raising it as in the acyclic series.



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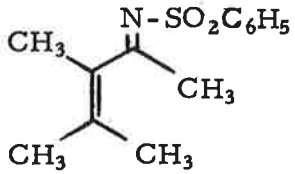
4. We have investigated the syn-anti isomerization of the N-phenylsulfonyl ketimine 6 using second order asymmetric transformation and following the relaxation toward equilibrium and are currently using complete line shape analysis for the same purpose. Preliminary results ($\Delta G^* \sim 16.3$ kcal/mole) indicate that the phenylsulfonyl group is even more effective than phenyl in increasing the rate of stereomutation at the C-N double bond.



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Sincerely yours,

Morton Raban

Morton Raban

Freeman Jones

Freeman Jones

George W. J. Kenney Jr.

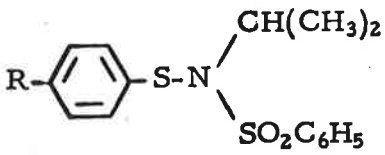
George Kenney

Eric Carlson

Eric Carlson

TABLE I

N.M.R. Parameters and Free Energies of Activation for Conformational Change



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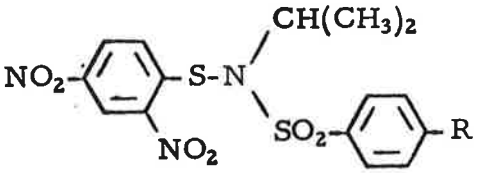

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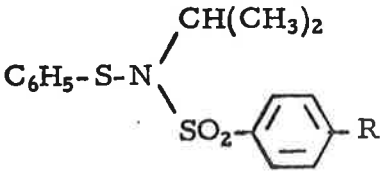

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Compound	R =	σp	Δν in Hz.	T_c in °C.	ΔG* in kcal/mole
1a	OCH_3	-0.27	17.6	-15	13.2
1b	CH_3	-0.17	18	-20	12.9
1c	H	0.00	17.8	-8	13.5
1d	Cl	0.23	18.5	0	13.9
1e	NO_2	0.78	18.1	32	15.6
2a	CH_3	-0.17	19.2	101	19.3
2b	H	0.00	20.0	99	19.1
2c	NO_2	0.78	18.8	31.5	15.6
3a	CH_3	-0.17	16.7	-11	13.4
3b	H	0.00	17.8	-8	13.5
3c	Cl	0.23	17.2	-16.5	13.1
3d	NO_2	0.78	15.4	-10.5	13.4

ABBOTT LABORATORIES. SCIENTIFIC DIVISIONS

NORTH CHICAGO. ILLINOIS 60064

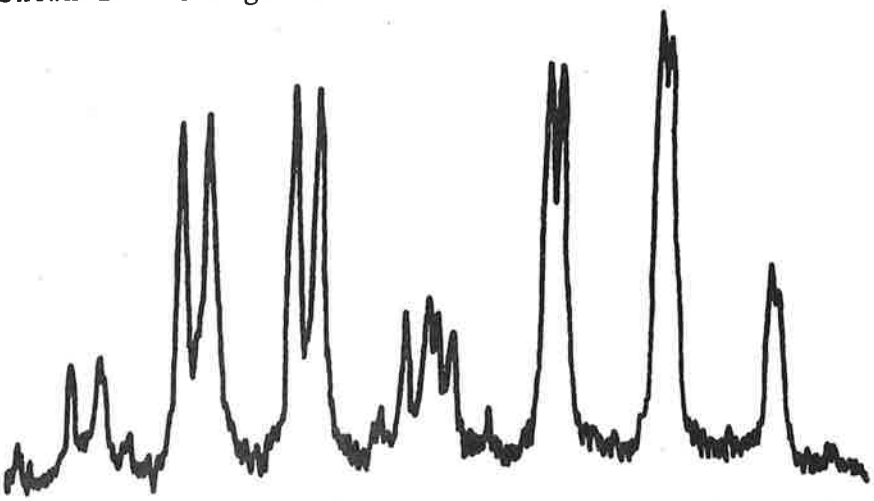
February 20, 1969

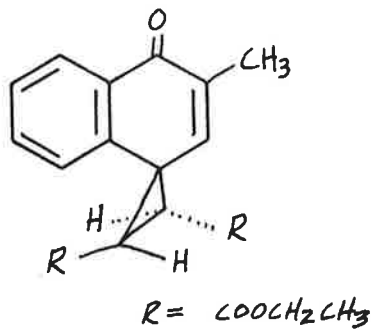
Dr. Bernard L. Shapiro
Texas A & M University
College of Science
Department of Chemistry
College Station, Texas 77843

Dear Professor Shapiro,

LONG-RANGE NON-EQUIVALENCE

An interesting case of methylene non-equivalence in which the methylene group is not α to an asymmetric center was encountered in our laboratory. The methylene resonances in $CDCl_3$ of trans-2,3-diethoxy-2'-methylspiro /cyclopropane-1,4'-naphthalenone)/ are shown in the figure.





The extra "splitting" on each quartet was not attributable to spin-spin coupling with the cyclopropyl protons as the AB quartet arising from these protons was visible to slightly higher field and showed no evidence of this separation. When the spectrum was obtained in C_5D_5N the separation was much smaller and independent of changes in temperature.

We assign this "splitting" to chemical shift non-equivalence of each proton in the methylene group ($J_{AB} \sim 10.8$Hz). Since the non-equivalence was not temperature dependent, we attribute the effect to induced asymmetry from the asymmetric center 3 bonds away at the cyclopropyl ring rather than to restricted rotation or conformational changes.

Although this effect has been reported in cases where the asymmetry is "transmitted" through ether linkages (E. Bullock, E.E. Burnell and B. Gregory, Chem. Conrm., 193 (1967); F. Kaplan and J.D. Roberts, J. Am. Chem. Soc., 83, 4666 (1961), we are unaware of other examples involving ester linkages.

We thank Mr. James W. Pavlik, Ass't. Prof. of Chemistry, Haile Sellassie I Univ., Addis Ababa, Ethiopia for the sample.

Sincerely,

Richard S. Egan
nmr Lab. D-408

126-18

University College of Swansea

Department of Chemistry

Professor C H Hassall PhD ScD FRIC
Professor and Head of Department
Professor J H Purnell BSc PhD MA PhD
Professor of Physical Chemistry

SINGLETON PARK SWANSEA
TEL SWANSEA 25678

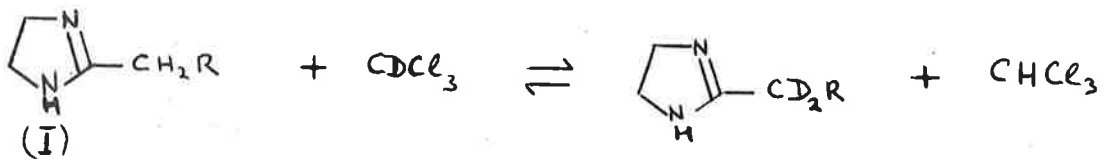
19th February, 1969.

Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station,
Texas 77843,
U.S.A.

Proton-deuterium exchange in imidazolines.

Dear Barry,

We have recently completed a study of some unusual proton-deuterium exchange reactions of strong organic bases with deuterochloroform. Deuterium exchange in $CDCl_3$ has previously been observed with sodium hydroxide solutions as the base, and infrared spectroscopy as the technique for following the rates of exchange (1). The exchange observed in this work is of the general type:-

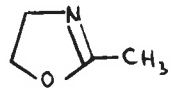


(I)

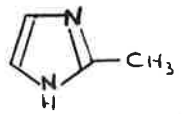
This unusual reaction occurs at ambient temperatures, and is a fairly slow process relative to the n.m.r. time scale, enabling the reaction to be readily followed by p.m.r. spectroscopy. In the case of 2-methyl-Δ^2-imidazoline (I) (R=H), equilibrium is reached in as little as ca. 3 days, for high concentrations, although in more dilute solution equilibrium is reached in ca. few weeks. Initially the spectrum consists of three singlets corresponding to the N-H, the four methylene protons and the methyl group. The methylene protons are

made equivalent by the rapid tautomerism of the N-H proton, which is still apparently rapid at -80°C. By examining the spectrum at regular intervals, it is clear that relative to the methylene proton singlet, the methyl peak reduces in intensity, broadening as it does so, and that a new sharp singlet is appearing at ca. τ 2.6, clearly due to $C\underline{H}Cl_3$ protons. By integrating the spectrum at regular intervals, the exchange is followed until equilibrium is reached.

In the Table, the chemical shifts and rate constants for various equimolar solutions in $CDCl_3/CCl_4$ of imidazolines are recorded. It is clear from the results that the rate of exchange depends not only on the concentration, but also on the basicity of the heterocycle. Compound (I), for example has a pK_a of 11.1 in aqueous solution at 25°C (2) and is therefore strongly basic. An examination of 2-methyl-Δ^2-oxazoline (V) and 2-methyl-imidazole (VI) in $CDCl_3$ shows that very little exchange occurs in (V) over several days, whereas in (VI) only the N-H proton exchanges, but very slowly compared to the imidazolines.



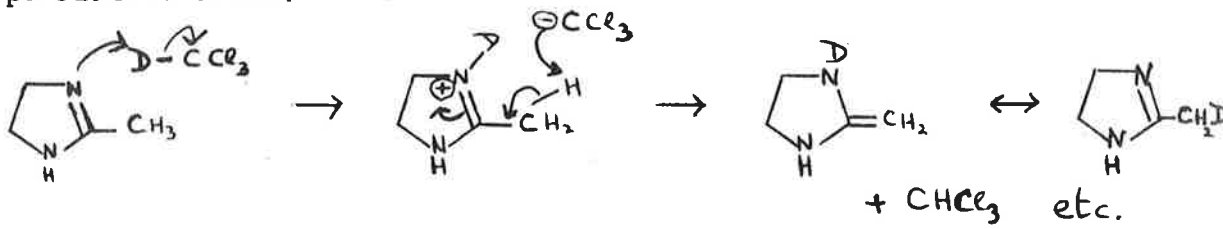
(V)



(VI)

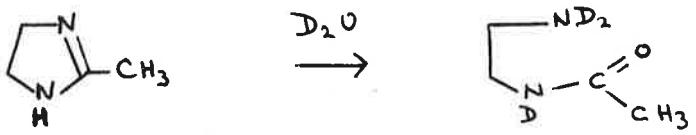
This very slow exchange can be attributed to the lower basicities of these compounds pK_a 5.5 in the case of (V) and 7.85 for (VI) (2).

A tentative mechanism for the reaction seems to follow the steps outlined below.



However in this mechanism in the final step presumably either the N-D or N-H bond is broken, leading to extensive exchange of the N-H proton. In practice only ca. 1/3 of the N-H proton peak is lost. This and other features will be discussed in a full paper.

In d_6-acetone where the deuterium atoms are more acidic, very rapid exchange with the methyl group of (I) is observed, exchange being complete in a few hours. Finally, the p.m.r. spectrum in aqueous solution indicates that ring opening occurs. The sharp singlet for the methylene protons is rapidly replaced by an AA'BB' pattern, indicative of the methylene protons of mono-acetyl ethylene diamine (VII).



(VII)

I hope this qualifies as a subscription to your Newsletter.

Best regards.

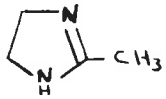
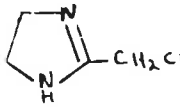
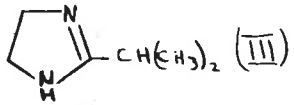
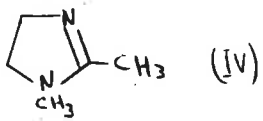
Tony Graham Griffin

W. A. Thomas G. E. Griffin.

1. J. Hine, R. G. Peek, Jr., and W. D. Oakes, J.Amer.Chem.Soc., 1954, 76, 827.

2. D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution", London, Butterworths, 1965.

TABLE

Compound [a]	N-H[c]	2-CH_3	2-CH_2-	2-CH	-$(CH_2)_2$-	βCH_3	Rate constants[d]
 (I)	5.20[b]	8.05	-	-	6.37	-	7.00×10^{-1}
 (II)	5.40	-	7.70	-	6.35	8.77	4.81×10^{-1}
 (III)	5.20	-	-	7.37	6.32	8.12	0.28×10^{-1}
 (IV)	7.02 (N-CH_3)	8.11[f]	-	-	<6.35-6.65>[g]	-	0.27×10^{-1}

(a) Rate measurements were obtained using a 0.7M imidazoline solution in $CDCl_3$, diluted with CCl_4

(b) τ values obtained on a Perkin-Elmer R.10 spectrometer.

(c) Very concentration dependent.

(d) Measured in $l.hr.^{-1}$ $mole^{-1}$, with accuracy limited generally by errors in integration.

(e) In all cases, the $CHCl_3$ singlet appears between τ 2.46 and 2.58.

(f) Triplet $^5J_{HH}$ = 1.1 c/s.

(g) Approximate shifts.

126-22

THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175
CINCINNATI, OHIO 45239

February 24, 1969

Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Subjects: (1) Computer Retrieval of Reprints of NMR Papers:
(2) Spectrum of Ethanol Oriented in a Lyotropic Nematic Phase

Dear Dr. Shapiro,

For some time now we have been using the Preston NMR Abstracts tape and COBOL search program compiled by Ted Becker and Ernest Lustig. (IITNMR 91-24, 99-45.) We have found it useful when using the search program to generate a list of abstracts which indicates whether or not we have a reprint on file, as most of our NMR reprints are stored in order of their P.A. number. This was achieved by writing two short COBOL programs and modifying the original search program.

Program No. 1 increases the size of each record on the original data tape from 227 characters to 228 by adding a "blank" at the end of each record.

Program No. 2 reads a bunch of cards which contain the P.A. numbers of the reprints on file and writes the letter "R" on the data tape at the end of the appropriate record.

Program No. 3 is the modified original search program and its printed output is the same as before except for an "R" appearing at the end of each record if a reprint of that particular abstract is on file.

Programs 1 and 2 are only used occasionally for updating purposes, and Program 3 is used quite frequently. IBM-360/65 listings of these programs are available to anyone interested (RER).

Since the original article by Lawson and Flautt[1] describing the use of a lyotropic liquid crystalline mixture as an orienting matrix for NMR studies, we have carried out a number of further experiments with the aim of investigating the potentiality of this kind of mesophase as an alternative to the thermotropic liquid crystals usually employed.

The accompanying figure shows a "typical" example of the results possible. This spectrum is that of ethanol (3% by weight) in a nematic mesophase (composition 36% sodium decyl sulfate, 7% decyl alcohol, 7% sodium sulfate and 50% D_2O). The instrument used was a Varian HA-100 (External H_2SO_4 lock). The sample, kept at the probe temperature, was spun in the normal high resolution manner. This ability to be spun in the field without destruction of the field-induced orientation is the most distinctive feature of this type of mesophase.

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The spectrum was analyzed using a version of LAOCN3 modified to include direct dipole-dipole couplings in the spectral calculation and iterative fitting (a listing is available to anyone interested). The parameters obtained for this A_3B_2 system were:

$$\tau_A - \tau_B = 2.462 \pm 0.11 \text{ ppm.}$$
$$J_{AB} = 7.05 \pm 0.07 \text{ Hz.}$$
$$D_{AA} = -46.38 \pm 0.14 \text{ Hz.}$$
$$D_{BB} = -780.69 \pm 0.13 \text{ Hz.}$$
$$D_{AB} = -62.59 \pm 0.11 \text{ Hz.}$$

(J_{AB} is assumed positive, the signs of the D's are then established by the analysis.)

A motional constant analysis then indicates that the preferred orientation of ethanol in this mesophase is with the applied field perpendicular to the C-C-O plane.

A more detailed account of this work will be published shortly. Please credit this item to the Miami Valley Laboratories' subscription.

Sincerely,

R. E. Reavill

R. E. Reavill

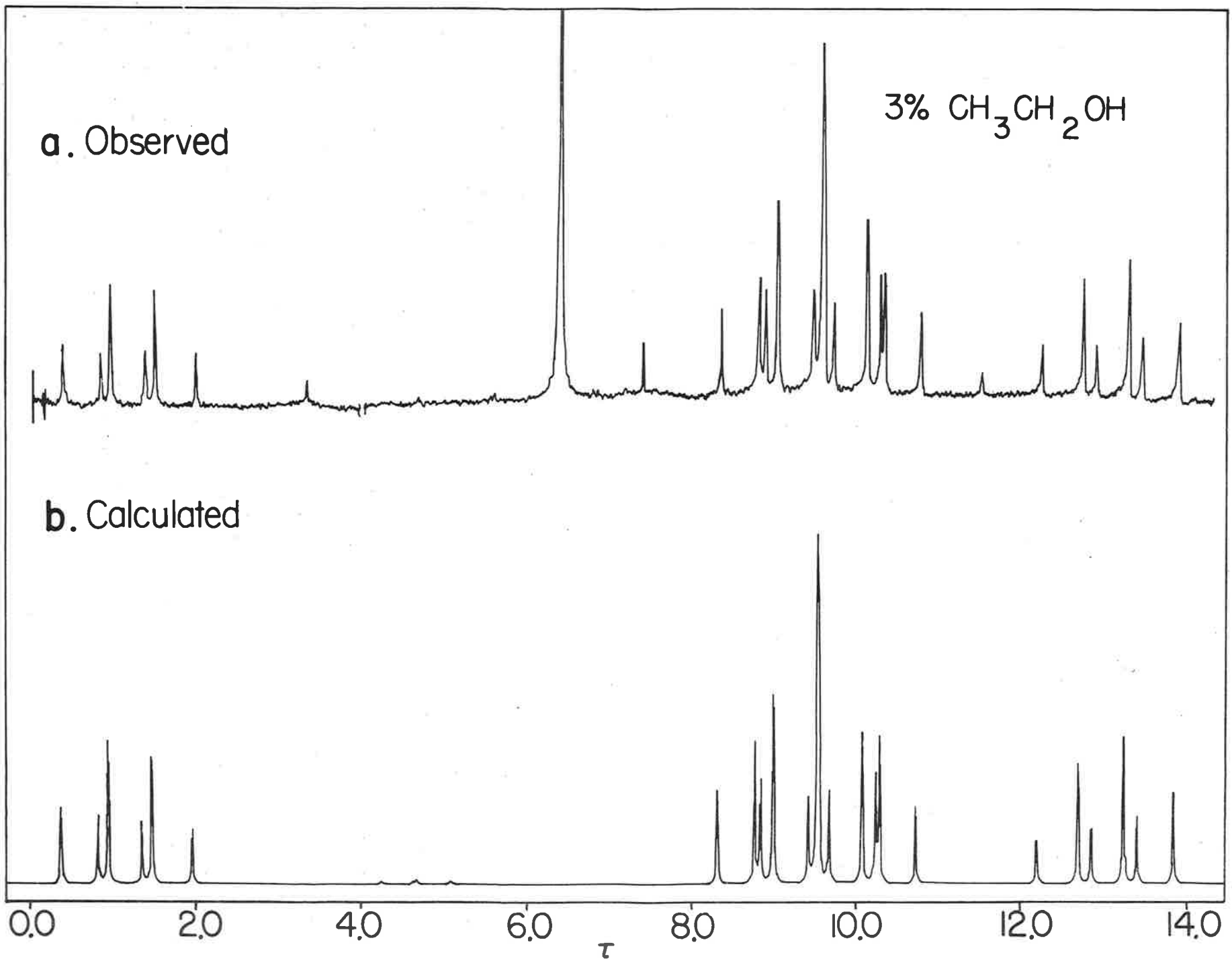
P. J. Black /KDL

P. J. Black

cj

References:

1. K. D. Lawson and T. J. Flautt, J. Am. Chem. Soc. 89, 5489 (1967).


a. Observed
3% CH_3CH_2OH
b. Calculated
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
τ

Institut für Physikalische Chemie
Rhein.-Westf. Techn. Hochschule

Doz. Dr. R. Kosfeld

51 Aachen, den 25.2.1969
Klosterbongard 12

Tel.: 422/2154

Mr.

Prof. Bernard L. Shapiro
Department of Chemistry
Texas A+M University

College Station

T e x a s 77 843

U.S.A.

Sixth NMR-Workshop

Dear Prof. Shapiro!

The sixth Workshop on Nuclear Magnetic Resonance Spectroscopy will be take place at Aachen, Germany, on Monday through Saturday, March 24 - 29, 1969.

I include a program for the above workshop.

With best wishes

R. Kosfeld

(R. Kosfeld)

6. Kolloquium über Kernresonanzspektroskopie in Aachen vom 24. - 29.3.1969

PROGRAMM

Montag, den 24.3.1969

9.00 h: Begrüßung

9.15 h: H. Günther, Köln
Zur Analyse von Vierspinsystemen

10.45 h: J.C. Jochims, Heidelberg
Über stereospezifische ^{4}J- und ^{5}J-Protonenkopplungen in gesättigten Systemen

14.00 h: D. Jung, Darmstadt
Rotationsisomerie und NMR

15.30 h: S. Castellano, Pittsburgh, USA
Proton-proton coupling constants in monocyclic aromatic systems

Dienstag, den 25.3.1969

9.15 h: W. v. Philipsborn, Zürich, Schweiz
NMR-spektroskopische Strukturbestimmung stickstoffhaltiger Naturstoffe

10.45 h: R.F. Zürcher, Basel, Schweiz
Probleme der chemischen Verschiebung

14.30 h: J.F.M. Oth, Brüssel, Belgien
Conformational mobility and valence-bond isomerism in the annulenes

Mittwoch, den 26.3.1969

9.15 h: H. Dreeskamp, Stuttgart
Die Bestimmung von ^{31}P-Kopplungskonstanten und ihre Interpretation

10.45 h: A. Schmidpeter, München
^{31}P-NMR-Verschiebung und Effektübermittlung in P-N-P-Systemen

14.30 h: R. Schmutzler, Braunschweig
NMR-Untersuchungen an Phosphor-Fluor-Verbindungen

15.30 h: H. Schmidbaur, Würzburg
^{1}H- und ^{31}P-NMR-spektroskopische Untersuchungen an Yliden des Phosphors, Arsens und Schwefels

Donnerstag, den 27.3.1969

9.15 h: R. Hoffman, Uppsala, Schweden
Relaxationsvorgänge in der hochauflösenden Kernspektroskopie

10.45 h: F. Noack, Stuttgart
Kernmagnetische Relaxationserscheinungen in kondensierten Systemen

14.30 h: U. Haeberlen, Cambridge, USA
Impulszyklen zum Messen von chemischen Verschiebungen in Festkörpern

Freitag, den 28.3.1969

9.15 h: P. Diehl, Basel, Schweiz
Kernresonanzspektren orientierter Moleküle in nematisch-kristallinflüssiger Lösung

10.45 h: A.D. Buckingham und C.A. de Lange, Bristol, England
Chemical shift anisotropies from NMR studies of oriented molecules

14.30 h: C. McLean, Amsterdam, Holland
NMR of molecules oriented in the electric field

16.00 h: C.L. Khetrapal, Basel, Schweiz
NMR of oriented aromatic molecules with C_{2v} symmetry

Samstag, den 29.3.1969

9.15 h: P.J. Black, Cincinnati, USA
NMR of molecules oriented in the lyotropic mesophase

10.30 h: H. Spiesecke, Ispra, Italien
Bestimmung molekularer Strukturen in nematischen Lösungen

126-28

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Research Laboratory · Service Center · Klausstrasse 43 · Tel. 051 / 47 24 20 · Zürich 8 · Telex 58 444

Zürich, 27 February, 1969

Professor B.L. Shapiro
Department of Chemistry
Texas A + M University
College Station / Texas 77843
USA

INDOR MODIFICATION FOR HA-100 AND HA-60IL

Dear Professor Shapiro,

Many people have modified their HA-100 and HA-60IL spectrometers to record homonuclear INDOR experiments. This is a relatively simple procedure, and we have prepared a description of the necessary modification which we are prepared to supply to anyone interested.

In the INDOR experiment we require that ω_1 be held constant at the frequency of a chosen line and that ω_2, the perturbing radiofrequency, be swept through the desired portion of the spectrum. The modification to the V-4354A unit (Internal Reference NMR Stabilized Controller) requires the installation of two rotary switches and a new adder amplifier card (see figure 1). Switch 1 is a 3 position rotary switch (shim on / normal / INDOR) and is replacing the shim on / off switch S 1309. The third position of switch 1 is wired to allow the desired signal to be monitored while ω_2 is swept synchronously with the recorder. The second switch assembly is of the same type as used for the swept and manual oscillator and is best placed in the upper center of the V-4354A unit. It is wired such that it controls the amplitude of the observing field ω_1 (provided by an external audio oscillator).

A revised schematic for the modified V-4354A unit is available on request.

Sincerely yours,

U. Scheidegger

Ulrich Scheidegger

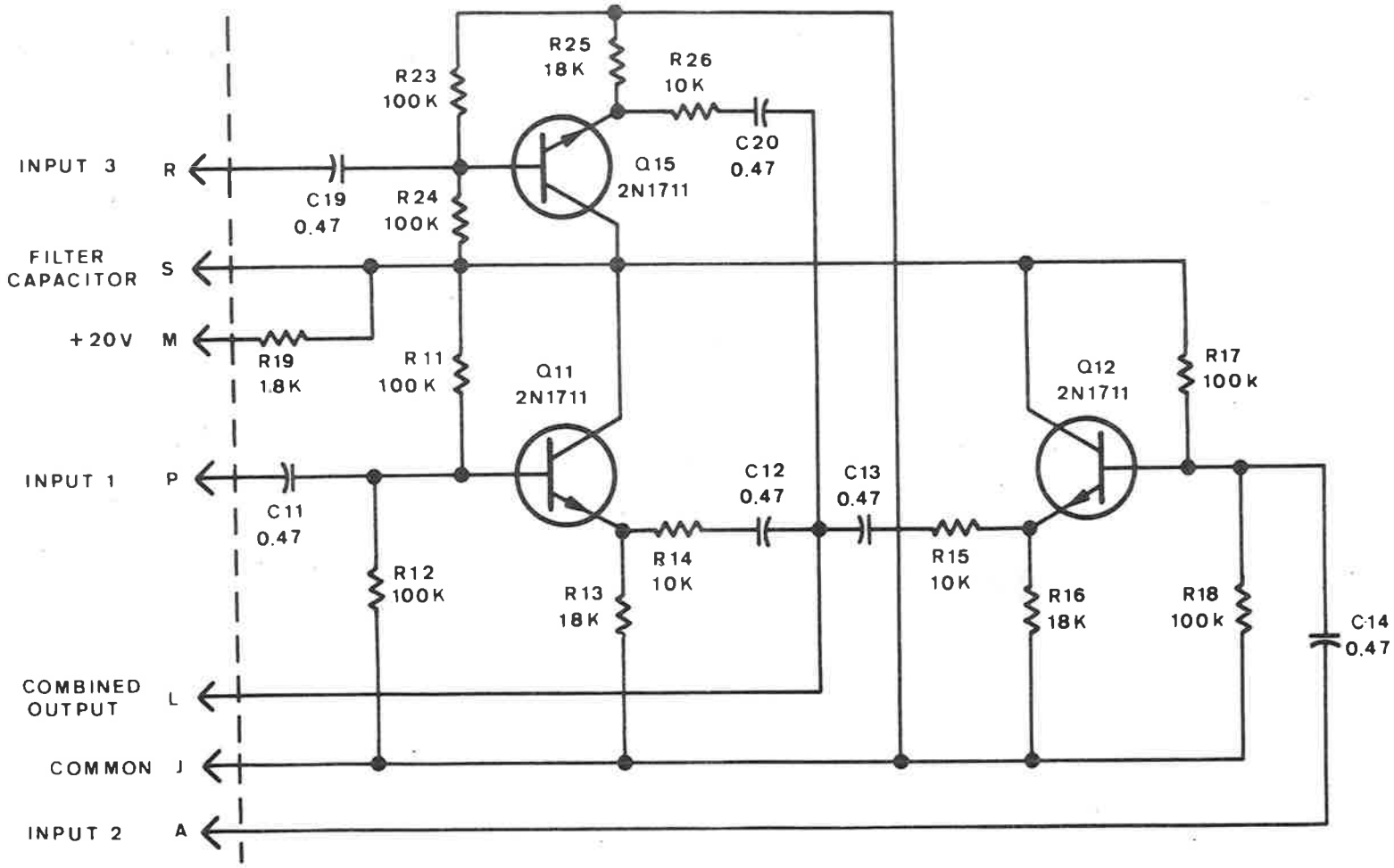


FIGURE 1 : ADDER AMPLIFIER SCHEMATIC FOR INDOR RECORDING

CSIRO

DIVISION OF PLANT INDUSTRY

P.O. BOX 109, CANBERRA CITY, A.C.T., 2601, TELEPHONE 4-0455 — TELEGRAMS CORESEARCH CANBERRA

WPAP:IVS.
Refer.:

4th February, 1969.

Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station,
Texas. 77843. U.S.A.

"The Range of Proton Chemical Shifts for N-CH_3 Groups"

Dear Professor Shapiro,

We have been interested in compounds containing N-methyl groups and as some of these protons have chemical shifts at variance to the previously published tables we would like to suggest an extension of the range in which these are given (2.16δ -3.33δ) to cover 2.16δ - 4.30δ. The chemical shifts for the protons of trimethylamine and nitromethane lie at the extremes of this range.

Numerous examples of chemical shifts which lie outside of the previously published ranges are available in the literature. Where the N-CH_3 group is part of a more highly conjugated planar system, the proton chemical shifts more closely approximate the observed value for nitromethane. The accompanying diagram shows some of the available values compared with the previously published ranges for N-CH_3 proton chemical shifts.

It may be noted that the suggested N-CH_3 range now overlaps that for O-CH_3 shifts.

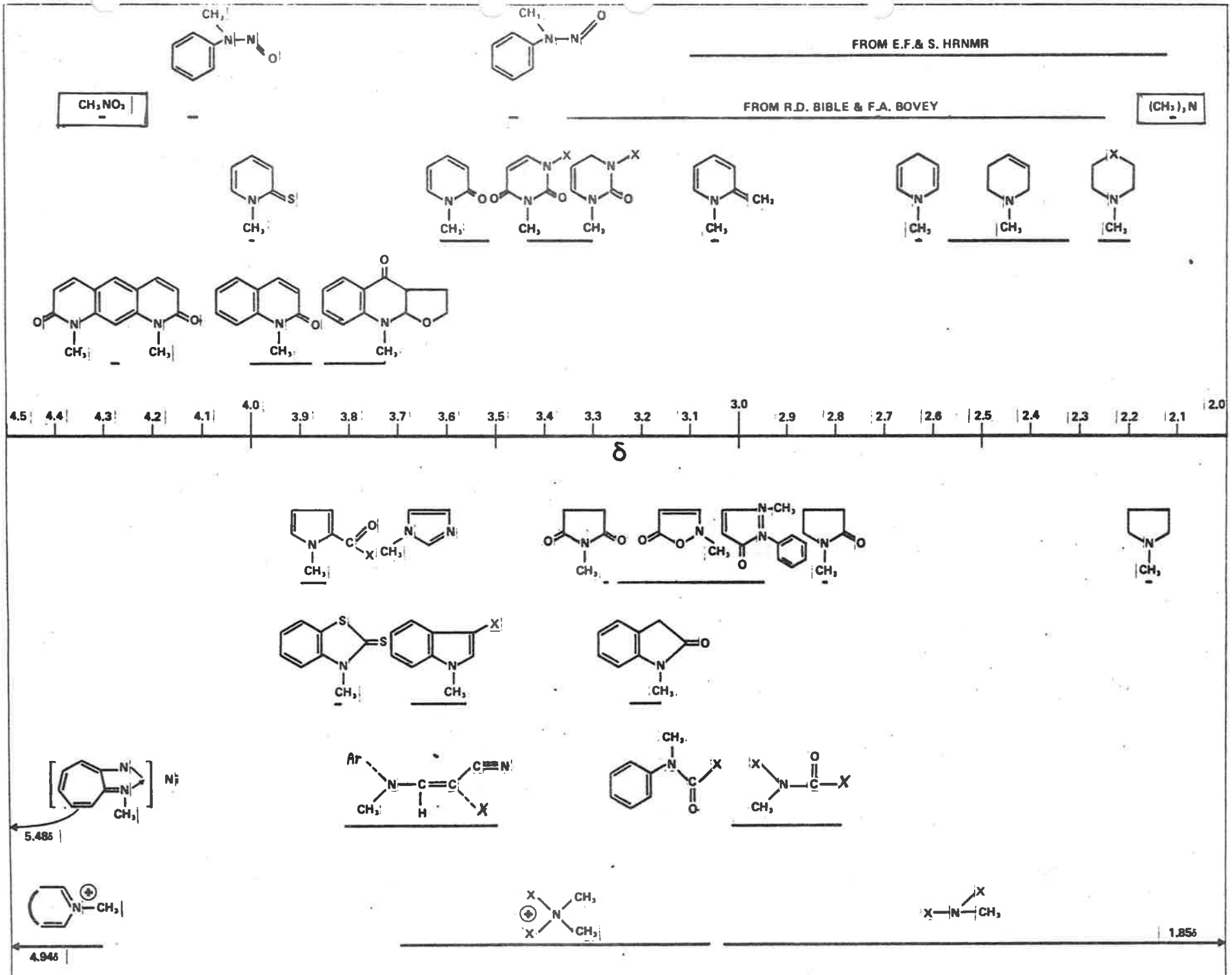
Sincerely yours,

C.P. Whittle

(C.P. Whittle)

W.P.A. Pascoe

(W.P.A. Pascoe)


FROM E.F.& S. HRNMR
FROM R.D. BIBLE & F.A. BOVEY
CH_3NO_2
$(CH_3)_4N$
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0
δ
5.48δ
4.94δ
1.85δ

KEMISK INSTITUT
AARHUS UNIVERSITET

LANGELANDSGADE
8000 AARHUS C
DANMARK

AARHUS, den February 26 1969

Telefon (06) 12 46 33

Efter kontortid kaldes afdelingstlf. nr.:
124106 — organisk kemi
124578 — uorganisk kemi
124761 — fysisk kemi
124892 — kemisk fysik
124312 — radiokemi

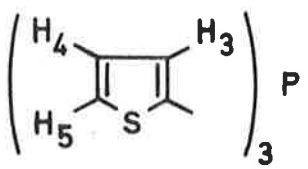
Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843
USA

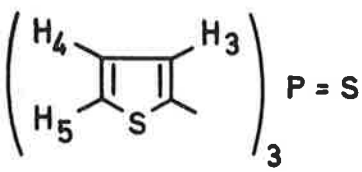
^{1}H-^{31}P SPIN COUPLINGS IN TRITHIENYLPHOSPHINES

Dear Professor Shapiro,

For some time we have been concerned with the analysis of the PMR spectra of the two trithienylphosphines and some of their tetracoordinated derivatives such as the oxides, the sulphides, the selenides, and phosphonium salts in order to obtain the magnitudes and signs of the ^{1}H-^{31}P spin coupling constants. The assignments of the energy level diagrams were generally carried out using the technique of double quantum transitions and the best values of chemical shifts and coupling constants were obtained by computer iterations on the assigned transitions (r.m.s. errors ~ 0.02 Hz). The PMR spectrum of tri-3-thienylphosphine is shown in the figure.

All ^{1}H-^{31}P spin coupling constants are of the same sign, presumably positive, and the values for tri-2-thienylphosphine and its sulphide are:[1]



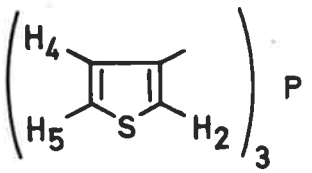


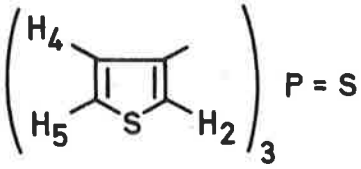
$J_{P-H(3)}$	= 6.10 Hz	$J_{P-H(3)}$	= 8.90 Hz
$J_{P-H(4)}$	= 1.30 Hz	$J_{P-H(4)}$	= 1.90 Hz
$J_{P-H(5)}$	= 0.33 Hz	$J_{P-H(5)}$	= 4.39 Hz
J_{34}	= 3.50 Hz	J_{34}	= 3.67 Hz
J_{35}	= 1.09 Hz	J_{35}	= 1.17 Hz
J_{45}	= 4.94 Hz	J_{45}	= 4.84 Hz

HJJ/EL

.../cont.

and for tri-3-thienylphosphine and its sulphide:



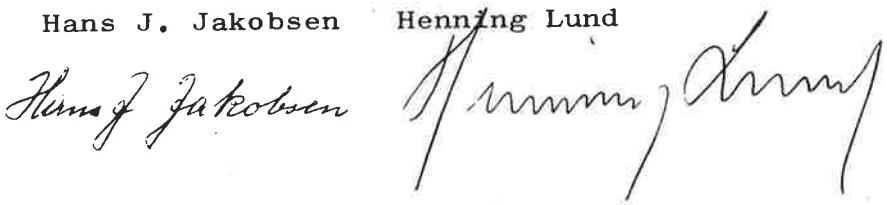


$J_{P-H(2)}$	= 4.22 Hz	$J_{P-H(3)}$	= 8.80 Hz
$J_{P-H(4)}$	= 2.58 Hz	$J_{P-H(4)}$	= 4.34 Hz
$J_{P-H(5)}$	= 0.99 Hz	$J_{P-H(5)}$	= 2.07 Hz
J_{24}	= 1.22 Hz	J_{24}	= 1.25 Hz
J_{25}	= 2.84 Hz	J_{25}	= 2.91 Hz
J_{45}	= 4.92 Hz	J_{45}	= 5.03 Hz

In general the magnitudes of the $^{1}H-^{31}P$ coupling constants in the phosphines are smaller than the corresponding values in the tetracoordinated analogues; this is especially pronounced for $J_{P-H(5)}$ in tri-2-thienylphosphine and its sulphide. This increase in $^{1}H-^{31}P$ coupling constants for tetracoordinate organophosphorus compounds relative to trivalent analogues is in accordance with earlier observations in the benzene series.[2]

Sincerely yours,

Hans J. Jakobsen Henning Lund



[1] H.J.Jakobsen and J.AA.Nielsen, J.Mol.Spectry. (in press).
[2] C.E.Griffin, Tetrahedron 20, 2399 (1964).

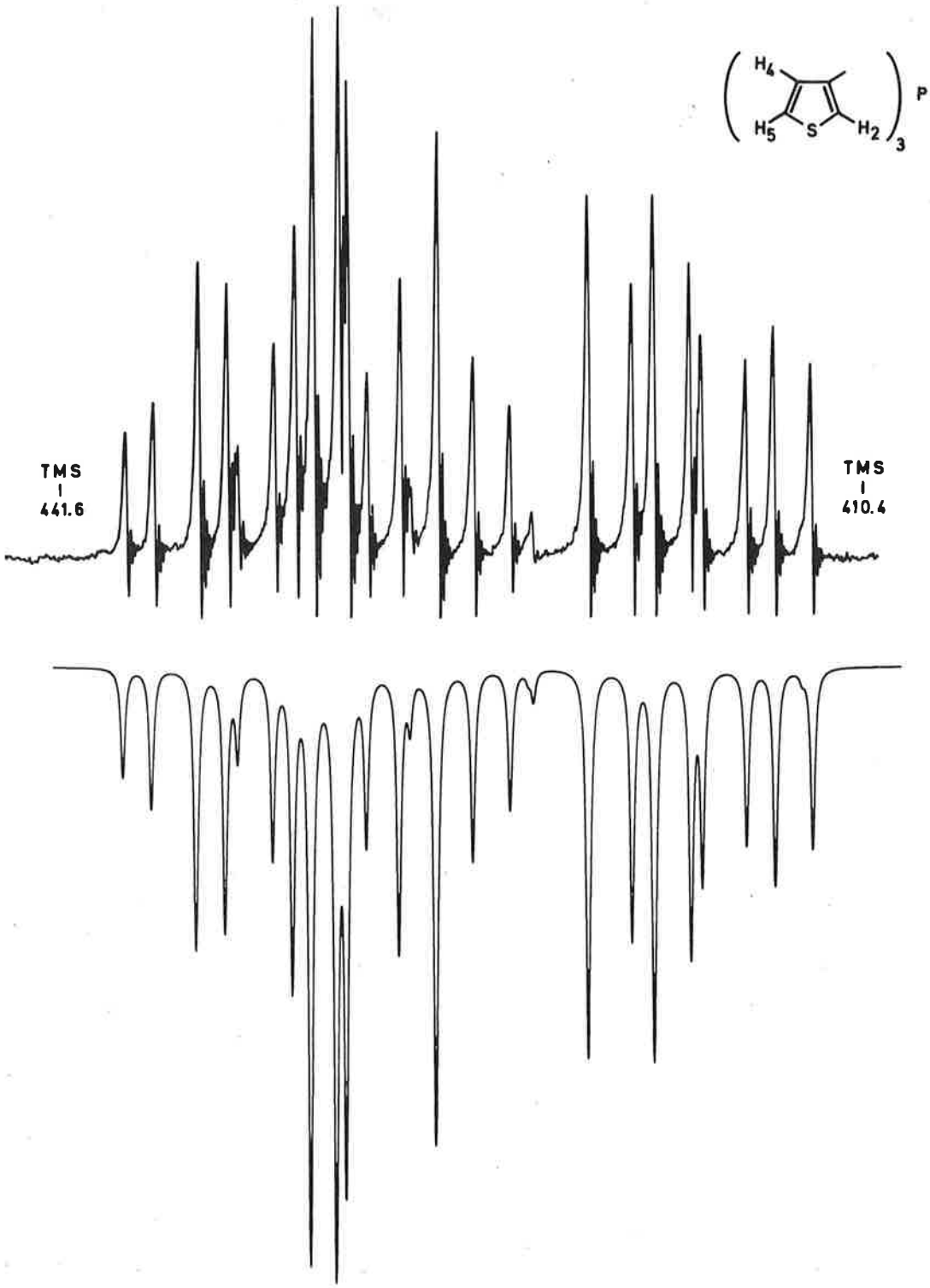


Figure. Observed (above) and calculated (below) 60 MHz PMR spectrum of a 14% w/w degassed solution of tri-3-thienylphosphine in CCl_4.

NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20390

IN REPLY REFER TO:

6110-90:WBM:vmg
3 March 1969

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry:

Procedures, Observations and Equipment Modifications
from Washington Area Government NMR Laboratories

Subscribers who did not attend the 10th ENC where copies of POEM were available may obtain copies by writing to me.

The compilation came about because we in the Washington area discovered that despite the availability of the Newsletter, here were a dozen or more items of potential value that lay unpublicized. From the comments of several ENC attendees, it is apparent that many other modifications are in the same category.

I believe that were Newsletter readers to give the matter some thought, many useful contributions relating to POEM's would be forthcoming. Incidentally, in compiling the handout, we tried to be as explicit as possible, list all components, and include detailed drawings. While more work is required in preparation, and more paper in publication, the necessity for correspondence is hopefully eliminated.

Sincerely yours,

Bill

W. B. MONIZ, Head
NMR Spectroscopy Section
Chemistry Division

The following several-page document is being reproduced in full in the Newsletter at my suggestion and with Bill Moniz' concurrence. The appearance of this lengthy contribution is not to be construed as establishing a general precedent. Economic necessity and my own peculiar sense of aesthetics will continue to make contributions longer than four pages as welcome as rain in Southern California.

BLS

PROCEDURES, OBSERVATIONS AND EQUIPMENT MODIFICATIONS

from

Washington Area Government NMR Laboratories

Collated by Dr. W. B. Moniz, Chemistry Division
Naval Research Laboratory

Index

CONTRIBUTING LABORATORIES

ARDL: U. S. Army Electronics Command
Night Vision Laboratories
Bldg. 317
Ft. Belvoir, Va. 22060
Attn: Mr. William Lightel

FDA: Dr. Ernest Lustig
Food and Drug Administration
200 C St., S. W.
Washington, D. C. 20204

NBS-J: Dr. Rolf B. Johannesen
National Bureau of Standards
A329 Materials
Washington, D. C. 20234

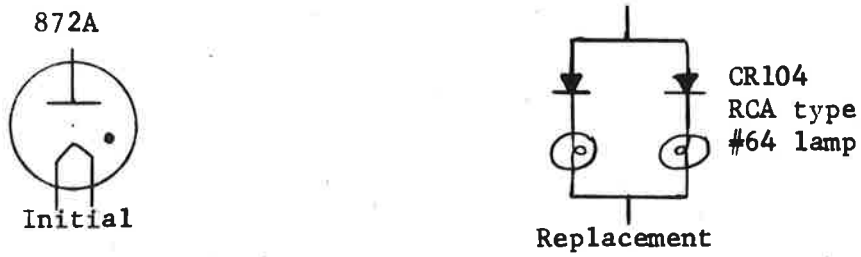
NOL: Dr. Lloyd A. Kaplan
Advanced Chemistry Division
U. S. Naval Ordnance Laboratory
Silver Spring, Md. 20910

NRL: Dr. William B. Moniz
Code 6110
Naval Research Laboratory
Washington, D. C. 20390

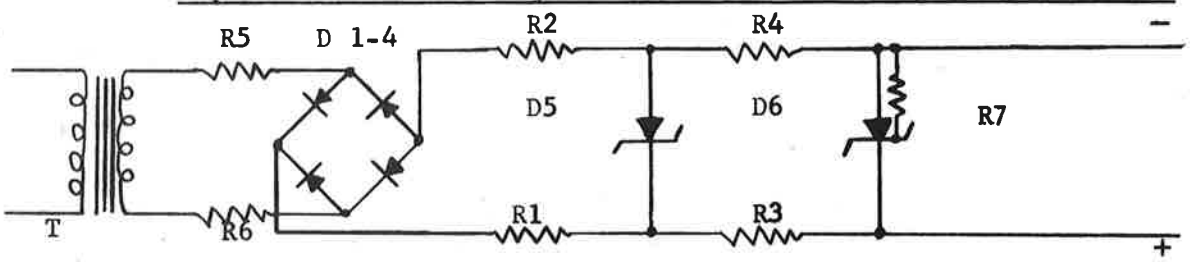
Magnet Power Supply (V2100B)

1. Diode Replacement for 872A Mercury Rectifiers in V2100B (NBS-J)

2 - CR104 in parallel replace each 872A. The #64 bulbs are load equalizer resistors which give a visual indication that current thru each leg is equal.



2. Replacement for Mercury Reference Batteries in V-2100B (NBS-J)



T	Transformer, 110-110V, 25 ma
D1-4	Rectifier diodes
R5,R6	10 Ω 1/2W
R1,R2	3,000 Ω 5W
R3,R4	560 Ω 1W
R7	Trimming resistor to adjust output voltage. 1/2W, fixed. Select value to obtain desired voltage (33K Ω used by NBS).
D5	Zener 25V, 5W
D6	"Superreg" zener 9.4V. "Superreg" - integrated circuit. 75E10 Trio Labs., Plainview, N. Y.

3. Installation of 15 KVA Variable Voltage Transformer in the V-2100B (NRL)

Complete plans and instructions for the replacement of the 10 KVA transformer with a 15 KVA unit are available. The larger unit gives more reliable operation, especially at 23 KG.

Magnet Flux Stabilizer (V3506)

1. Permanent Cure for Many Flux Stabilizer Problems? (NRL)

We had been plagued with the necessity for cleaning the printed circuit portion of the balance-operate switch in the V-3506 Magnet Flux Stabilizer every two or three months. Various symptoms were

displayed when it was dirty: undamped oscillation of the galvonometer for long periods of time; frequent "jumping out" of the galvanometer; inability to switch to the operate position, except on the nth attempt, without the galvanometer going off scale, etc., etc.

Recalling an item, either from an early ENC or a publication which must remain unnamed, in which gold-plating of the balance-operate switch contacts was alleged to cure these problems, we had the two parts of the printed-circuit portion of S1 gold-plated.

In over two years of operation we have not had a single recurrence of any of our previous difficulties with switch operation.* No adjustments have had to be made to the stabilizer gain or reg. settings during this period; and coincidentally or not, the OC3's in the chopper of the V2100B have not had to be replaced so frequently.

We believe that many problems reported with the flux stabilizer reflect nothing more than marginal operating conditions brought about by dirty switch contacts.

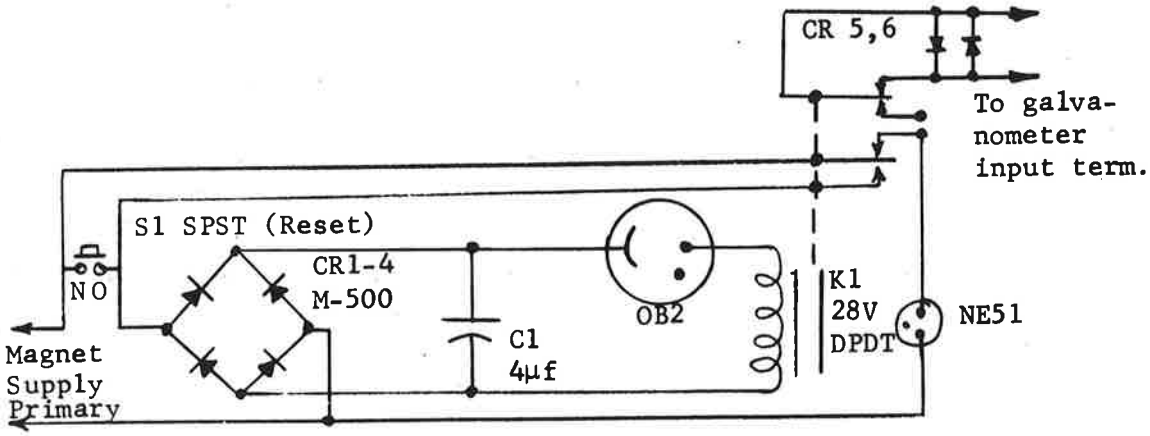
If the originator of the idea for gold-plating the switch will get in touch with me, I will be happy to give him proper credit; I have been unable to locate the original reference.

---

*Dr. E. Lustig (FDA) had his V3506 switch gold-plated about a year ago, and reports similar results. He reports that the cost was less than $5.00 for heavy gold-plating. A Washington Area source is Universal Electro-Plating Co., 1067 Wisconsin Ave., N. W., Washington, D. C.

2. Galvanometer Protection Circuit (ARDL)

The circuit shown below will protect the galvanometer from large current surges in the event of AC power interruptions sufficient to cause the galvanometer to "kick out". If it is desired to open the feedback loop to the console as well, an additional pair of relay contacts is required. (Circuit design by Dr. John Muller.)



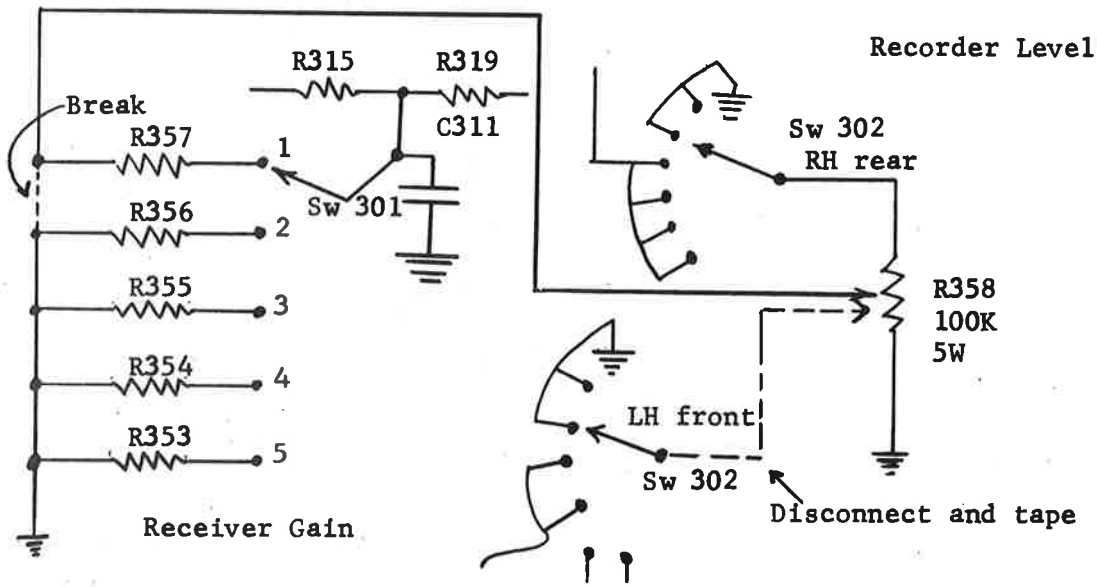
Console Modifications

1. Fine Adjustment of Detector Zero (A-60) (FDA)

Adjustment of this control for integration was found to be too coarse. Thus the variable resistor R 821 which also contains an on-off switch was replaced by a 5-turn variable resistor. Since no multiturn variable resistor with on-off switch could be obtained, a separate switch (SPST, toggle) was installed on the front panel of the console right above the Detector Phase control. Part: Bourns variable resistor, 5 turn, 10 k, 3520 S - 1 - 103.

2. V-4311 Variable Gain Control for Decoupling (NOL)

The modification shown below permits variable gain in the receiver gain 1 position. Follow directions in the manual for spin decoupling, but attenuate gain with R358 to obtain a stable lock signal. Then proceed with irradiation. Finer control can be obtained by replacing R358 with a 10 k multiturn potentiometer.



3. Non-Mechanical Sweep of HA-100 for Time-Averaging with C-1024 (FDA)

We are grateful to Dr. J. J. Katz and Messrs. D.J. Matter and G.D. Norman (Argonne National Laboratory) for the basic idea of this sweep system and for a number of constructional details; and to Dr. R. E. Lundin (U.S.D.A. Western Regional Laboratory, Albany, Calif.) for pointing out to us the high linearity of the voltage-to-frequency converter made by Vidar Corporation.

A. Purpose.

To separate the C-1024 from the HA-100 sweep controlled by

recorder arm movement. Sweep rate and width can now be controlled by a voltage-to-frequency converter which receives a ramp voltage from the C-1024 and supplies the sweep frequency to the HA-100. Mechanical movement of the recorder arm is avoided, and thus wear of the recorder.

B. Voltage-to-Frequency Converter. From Vidar Corporation, Mountainview, Calif.

a. 211-06 Converter, 5,000 kHz square-wave output; 0.025% linearity, fixed offset; zero bias at 2,400 Hz.

b. 101 Power Supply for 211-06.

c. 904 Housing for 211-06 and 101.

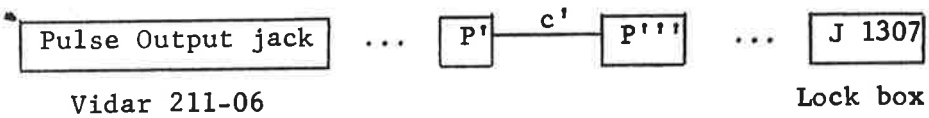
C. Instructions for Use. In preparation.

D. Cabling

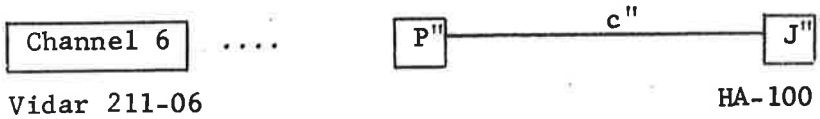
a. Between C-1024 and HA-100: as usual.

b. Between Vidar 211-06 and

1. V-4354 lock box



2. C-1024



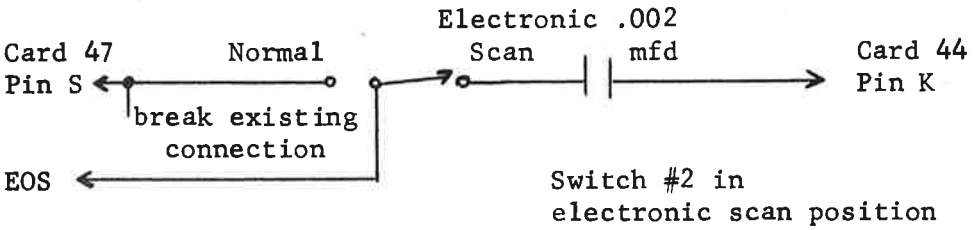
Plugs:	P'	Cannon, 25 P connector, DMB; with DD-24659 clamp.
	P"	Winchester M4 connector, 4 MS-LSN.
	P'''	BNC
Jack:	J'	Jack for connection with C-1024, usually located on the left side of the HA-100 console.
Cables:	c'	Coaxial cable. Shield to 14 on P', axial lead to 6 on P'.
	c"	Two-wire cable, wired directly into rear of J'; lead #1 from B of P" to A of J', lead #2 from A of P" to D of J'.

E. Switches.

a. #1 on HA-100, located on front panel of lock box between Signal Monitor and Spectrum Amplitude controls. SPST,

between J 1323 M and J 1324 M (underside of lock box chassis). For operation with converter, use open switch position (EL.SCAN) which cuts the power off the HA-100 sweep oscillator; otherwise use closed position (NORMAL).

b. #2 on C-1024, located on front panel of C-1024, between the two Sweep Width controls.



4. Increased Output from Integrator/Decoupler (NRL)

When dealing with weak signal, it is sometimes desirable to have a higher gain capability for recording spectra than is provided by the V-3521A Integrator/Decoupler. This can be accomplished by a change in the value of resistor R423 in the feedback loop of the USA-3. In our case, we used 40 meg in place of the 18 meg resistor, providing a gain increase of 2.2 (in the spectrum position only).

5. Oscilloscope Display Selector (ODS) (FDA)

A. Purposes.

1. To monitor sample spinning.
2. To observe HR-mode signals without modulation side bands. This is often desired, if resonance signals are separated by more than the sideband frequency, so that under normal operating conditions it may be difficult to disentangle centerband signals from sideband signals.

B. Switch Positions of ODS*

1. Normal, that is, as though no changes had been made in the cabling of the HA-100 (see D.1 for normal cabling) because of the installation of ODS.

2. Monitoring of Spinning, that is, of wobble of spinning sample (frequency and amplitude). This position is used when the spectrometer is operated in a locked mode.

3. a. HR-Mode w/o sidebands from the V-3521 integrator-decoupler. Spinning must be stopped (see also C.3)1.); otherwise there is modulation of the oscilloscope trace.

b. As Position 2); sample must, of course, be spinning.

*The switch was constructed in several stages, and the final setup as described may not be the most efficient device to obtain the desired displays.

C. Instructions for Use.

1. Normal position is used for oscilloscope displays as recommended in the Varian manuals. Note that signals are fed into the Vert. of the oscilloscope by d.c. coupling.

2. Change oscilloscope setting to the following:
   Coupling: a.c. Horiz.: 10 msec/cm Vert.: 10 mV/cm

   A sine wave (not too clean) will appear on the oscilloscope. The spinning rate is equal to the wobble frequency of the sample as deduced by the separations of the maxima of the sine wave: SR = 100/d (Hz).

   The wobble amplitude is related to the amplitude of the sine wave. Large wobble amplitudes produce undesirable audio noise. To minimize wobble, rotate sample tube with respect to spinner.

   Note 1: If a sufficiently strong lock signal is present, it will restore itself, after the sample has been reinserted into the probe.

   Note 2: Excessive wobble may also be caused by a bad spinner, by misalignment of the spinner housing or by sample tubes which are too long or eccentric.

3. a. HR-Mode signals w/o Sidebands

   Stop spinning the sample.
   V-4311: Switch from WLØ Detector to HRØ Detector (1,2..), adjust receiver gain and rf attenuation as needed.
   Oscilloscope: see C.2. above.

   b. Monitoring of Spinning in HR-Mode

   Stop sweeping (in V-4352 A, Linear Sweep: Sweep Field Off).
   Oscilloscope: see C.2. above.

D. Connection for and in ODS

1. Connections in HA-100 before installation of ODS

   a. V-4311/J 314 rf unit with V-4354/P 314 lock box

b. V-4391/VERT mode selector with Oscilloscope, vert.

c. V-4391/VERT mode selector with V-3521/J 201 integrator-decoupler

2. Panel, containing ODS (rotary switch, three positions) and jacks (j1, j2, ... j7). View from rear of console:

j1	j2	j3	j4	ODS	j5	j6	j7

The panel is mounted in the lower left half of the console above the oscilloscope (see "Relocation of Oscilloscope"). ODS is operated from the front of the console.

3. New cabling

	From	To		From	To
in	V-4311/J 314	j1	out	j5	V-4354/P 314**
	V-3521/J 201	j2		j6	V-4391/P 201***
	V-3521/J 301*	j3		j7	Oscilloscope, J Vert
	V-4391/VERT	j4			

*insert a T into existing connection on V-3521/J 301.
**see D.1.a.
***existing cable is long enough.

4. Connections of Jacks j1 through j7 in the Various Switch Positions

Position 1: j1 and j5, j2 and j6, j4 and j7; j3 is not connected

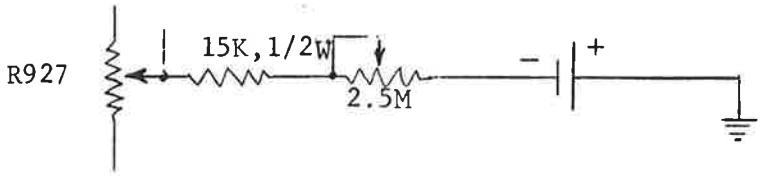
Position 2: j1 and j5, j2 and j6, j3 and j7 j4 is not connected

Position 3: j1 and j7 no other connections

We gratefully acknowledge the information on which the construction of the Oscilloscope Display Selector is based. The suggestion to monitor the sample spinning by displaying the output of the V-4311 rf unit (going into the V-3521 integrator at J 301) stems from Dr. R. E. Lundin (USDA Western Regional Laboratory, Albany, Calif.). Dr. W. B. Moniz (U. S. Naval Research Laboratory, Washington, D.C.) supplied us with the information on how to observe HR-mode signals without modulation sidebands.

6. Mars Recorder Zero Offset (NRL)

At very high audio and rf gains, the zero offset control of the Mars recorder sometimes does not have sufficient range for full scale control of the baseline. The circuit shown below increases the offset range (zero suppression). To avoid damage to the capacitors in the filters, battery voltage should not exceed 22V. Since only occasional need for this circuit exists, means should be provided to disable it.



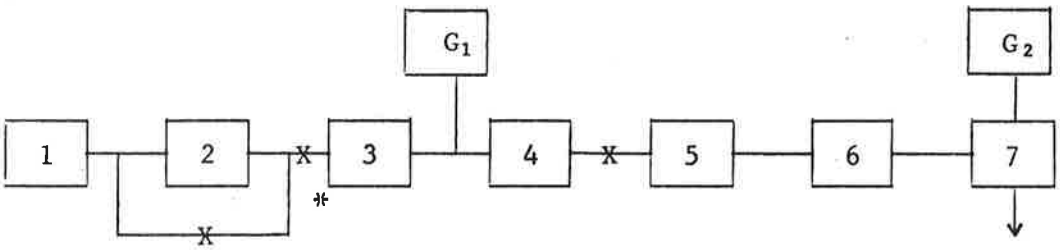
7. Voltage Regularor for HA-100 Console (FDA)

A 2 KVA regulator (e.g., Sorenson ACR 2000) regulates the voltage for all devices in the console, for all outlets of the console, and for the C-1024. Only with regulated voltage have we been able to avoid dropped counts in the C-1024. Note: To avoid hum pickup, regulator case should be insulated from the console frame.

General

1. Spinner Air Supply (FDA)

Since air free of oil, moisture and particles has not been available from the house supply, we have been using the following setup.



X = valve
G = pressure gauges; G_1 to read 10 psi
G_2 to read 6 psi

1	Compressor	5	Filter a
2	Dryer	6	Filter b
3	Regulator	7	Regulator
4	Drying tower		

Another train of equipment, starting with item 3, is branched off at * to supply another spectrometer (the capacity of items 1 and 2 is sufficient for drying the spinner air in the A-60 and the HA-100).

Details

1. Oilless compressor, Bell and Gosset, SYC 8 - 1
2. Puregas Heatless Dryer, HF 200-9; Puregas Equipment Corp., Copiague, N. Y. 11726, Industrial Products Division
3. Regulator, Conoflow Corp., Phila., Pa.; model H-10 XT - HXXB
4. Drying tower, Laboratory Gas and Air Drying Unit. A. Hammond Drierite Co., Xenia, Ohio
5.) Filters supplied by Varian (from Monnier Bros., Algonac,
6.) Mich.)
7. Regulator, with gauge G_2, supplied by Varian (see items 5 and 6)

Notes

a. Use copper tubing from 1 through 4; from then on, tygon tubing.
b. The compressor has not required any repair in the four years of operation. Since it is noisy as is item 2, items 1 and 2 are installed outside the laboratory. Condensation needs to be drained regularly, particularly during the humid summer months.
c. Repairs of drier consisted in the replacement of solenoid valves (X-8314A-99) and cleaning of stopped-up valve openings.
d. The purpose of the drying tower is to indicate the presence of moisture. If moisture is present, it is due to lack of draining of the compressor or malfunction of the drier. The silica-gel of the drying tower does not need to be regenerated by heating; it will regain its blue color when dry air has passed through it for a while.

2. Recorder Pen (FDA)

General: Varian penholder 914-197 has a rubber grommet which deteriorates in time. It was replaced by a nylon bushing into which a Leroy pen can be screwed (see sketch next page).

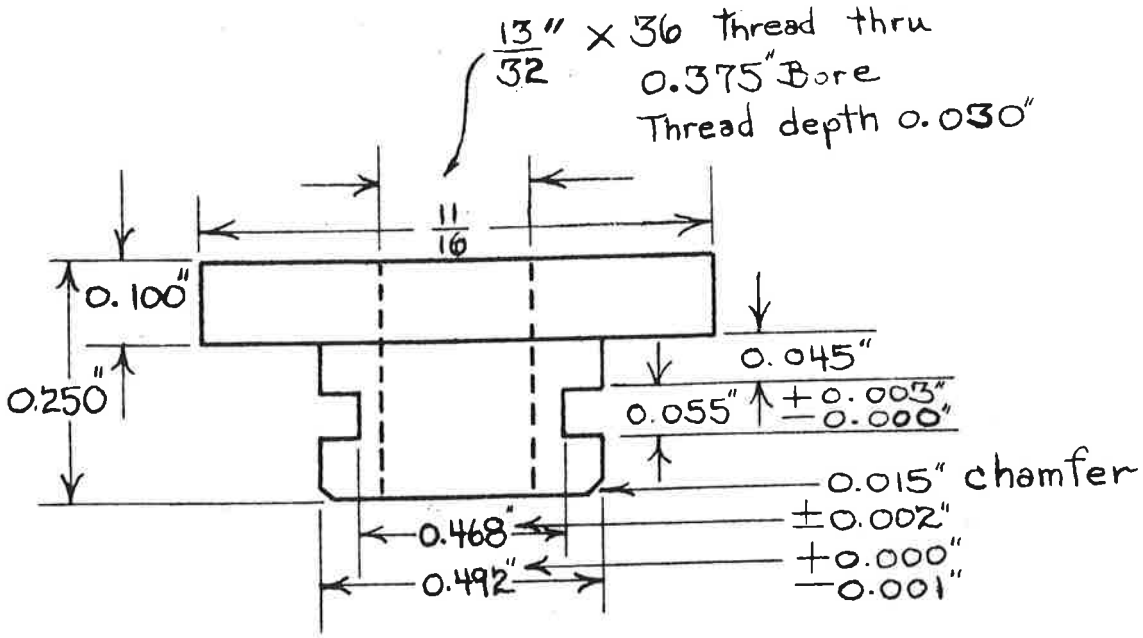
Pens: Leroy lettering pens #0 for routine use, #00 for precision measurements (61-0015-0 and -00).

Ink: Any writing fluid except India ink, which clogs pen; no cleaning of pens is necessary. Pen tips need not be covered. We find it useful to have traces of different colors on one recorder chart and keep on hand several pens with different colors. Each pen has its own pen holder. Change of pens is easy on the HA-100, where the penholder is attached magnetically. For an adaptation of this system to the A-60 see next page.

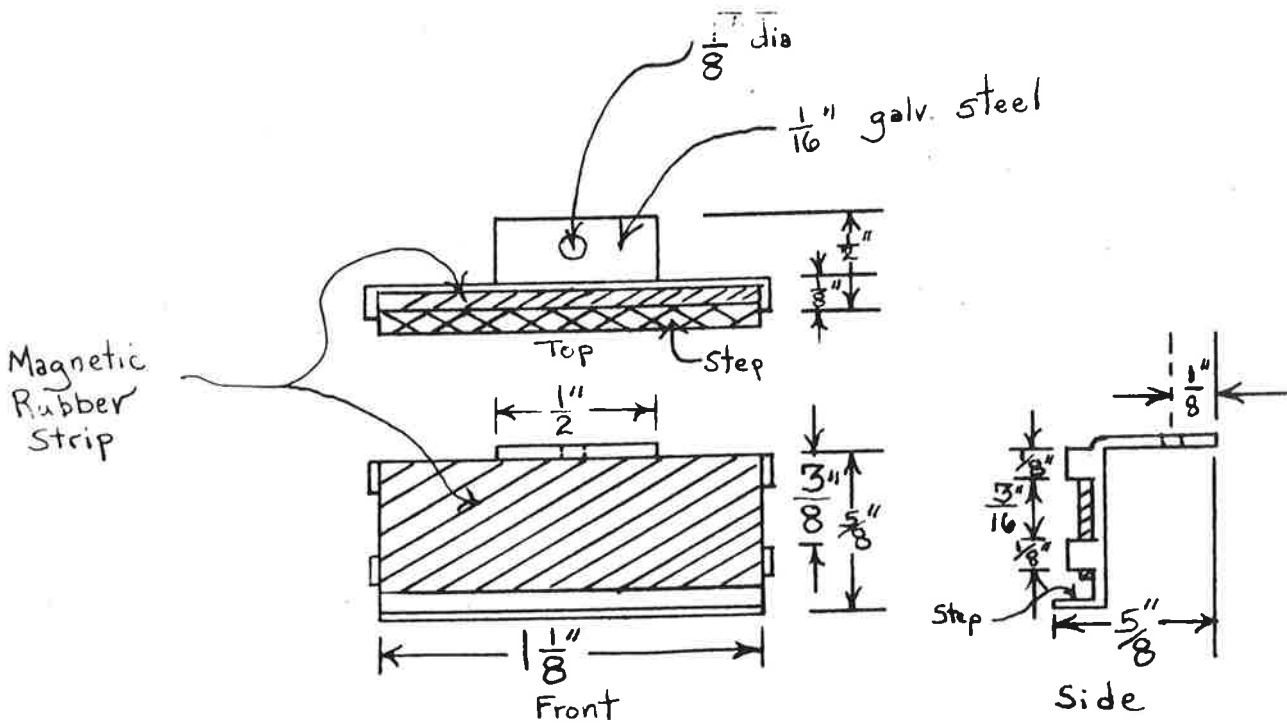
Penholder bracket: On the A-60, the Varian penholder bracket was replaced by that shown in the sketch on the next page, so that Varian penholder 914-197 can be used. The new bracket holds the penholder by magnetic attraction.

We gratefully acknowledge Dr. Johannesen's (NBS) making available to us a sketch of the penholder bracket.

Penholder: Make of aluminum of nylon. Use #3101-50 retaining ring.



Penholder bracket:

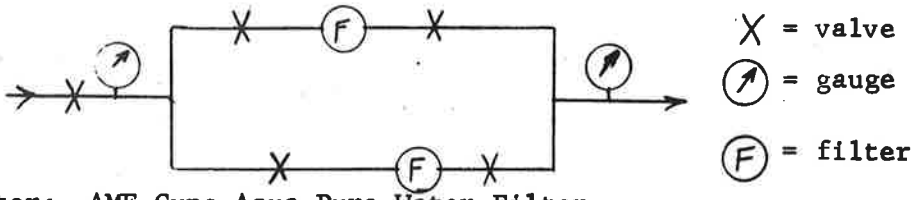


3. Magnet Cooler Solenoid Valve (FDA)

The three-way solenoid valves used in magnet coolers can be rebuilt with a spare part kit, #68-046, available from an ASCO representative. D.C. area: J. C. Soraghan and Assoc., 20 E St., N. W., Washington, D. C. Price: $5.-.

4. Filtering of Raw Water for Magnet Cooling (FDA)

A set of two filters in parallel, with only one filter being used at a time, allows one to change the filter cartridges without cutting off the cooling water.



Filter: AMF Cuno Aqua-Pure Water Filter
Whole unit: P 10-1
Cup* : 32318-31
Cartridge : P 110

*Filter cups ("sumps") tend to crack at the top after a few years of use; it is recommended that a spare cup be kept on hand.

Filter change: The pressure drop across new cartridges varies, probably due to variations in porosity of the cartridge material. Therefore, the criterion for changing a cartridge is the change in pressure drop. When this drop has increased by 3 psi, the cartridge is changed. Discoloration of the cartridge occurs much sooner than, and need not be taken as an indication of, filter clogging. To unscrew the cup of the filter assembly, a strap wrench should be used.

Operating Instructions

1. Instructions for C-1024/HA-100 Combination (FDA)

These were drawn up on the basis of our own experience with this setup. They are more compact than those given by Varian and, at the same time, somewhat more explicit.

Copies available upon request.

Author Index - TAMU NMR Newsletter No. 126

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