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No. 33

Author Index

ANALYSIS OF COMPLEX NMR SPECTRA: EPICHLOROHYDRIN

C. A. Reilly and J. D. Swalen

Shell Development Company, Emeryville, California

In previous publications[1,2,3] the authors have developed an iterative method for calculating accurate parameters from high-resolution NMR spectra. In the present letter we illustrate the utility of the method by giving some preliminary values for the NMR parameters of epichlorohydrin (5 non-equivalent protons).

Two FORTRAN programs, which greatly facilitate the calculations have been written for the IBM 7090 computer. Trial values of the shielding parameters and the spin-spin coupling constants are first entered and the main program (NMRIT) compiles the matrix of the spin Hamiltonian, diagonalizes it and calculates the frequencies and intensities of the allowed transitions. The energy levels from which each transition originates are also indicated. With a judicious choice of these trial parameters an assignment of the observed spectrum is usually possible[2].

A second program (NMRLS) utilizes the assignment of the observed transition frequencies to calculate numerical values for the spin energy levels and their precision by a least-squares technique. These energy levels, the initial trial parameters, and the observed frequencies are now used as input data for NMRIT. By an iterative process already described[2,3] NMRIT calculates new parameters, the

process being continued until a predetermined convergence limit is reached, a serious divergence occurs, or a prescribed number of iterations is performed. At present the program allows for a maximum of ten iterations in any one calculation. The final values for the parameters, or extrapolations from them, may be used as initial values for further iterations, if desired.

The above programs have been used to advantage in analyzing the 60 Mc/sec and 40 Mc/sec NMR spectra of epichlorohydrin (these spectra have been published as Serial Nos. 3 and 4 of the API Catalogue). Values for the parameters are given below and are believed to be accurate to one or two units in the last place quoted. More precise values must await the availability of more precise experimental data.
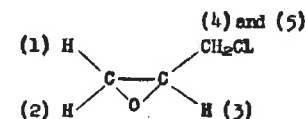
δ_1 2.65 ppm from TMS
δ_2 2.84 "   "
δ_3 3.20 "   "
δ_4 3.47 "   "
δ_5 3.74 "   "

$J_{12} = 5.0$ cps	$J_{23} = 4.0$ cps	$J_{34} = -6.6$ cps
$J_{13} = 2.4$ "	$J_{24} = 0.6$ "	$J_{35} = -4.0$ "
$J_{14} = -0.2$ "	$J_{25} = -0.1$ "	$J_{45} = 11.7$ "
$J_{15} = -0.1$ "		

33-1

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

ADDRESS REPLY TO

NATIONAL BUREAU OF STANDARDS

WASHINGTON 25, D. C.   June 12, 1961

Attn: Dr. L.H. Bennett

IN YOUR REPLY
REFER TO FILE NO.

EF, SES/IH

Dr. A.A. Bothner-By
Mellon Institute
440, Fifth Avenue
PITTSBURGH 13, Pennsylvania
USA

Dr. Aksel A. Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

I just learned from my colleague here at N.B.S., Dr. Ernest Lustig, of your M.E.L.L.O.N. M.R. mailing list. I think it is a wonderful idea, and I would like to be included on it. I would be very happy to make an occasional contribution, though I have one hesitation. I note that high-resolution NMR is the predominant interest of your correspondents. Do you want a wide-line resonator?

As an initial contribution, I would like to mention an experiment I plan this summer together with my assistant, Rex J. Snodgrass, who will use this research as his Ph.D. thesis at the University of Maryland. We plan to search for oscillations of the de Haas-Van Alphen type in the Knight shift of metals. This effect was predicted by Das and Sondheimer about a year ago. We have a helium dewar which we insert in the probe of the Varian wide line spectrometer. We expect to hold the field constant and sweep the spectrometer in frequency with frequency readings from a Beckman counter being simultaneously printed on tape and pips marked on the recorder. This permits quite accurate determinations of the Knight shift to be made.

Please let me know if you are interested in this sort of thing.

Sincerely yours,

L. H. Bennett

Lawrence H. Bennett
Physicist
Metal Physics Section

Dear Dr. Bothner-By:

Together with Dr. J. Krogh-Moe of the Swedish Institute of Silicate Research in Gothenburg we have recently made an NMR study of boron coordination in potassium borate glasses which might have a bearing on the general problems related to the evaluation of weak quadrupole effects in wide line spectra.

The coordination of boron in the alkali borate glasses has earlier been studied with NMR by Silver and Bray (J.Chem.Phys. 29, 984 /1958/ and J.D. Mackenzie, Modern aspects of the vitreous state /Butterworths, London 1960/ Vol. I). The B^{11}-resonance indicates that the boron nuclei in these glasses have two different local environments. Due to an anisotropic distribution of electronic charge around the boron nucleus, the resonance line in vitreous boron oxide shows a second order broadening effect of nuclear quadrupole interaction, and this broad line is assigned to boron in three-fold oxygen coordination. By addition of alkali oxide a sharp resonance line is produced which is attributed to the appearance of boron in four-fold coordination belonging to BO_4 tetrahedra with low quadrupole interaction. It would in principle be possible to calculate the amounts of three-fold and four-fold coordinated boron in the sample after separation of the overlapping resonance lines and evaluation of the areas under each line. The results of Silver and Bray, however, were evaluated in a very simplified manner from the observed signal amplitudes. As pointed out by the authors themselves their method is likely to overestimate the fraction of four-fold coordinated boron at high alkali content, since the width of the broad line increases with increasing alkali content and, indeed, their measurements (filled

circles in fig. 1) lead to a fraction of four-fold coordinated boron definitely higher than that assumed by Warren (J.Amer.Ceram.Soc. 24, 256 /1941/) and the one observed in some crystalline borates investigated by Krogh-Moe (Arkiv Kemi 14, 439 /1959/ and Acta Cryst. 13, 889 /1960/).

Warren assumed that boron changes from three-fold to four-fold coordination as alkali oxide is added to the glass, supposing each oxygen bonded to two borons at low alkali content, all oxygens being engaged in boron-oxygen bonds. Krogh-Moe (Acta Cryst. 13, 889 /1960/) has shown that the boron-oxygen networks of crystalline potassium pentaborate (Arkiv Kemi 14, 439 /1959/) cesium triborate (Acta Cryst. 13, 889 /1960/) and lithium diborate (To be published) are built in agreement with the following rule regarding the coordination of boron and oxygen: Each "molecule" of alkali oxide added to boron oxide converts two boron atoms from three-fold to four-fold coordination. This corresponds to a fraction of boron in four-fold coordination $N_4 = S/1-S$ (shown by the solid line in fig. 1), where S is the molar alkali concentration. The above rule and expression for N_4 follows from the Warren scheme for the region of low alkali oxide content (< 15 mole-%). At higher alkali content, however, Warren assumes that some oxygens are bonded only to one boron in which case the fraction of four-fold coordinated boron should be less than that given by the ratio S/1-S. The dashed line in fig. 1 indicates the values expected by Warren.

In order further to investigate the discrepancy between experimental and theoretical data we have repeated and extended some of Silver and Bray's measurements. During this work we made the observation that there is a close agreement between the spectra of crystalline boron oxide and vitreous boron oxide, from which we infer that the similarity of the spectra is based on a corresponding similarity of the two states with regard to the boron coordination. These findings, on the other hand, suggest the existence of corresponding relationships between other crystalline and vitreous boron compounds. Since the crystalline compounds, so far investigated, all lie on the theoretical $N_4(S)$ curve the corresponding vitreous states are expected to yield N_4-values in the close vicinity of the theoretical line, an assumption which is actually born out by experiment.

In particular, we may refer to a study of potassium borate glass at room temperature. The samples were prepared by melting boric acid and potassium carbonate in a platinum crucible. After solidification, the samples were coated with a plastic to be protected against moisture. The cylinders prepared were 16 mm in diameter and of 70 mm length. The compositions were determined by analyses within 0.1 %. Spectra were recorded with a Varian-4250 wide line spectrometer at 13.0 Mc/s and three different settings of the radiofrequency field. Our recorded spectra were in agreement with those reported by Silver and Bray (J.Chem. Phys. 29, 984 /1958/). A rigorous calculation of the fraction of four-fold coordinated boron based on a detailed analysis of the two lines would, however, require a considerable amount work, while still yielding values of limited accuracy due to the poor signal-to-noise ratio of the recorded broad line spectrum. As the signal-to-noise ratio of the sharp line much exceeds that of the broad one, we have therefore, to a first approximation, chosen to calculate only the area under the sharp absorption line as a measure of the changes in the amount of four-coordinated boron. The area is estimated to be of the magnitude $y_m' \cdot x_m^2$, where y_m' is the ordinate and x_m the abscissa of the maximum of the experimental sharp line derivative, taking the center of the line as origin. For absorption curves of Gaussian or Lorentz line shapes, the area is proportional to this quantity. As y_m' and x_m refer to the central part of the sharp line, the influence on these quantities from the superposition of the broad line could be neglected. The calculated absorption line area is taken to be proportional to the fraction of four-fold coordinated boron and to the volume density of boron atoms in the sample. In this way it was possible to calculate the ratio between N_4-values for samples of different K_2O-content. The method, of course, does not allow an absolute determination of N_4. Our values, shown in fig. 1 by open circles, have therefore been fitted to the theoretical line $N_4 = S/1-S$ by the method of least squares, yielding a standard deviation from the theoretical value of 3 %. A significance test of the deviation indicates that the boron-oxygen coordination in the potassium borate glass is in agreement with the S/1-S-rule, in contradiction to the results obtained by Silver and Bray (J.Chem.Phys. 29, 984 /1958/ and J.D. Mackenzie, Modern aspects of the vitreous state /Butterworths, London 1960/ Vol. I).

In connection with a general study of new methods for the analysis of wide line NMR spectra taken up by our group we plan to extend the results so far obtained towards a more rigorous analysis of the quadrupole effects in alkali borate glasses.

Yours sincerely,

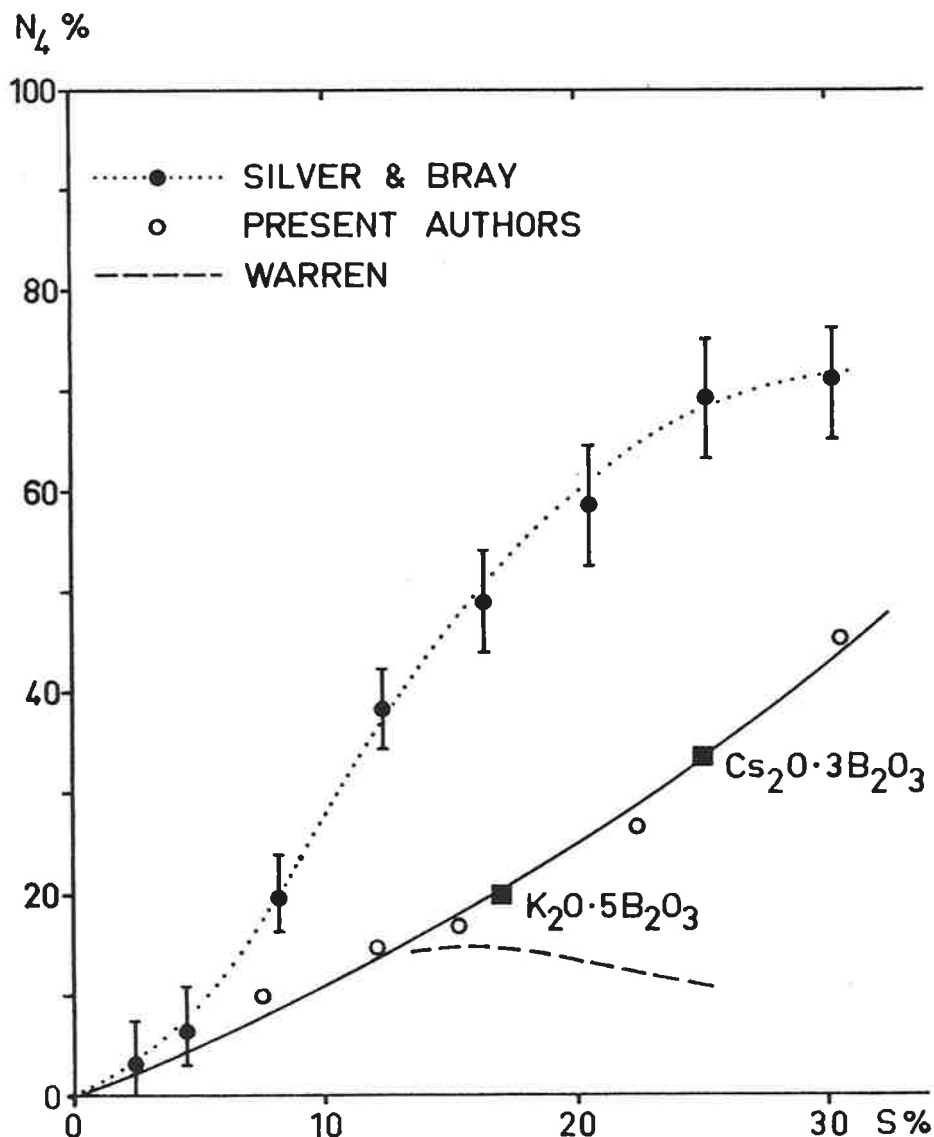Erik Forslind   Sven-Erik Svensson

Fig. 1. The fraction of four-fold coordinated boron atoms, N_4, as a function of the molar K_2O concentration S. The solid line represents the theoretical curve $N_4 = S/1-S$.

THE STEREOCHEMISTRY OF SOME MANOYL OXIDES

Ernest Wenkert and Peter Beak[1]

Department of Chemistry, Iowa State University

Ames, Iowa, U. S. A.

P. K. Grant

Dominion Laboratory
Department of Scientific and Industrial Research

Petone, New Zealand

A recent proton magnetic resonance spectral analysis of pimaradienic diterpenes (I)[2] revealed that the stereochemistry of their vinyl groups is reflected by the resonance behavior of the vinyl protons. A difference in the intramolecular shielding of the vinyl hydrogens by the nuclear double bond was assumed to be responsible for the distinguishing features of the vinyl region of the p.m.r. spectra of 13α- and 13 - β vinyl compounds. On the supposition that a similar internal shielding effect (of the vinyl hydrogens by the nuclear oxygen atom) should prevail in manoyl oxide (II) and its stereoisomers, the p.m.r. spectra of manoyl oxide and epimanoyl oxide (III), its 13-epimer[3], were inspected. As both Table I and Figure I

[1] Public Health Service Predoctoral Research Fellow, 1960-1961.

[2] E. Wenkert and P. Beak, J. Am. Chem. Soc., 83, 998 (1961).

[3] R. Hodges and R. I. Reed, Tetrahedron, 10, 71 (1960).

indicate, the twelve-line vinyl regions (analyzed as ABC sy-
stems) of the spectra of the two epimers are distinctly diff-
erent.

I   II   III
                  TABLE I
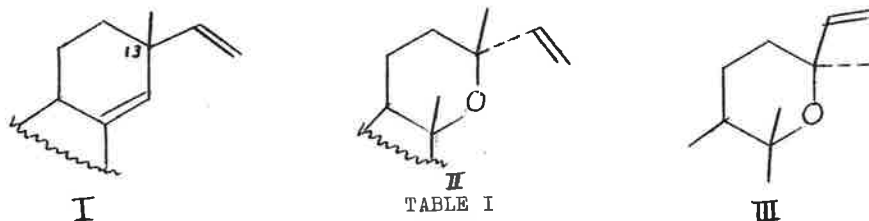
CHEMICAL SHIFTS (IN δ) AND SPIN-COUPLING CONSTANTS

(IN C.P.S.) FOR COMPOUNDS II AND III

	H_A	H_B	H_C	J_{AB}	J_{AC}	J_{BC}
II	5.90	4.88	5.09	10.1	17.3	1.7
III	6.04	4.89	4.96	10.9	18.5	1.4

The p.m.r. spectra of 2-ketomanoyl oxide (IV, carbonyl group
at C-2), of a new ketomanoyl oxide[4], a plant constituent of
Xylia dolabriformis, and of colensone oxide[5], a ring A-nor
ketomanoyl oxide constituent of Dacrydium colensoi, show these
natural substances to be of the manoyl oxide (II) stereochemical

type. While these results confirm previous structural assign-
ments, based on chemical data, for 2-ketomanoyl oxide[6] and
the Xylia oxide,[7] they represent new stereochemical inform-
ation for colensone oxide.
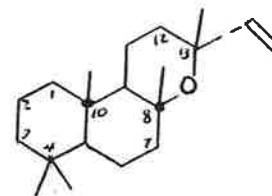
IV

As illustrated by Table II, the position of the down-
field methyl peaks, those of the methyl groups on the oxide-
bearing carbon atoms, can serve also as a diagnostic test of
the C-13 stereochemistry of the oxides. Indeed, the chemical
shifts of the C-8 and 13 methyl functions of the keto-oxides
are in full agreement with the latter's assigned stereochemistry.

[4]Dr. John Morgan (D.S.I.R., Forest Products Research Laboratory,
Princes Risborough, Aylesbury, Bucks., England) kindly furnished
a sample of this oxide.

[5]R. M. Carman and P. K. Grant, J. Chem. Soc., in press.

[6]J. R. Hosking and C. W. Brandt, Ber., 68, 286 (1935).

[7]Private communication from Dr. J. Morgan.

TABLE II

CHEMICAL SHIFTS (IN δ) OF METHYL GROUPS

Oxide	At C-8 and 13	At C-4, 4 and 10
Manoyl	1.27, 1.27	0.78, 0.78, 0.85
Epimanoyl	1.08, 1.17	0.68, 0.74, 0.81
2-Ketomanoyl	1.28, 1.28	0.83, 0.89, 1.06
Xylia	1.27, 1.32	0.91, 1.02, 1.08
Colensone	1.29, 1.32	0.82, 0.97, 0.99

Additional structural information about the keto-oxides could be gained from an inspection of the α-ketomethylene region of their p.m.r. spectra. 2-Ketomanoyl oxide exhibits a four-proton quartet centered 2.22δ(J=14.3 c.p.s.) (an AB, almost A_2, system), characteristic of a carbonyl group flanked by two isolated methylene functions.[8,9] The Xylia keto-oxide reveals a two-proton unsymmetrical multiplet centered at 2.49δ, characteristic of a $RCH_2CH_2COCR'_3$ moeity. While this would permit the carbonyl group to be located at C-1, 3, 7 or 12, the last two positions are excluded because of the lack of an expected change of the chemical shifts of the neighboring C-8 and 13 methyl groups and because of a noticable down-field shift of the ring A methyl signals. Hence, the Xylia product is 1- or 3-ketomanoyl oxide. Colensone oxide shows a two-

proton quartet centered at 2.04δ(J=15.8 c.p.s.), characteristic of a carbonyl group flanked by only one isolated methylene function. This fact as well as arguments similar to those used for the Xylia compound speak in favor of colensone oxide being a ring A-nor ketone. The down-field position of the α-ketomethylene signals of this substance also support a cyclopentanone structure.[10,11]

[8] P. K. Grant and R. Hodges, Chemistry and Industry, 1300 (1960).

[9] C. Enzell, Acta Chem. Scand., 14, 2053 (1960).

[10] Cf. L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Ltd., London, England, 1959, p. 57.

[11] All spectra were obtained with ca. 25% deuterochloroform solutions on a Varian Model HR60 spectrometer at 60mc./sec. with tetramethylsilane acting as internal standard. Position of the major peaks was determined by the audiofrequency side band technique, that of minor peaks by linear interpolation.

RF/DMT

Department of Scientific and Industrial Research

NATIONAL PHYSICAL LABORATORY

TEDDINGTON, Middlesex

Telegrams: Physics, Teddington   Telephone: TEDdington Lock 3222, ext. 199

BASIC PHYSICS DIVISION

Please address any reply to
THE DIRECTOR
and quote: BP.A.F1.
Your reference:

7th June, 1961.

Dear Dr. Bothner-By,

There are four or five of us working on various aspects of nuclear resonance here at NPL, and we all greatly appreciate your newsletter. Although my name does not appear on the mailing list, I wonder if I may be allowed to contribute something?

About a year ago we started some proton spin decoupling experiments mainly directed towards the simplification of complicated high resolution spectra. The project took a new turn when we heard from Dr. D.F. Evans (Imperial College, London) how he had used a double irradiation experiment to determine relative signs of spin coupling constants[1] He was able to show that in the thallium diethyl cation the two thallium-hydrogen couplings were of opposite sign. Now thallium-proton spin coupling constants are very much larger than proton-proton coupling constants and it was clear that an extension of the method to determine the relative signs of proton-proton couplings would be trickier experimentally. However when Dr. Whiffen and I tried it we were surprised how neatly the method worked.

In a system of only two coupled nuclei, it is clear that the sign of the coupling constant must remain ambiguous. For this experiment it is necessary to have three nuclei coupled together, and a convenient practical example is 2-Furoic acid (Figure 1 shows spectrum of ring protons). We find $|J_{AB}| = 3.5$ c/s, $|J_{BX}| = 1.8$ c/s, $|J_{AX}| = 0.8$ c/s.

Assuming, to begin with, that all J's are positive, it is possible to write down for each transition of Figure 1 the spin states of the two neighbour protons, each of which could have spin state α or β. The argument is unaffected by interchanging α and β throughout Table I.

Dr. A.A. Bothner-By   7th June, 1961.

		X				A				B			
		12	11	10	9	8	7	6	5	4	3	2	1
Spin states of neighbours	A	α	β	α	β					α	α	β	β
	B	α	α	β	β	α	α	β	β				
	X					α	β	α	β	α	β	α	β

Table I

A spin coupling can be destroyed by irradiation of one of the multiplet patterns with a field $\frac{\gamma}{2\pi} H_2 \sim J$. It is experimentally feasible to irradiate near transitions 7 and 8 of 2-Furoic acid with only a slight perturbation of transitions 5 and 6, while still satisfying the condition $\frac{\gamma}{2\pi} H_2 \sim J_{AX}$. Physically this means that protons A and X are decoupled only in those molecules that have proton B in spin state α (see Table). Consequently if the X spectrum is recorded at the same time, we would expect to see lines 11 and 12 coalesce but lines 9 and 10 remain unaffected.

Table I has been drawn up for the case that all the coupling constants have like sign. If J_{AB} and J_{BX} were of opposite sign, either row B of Column X or row B of column A should have α and β interchanged. Then strong irradiation of lines 7 and 8 causes lines 9 and 10 to coalesce, and this is how the experiment determines the relative signs of J_{AB} and J_{BX}.

Analogous experiments may be carried out where the J_{BX} coupling is destroyed by irradiation of lines 1 and 2. Then lines 9 and 11 coalesce (and sit on top of line 10) if J_{AB} and J_{AX} have like signs. In this particular example all the coupling constants have like signs (presumably positive). Figure 2 shows typical observed patterns of the X spectrum under conditions of double irradiation.

The only other method of obtaining relative signs of coupling constants depends on the analysis of strongly coupled systems of at least three non-equivalent protons. The double irradiation method has the advantage of being applicable to

Dr. A.A. Bothner-By   7th June, 1961.

"first order" spectra, and we feel it could be applied rather generally. Only very slight modification of the spectrometer is required[2].

Yours sincerely,

R. Freeman.

R. Freeman
Basic Physics Division

(1) D.F. Evans and J.P. Mahler - Proc. Chem. Soc., to be published.

(2) R. Freeman and D.H. Whiffen- Molecular Physics, to be published.

Dr. A.A. Bothner-By,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13,
Pennsylvania,
U.S.A.

FIGURE 1

FIGURE 2 THE X SPECTRUM RECORDED WITH SIMULTANEOUS STRONG IRRADIATION OF (a) TRANSITIONS 5 & 6, (b) 7 & 8, (c) 1 & 2, (d) 3 & 4.
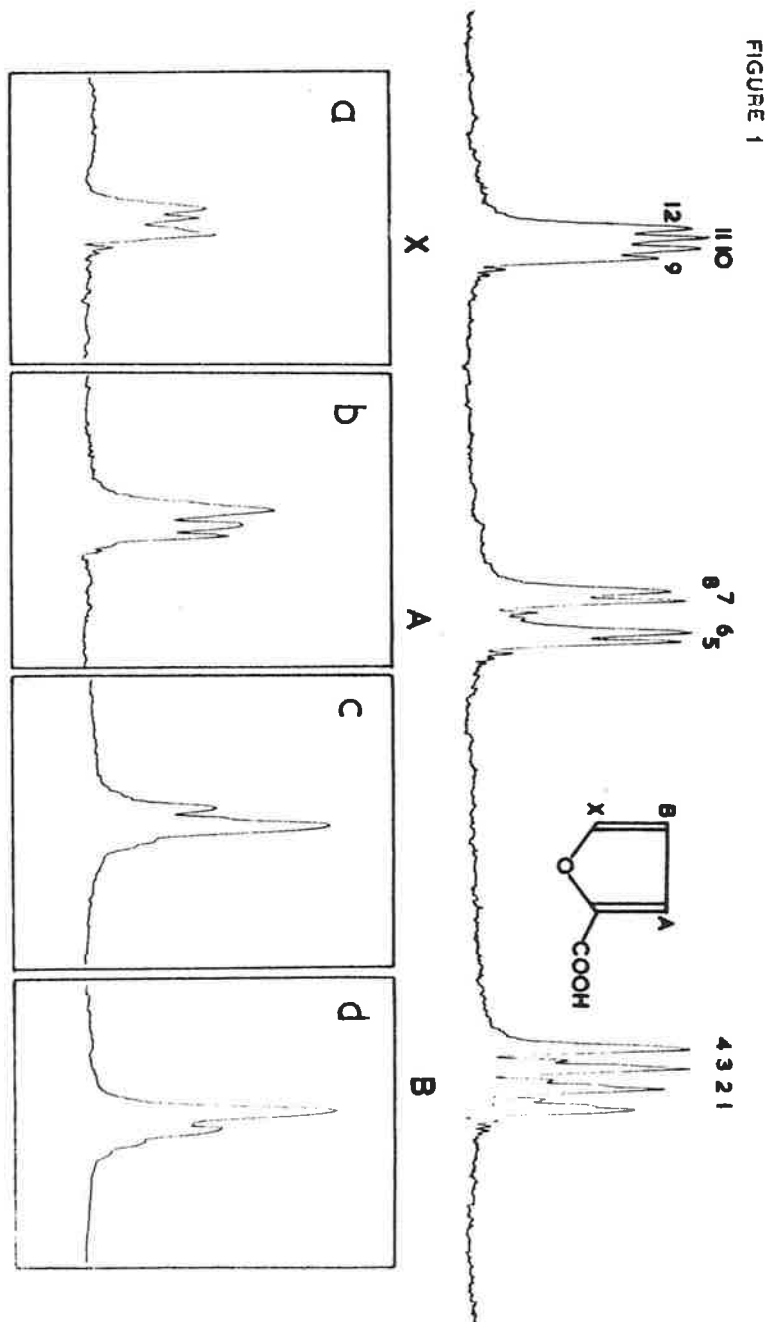
33-9

June 15, 1961

The existence of tetracoordination of boron has been proposed in organic and inorganic borate systems (1,-4). Sodium salts of several diglycol borates have been recently reported (5), and an investigation of the structure of these compounds has been conducted using nuclear magnetic resonance and infrared techniques.
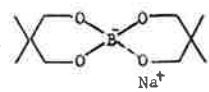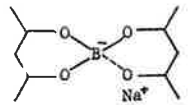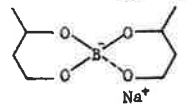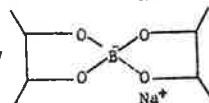
B'' Studies

The use of Boron Magnetic Resonance to study tetracoordination in boron compounds has been previously reported (6, 7). As the tetrahydral character increases, δ (the chemical shift) becomes more positive relative to a tricoordinated similar boron compound. Relative to $B(OCH_3)_3$, the δ's for the following known tetracoordinated species are: tetra acetyl, +17.0; $B(OH)_4^-$, +16.8; $LiB(OCH_3)_4$, 15.2; BF_3, etherate, +17.0 (3). All of the diglycol borate salts described (5) were investigated by B''MR to establish the existence of tetracoordination of B in these compounds.

The B'' spectra were obtained with a Varian V-4300 B Spectrometer operating at 12.8 MC. Methyl alcohol was employed as the solvent and the spectra were calibrated relative to the B resonance line of $B(OCH_3)_3$ using the side band technique (8). The results are shown below in Table I. The proton results (described later) were obtained at 60 MC using CD_3OD as the solvent and the spectra were calibrated relative to tetramethylsilane again using the side band technique (8).

TABLE I

Compound		δ*	% Tetra Coordination+	Na Salt Prep. NaOH	Na
I		0 +17 +17	0 (glycol borate) 100 100	X	X
II		+16 +16	100 100	X	X
III		+17 +12	100 65	X	X
IV		+11 +11	60 60	X	X

* The chemical shift δ is given in ppm above $B(OCH_3)_3$

+ % tetracoordination defined as $\delta/17 \times 100$

We have assumed that a δ of 17 represents complete tetracoordination, since in all of these borates the B environment (at least for the 6 member rings) is essentially identical. This value is also consistent with the results of Onak at al (7). The deviation of the values of δ are estimated to be ±0.5 ppm and consequently a $\Delta\delta$ of 1 ppm is not considered significant. It should be noted - all of the 6 membered ring compounds are highly tetracoordinated (except one) and this is probably due to ring stabilization. Results, utilizing molecular models, are compatible with this. Edwards and Ross (3) postulate that in the solid hydrated borates, boron exists in three and four-fold coordination by oxygen. Also that the ratio of tetrahedral boron to total boron is equivalent to the ratio of cation charge to total boron. The data which are being presented here not only support their postulate, but provide an extension of it to include solutions. Referring to the table on elemental analysis (Table II) one finds that the ratio of cation ion charge (Na) to total boron is unity which indicates all of the boron is tetracoordinated. Furthermore, the first compound shown in Table II was examined both as the diglycol borate and as Na salts (from each preparation method). The diglycol borate has a cation to total boron ratio of 0, consequently the postulate predicts no tetracoordination and none was observed by Boron Resonance. Presumably, the cation stabilizes the charge on the tetrahedral boron.

The last compound in Table I appears to be half tetracoordinated, if true, this could be due to ring strain effects being somewhat stronger than the charge stabilization. If this is the case, it would be interesting to know whether the Na+ is exchanging between the tri and tetra-valent forms or if a B atom remains tetracoordinated once it happens. Another possibilitiy is that this compound is

completely tetracoordinated, but due to ring strain the B may be in a distorted tetrahedral configuration. One then would not expect the chemical shift for the 5 membered-rings to be equivalent to that in the 6 membered-ring systems. Further work on this system is necessary and is planned.

TABLE II

ELEMENTAL ANALYSIS AND SODIUM-BORON RATIO

Compound Number *	Glycol	% B (Wt.)	% Na (Wt.)	Na/B (Atomic)
I	2,2-Dimethylpropanediol-1,3	4.55	9.99	1.0
I	2,2-Dimethylpropanediol-1,3	4.48	9.62	1.0
II	Pentanediol-2,4	5.02	9.15	0.86
II	Pentanediol-2,4	4.91	.9.64	0.93
III	Butanediol-1,3	5.11	11.10	1.0
III	Butanediol-1,3	4.92	11.32	1.1
IV	Butanediol-2,3	4.99	10.70	1.0
IV	Butanediol-2,3	5.16	11.46	1.0

* First row in each of the four cases is for NaOH preparation.

Proton Spectral Evidence for Tetracoordination

If proton line shifts due to the tetracoordination of boron are to be observed, one must look to the protons attached to carbons which are β to the boron (there are no α's in these compounds). The shift would be expected to be small as the effect must be transmitted through 3 bonds which normally falls in the range of 0.1 to 0.5 ppm. (As an example, the difference in δ's for the methyl protons in ethylbenzene and n-hexane is about 0.4 ppm). Obviously, a

detectable shift would not be expected if the effect involved one more bond. Within the limits of experimental accuracy the above was observed. Six of the eight borates contained a tert H on the β carbon and peak assignments for these protons in the tetra- and tri-coordinated borates were 3.4$_7$ and 3.7$_5$ ppm _below_ tetramethylsilane, respectively. The ratio of these peak areas times 100 was taken as the % tetra coordination. The results are shown in Table III. The larger errors in the proton results are due to line broadening. The results correlate rather well with the B" probe and strongly support the contention that the proton results are a measure of the amount of tetracoordination of the boron in these borates. These results also suggest that there are no unusual or large electrostatic effects associated with the tetracoordination of the boron atom as otherwise a larger shift would have been detected. Further work is planned to substantiate these observations.

TABLE III

PERCENT TETRACOORDINATION IN NA BORATES

Compound No.	B" Results	H' Results
II	100 ±5	100 ±10
II	100 ±5	100 ±20
III	65 ±5	65 ±10
III	100 ±5	100 ±10
IV	60 ±5	55 ±5
IV	60 ±5	50 ±5

1. Dale, J. Chem. Soc. 922 (1961)
2. Edwards, Morrison, Ross, and Schultz, J. Am. Chem. Soc. 77, 266 (1955)
3. Edwards, and Ross, J. Inorg. & Nucl. Chem. 15, 329 (1960)
4. Boescken, Vermaas, & Kuchlin, Rec. Trav. Chem., 49, 711 (1930)
5. Liao and Denny, 140th A.C.S. Meeting, Chicago, Sept., 1961
6. Phillips, Miller, and Muetterties, J. Am. Chem. Soc. 81, 4497 (1959)
7. Onak, Landesman, Williams, and Shapiro, J. Phys. Chem. 63, 1533 (1959)
8. Arnold and Packard, J. Chem. Phys. 19, 1608 (1951)

Sincerely,

Bill

W. M. Ritchey

WMRitchey:gls
Enclosure

Proton Magnetic Resonance II
Triphenylmethane Dyes*

David J. Wilson

Department of Chemistry
University of Rochester
Rochester 20, New York

The nuclear magnetic resonance spectra of the triphenylmethane
dyes pararosanilin and crystal violet and their corresponding leuco
forms provide verification of certain aspects of the theory of
chemical shifts and yield empirical information useful in the
determination of organic structures.

The spectra were taken at 27°C on a 60 Mc. Varian Associates
4300 B spectrometer, and were calibrated by the usual side-band
technique due to Arnold and Packard[1]; a Computing Measurements

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1. J. T. Arnold and M. E. Packard, J. Chem. Phys. 19, 1608 (1951).

Corporation Model 201-B frequency-period counter and Knight-Kit
audiogenerator were used. The dyes were obtained from Distillation
Products Industries, Rochester 3, New York, and were used without

further purification. They showed no spurious peaks in their NMR
spectra. Solvents (methyl alcohol and 1-4 dioxane) were analytical
reagent grade; the dioxane was distilled over sodium to remove
peroxides.

The ring proton shifts observed in the four compounds are listed
in Table 1. All four showed the characteristic four-line spectrum
of an AB group in the aromatic region of the spectrum. All data
are tabulated in cycles per second and are accurate to $\pm$ 0.5 c.p.s.
The centers of the AB quartets are reported relative to the methyl
peak in methyl alcohol. The solvent used was a 50% dioxane - 50%
methyl alcohol (by volume) mixture, which dissolved sufficient
quantities of both the leuco forms and the dyes themselves to permit
spectra to be taken. Saturated solutions were used and were run
immediately after preparation.

For both dyes the center of the quartet spectrum of the oxidized
form lies some twenty cycles below the center of the quartet of the
leuco form. For both dyes the spin coupling constants are essentially
independent of the oxidation state, and have values of about 8-9 c.p.s.
reasonable for ortho-proton coupling constants. And for both dyes
the chemical shift δ_{AB} increases about seven cycles on oxidation.

The assignment of the doublets at higher fields in the leuco
forms we make by analogy with the spectra of aniline and N N-di-
methylaniline reported by Corio and Dailey,[2] who found that ortho-

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2. P. L. Corio and B. P. Dailey, J. Am. Chem. Soc. 78, 3043 (1956)
----

protons appear well upfield from protons <u>meta</u> to the amine group, in these compounds. This is what is predicted for an electron-donating substituent.[3]

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3. J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Company, Inc., New York, 1959, p. 260.

On oxidation, these doublets shift downfield; the nitrogens are now positively charged, and therefore are somewhat electron-withdrawing, so this is to be expected. What is rather startling is the fact that the doublets due to the protons <u>meta</u> to the amine group shift even further downfield than do the ortho-protons; this, as indicated in reference 3, should not be.

A probable explanation of this apparent anomaly is the following. In the leuco forms, the central carbon atom is presumably nearly tetrahedral, and the rings are nowhere near coplanar. If one makes models, it is evident that ring current effects[4] between protons and

---

4. C. E. Johnson, Jr., and F. A. Bovey, <u>J</u>. <u>Chem</u>. <u>Phys</u>. <u>29</u>, 1012 (1958)

---

rings to which they are not attached should not be very large, on the average. In the oxidized forms, however, the central carbon atom is trigonal, and the partial double bond character of its bonds would make a structure in which the three rings are nearly coplanar quite

stable. Each proton <u>meta</u> to an amine group is now subject to strong ring current effects from one of the other rings, and is located in such a position that this additional ring current effect will push its spectrum to lower fields, as is indeed observed.

One can calculate an approximate value for the decrease in electron density at the aromatic protons brought about by oxidation by using modification of a formula given on page 175 of reference 3;

$$\Delta\lambda = \Delta\bar{\delta}/21.4 \qquad \text{where} \qquad \Delta\lambda$$

is the change in the effective number of electrons about the protons; and $\Delta\bar{\delta}$ is the corresponding change in average chemical shift for the ring protons. This ignores, of course, the ring-current contributions, which cannot be calculated with certainty. Each ring proton in the oxidized form of the dyes has about 0.013 less electrons than it has in the reduced form. The inclusion of ring current effects would reduce this value somewhat.

TABLE 1

	$\bar{\delta}$	δ_{AB}	J
Pararosaniline-HCl	-222.0	28.9	8.0
leuco form	-203.7	21.2	7.5
Crystal Violet	-228.5	20.7	10.0
leuco form	-208.5	13.5	9.5

Spectral parameters of triphenylmethane dyes.

THE FLORIDA STATE UNIVERSITY

TALLAHASSEE

R. E. Glick
DEPARTMENT OF CHEMISTRY

June 23, 1961

Dr. A. A. Bothner-By
Mellon Institute
4400 - 5th Avenue
Pittsburg 13, Pennsylvania

Dear Aks:

Your readers might be interested (at least your recent correspondents refer to such belief) in some exact nuclear magnetic resonance shielding constants we have computed from the twenty-term Hylleraas-type wave functions of Hart and Herzberg; $\sigma(H^-) = 2.4670 \times 10^{-5}$, $\sigma(He) = 5.9935 \times 10^{-5}$, $\sigma(Li^+) = 9.5459$ and $\sigma(O^{+6}) = 27.289$. Although these "diamagnetic" shielding values may not have much intrinsic value, they may be examined with reference to those obtained from wave functions of recent interest using $\langle \frac{1}{r} \rangle$ as a measure of the "quality" of the wave function near the nucleus. In addition, the change in σ from that of a neutral atom to that of the monovalent negative ion has been determined to be of the order of 1×10^{-5} for O_2 to O^- with $\sigma(O^-) > \sigma(O_2)$. A similar effect, but less than previously estimated, would be expected for shielding (DIAMAGNETIC) in F_2 as compared to F^-.

We've enjoyed and profited from your nmr letter and look forward to receiving future copies.

Very truly yours,

Dick

REG/jc

PURDUE UNIVERSITY
DEPARTMENT OF CHEMISTRY
LAFAYETTE, INDIANA

June 23, 1961

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Aksel:

I hope that this will reach you in time for inclusion in the June M.E.L.L.O.N.M.R. because I have found a rather large error in one of the $J(C^{13}-c-H)$ values which I sent you last month and would like to set the record straight without delay.

With improved resolution we can measure these couplings better now than when the data I sent were obtained, and I became suspicious of the old value for acetonitrile yesterday after finding that for malononitrile $J(C^{13}-C-H)$ is 11.8 plus or minus 0.2 c/sec. When I put the acetonitrile sample in the spectrometer for a recheck, I found that we had been fooled by some small impurity lines, always a danger when hunting C^{13} sidebands. We won't know the coupling exactly for acetonitrile until I get a really clean sample made up, but it looks as if the value is about 9.8 c/sec and not 27 c/sec. My apologies to anyone who has come up with a theoretical "explanation" of the high value! The situation looks a little less confused now that the available coupling constants for near-tetrahedral C-C-H angles are all comparable.

I hope within a few days to have preprints available of a note on bonded C^{13}-H couplings which I'm sending to the J. Chem. Phys. It will be called "C^{13} Splittings in Proton Magnetic Resonance Spectra. III. Formyl Compounds."

With best regards,

Sincerely

Nobby

Norbert Muller

THE WORCESTER FOUNDATION FOR EXPERIMENTAL BIOLOGY

Shrewsbury, Massachusetts

June 22, 1961

Dr. Aksel A. Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Dr. Bothner-By:

Our contribution to the Mello N-M-R will be a series of rambling notes on the subject of NMR as practiced at the Worcester Foundation.

When we purchased our Varian high resolution instrument about two years ago we decided that the 5 inch chart was too small. This may have been psychological but our decision seems to be borne out by Varian's use of the wider chart paper in their A-60 instrument. For our permanent records we use a 10 inch chart as obtained from a Sargent recorder, (model MR) operating at 4 inches per minute. We use the smaller recorder for tuning up purposes.

The spectra are recorded in duplicate on blank paper - one copy goes to the investigator requesting the analysis along with a report sheet giving the interpretation and the other is filed. Sample and operating data are filled in on each sheet using a rubber stamped form. Each spectrum is numbered consecutively on the outer end of the sheet using a hand numbering machine.

The sheets are filed consecutively flat and face up in blueprint drawers, with the latest number on top. A suitable 5 drawer cabinet is obtained from the Cole Co. It measures 40 1/4" long 28" deep and 15 3/4" high. Using two dividers per drawer and 400 spectra per section this cabinet will hold 6000 spectra.

HUDSON HOAGLAND, Ph. D., Sc. D
Executive Director

GREGORY PINCUS, Sc. D
Research Director

RALPH I. DORFMAN, Ph. D
Director of Laboratories

BRUCE CRAWFORD
Business Manager

In order to locate any spectrum we make use of an empirical formula card index. The empirical formulae are listed in the order P, N, S, O, I, Br, Cl, F, C, H as suggested by J. H. Fletcher and D. S. Dubbs C & E News 1956, 5888. By using this index we can locate any spectrum on file in a few minutes.

Some small accessories we have added, which we believe simplify the operation are:

(a) A Conoflow diaphragm reducing valve (Type H-10-XT) is used instead of a needle valve in the air supply to the spinner. This gives a more constant sample spinning rate which seems to improve the stability of the instrument when fluctuations in the air line pressure occur.

(b) We have adopted the idea of Dr. W. M. Ritchey, Sohio, Cleveland, by installing a lucite panel in the lower front of the magnet power supply. In addition, we have installed one on the upper right hand panel. We find that the heat from the 304 TL tubes does not affect the plastic. Our electronics specialist has been able to detect two defective 304 TL tubes visually, as a result of this.

(c) Running time meters have been placed on the recorders and we keep weekly records of the instrument operation. Some of the records averaged over the past 3 months may be of interest.

One spectroscopist (Tom Wittstruck) prepares samples, operates the instrument, measures and interprets the spectra.

	3 month weekly average
Recorder operating time	10.5 hr.
Samples reported	10.6
Reporting time	12.8 days
Down time	1.5 hours
Backlog	25 samples

The weekly records are conveniently kept on a "Boardmaster" sold by Graphic Systems, Yanceyville, N. C.

We hope that the above notes will prove of interest.

Yours sincerely,

Neal L. McNiven

Neal L. McNiven

NLM:je

THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 175
CINCINNATI 39, OHIO

June 21, 1961

Dr. Aksel A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Bothner-By:

Enclosed is my subscription for MELLONMR. It consists of
three circuit diagrams which describe useful modifications
to a Varian 4310 transmitter-receiver unit. The modifications
include: 1) a precision attenuator, 2) a "phase detector" ---
really a leakage control which is independent of the probe,
sample, and rf level, 3) a monitor for the transmitter power,
and 4) a differential amplifier to cancel spurious modulation
of the spectrum from the transmitter when high leakage voltage
is used. We have found that these modifications take most of
the inconvenience out of operating the 4310 unit.

Figure 1 represents a schematic of the system. Figure 2 repre-
sents changes made in the receiver section. Figure 3 repre-
sents a separate box which contains the leakage control system
and transmitter level diode. In our unit, this box has been
located at the spot that the original rf level switches were
located. The precision attenuator (Hewlett Packard 355 A/B) is
mounted above the chassis. The box is connected by 50 ohm co-
axial cable to the transmitter and receiver units.

To use the phase detector, the probe is balanced to null with
the leakage switch (SW in Figure 3) off. Then it is switched
on and leakage is adjusted to make the dc amplifier balance.
This occurs at around 6 volts dc on the diode resistor. The
phase is then adjusted by changing C in Figure 3 until a pure
mode is seen from a sharp signal. (When C is adjusted, a corre-
sponding amplitude change occurs which is compensated for by
adjustment of P1 or P2.) The LC circuit in the leakage box is
the only frequency sensitive element in the circuit: it is tuned
to the spectrometer frequency. Hence this modification can easily
be applied to any 4310 unit.

I recommend one change from the system described here. The
transmitter level diode and the receiver diode should be at
precisely the same temperature. Some thermal drift has been
observed with the two diodes separated although both were en-
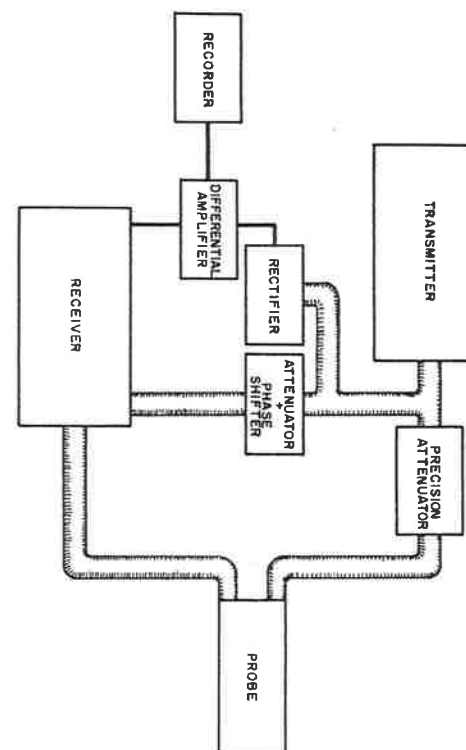closed in the same chassis. Mounting both in the same copper

Figure 1

T. J. Flautt
Review of Scientific Instruments

33-16

Dr. Aksel A. Bothner-By   Page 2   June 21, 1961

block would probably solve this difficulty.

Beside the above mentioned difficulty, the system operates satisfactorily. A more complete description of the modifications are available for those interested.

I would like to join the other subscribers who have expressed appreciation to you for making this method of communication possible. It is invaluable in keeping abreast of recent developments.

Sincerely yours,

THE PROCTER & GAMBLE COMPANY
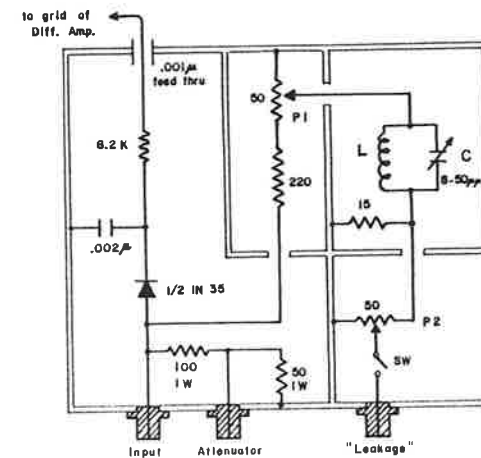Research & Development Department

T. J. Flautt
Research Division

CW

Enc.

RF Amplifier

Output Amplifier

Figure 2

T. J. Flautt
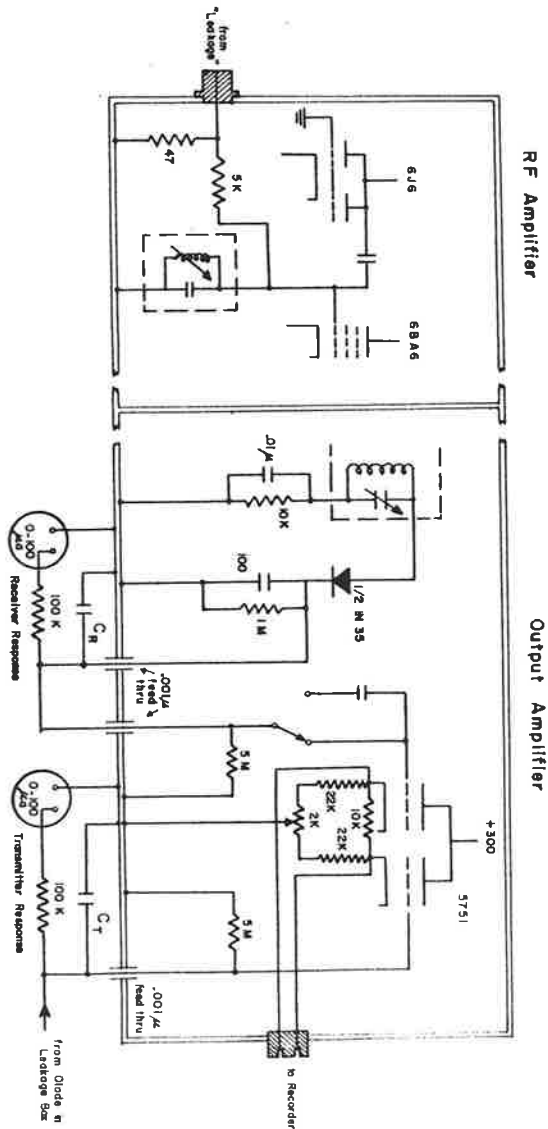
Review of Scientific Instruments

Figure 3

T. J. Flautt

Review of Scientific Instruments

HARVARD UNIVERSITY

DEPARTMENT OF ~~CHEMISTRY~~ PHYSICS

12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.
June 20, 1961

Dr. A. A. Bothner-By
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Aksel,

      Some months ago I expressed disbelief in Dr. F. A. L. Anet's inter-
pretation of <u>long-range</u> (H-C-C-C-H) coupling in the saturated system of a diol
of bicyclo-2,2,1-heptane. I must withdraw my objection, which at the time was
just one of faith, and submit the attached figure of the fenchols, where no <u>short-</u>
<u>range</u> (H-C-C-H) coupling is possible, as further and more conclusive justifica-
tion of Dr. Anet's statement. These are just a few examples of the ones we have
studied some of which are not trivial to interpret. The samples are all courtesy
of Prof. N. J. Toivonen of the University of Helsinki and the coupling constants
are probably as indicated. The borneol, however might have been interpreted
as virtual long-range coupling from the 4-proton which might have had the same
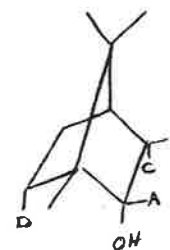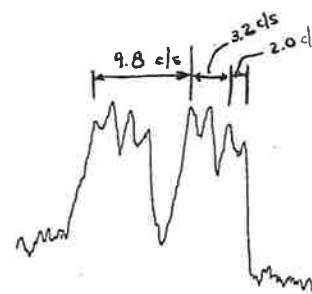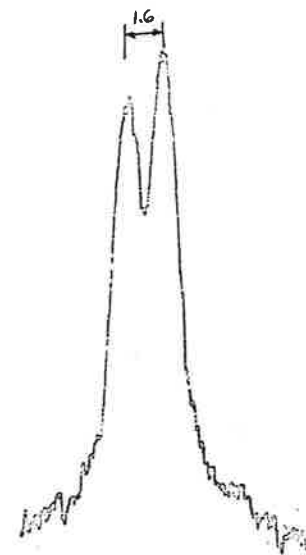chemical shift as the endo-3 proton and could have caused the same effect.

      In mad haste, as I leave for Europe tomorrow: I will be on vacation
in Perugia for July and at the NATO Statistical Conference in Breukelen, Holland
in August, and with best wishes for the summer, etc.

          Sincerely,

          J. I. Musher

For MELLONMR.

Exo-(β)-Fenchol

$J_{HH'} \stackrel{?}{=} 1.6$ c/s

Endo-(α)-Fenchol

$J_{HH'} \stackrel{?}{=} 1.6$ c/s

9.8 c/s   3.2 c/s   2.0 c/s

$J_{AD} = 2.0$ (or 3.2) c/s

$J_{AB} + J_{AC} = 13.0$

(or 11.8) c/s

Borneol

Laboratorium
für physikalische Chemie
Eldg. Technische Hochschule
Zürich
H. Primas
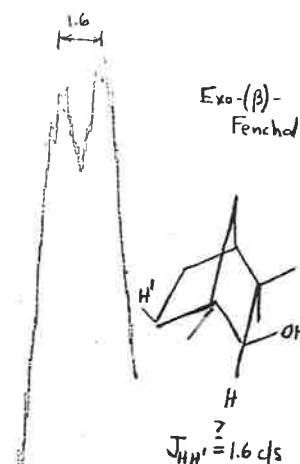
ZÜRICH,   May 27, 1961
Universitätstrasse
Tel. (051) 32 73 30

A new type of nmr-stabilizer for high-resolution nmr-spectrometers

The need for nmr-stabilization of high-resolution nmr-spectrometers
has been realized for a long time — there is something every nmr
worker can say about that. The principle of nmr stabilization is
well known, too, and was sucessfully applied in 1957 by BAKER and
BURD (Rev.Sci.Instr. 29,313,1957) to get a high stability high-
resolution spectrometer. This construction was a spectrometer with
two spatially separated probes. Although this system was a remarkable
improvement in field stability it never became very popular. The main
reason for this was the need for using two separated probes. This
means a severe restriction in flexibility of the whole equipment and
does not give an absolute stability and an absolute calibration of
spectra because any change in the field geometry refects itself in a
change of calibration.

It can be shown that all information of chemical interest that can
be gained by any nmr-investigation can also got fully with an nmr-
spectrometer with just a single probe — regardless of fluctuating
fields, inhomogeneous fields and so on. But this is just an existence
theorem and gives no hint how to realize it. The nmr stabilized
spectrometer I would like to describe here is just a first step in
the direction to get an optimal system and is by no means already a
theoretically optimal system. But the improvement we can get over
the more conventional type of spectrometer is quite remarkable. Our
aim was not to build a complete new nmr-spectrometer but an additional
device that converts a conventional nmr-spectrometer to a nmr-stabilized
instrument without any changes in the construction of the measuring
head or the probes and without restricting the flexibility of the
conventional instruments. In order to facilicate routine measurements
there should be an automatic calibration of the spectra with an
accuracy of about o.1 cps without any adjustments or corrections.

Because we have an nmr-spectrometer with a flux-stabilizer at our
disposal, the conversion to an nmr-stabilizer of servo-type 1 ist
quite simple (cf.fig.1). We are setting our spectrometer to work in

the dispersion mode. If we now connect the output of the spectrometer
with the correct phasing to the input of the flux-stabilizer (i.e.
directly to the galvanometer of the superstabilizer), then we will
get an integrating servo system of type one with no residual error.
For example: if the field is too low, the signal output will always
be negative and the fluxstabilizer will drift upwards to the exact
resonance position. The overall discriminator curve is now not the
dispersion curve $x/(1+x^2)$ but the flux-stabilizer performs an inte-
gration and the discriminator curve is now $\int dx \cdot x/(1+x^2)$ which is indeed
an excellent characteristic. The look-in and holding range is extremely
large - even at a distance of several hundred line-widths from the
reference line the feedback system will quickly go to its final value.
Our system can easily handle a drift of 1 ppm/min (which is about
equal to the conventional sweep rate) without nmr stabilizer and we
will get a drift free system with a residual error of about o.ool ppm.
So we can get easily an excellent nmr-stabilizer, but how can we
manage to get both the stabilizer signal and the measuring signal with
one probe and one rf-channel ? Nowadays we usually work with an in-
ternal standard for proton resonance, mostly with tetramethylsilane.
Obviously it would be nice to use just this internal standard as a
reference line for the nmr stabilizer. A simple calculation shows
that the usual concentrations of tms is ample to get a good signal-to-
noise ratio for an nmr-stabilizer with high accuracy. Fig.2 shows a
somewhat simplified diagram of a high-resolution nmr-spectrometer
with an nmr-stabilizer having a single probe. The usual crystal-control-
led rf-transmitter is used for the stabilizer channel. With the stabi-
lizer working we have a fixed relation between the magnetic field and
the rf-frequency. In order to record an nmr-spectrum we are now
changing the frequency by means of a single-sideband modulator that
converts the original frequency ω (in our case 25 Mc/s) to a variable
frequency $\omega + \varepsilon$ (or if we like, to $\omega - \varepsilon$). ε is an audiofrequency
(in our case variable between 5 cps and 25o cps). Both channels have
the same rf-part, but each channel has its separate rf-phase-sensitive
detector (PSD). Experience has shown that there is no disturbing inter-
ference between the two channels and we can easily work with a fre-
quency difference of just a few cycles between them. In this type of
arrangement the most critical device is the RC-audiooscillator. In
order to change the frequency of this oscillator we would of course
like to couple a precision potentiometer to a synchromotor. But the
usual RC-oscillator have an inverse relationship between frequency
and resistance. In order to get a linear sweep we were forced to

built a new type of RC-oscillator with a _linear_ relationship between
frequency and resistance. We could achieve a linearity of better
than o.1 cps in the range of 5 to 25o cps and as a by-product of
this new construction we got an excellent long-time stability of the
frequency - better than o.1 cps over several months. The actual
stabilizer we built is a little bit more elaborate than shown on
fig.2. We are using a double conversion; further a magnetic side-
band-modulation in both channels. That does not change the principle
but improves the performance of the spectrometer considerably and is
almost indispensable for a perfect operation.

If you would like to convert your conventional spectrometer to an
nmr-stabilized spectrometer you have to add

firstly a single-side-band modulator and a high precision
RC-oscillator, driven by a synchromotor and some device
to write calibration marks,

secondly an additional high-frequency phase-sensitive detector and
a further phase-sensitve detector for the side band
modulation.

Further you have to connect the output this second channel to the input
of the fluxstabilizer via a simple phase-correcting network. Maybe
you have to make shure tha t you get no phase-shifts in the measuring
channel because of the varying frequency. Perhaps some bandfilters
needs a readjustment.

Fig.3 shows the long-term stability of our stabilizer. We were
standing on the side of a sharp line and recorded the fluctuations
over more than one day: peak to peak fluctuations < o.oo14 ppm ,
rms-fluctuations < o.ooo3 ppm , practically no drift over one day.
Because of the good long-term stability we can increase the scope
of useful nmr-measurements. For example, its now easy to get very
accurate measurements of line positions: with _one_ single measurement
we can get an accuracy of about o.o2 cps. One point that can be very
important for the biological chemist is the possible lowering of the
amount of substance necessary for a useful nmr spectrum. If we in-
crease the usual recording time of say 6 minutes to 1o hours we can
increase the filtering time constant by a factor of one hundred and
therefore get an increase in sensitivity of a factor of ten. Fig. 4
shows an proton resonance spectrum of 85 gammas of a steroid at 25 Mc/s.
We should be able to decrease this minute amount of substance by a
further factor of ten when we will work at higher frequencies.

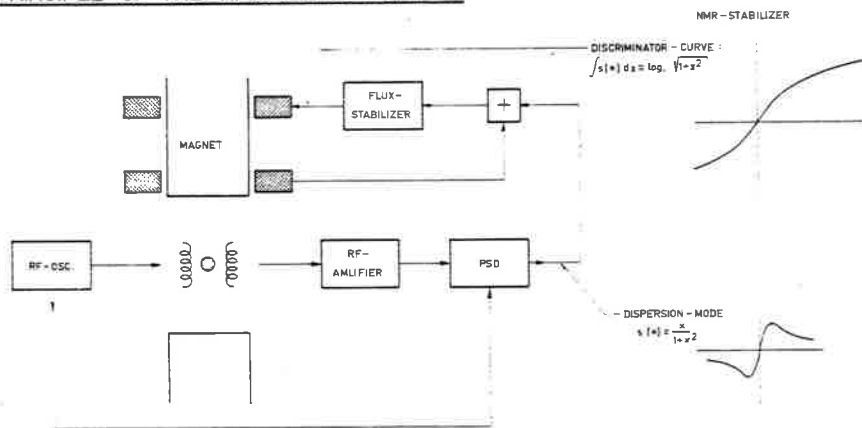Accuracy of the single probe nmr-stabilizer

measured at 25 Mc/s with o.5 mgr $Si(CH_3)_4$ as a internal standard

overall long term stability overall long term calibration (without any adjustments)	o.1 cps over one month
change of mode change of line shape	gives an error of less than 1/1o of linewidth
accuracy of calibration marks	better than o.oo1 ppm
with the aid of a frequency counter: line position measurements	better than o.oo1 ppm (or with broad lines: 1/3o of line width)

**A more technical description of our stabilizer is in pre-
paration and will appear either in Helvetica Physica Acta,
Helvetica Chimica Acta _or_ in the Review of Scientific
Instruments.**

Figure 1

PRINCIPLE OF THE NMR–FIELDSTABILIZER

NMR – STABILIZER

DISCRIMINATOR – CURVE :
$$\int s(x)\,dx = \log \sqrt{1+x^2}$$

MAGNET

FLUX–STABILIZER

$+$

RF–OSC.

RF–AMLIFIER

PSD

– DISPERSION – MODE
$$s(x) = \frac{x}{1+x^2}$$

EXAMPLE : A DRIFT OF 1 ppm / min   (WITHOUT NMR – STABILIZER)

GIVES A RESIDUAL ERROR OF 0,001 ppm   WITH NMR–STABILIZER   (WITHOUT DRIFT)

Figure 2

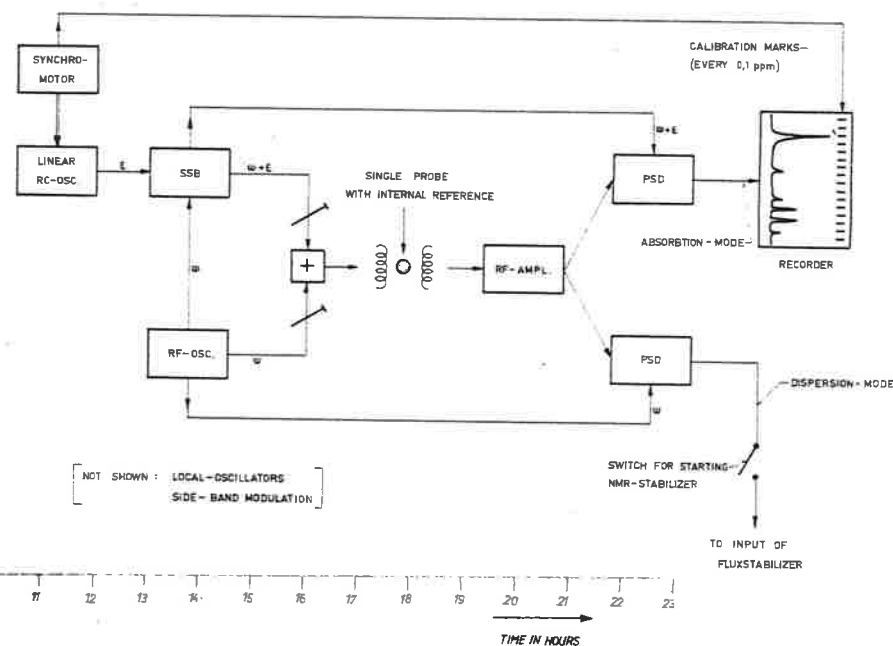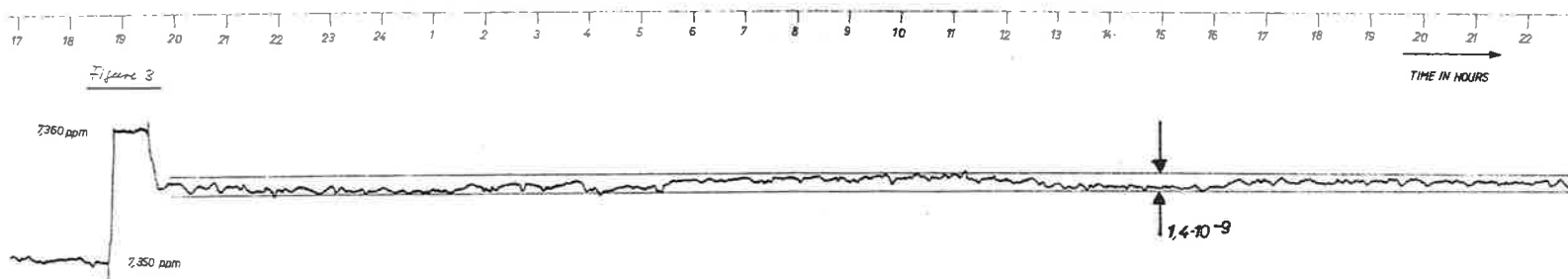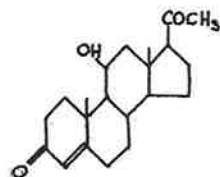# PRINCIPLE OF A NMR–STABILIZED NMR-SPECTROMETER WITH A SINGLE PROBE

SYNCHRO-MOTOR

LINEAR RC–OSC.

SSB

$\omega + \epsilon$

SINGLE PROBE WITH INTERNAL REFERENCE

CALIBRATION MARKS–
(EVERY 0,1 ppm)

$\omega + \epsilon$

PSD

ABSORBTION – MODE–

RECORDER

$+$

RF–AMPL.

RF–OSC.

PSD

DISPERSION – MODE

SWITCH FOR STARTING–
NMR–STABILIZER

TO INPUT OF
FLUXSTABILIZER

NOT SHOWN : LOCAL–OSCILLATORS
SIDE– BAND MODULATION

Figure 3

17 18 19 20 21 22 23 24 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23

TIME IN HOURS

7,360 ppm

$1,4 \cdot 10^{-9}$

7,350 ppm

LONG TERM STABILITY OVER ONE DAY : 3 PARTS IN 10^{10} rms

Figure 4

85 MICROGRAMM HYDROXY PROGESTERON

H¹-SPECTRUM AT 25 MCPS
RC-TIME CONSTANT = 50 SEC
SWEEP RATE = 1 PPM PER HOUR

0,26 gamma protons
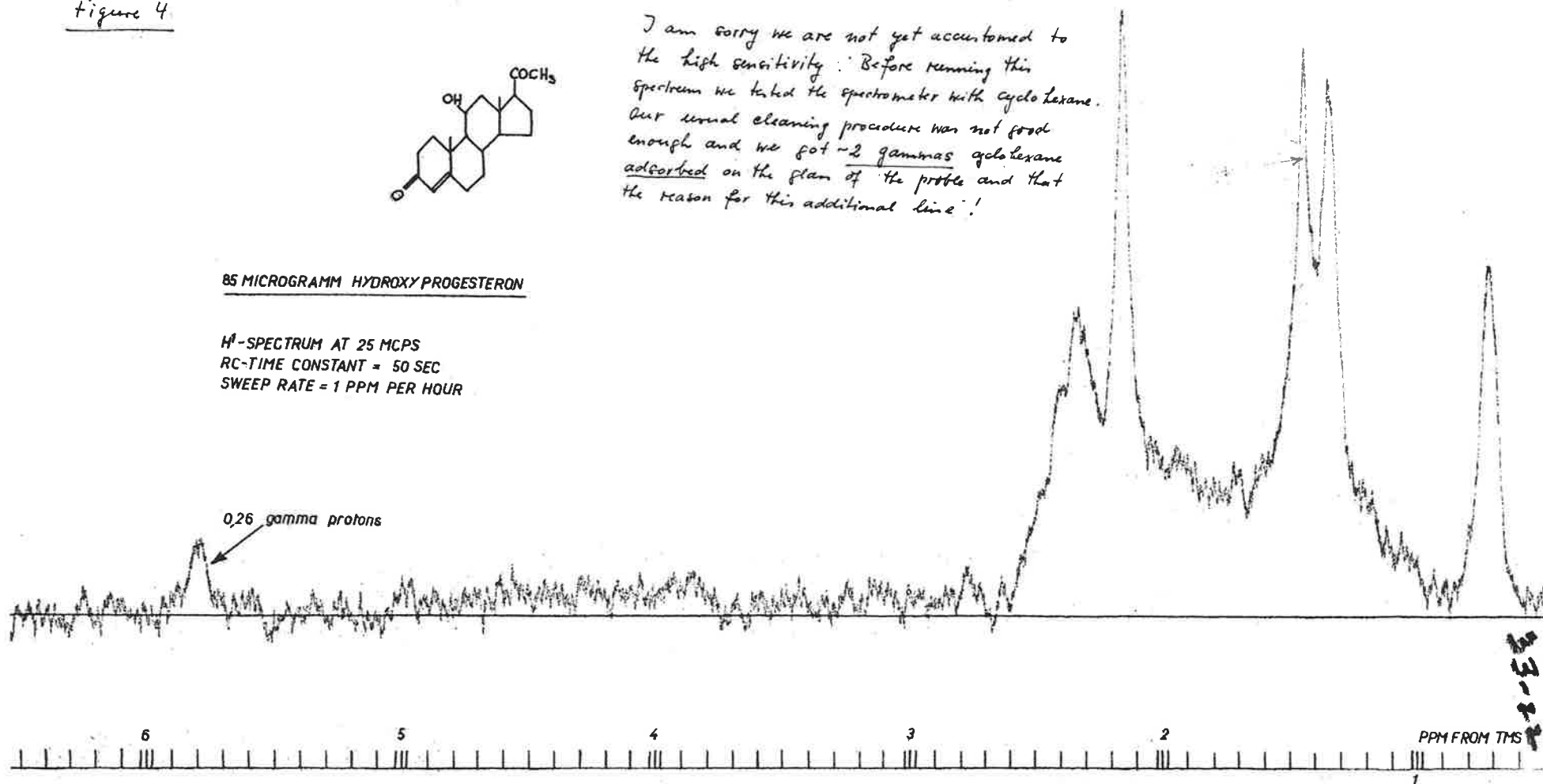
I am sorry we are not yet accustomed to
the high sensitivity. Before running this
spectrum we tested the spectrometer with cyclohexane.
Our usual cleaning procedure was not good
enough and we got ~2 gammas cyclohexane
adsorbed on the glass of the probe and that
the reason for this additional line!

PPM FROM TMS

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

National Physical Laboratory

TEDDINGTON · MIDDLESEX

Please reply to the DIRECTOR and quote our reference   Telegram : Physics, Teddington   *Teddington Lock 3222*   Telephone : Molesey 7900   Ext. **199**

OUR REF:

YOUR REF:

BASIC PHYSICS DIVISION

2nd June, 1961.

Dear Dr. Bothner-By,

One of the topics we have been looking at here is a study of solvent effects in P.M.R., with particular emphasis on those solvents which give rise to "anomalous" solute chemical shifts (i.e. aromatic solvents). The solutes used were cyclohexane, methyl iodide and iodoform and the solvent shifts of the latter two solutes in aromatic solvents have been postulated to be due to the formation of solute solvent complexes. To confirm this the effect of temperature on the chemical shifts of these solutes in toluene was studied. The solute peaks were measured from that of the phenyl protons of the solvent. Whilst the position of the cyclohexane peak was constant over the entire temperature range (-60 to 100°C), thus demonstrating the lack of any complex formation for this solute, the positions of the methyl iodide and iodoform peaks change considerably, that of iodoform by almost 1 p.p.m., both moving to high field as the temperature is lowered. They confirm the postulate of solvent solute complex formation and, in addition, the energy and entropy of formation of the complexes can be obtained. The values of these parameters are:

(a) For the iodoform toluene complex $H = 1.6 \pm 0.2$ kcals/mole,
$S = 6.4 \pm 0.2$ e.u.

(b) For the iodoform methyl iodide
complex $H = 1.3 \pm 0.5$ kcals/mole,
$S = 4.9 \pm 0.4$ e.u.

The type of complex envisaged here is one in which the dipole axis of the solute lies along the hexagonal axis of symmetry of the benzene ring with the protons towards the ring.

This explains the high field shift of the solute protons in the complex, and by assuming this high field shift is solely due to the ring current it is possible to estimate the distance of the solute protons from the plane of the ring. A full account of this work has been submitted (1). However what may be emphasised here is the large temperature dependence of these solute proton chemical shifts. That of iodoform changes by approximately 1/3 c.p.s. per °C at room temperature. Although this is a rather unique system this does emphasise the necessity of accurately known sample temperatures for very accurate chemical shift measurements.

Also Dr. McLauchlan and I have been investigating the spectra of some derivatives of L proline. The spectra obtained are often too complex for a full analysis, but those of L hydroxy proline and allo L hydroxy proline can be analysed completely, giving the coupling constants between adjacent protons all round the ring. Figure 1a shows the formula of allo L hydroxy proline (in D_2O) and the coupling constants obtained. These coupling constants show a large

/variation

Dr. A.A. Bothner-By   2nd June, 1961.

variation, changing from one to ten c.p.s. Assuming that the molecule exists in one conformation, and using the Karplus equation $J = k \cos^2 \phi$ relating the J's with the dihedral angles between the C-H bonds, it is possible to determine the conformation of the molecule in solution. The molecule is bent in solution as shown in Figure 1b and the angle of bending which gives best agreement between the observed J's and those calculated using the Karplus equation is approximately 60°.

Two points of interest emerge. (a) The angle of buckle seems much larger than is generally accepted for five membered rings, and (b) the substituent on C_4 attains a pseudo axial position, again an unusual result. These results are discussed in more detail, together with the possible errors that can arise in this type of investigation elsewhere (2).

Yours sincerely,

R.J. Abraham
Basic Physics Division

(1) R.J. Abraham   }
                                          }   Submitted Mol. Phys.
(2) R.J. Abraham and K.A. McLauchlan   }
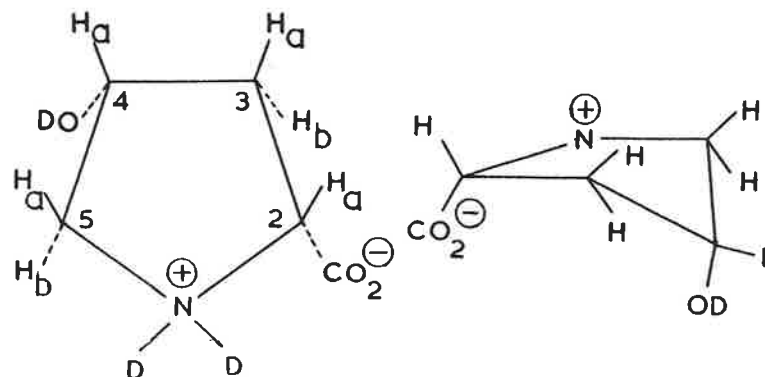

Figure   1(a)   1(b)

$J_{2a-3a} = 10.1 \pm 0.3$ cps $J_{3a-4a} = 4.4 \pm 0.5$ cps $J_{4a-5a} = 4.7 \pm 0.8$ cps

$J_{2a-3b} = 4.7 \pm 0.3$ cps $J_{3b-4a} = <2$ $J_{4a-5b} = 0.9 \pm 0.8$ cps

Dr. Askel A. Bothner-By
Director of Research
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania

Dear Dr. Bothner-By:

This is the tale of a minor innovation in N-M-R instrumentation that may be of some interest to your Mello-N-M-R readers.

Last fall we replaced the V-4310C 40Mc RF Unit of our Varian Dual-Purpose Spectrometer with a 40Mc V-4311. The R-F phase detector feature of this new unit was splendidly suited to our needs (principally broadline measurements at a variety of temperatures) with one exception: When dealing with certain materials whose broadline spectra could be expected not to be perfectly symmetric, it was quite tedious to ascertain the optimum setting of the R-F Reference Phase Dial required for a pure absorption derivative to be plotted. Furthermore, it was found that this optimum dial position was some 'unknown function of several variables, including 1) sample size and composition, 2) sample temperature, 3) strength of H_1 applied, and 4) time of day (probably related to local room temperature fluctuations). Clearly, some quick and simple means was needed to determine the proper setting of the R-F Reference Phase Dial.

In order to use larger samples, as well as to eliminate the bothersome false proton N-M-R signals built into the Varian V-4331 probe, we have for some time used a single coil r-f bridge for most broadline work. Recalling the ingenious "Automatic N-M-R Bridge Balancer" of R. L. Collins (Rev. Sci. Instr. 28, 502 (1957)), it was felt that a similar

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Dr. Askel A. Bothner-By   -2-   May 16, 1961

modification of our Twin-T r-f bridge could be used to provide a precise indication of the pure absorption mode position(s) of the R-F Reference Phase Dial. Accordingly, a high Q voltage-variable capacitor was added to the r-f bridge, as shown in Figure 1. (No attempt has as yet been made to incorporate additional instrumentation, a la Collins, to complete the servo loop in order to have "automatic reference phasing".)

The principle of operation of the present circuit differs only slightly from that of Collins; in both cases, the working criterion for pure absorption mode is that infinitesimal changes in the reactance (as distinguished from resistance) of the sample arm of the bridge should produce exactly zero change in the receiver output signal.

In use, the bridge is first balanced as well as possible--at least well enough to keep the needle of the Detector Level Meter of the V-4311 on-scale for the Receiver Gain setting used--after which an audio signal is applied to the Bridge Modulation Input terminals. The R-F Reference Phase Dial on the V-4311 R-F Unit is then rotated for a null of the audio signal observed on the spectrometer oscilloscope, completing the operation. A tuned audio amplifier (such as the Model 107B, manufactured by Custom Electronic Services, San Diego, California, operating at 1000 cps), used while modulating the bridge with the same audio frequency, has proved helpful in pinpointing the null position.

Our V-4311 R-F Unit is sufficiently stable that once the proper dial setting is found, no further attention is normally required for several hours. During the period, the r-f bridge normally requires rebalancing several times (merely to keep the Detector Level Meter near mid-scale); however, it has been found that even rebalancing the bridge during the scanning of a broadline spectrum does not measurably affect the record, such are the virtues of r-f phase-sensitive detection.

So much for success. We wondered after this if we could not do as well with the Varian probe, using a somewhat different approach. For simplicity, we tried first audio modulation of the V-4311 transmitter (obviously to no avail, as we later decided). Then we ran out of simple ideas. Currently, the best method I can think of to optimize the R-F Reference Phase dialsetting when using a Varian V-4331 Probe would consist of a "double modulation" of the V-4311: First, an a-f signal in the frequency range of 10-30 kc should be applied to the Modulation Input terminals of the V-4311; second, the amplitude of this higher a-f signal should be varied at a lower a-f rate, say 100-1000 cps. Using appropriate filtering to permit only the observance of the lower a-f rate on the signal oscilloscope, two nulls should be found on the R-F Reference Phase Dial as it is rotated through 360°; these nulls should then correspond to perfect absorption mode settings.

We have not yet put together the apparatus to test out this "double modulation" scheme. If anyone has a more ingenious (i.e., simpler) idea about how to solve this basic phase-setting problem, I should be delighted to hear about it.
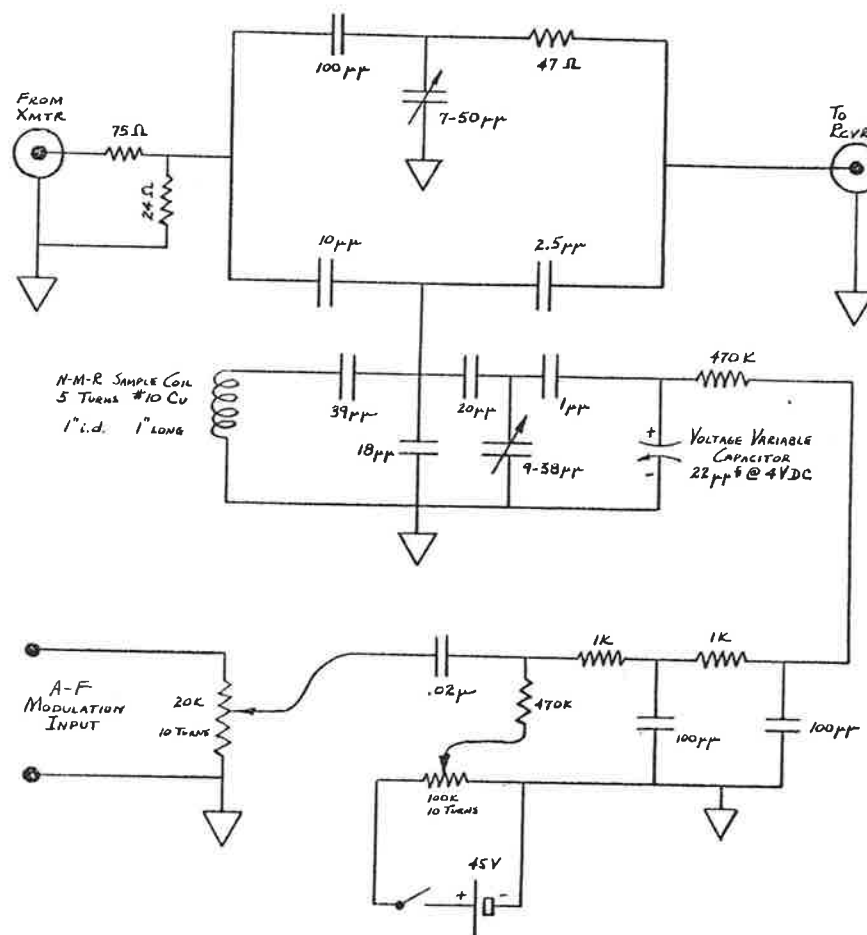
Sincerely,

Charlie

Charles W. Wilson III/sw

FIGURE 1: 40 Mc R-F BRIDGE WITH AUDIO MODULATION