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Mailed: APR 3 - 1961

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L etters from
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No. 30

A monthly collection of informal private letters from laboratories of nmr.
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HARVARD UNIVERSITY

DEPARTMENT OF PHYSICS

LYMAN LABORATORY OF PHYSICS
CAMBRIDGE 38, MASSACHUSETTS

26 February 1961

Drs. Bothner-By, Shapiro and Lauterbur
Hollor Institute
1100 Fifth Avenue
Pittsburgh, Pa.

Dear Drs. Bothner-By, Shapiro and Lauterbur,

I have just been thinking through John Baldeschwieler's
Memorandum since June and wanted to send along a few comments.

First is on Dr. Anet's note (#20) on coupling constants
in norbornenes. I must admit that the long-range coupling is
very surprising. The instance cited is rather convincing mainly
because he can see two protons (A') of the larger (ABXYZetc)
spectrum. We have seen such a multiplicity in a few cases but
do not yet think that this can account for it. I wanted to
comment, though, that the agreement of these c.c.'s with the
Karplus theory might be somewhat fortuitous. I cite two examples:



both of whose protons are coupled to a proton with an H-C-C-H
angle of 0° as well as to another proton. Because we only see
the A proton of ABXYZetc spectrum a complete analysis is not
possible. However because A appears (grossly at least) as a
doublet, its splitting must arise from only one proton and this
pattern cannot be caused by other couplings around the ring.
Thus we have:

$$J(\phi=0) \sim 9.5 \text{ and } 6 \text{ c/s} \quad J_{\text{calc}} = 8.2 \text{ c/s}$$

$$J(\phi=120) \sim 0 \text{ and } 0 \text{ c/s} \quad J_{\text{calc}} = 2.1 \text{ c/s.}$$

We have seen quite a few other amusing things with the molecules
in this series.

Now for #19. I was very pleased and excited to see Dr.
Thomas' note on the perfluorodecalins (#24). In particular
the cis-decalin which shows separate peaks (non-coupled for F's)
for the bridgehead F's, those α to the bridgehead and those
 β to the bridgehead. This points up the accidental degeneracy,
that I mentioned in a footnote (JACS, Feb. 20, 1961 ?), of such
peaks, which as shown by Dr. Richards and myself (Proc. Chem. Soc. 1958),
gives a single sharp line. Both this work and that of Drs.

- 2 -

Feeney and Sutcliffe (#21, T.F.S. 36, 1539 (1960))
appeared before Piers' low temperature study. I have commen-
ted in detail on the TFS article to Dr. Sutcliffe. One
of the conclusions of those comments is that only one of
the six dihydrodecafluorocyclohexanes has a quartet AB
pattern in its spectrum exactly as that of perfluorocyc-
lohexane, and that this probably belongs to the 4 and 6
F's of the cis 1H,3H isomer. This is so because only here
does an axial F "see" two other axial F's on the same side of
the molecule thus simulating closely the perfluorocyclohexane
situation. This might well carry over to the trans-perF-
decalin where the AB quartet would belong to the fluorines
beta to the bridgehead and the incompletely resolved quartet
to those alpha. The axial ones of the latter "see" 3 axial
F's instead of 2, whereas the beta F's "see" only the
immediate environment of perF-cyclohexane. Incidentally
the large delta_{ax-eq} in perF-cyclohexane is most probably

caused by distortion of the axial CF bond's electrons' and
F electrons' distribution by each other. Were the 10×10^{-6}
caused by bond anisotropy, delta chi would be 1.9×10^{-4}
cc³/mole, many times its total susceptibility. Also it could
not be accounted for by the recent expansion of Karplus and
Das' (JCP? to appear) in terms of ionic strength, hybridization
and double bond character since these parameters are all
the same here.

Sorry about the length of this. Got carried away at
the typewriter.

with best regards.

Yours sincerely,

G. I. Musher
G. I. Musher

3 March 1961

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

Dear Dr. Bothner-By:

We are beginning to do some NMR work here and we would like to vie for a position on your M.E.L.L.O.N.M.R. mailing list with the following meager contribution and the promise of more to come.

We have been using your IEM 704 program on some problems in collaboration with Professor John D. Roberts and on some of our own problems. At one stage, we had a deck of cards and a thermofax copy of your letter from C. P. Saalbach. It took some talking to get our computer people to run the program. Our IEM 704 was a 32K machine and the program performed satisfactorily except for a few hitches which were dependent on the nature of the input data. We found that there are certain combinations of chemical shifts (i.e., if there are too many zeros) which cause the program to stop or give meaningless answers. This happened several times when W_1 and W_2 of an A_2B_2 system were zero or when an A_2BC system is programmed with W_1 and W_2 and W_3 equal to zero. We have tried many five, several six, and several seven spin systems without any difficulties. We recently had our IEM 704 replaced by an IEM 7090. After surmounting another activation energy barrier with our computing people we are running the NMR program again. We would like to thank you very much for sending the extra subroutines for compiling the output data. This will cut down the plotting time of the data several orders of magnitude. Possibly our curve plotter may work with your line shape subroutine.

The NMR instrument at JPL is now equipped with a proton spin decoupler which uses a technique similar to that described by Reinhold Kaiser.¹

1. R. Kaiser, Rev. of Scientific Inst., 31, 963 (1960).

Dr. Aksel A. Bothner-By

-2-

3 March 1961

We found it quite convenient to use the phase detector that we have^d previously constructed for a resonance line integrating system.²

2. W. A. Anderson and L. F. Johnson, Special Operating Techniques, Varian Associates.

A diagram of our phase detector is shown in Figure 1. We found that it was advantageous to use matched pairs of 10K and 20K resistors; also the 1N216 diodes were matched. The diodes are also imbedded in a block of copper so as to maintain them at nearly constant temperature. The input to the phase detector was taken from either J314 or J302 of V4311 and switch SW302 of V4311 was placed in W1 diode position. This was done to by-pass the filter network of the r-f unit. When the phase detector was used with the spin decoupler, it was necessary to use an extremely small audio modulation amplitude on the sweep coils of the 60 Mc probe. When H_1 , the r-f field, was of the order of 3 milligauss or larger, it was necessary to attenuate the audio signal across the modulation coils to 100 μ volts or less. If a larger audio signal is used, the side bands of the resonance lines which one observes will saturate.

We found that it was necessary to calibrate the H_1 field in terms of db attenuation of the r-f unit. We used the phase detector for this calibration in a manner similar to that described by Anderson.³ It was

3. W. A. Anderson, Phys. Rev. 102, 151 (1956).

quite convenient to adjust the audio detector and the r-f phase detector with a doped water sample ($T_1 = 0.1$ sec.) in the probe. The r-f phase was adjusted for a large H_1 . The small additional changes of H_1 do not introduce any appreciable phase change. However, for any change in the audio frequency, one must readjust the audio phase.

One difficulty which has plagued us is that 60 cps modulation was appearing on the field and it produced side bands comparable to the signal. On some spectra, these side bands overlapped some of the resonance lines of interest. Another difficulty has been that if the chemical shift of the two groups of protons being decoupled is 60 cps or a multiple of 60 cps, the audio signal and the unwanted 60 cps modulation produce a beat that fluctuates the base line at the beat frequency. We found that our super stabilizer was oscillating and producing the 60 cps modulation of the field. We decreased the gain of the super stabilizer and this has greatly reduced the 60 cps modulation. We are now in the process of building a new phase detector system which we hope will give even better performance than the present model. Even with the difficulties described, we have found the present decoupler to be a very useful addition to the spectrometer.

Dr. Aksel A. Bothner-By

-3-

3 March 1961

Enclosed you will find some spectra exhibiting our present attainable resolution and the use of our spin decoupler. Our magnet is equipped with a Varian Field Homogeneity Unit which is invaluable. We do not thermostat our magnet water but we will when our instrument is transferred to its new quarters. Our biggest trouble is sweep linearity which is very poor at slow sweep rates. We are doing something about this and will report on this improvement in a future letter.

We have included some spectra of propylene oxide. We looked at its NMR spectrum and decided that it was a good candidate on which to try the spin decoupling technique after having been able to repeat the results described by Kaiser.⁴ Figure 2 shows the complete spectrum; the doublet at high field is the methyl protons and the region at low field the other three protons.⁴ Assignments for the latter three protons were based on Reilly and Swalen's work where proton ① is at lowest field and proton ③ is at highest field.

4. Due to the raging controversy over referencing systems, we have reported, for the time being, only the relative chemical shifts in cps at 60 Mc.

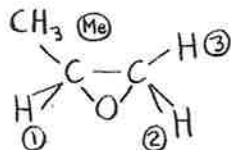


Figure 2 was drawn from a spectrum and the fidelity of reproduction was very poor. Figure 3 shows the slow sweep of the three proton region and shows nearly all the lines but it points up our horrible nonlinearity of sweep. The region which we set ourselves about to untangle was the ① proton region. Figure 4 shows the ①, ②, and ③ proton region at a much more linear sweep and shows the spectrum of the ① proton decoupled from the methyl protons (audio

frequency 92 cps and H_1 about 33 db down). Measurement of several decoupled spectra gave good checks of J_{12} and J_{13} as obtained from undecoupled spectra. The 2-proton region is partially decoupled in Figure 4 due to some spill over of the large H_1 . Listed below is a set of parameters which fit the propylene oxide spectrum pretty well so far:

Coupling Constant

J_{12}	3.86 Cps
J_{13}	2.48
J_{23}	5.25
J_{1Me}	5.1
J_{2Me}	0.47
J_{3Me}	0.34

Chemical Shifts*

H_1	0.0 Cps	*Relative at present
H_2	15.5	
H_3	35.9	
H_{Me}	98.0	

Dr. Aksel A. Bothner-By

-4-

3 March 1961

It should be pointed out that the coupling constants and chemical shifts for propylene oxide could be obtained quite straight forwardly from the undecoupled spectrum.

Figure 5 is a spectrum of cyclopentadiene with one pair of the vinyl protons decoupled from the methylene protons. The low field region shows eleven lines of significant intensity. The high field side is also partially decoupled from the methylene group because of the small chemical shift (about 7-9 CPS) between the vinyl protons.

With our spin decoupling system we have looked at a number of other systems such as bicycloheptadiene, allyl acetate, indene, acetaldehyde diethylacetal, propylene glycol acetonide, and epichlorohydrin. In epichlorohydrin, two groups about 40 cps apart at 60 Mc were successfully decoupled. We will report on some of the other systems at a later time.

We hope we have convinced you that our intentions with NMR are honorable and that we may gain a place on the M.E.L.L.O.N.M.R. mailing list.

Very truly yours,

JET PROPULSION LABORATORY

Stanley L. Manatt
Senior Scientist
Physical Sciences Division

Daniel D. Elleman
Senior Scientist
Physical Sciences Division

SIM.DDE.mco

← H

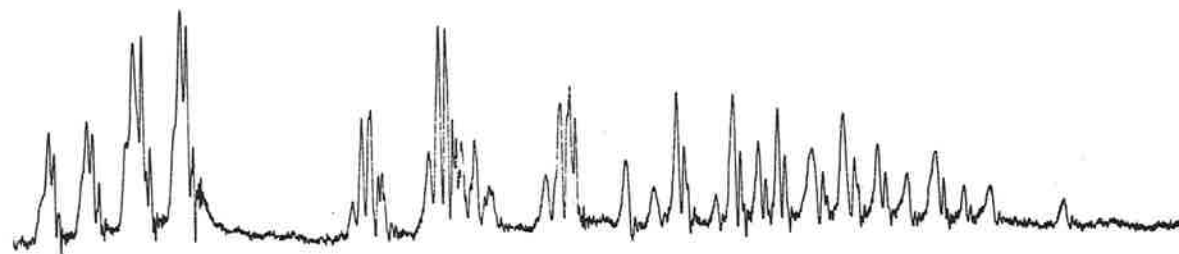
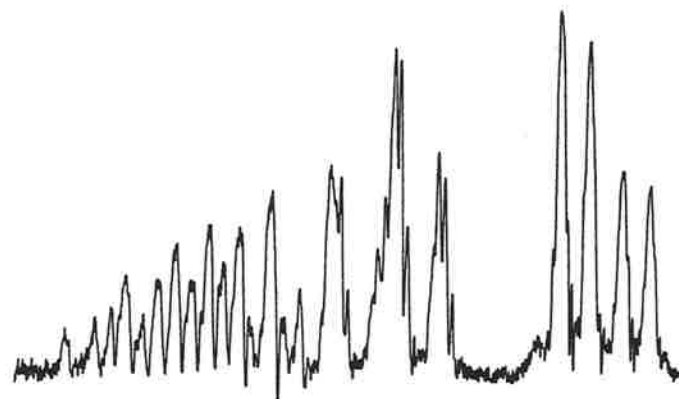
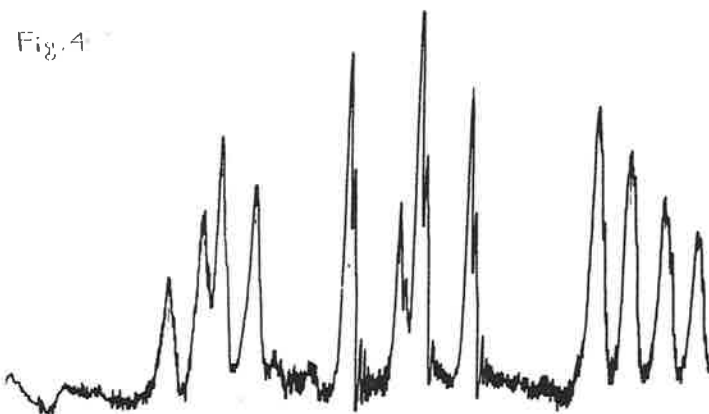


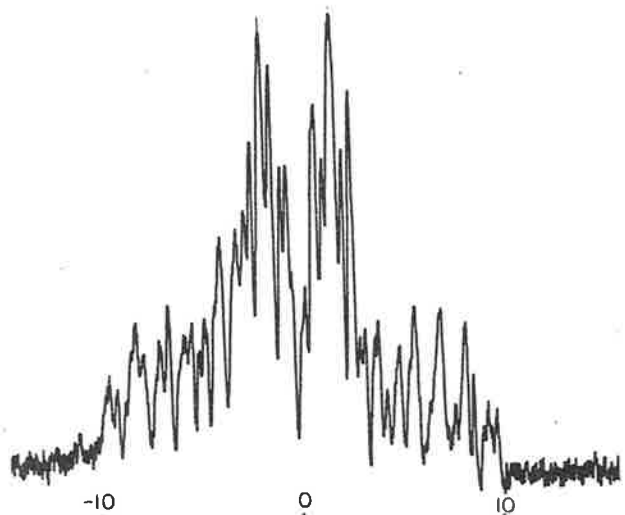
Fig.3



PROPYLINE OXIDE

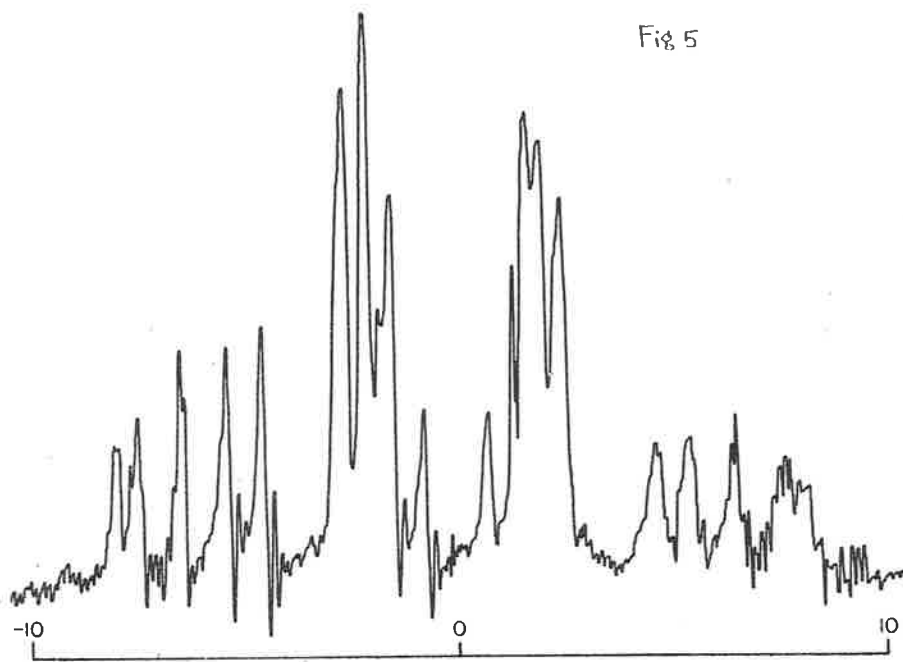


DECOUPLED SPECTRUM OF PROPYLINE OXIDE



VINYL PROTONS OF CYCLOPENTADIENE (60 mc)

Fig 5



DECOUPLED VINYL PROTONS

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

ADDRESS REPLY TO
NATIONAL BUREAU OF STANDARDS
WASHINGTON 25, D. C.

March 21, 1961

IN YOUR REPLY
REFER TO FILE NO.
15.7

Dr. Aksel A. Bothner-By
Mellon Institute
4100 Fifth Avenue
Pittsburgh 13, Pa.

Dear Dr. Bothner-By:

Your Mellon Letters render an extremely useful service through the publication of monthly bibliographies. I personally would not know how to manage without them at all. But I believe that some organization should go further and bring out an indexed NBS bibliography. One simply cannot read every paper containing NBS material; on the other hand, "selective" reading never provides sufficient knowledge of work related to one's current or transitory interest.

A public angry or desperate (or both) statement on this situation was made at the Second Conference on Experimental Aspects of NMR by George Tiers, when he said "I simply don't know where to find the time to read what I should really read", or words to that effect.

I plan to submit some specific proposals along these lines to the staff of the NBS library. But before doing this, I should like to have the opinion of as many NMR-tists as possible - and of other well-meaning people - and therefore I am asking you to include this letter in the next MELLONER.

Some of the questions that arise in connection with such an undertaking are these:

- 1) How often should such a bibliography appear? Monthly? Bimonthly?
- 2) Should all NMR material be included or only that from specific areas, e.g. high resolution?
- 3) What kind of indexes should there be, in addition to an author index: subject? formula?
- 4) What experience in similar bibliographies or card files (punched etc.) should or might be considered here?
- 5) Are there any files, bibliographies (apart from those published in books or journals) or reference collections in existence which could be made available to the group that is to embark on a pilot study or a full-fledged program?

Any further utterances on this subject are also welcome. The desires of the interested people are of prime importance at this stage, however impossible, far-fetched or trivial they may sound. I should also like to hear about any misgivings, although for instance those on manpower or the economic aspects ought not to be in the foreground of the discussion right now.

Sincerely yours, *Ernest Lustig*
Ernest Lustig



THE JOHNS HOPKINS UNIVERSITY • BALTIMORE 18, MARYLAND

DEPARTMENT OF CHEMISTRY

March 9, 1961

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

Dear Dr. Bothner-By:

Thank you for your letter of March 1. We have found the M.E.L.L.O.N.M.R. Newsletter very useful and informative, and we appreciate receiving it.

As a contribution from our Laboratory, I would like to make a preliminary report on some high resolution proton resonance work that we are carrying out in cooperation with our Physiological Chemistry Department. This work is not complete as yet; however, most of the assignments are firm although some of the hyperfine splittings are not accounted for to our complete satisfaction.

This work was undertaken not only because of the interesting nmr and structural problems involved in this class of compounds, but also we are interested in using this technique to identify the peripheral groups in naturally occurring porphyrins.

The results are summarized (Table I) in the form of chemical shifts relative to tetramethyl silane as an internal standard. Deuterated chloroform was the solvent and the work was done at 40 Mc/sec with solutions approximately 0.05 molar. It will be noticed that with the exception of N-H all of the proton resonances fall on the low-field side relative to the standard. The wide range of proton chemical shifts can be explained semi-quantitatively by simple ring current theory. It also appears that these results can be correlated well with porphyrin chemistry. The present indications are that nmr will prove to be a very useful analytical tool for studying this family of compounds. In Fig. 1 a typical spectrum obtained for mesoporphyrin IX diethyl ester is shown.

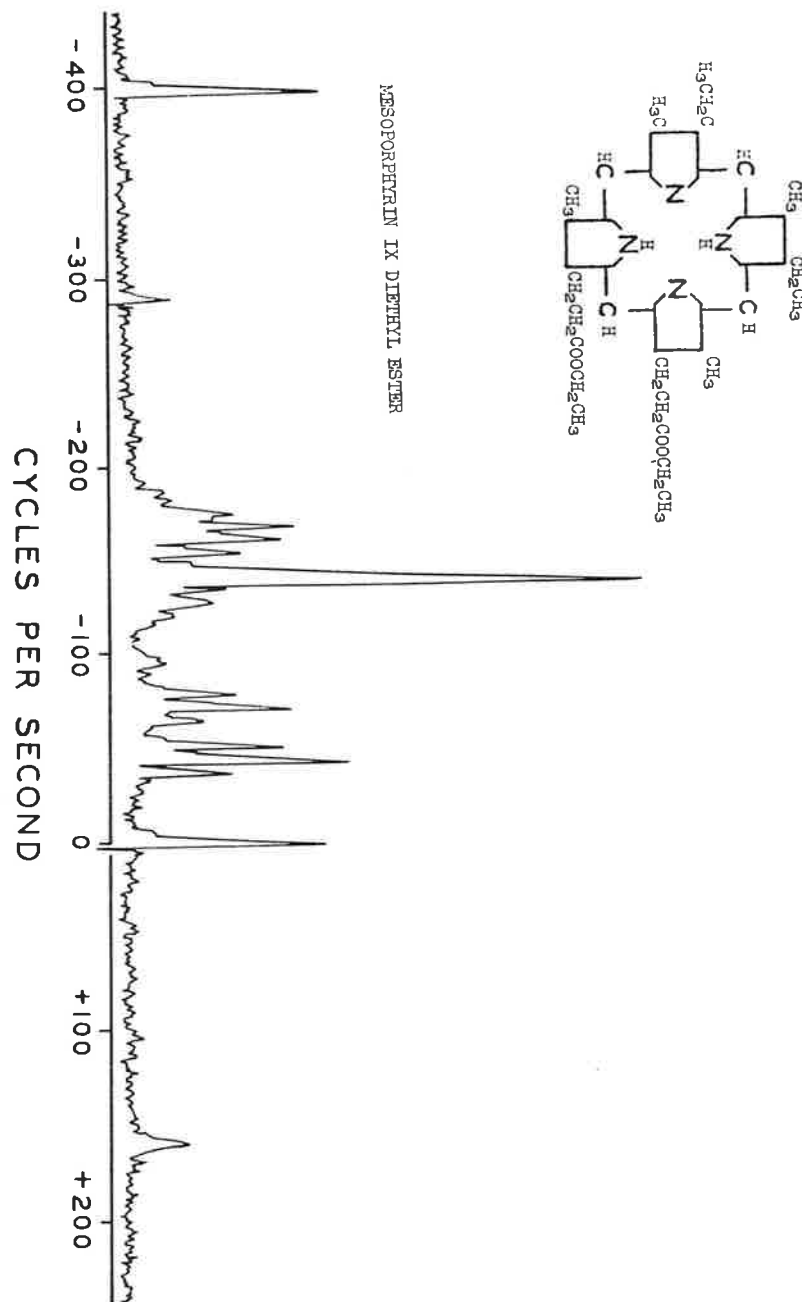
Please give my regards to Dr. Shapiro.

Very truly yours,

Walter S. Koski

Walter S. Koski
Professor of Chemistry

enclosures-2



Proton Chemical Shifts in Some Porphyrins

Com- pound	Type H	bridge H	pyrrole H	-CH ₃	-CH ₂ -CH ₃	-CH ₂ -CH ₃	-OCH ₃	-OCH ₂ -CH ₃	OCH ₂ -CH ₃	-CH=CH-	=CH ₂ -CH ₂ -	-N-H
1		10.08	----	3.61	4.09	1.85						3.74
2		9.56	8.67	3.24	----	----		1.08	4.07	----		4.48
3		9.54	8.70	3.47- 3.22	----	----	3.56	----	----	----	4.0 3.06	4.59
4		9.57	9.42 9.37	3.28	----	----		1.12	4.1	6.45- 5.85	4.31 3.12	4.81
5		9.92 9.80	----	3.52	----	----	3.66	----		6.47- 5.98	3.21	4.28
6		9.99	----	3.56	4.14	1.83	----	1.13	4.14	----	3.27	3.91
7		9.94	----	3.52	4.25	1.78	3.61	----	----	----	3.19	3.88
8		9.39	8.62	3.42 3.32	----	----		1.14	4.12	----	3.02	----

All chemical shifts are negative relative to tetramethylsilane except those listed for NH in the last column.

1. etioporphyrin II 2. deuterioporphyrin IX dimethyl ester
 3. deuterioporphyrin IX diethyl ester 4. protoporphyrin IX diethyl ester
 5. protoporphyrin IX dimethyl ester 6. mesoporphyrin IX diethyl ester
 7. mesoporphyrin IX dimethyl ester 8. nickel deuterioporphyrin IX diethyl ester

DARTMOUTH COLLEGE

Department of Chemistry

HANOVER · NEW HAMPSHIRE

March 23, 1961

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

Dear Dr. Bothner-By:

At the recent Conference on Experimental Aspects of NMR Spectroscopy (Mellon Institute, Feb. 24-25, 1961) I described a variable temperature system (roughly, ambient to 200°C) suitable for high resolution work with sample spinning which was designed for the 60 Mc Varian Spectrometer at the California Institute of Technology. There seemed to be sufficient interest to warrant a brief description in NMR Letters.

The insert assembly (Fig 1, 2) uses a standard Varian insert (for 5 mm. sample tubes), lengthened to 9.7 cm overall, with slots or holes cut through the tube as near the coax plug as permitted by a cut down lower bearing. The upper and lower insert seals align and support the insert with respect to the dewar, the probe and the superstructure. The upper seal consists of a retaining ring, an O-ring and a flat silicone rubber washer. The nylon superstructure (Fig 2) supports the quartz dewar, the insert and a standard Varian air turbine, and brass pins afford automatic alignment for spinning. A cross flow of dry air is drawn through the ventilation chamber to bring the insert exhaust to about room temperature.

The aluminum probe mounting unit supports the inlet dewar tube which is clamped to the upper bar with split nylon blocks. The lower bar, the probe and the probe carriage extension are fastened in rigid alignment and since this bar is always left in place, the magnet is shifted accordingly. The shop must be warned that all parts of this system must be free from imbedded steel chips.

For routine work at room temperature, the inlet dewar and its support are removed, but the insert assembly (dewar and superstructure) are left in place. This does not effect the resolution and makes it very convenient to shift over to other temperatures by simply replacing the inlet dewar tube. To simplify changing frequencies between 50.4 and 60 Mc/s, a small hole, protected with a nylon plug, may be drilled in the top probe cover plate just over the transmitter input tuning condenser.

The Cal Tech unit has worked very successfully since it was installed about eight months ago and has been operated between -175° and $+175^{\circ}\text{C}$. For low temperatures, we boil liquid nitrogen using a 10 ohm coil regulated with a variable transformer as a heat source. Starting at room temperature, about 10 minutes is required to reach and maintain stable operation at -60° with a boil off rate of about 1 lb. N_2/hour . At -150°C , the rate is about 4 lb. N_2/hour . Temperature stability is about ± 0.1 to $0.5^{\circ}\text{C}/\text{hour}$ depending upon the care with which adjustments are made. For elevated temperatures we use tank nitrogen and a conventional heating coil in the inlet dewar tube.

I will be glad to supply a set of shop drawings to anyone who may be interested.

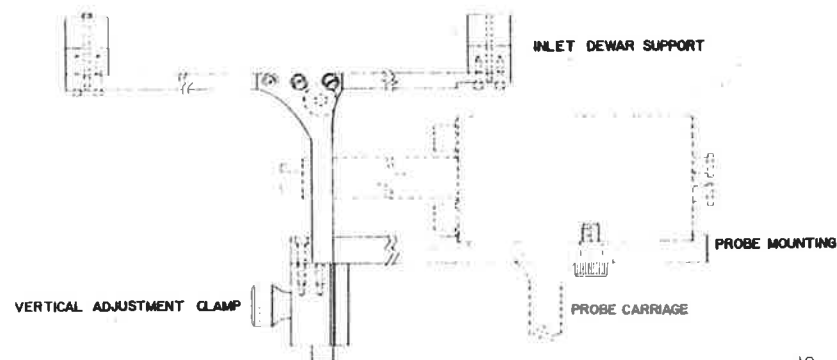
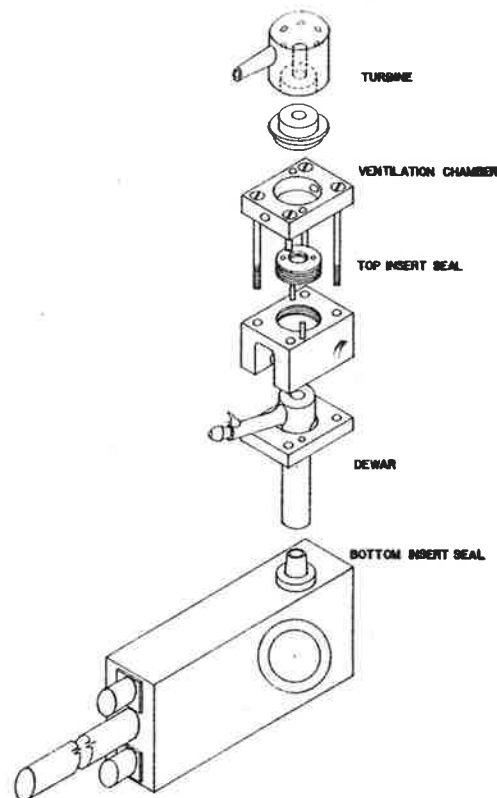
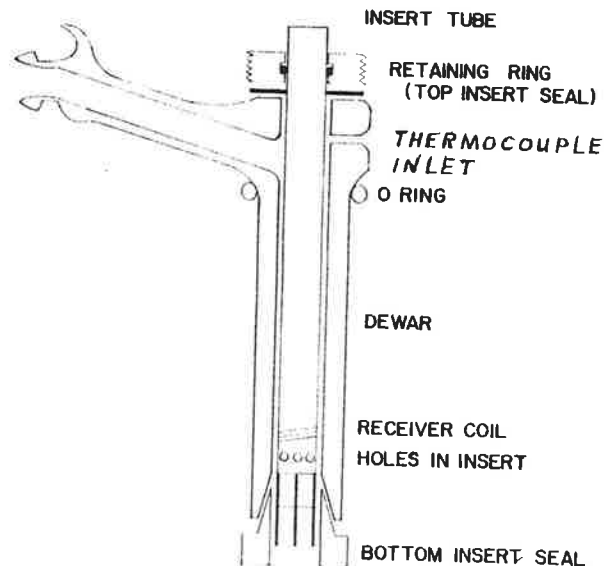
Sincerely yours,

Paul R. Shafer
Paul R. Shafer

PRS:rl

¹At the time of my talk I was unfortunately not aware that a basically similar design had previously been described by Dr. Brownstein, Can. J. Chem. 37 1119 (1959).

²Co-designers of this system were Mr. Donald Davis, Grellin Laboratories, California Institute of Technology, and Prof. Gideon Frenkel, Department of Chemistry, Ohio State University.



MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH 13, PA.

March 20, 1961

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Barry:

Enclosed is a sketch of a pen reservoir which we are using in conjunction with our Varian G-10 recorder. We find that this pen is economical since when a pen point becomes damaged or worn one need only replace the lettering pen. This type of reservoir is also time-saving since if it is not allowed to become empty the problem of clogging is negligible and we have operated as long as a month without having to remove the pen for a major cleaning.

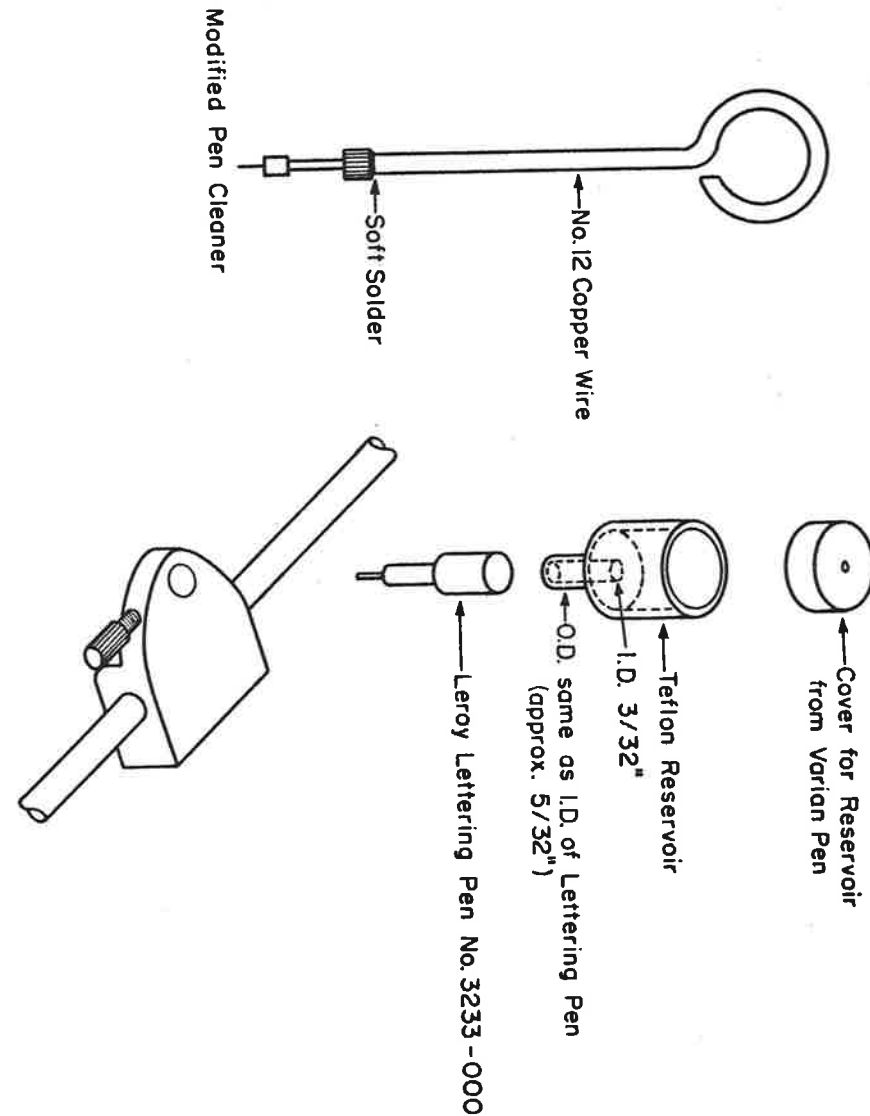
We have used Higgins india ink with this pen and found it to be very satisfactory. Recently we tried some K & E drawing ink #3015, and it also appears to be quite acceptable.

Very truly yours,

John J. Burke

Junior Fellow

JJBurke:pok





THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY

(Faculty of Technology in the University of Manchester.)

MANCHESTER 1 · TELEPHONE CENTRAL 3266

Department of Chemistry

Dr. J. Lee.

20th. March, 1961.

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

Dear Dr. Bothner-By,

Please accept my apologies for having been so long in contributing to your excellent newsletter, which we find very useful. We have just received our new A.E.I. (60 and 25 Mc/s) Spectrometer and among the research projects which we are undertaking are the following two.

(i) Hindered rotation in inorganic systems.

Preliminary investigations of the 40 Mc/s ^1H spectrum (using a Varian instrument) of phenyldimethylaminoboron chloride



have indicated a potential barrier of about $18 \text{ k cal mole}^{-1}$ about the B-N bond. In the preliminary analysis on the variation of methyl absorption with temperature, we have used four different approaches. Three of these (a. coalescence temperature + transition state theory, b. separation of band maxima, c. "fast exchange approximation" analysis above coalescence temperature (Piette and Anderson: J. Chem. Phys., 1959, 30, 899)) have yielded results between 16 and 20 k cal mole^{-1} . The fourth approach (d. maximum/central minimum intensity ratio) has given a value of 5 k cal, which seems unreasonably low. So far (with the exception of approach c.) we have not allowed for natural band width; this may well account for the low value of d.

(ii) Six-membered N-heterocyclics.

In the course of investigating a number of fluorinated pyridines, preliminary work on 2-fluoropyridine at 60 Mc/s has revealed a complex ^1H spectrum. Although some analysis has been possible, we are strongly convinced that H-F double resonance will assist considerably in analysis of the absorption and of spectra for similar compounds. We therefore intend to construct the requisite auxiliary equipment. A curious feature in the 2-fluoropyridine spectrum is a very broad doublet at lowest field. Could this be due to ^{14}N quadrupolar broadening of a hydrogen atom not directly attached to nitrogen or is it a chemical exchange effect? We hope to decide which is the case by (a) temperature variation, (b) N-H double resonance and (c) investigations on related compounds. Since we have not yet examined the fluorine absorption, we are not in a position to say whether this shows similar broadening.

We have created something of a problem for the people who have delivered our instrument by requesting installation of the 5 ton magnet on the fourth floor of our building.

Yours sincerely,

Contd.

March 23, 1961

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

Dear Dr. Bothner-By:

Here is a brief account of some work which we completed recently. A more complete report will appear in the J. Chem. Phys.

Phys. In 1956 Saika and Gutowsky¹ reported a near-zero coupling constant between the fluorine atoms on adjacent carbon atoms in the NMR spectrum of $\text{CF}_3\text{CF}_2\text{N}(\text{CF}_3)_2$. This appeared anomalous to them since F-F coupling constants were known to be large, and in particular since the coupling constant between the fluorine atoms in the two nonequivalent perfluoromethyl groups was found to be 6 cps. Since that time several other similar cases have been reported in the literature^{2,3,4,5}. Furthermore, it has been assumed that the restrictions upon rotation are responsible for these near-zero coupling constants. This was presented in the literature by Crapo and Sederholm².

Little has been said explicitly in the literature concerning the mechanism for fluorine-fluorine coupling, but it seems to be generally assumed that as in the hydrogen case⁶, the coupling takes place through the bonds. Data are presented below that have led us to believe that (i) near-zero coupling constants can not be explained by an accidental, mutual cancellation of nonvanishing coupling constants averaged over the three staggered configurations; (ii) in the case of fluorine the coupling proceeds primarily not through the bonds, but is rather due to a direct-through-space electron-coupled interaction.

Table 1

Serial Number	Compound	Coupling constants (cps)
1	$\begin{array}{c} \text{CF}_3-\text{CF}_2 \\ \quad \quad \quad \diagup \text{N}-\text{CF}_3 \\ \text{CF}_3-\text{CF}_2 \end{array}$ <p style="text-align: center;">a b c</p>	$J_{ab} = 5.1$ $J'_{ab} = 5.1$ $J_{ac} = 6.8$ $J_{bc} = 15.8$
2	$\begin{array}{c} \text{CF}_3-\text{CF}_2 \\ \quad \quad \quad \diagup \text{N}-\text{CF}_2-\text{CF}_3 \\ \text{CF}_3-\text{CF}_2 \end{array}$	$J_{ab} = 6.8$ $J'_{ab} = 6.8$

3	$\text{CF}_3-\text{CF}_2-\text{O}-\text{CF}_2-\text{CF}_3$ a b b a	$J_{ab} = 1.7$ $J'_{ab} = 1.7$
4 ³	$\text{CF}_3-\text{CF}_2-\text{COOH}$ a b	$J_{ab} = 1.38$
5 ¹	$\text{CF}_3-\text{CF}_2-\text{N} \begin{array}{l} \nearrow \text{CF}_3 \\ \searrow \text{CF}_3 \end{array}$ a b c	$J_{ab} \leq 1$ $J_{ac} = 6$ $J_{bc} = 16$
6	$\text{CF}_3-\text{CF}_2-\text{CF}_2-\text{NF}_2$ a b c d	$J_{ab} \leq 1$ $J_{ac} = 8.6$ $J_{ad} = 2.2$ $J_{bc} \leq 1$ $J_{bd} = 10.5$ $J_{cd} \leq 1$
7	$\text{CF}_3-\text{N} \begin{array}{c} \nearrow \text{CF}_2-\text{CF}_2-\text{O} \\ \searrow \text{CF}_2-\text{CF}_2 \end{array}$ a b c	$J_{ab} = 13.6$ $J_{ao} \leq 2$ $J_{bc} \leq 2$ $J'_{bc} \leq 2$
8	$\text{CF}_3-\text{CF}_2-\text{N} \begin{array}{c} \nearrow \text{CF}_2-\text{CF}_2 \\ \searrow \text{CF}_2-\text{O} \end{array}$ a b c e d	$J_{ab} \leq 1$ $J_{ac} = 6.5$ $J_{ad} = 6.5$ $J_{ae} \leq 1$ $J_{bc} = 9.9$ $J_{bd} = 9.9$ $J_{be} \leq 1$ $J_{cd} \leq 1$ $J_{ce} \leq 1$ $J_{de} = 3.5$

It is apparent from Table 1 that there is no set type of molecule which always yields near-zero coupling constants. Such near-zero coupling constants appear in molecules where relatively free rotations are allowed about the carbon-carbon bonds, as well as in molecules where rings limit such free rotation. It has been assumed that the near-zero coupling constants are the time average of nonvanishing J's averaged over the three stable configurations. Due to the common

occurrence of this phenomenon, if this explanation is valid, one must assume that the J does not vary much from compound to compound but it is only a function of the dihedral angle, as in the case of hydrogen⁶. However, this would lead one to predict that the J in all compounds having the $\text{CF}_2\text{-CF}_2$ -group would always be near-zero, which is not the case.

One readily accounts for all fluorine-fluorine coupling constants in saturated compounds thus far investigated if one assumes that the major contribution to the coupling constant comes about as a direct-through-space, electron-coupled interaction rather than a through-the-bonds effect. The large excursions of the p electrons in fluorine atoms make it reasonable to assume that such an effect could be significant in the case of fluorine-fluorine coupling and not significant in the case of hydrogen-hydrogen coupling constants. (Note: however see Roberts⁷)

Assuming all bonding to be tetrahedral, the carbon-carbon bond distance to be 1.54\AA , and the carbon-fluorine bond distance to be 1.33\AA , and assuming that the staggered configurations are the favored ones, the closest fluorine-fluorine approach between the two sets of fluorine atoms in the $\text{R-CF}_2\text{-CF}_2\text{-R'}$ group is 2.73\AA . We propose then that the coupling through the bonds is small as in the case of the hydrogen analogs; that 2.73\AA is too great a distance to result in any appreciable through-space contribution; and that 2.73\AA is just outside the radius at which through-space coupling becomes important. (This is quite reasonable since the sum of the Van der Waal radii for two fluorine atoms is 2.70\AA .)

The fluorine-fluorine distance between gem-fluorine atoms in perfluorocyclohexane is 2.17\AA . The coupling constant is 2.84 cps . Here again it is assumed that most of the 2.84 cps comes about through space as might be expected from the fluorine-fluorine distance which is much smaller than the sum of the Van der Waal radii. If we assume, as a first approximation, a linear relationship between J and the internuclear distance D of two interacting nuclei, we can readily calculate the coupling constant to be expected for 1,3 fluorine atoms (fluorines on skeletal atoms which are β to each other), and 1,4 fluorine atoms. The equation used is $J = (2.73\text{\AA} - D) 507\text{ cps}$, which is the straight line determined by the near-zero coupling in $\text{R-CF}_2\text{-CF}_2\text{-R'}$ and the coupling of gem-fluorines in perfluorocyclohexane.

In two of the nine possible staggered configurations of the $\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-}$ group, the 1,3 fluorines are 2.51\AA apart; thus they are closer to each other than the closest distance between 1,2 fluorines (fluorines on adjacent skeletal atoms). The coupling at 2.51\AA is 111 cps , but only two of the nine possible configurations yield fluorine-fluorine distances which contribute to the through-space coupling. Although there may be some small barrier against the configurations which do not correspond to a zigzag carbon skeleton, if we weight all nine configurations equally, the coupling to be expected is 24.5 cps . We may likewise extend this calculation with less precision to the J_{14} case. This leads to an expected value

of $J_{14} = 8\text{ cps}$. In both cases the calculated values are large compared to the observed ones, but this can be accounted for in terms of errors in the assumed amount of twist in dihedral angles from the staggered configurations, the errors in the assumed bond distances and angles, and the probable nonlinearity of J vs. D since it would be expected that J would increase somewhat more rapidly as the distance decreases. Over all agreement with the experimental values is good considering the approximations made.

In conclusion we would like to draw attention to some of the coupling constants listed in Table 1. In compound 5 the coupling constants are what would be expected on the basis of the model presented. In compounds 1 and 2 which are very similar to 5, the coupling constants are also similar except for J_{12} . In compound 1, $J_{12} = 5.1\text{ cps}$. This might be expected from a model of the compound since there are a large number of atoms crowded around the central nitrogen atom. This tends to increase the C-C-N bond angle, thus throwing the 1,2 fluorine atoms closer to each other, and increasing the coupling constant. One might expect this effect to be more pronounced in compound 2 where another perfluoroethyl group is taking the place of a perfluoromethyl group; and indeed this is the case. Here $J_{12} = 6.8\text{ cps}$ which would imply a further increase in the C-C-N angle as is expected. Likewise in compound 3, J_{12} is again nonvanishing because of the opening of the C-C-O bond angle due to steric hindrance between the two ends of the molecule.

Preprints of our publication are available discussing the basis for this model and the interpretation of coupling constants in a great many more compounds.

Let us add our words of thanks and praise for the great job you are doing with MELLONMR.

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Sincerely,

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ALPHABETICAL INDEX TO MELLONMR

AUTHORS

Becker, E. D.
13, 7

Bothner-By, A. A.
1, 1
2, 1, 14 (Errata: 3, 11)
4, 3, 4
5, 1
7, 1,2,9
9, 3,4
11, 9

Bovey, F. A.
2, 3
10, 3

Bradley, R. B.
13, 7

Brownstein, S.
2, 3
3, 2
11, 1

Chamberlain, N. F.
2, 10
8, 10

Conroy, H.
12, 5

Curphey, T. J.
12, 3

Feeney, J.
11, 5

Gillespie, R. J.
10, 5

Grant, D. M.
8, 3

Gronowitz, S.
13, 3,4,5

Gutowsky, H. S.
8, 3

Hoffman, R. A.
6, 4
13, 3,4,5

Jackman, L. M.
11, 4

Karplus, M.
8, 3

Kowalewski, V. J.
13, 6

Lauterbur, P. C.
3, 1
4, 7
5, 7,8,9
7, 2,9
9, 4

Lee, J.
11, 6

Lombardi, E.
13, 1,2

Lown, J. W.
11, 4

Martin, R. J.
12, 1

Mueller, N.
9, 1,2
14, 6,7

Authors Index, Continued

Naar, C.
2, 14

Nist, B. J.
6, 1

Petrakis, L.
14, 1,2

Pratt, L.
8, 11

Primas, H.
7, 5

Pritchard, D. E.
9, 1,2
14, 6,7

Reilly, C. A.
2, 5
10, 1

Richards, R. E.
6, 3

Ritchey, W. R.
11, 3

Roberts, J. D.
8, 1
12, 4

Rogers, M. T.
8, 13

Saunders, M.
2, 2

Schneider, W. G.
8, 5

Sederholm, C. H.
14, 1,2

Shapiro, B. L.
1, 1
2, 1
4, 7
5, 1
7, 1,2,9
9, 4

Sheppard, N.
2, 7
15, 3,4,5

Shoolery, J. N.
2, 6
7, 6
11, 8

Slomp, G.
14, 3,4,5

Sogo, P. G.
13, 1,2

Stout, G. H.
8, 6

Sutcliffe, L. H.
11, 5

Thomas, L. F.
11, 7

Tiers, G. V. D.
2, 9
4, 1
6, 5
10, 2,3
12, 8
13, 8,9

Waugh, J. S.
3, 4

Weinberg, I.
12, 6

Whipple, E. B.
15, 2,3

White, R.
15, 1

Wiberg, K. B.
2, 6
6, 1

Zimmerman, J. R.
2, 12