Mailed:

Monthly
  Ecumenical
    Letters from
      Laboratories
        Of
          N - M - R

          No. 21

MICHIGAN STATE UNIVERSITY EAST LANSING

KEDZIE CHEMICAL LABORATORY · COLLEGE OF SCIENCE AND ARTS · DEPARTMENT OF CHEMISTRY

June 23, 1960

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

Dear Aksel:

As the result of an intensive study of A_3B_2C and A_3B_2X systems in these laboratories the relative signs of the spin-spin coupling constants in a number of compounds have been determined from high resolution proton magnetic resonance spectra (P.T. Narasimhan and M.T. Rogers, J. Chem. Phys., 31, 1428, 1430 (1959), and unpublished results). The frequencies and intensities of the lines in the NMR spectrum are calculated from an exact solution of the Hamiltonian equation for both choices of sign. Comparison with the experimental spectrum then usually allows one to determine unequivocally the relative signs of the coupling constants. Data accumulated so far are shown in Table I.

Table I

SIGNS[a] OF SPIN-SPIN COUPLING CONSTANTS IN A_3B_2C AND A_3B_2X TYPE COMPOUNDS

Compound	J^b_{AB}	J_{AX} or J_{AC}	J_{BX} or J_{BC}
$(CH_3CH_2)_3P^{31}$	7.6 cps	13.7 cps	-0.5 cps
$(CH_3CH_2)_4Sn^{117}$	8.2	-68.1	30.8
$(CH_3CH_2)_4Sn^{119}$	8.2	-71.2	32.2
$(CH_3CH_2)_2Hg^{199}$	7.2	115.2	-87.6
$(CH_3CH_2)_4Pb^{207}$	8.2	124.0	-42.0
CH_3CH_2OH	7.15	0	4.8
CH_3CH_2SH	7.2	0	7.7
$CH_3CH_2C{\equiv}CH$	7.2	0	-2.4

a. Only relative signs are determined from analysis of the spectrum.
b. A,B,C, or X refer to the following:

   A = CH_3 proton; B = CH_2 proton; C = OH, SH, or ${\equiv}CH$ proton;
   X = P, Sn, Hg, or Pb nucleus with spin 1/2.

It may be noted that J_{AX} and J_{BX} have opposite signs in all A_3B_2X systems studied. For the A_3B_2C series J_{AC} has been nearly zero in our examples and J_{AB} and J_{BC} have the same sign except in ethyl acetylene where the triple bond is doubtless responsible for J_{BC} being negative. Absolute signs may be assigned if one has sufficient confidence in theoretical calculations. Since recent theoretical work supports the view that $J(CH_3-CH_2)$ is positive, the signs of J_{BC} for the last three compounds in Table I are probably as shown. Prof. Martin Karplus has indeed calculated a negative coupling constant for $J_{HH}(CH_3-C{\equiv}C-H)$ in methyl acetylene hence our conclusion that $J_{HH}(CH_2-C{\equiv}C-H)$ is negative in methyl acetylene receives additional support. The signs of J_{AX} and J_{BX} have been tentatively assigned on the basis of recent theoretical calculations carried out by Narasimhan and Karplus at the University of Illinois. It thus appears quite possible to determine with some confidence the absolute signs of many spin-spin coupling constants by a combination of experimental and theoretical data.

Sincerely,

P. T. Narasimhan

P. T. Narasimhan[+]

Max T Rogers

Max T. Rogers

[+] Present Address:
Noyes Chemical Laboratory
University of Illinois
Urbana, Illinois

MTR:o's

UNIVERSITY OF CALIFORNIA

DEPARTMENT OF CHEMISTRY
BERKELEY 4, CALIFORNIA

June 16, 1960

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

Dear Dr. Bothner-By:

An NMR analysis of CF_3CF_2CFICl, prepared by Haszeldine's method, yielded, upon examination at 56 megacycles, three distinct fluorine resonances. The CF group appeared at low field, separated from the CF_2 group by 2120 cps. and from the CF_3 group by 114 cps. The three fluorines of the CF_3 group appear to be equivalent, whereas the two fluorines of the CF_2 group are nonequivalent. Therefore, CF_3CF_2CFICl can be treated as an AB_3XY molecule.

The CF_2 group is a quartet, each member being further split into a doublet. This, in addition to the CF_3 part of the spectrum implies that $J_{BX} = J_{BY} = 0 \pm 0.3$ cps. Hence, this portion may be treated as the XY part of an AXY spectrum. Such a treatment yields $|J_{XY}| = 270.4 \pm 0.5$ cps., $|J_{AX}| = 14.6 \pm 0.1$ cps., $|J_{AY}| = 13.4 \pm 0.1$ cps., and $\omega_X - \omega_Y = 270.4 \pm 0.5$ cps, $\omega_X - \omega_A = 2255 \pm 3$ cps.

The spectrum of the CF_3 group is a doublet, each line being about 1 cps. wide. Interpretation of this portion of the spectrum treating it as the B_3 part of an AB_3 group yields $|J_{AB}| = 10.8 \pm 0.1$ cps.

Using the above data and assigning $\omega_B - \omega_A = 114 \pm 0.5$ cps. the spectrum of the CF group was calculated by first order perturbation theory, applying the perturbation $H' = J_{AX}I_A \cdot I_X + J_{AY}I_A \cdot I_Y$ to the exact solution for the AB_3 case. The observed and calculated spectra are shown on the attached drawing. Combination bands are not shown, but were observed. The close correlation supports our assignment of coupling constants. The additional lines in the observed spectrum are probably due to isotopic impurities.

The nearly zero coupling constant between the CF_3 and CF_2 groups, $J(CF_3CF_2)$, prompted a search of the literature for other such cases. Saika and Gutowsky reported $J(CF_3CF_2) = 0$ in $(CF_3)_2NCF_2CF_3$. Van Dyke Tiers implied that $J(CF_3CF_2)$ is very small in $CF_3CF_2CF_2H(D)$. Reilly has reported a small coupling constant in CF_3CF_2COOH, $J(CF_3CF_2) = 1.48$ cps.

The high resolution spectrum of $CF_3CF_2CF_2COOH$ consists of a triplet corresponding to the CF_3 group, a quartet corresponding to one CF_2 group and a singlet corresponding to the other CF_2 group. In line with the other cases presented here, we assert that $J(CF_3CF_2) \approx J(CF_2CF_2) \approx 0$, and that the splitting is due to the a-CF_2 group interacting with the CF_3 group.

On the basis of the above examples, we put forward the suggestion that the spin coupling constant between fluorine atoms on the adjacent saturated carbon atoms in the group -CF_2-CF_2- is usually very small when this group is in turn attached directly only to elements in the first row of the periodic table, or when one end

has a third fluorine attached giving it three fold symmetry; whereas, it is sizable if larger or smaller atoms are attached to one end of the group, and the other end lacks three fold symmetry.

The cause of these small coupling constants is not readily apparent. Their wide spread occurrence implies that there is a more fundamental reason behind them than pure chance. Variation of the electron withdrawing power of the attached groups does not seem to enhance these small coupling constants as can be seen from the cases sighted above. We feel that the cause of this effect must be connected with the hindered rotation about the carbon-carbon bond.

We suggest the following explanation. Consider two fluorine atoms attached to adjacent carbon atoms in the group A-CF_2-CF_2-B. The coupling constant, J, between these fluorine atoms is a function of the dihedral angle α. We assume that $J(\alpha)$ is of such a form that $J(\alpha) + J(120° + \alpha) + J(240° + \alpha) \approx 0$ if and only if $\alpha \approx 60°$, 180°, or 300°. The potential energy as a function of α has three minima. If A and B are in the first row of the periodic table, or if A = fluorine giving one end three fold symmetry, the three minima are near $\alpha = 60°$, 180°, and 300°, and are of nearly equal depth. Otherwise, the minima are substantially moved and are of unequal depth. If rotation occurs in a sufficiently short time, the observed coupling constant is the time weighted average of the instantaneous coupling constants. If $J(\alpha)$ is of the assumed form, this time weighted average is very small only for three equally spaced minima of equal depth, ie. when only atoms in the first row of the periodic table are attached directly to the group in question, or when A = fluorine. Further investigation of this hypothesis is now in progress.

Sincerely,

Charles Sederholm

Charles Sederholm

Larry Crapo   by C.H.S.
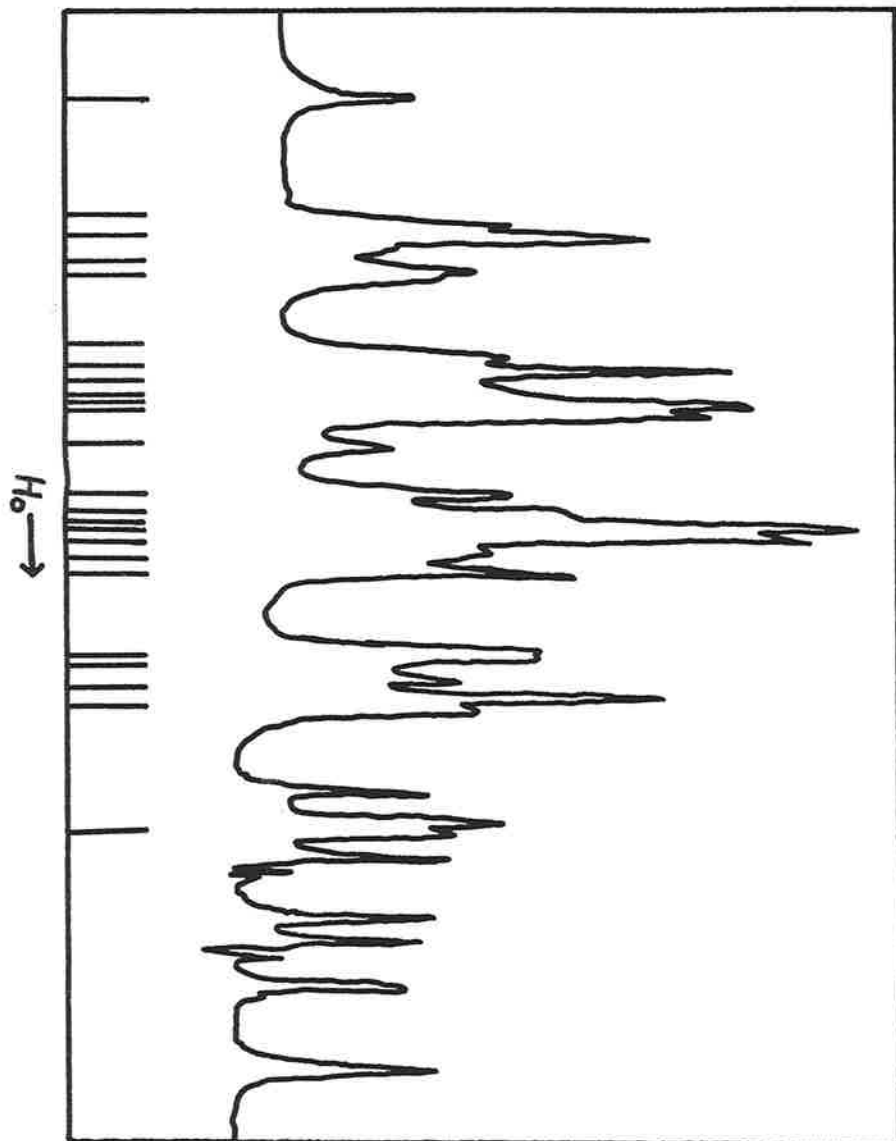
Larry Crapo

H₀ →

DEPARTMENT OF CHEMISTRY
BERKELEY 4, CALIFORNIA

June 16, 1960

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

Dear Dr. Bothner-By:

While I am at the typewriter I will drop you a second note
indicating the progress on another piece of research which is
just well started. In contrast to the other enclosed letter, this
will not be submitted for publication in the near future unless I
can find much more time for research than I have in the past.
Van Dyke Tiers and Gutowsky have reported chemical shifts
of hydrogen and fluorine resonances in various compounds, which
change when an isotopic substitution was made elsewhere in the
molecule. They have both stated that they believe this phenomenon
comes about as a result of the change in vibrational amplitude of
some modes of the molecule upon isotopic substitution. In order to
check the validity of this arguement, I have set about measuring
the temperature dependence of some chemical shifts. If the above
explanation is valid, molecules in excited vibrational modes should
exhibit different chemical shifts than similiar molecules in
their ground states, and this should result in a temperature
dependent chemical shift.
In order to avoid any variation in the chemical shift caused
be any variety of association, all compounds were studied in the
gaseous phase. The gases were sealed in thin walled sample tubes
at approximately two atmospheres pressure at room temperature.
Since all of the vibrational modes of methane lie at high
frequencies and are therefore very sparsely populated at room
temperature, it was felt that the proton resonance in methane would
serve as a good temperature independent standard. About equal
pressures of the sample under consideration and methane were therefore
sealed into the sample tubes. The above assumption that methane has
a temperature independent signal has not yet been checked, however,
judging from other compounds which have been investigated, this
may not be a good assumption since the chemical shift associated
with the excited vibrational modes may be very different from
that in the ground state.
Separations between the methane resonance and the sample
resonance were made using the technique described in MELLON 14.
Even on gaseous samples, the experimental points fall on a
straight line to better than 0.1 cps.
The following results have been obtained thus far:
Assuming methane to be temperature independent, all compounds
investigated thus far shift to low field as the temperature is
increased. This is the direction which would be predicted if
the existing theory for the isotope shift is correct.

DEPARTMENT OF CHEMISTRY
BERKELEY 4, CALIFORNIA

page 2

Compound	Downfield shift per 100° C.
cyclopentane	0.45 cps.
cyclobutane	0.71
cyclopropane	0.80
tetramethylmethane	0.61
tetramethylsilane	1.24
tetramethyltin	0.98

It is interesting to note that in the series tetramethyl-methane, silane, and tin, the tetramethylsilane has a larger shift than either of the other two, yet the tetramethyltin has the lowest vibrational frequencies. This then implies that in this case, at least, some of the higher frequency vibrational modes must have the the greater changes in chemical shifts which therefore outweigh the effect due to the low lying vibrational mode in the tetramethyltin.

An interesting calculation has been done on the cyclopropane. Assuming that any excited mode would have the same change in chemical shift from the ground state of the molecule, one can calculate what this shift would have to be to account for the observed temperature dependence. This number is then smaller than the largest actual change, and larger than the smallest one. In cyclopropane, at 60 megacycles, making this assumption, the protons in a molecule which is in an excited vibrational mode resonate on the average 9.7 cps. to the low field side of the protons in the unexcited molecule. This is a sizable shift, and makes the proposed explanation for the isotopic shift very reasonable.

Sincerely,

Charles Sederholm

Charles Sederholm

THE UPJOHN COMPANY

FINE PHARMACEUTICALS SINCE 1886

KALAMAZOO, MICHIGAN
May 31, 1960

RESEARCH DIVISION
301 HENRIETTA STREET

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

Dear Dr. Bothner-by:

We have obtained a device which has been very useful to us in the calibration of N.M.R. spectra. Since many spectroscopists calibrate spectra by interpolation between absorptions of known frequencies (reference materials and/or side bands), we are submitting this communication for your newsletter on N.M.R.

The device is a variable scale supplied by Gerber Scientific Instrument Company, 89 Spruce Street, Hartford, Connecticut. It is made from a spring which is expandable from 2 to 20 inches and which can be calibrated as desired. Ours measures 288 units in intervals of 2 (we record cps. at 60 mc. relative to water).

The scale has been useful for rapid calibration of spectra, for area measurements on electronically integrated spectra, and for reduction of spectra to hand-drawn facsimiles for filing purposes.

A photograph of a standard model selling for about $135 is enclosed.

Very truly yours,

George Slomp

George Slomp
Physical and Analytical Chemistry

GS:prv
Enclosure

THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY

(Faculty of Technology in the University of Manchester.)

MANCHESTER 1 . TELEPHONE CENTRAL 3266

Department of Chemistry

20th June, 1960

Dr. A. A. Rothner-by,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh, Pa., U.S.A.

Dear Dr. Rothner-by,

I hope the enclosed account of the spectrum of a fluorinated oxazetidine will be acceptable for the next issue of MELLONMR.

May I in addition make a few other comments.
(i) Might authors of published papers be a little more explicit about computational procedure adopted in the analysis of NMR spectra. Too often do we read statements of the kind, 'the – X – Hamiltonian matrix was solved by means of a ------ Computer' without saying whether the method was a trial and error one using estimated ranges of chemical shifts and coupling constants or whether the method was some sort of iterative one on the style of Reilly and Swalen (MELLONMR No. 17, p. 4). An additional few words could often be quite enlightening.
(ii) The controversial subject of the direction of a frequency scale could easily be resolved by labelling it

$$\nu_{ref} - \nu \quad .$$

The scale could then increase from low to high field, yet still satisfy those (including myself) who think of ν as representing the equivalent radiofrequency under conditions of fixed magnetic field and swept frequency. The latter concept then accords with Hamiltonian equation solutions for transition frequencies under fixed field conditions; I have never seen magnetic field solutions for fixed transition energy.
(iii) The idea of announcing complete computer programmes, given chemical shifts, coupling constants and perhaps transverse relaxation times, in your Newsletter is very commendable. I notice that the programmes are invariably for IBM Computers. I keep hoping that someone will offer a programme for a Ferranti Mercury, so that it would save me the trouble of writing one for myself.
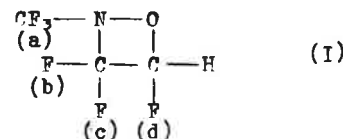
Finally, I should like to thank you for sending MELLONMR which we find very interesting and useful.

Yours sincerely,

J. Lee

The 40 Mc/s Spectra of a Fluorinated Oxazetidine:

(I)

The fluorine spectrum of I under conditions of low and high dispersion and its hydrogen spectrum, both at 40 Mc/s and at room temperature, are shown in Figs. 1 and 2, respectively.

It will be seen that although fine structure is evident in the $-CF_3$ and $>CFH$ absorption, the band associated with $>CF_2$ (on intensity grounds) is broad (ca. 30 c/s wide at half height) and structureless. One would expect two almost equally probable environments for each of the fluorine nuclei (b) and (c), these corresponding to the two minimum energy conformations in the nitrogen inversion vibration. Rapid vibration would average out each pair of chemical shifts and associated coupling constants, but not of course produce any (b)-(c) averaging. The observed (b)(c) band is strongly indicative of an intermediate rate of vibration, but gives the added indication that the averaged shifts for (b) and (c) differ from one another by less than ca. 30 c/s. Intermediate ^{14}N quadrupolar relaxation rate is probably not a prime contributor to the band broadening since one would expect the relaxation to affect the $-CF_3$ and $>CF_2$ absorption similarly: the increased broadness of the $-CF_3$ multiplet bands compared with the $>CFH$ bands may be attributable in part to the quadrupole effect, but it is more likely to arise from the inversion vibration (and possibly incompletely resolved structure due to (a)-H coupling).

We obtain additional confirmation of a small gem-fluorine chemical shift difference when we examine the fine structure of the fluorine and hydrogen absorption associated with the $>CFH$ group. We should not expect equality of J_{bd} and J_{cd} or of J_{bH} and J_{cH}, yet the hydrogen spectrum is apparently a doublet of triplets (1:2:1) and the fluorine spectrum a doublet of triplets (1:2:1) of quartets (1:3:3:1). In other words, $>CF_2$ is behaving like an AA' spin pair,
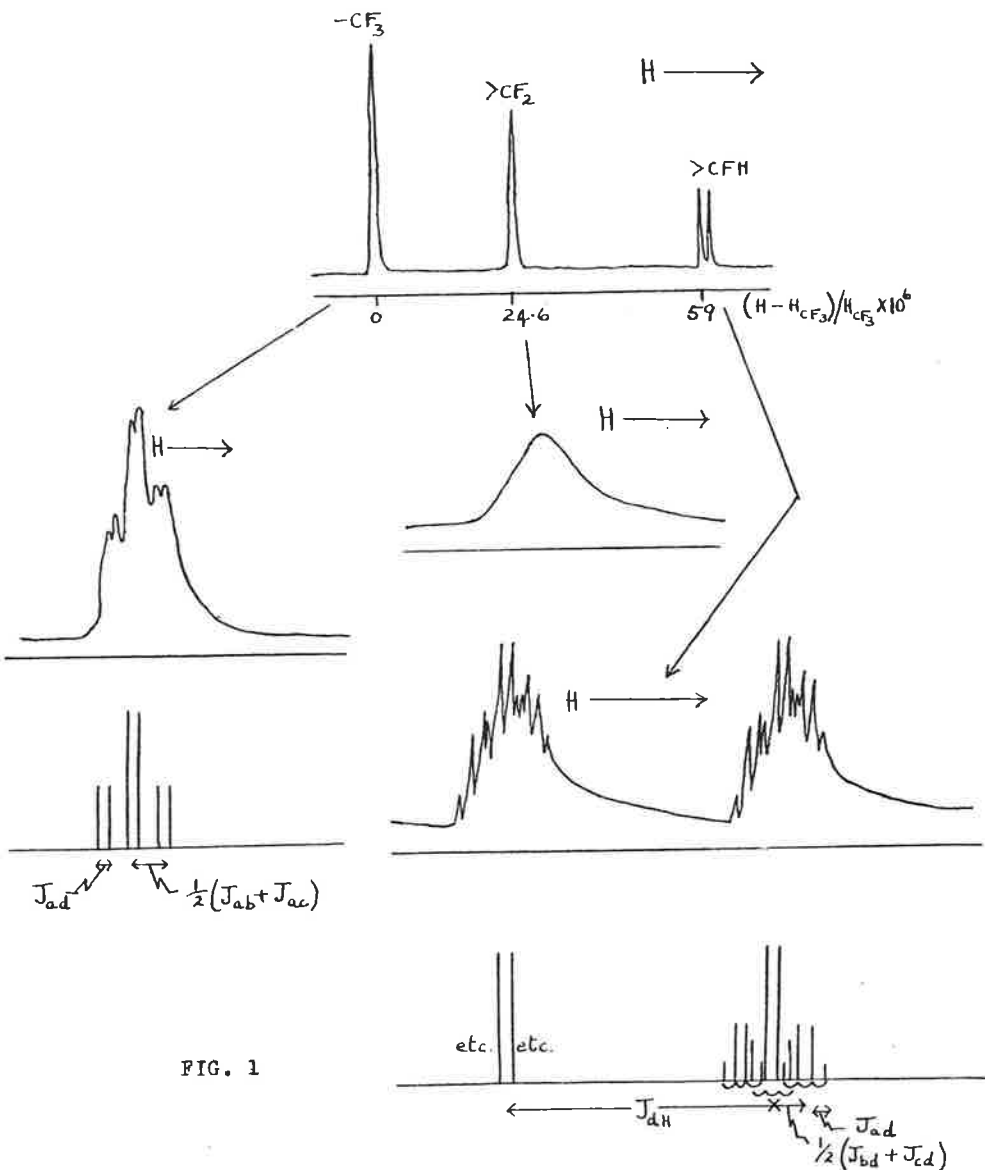
5.

FIG. 1

i.e. magnetically inequivalent but having fortuitously equal chemical shifts. The spin coupling origins of the splittings are indicated in the figures; first order perturbation theory was quite adequate in the analysis.. We might expect the $-CF_3$ absorption to give an indication of the near equality of the CF_2 chemical shifts, and indeed the observed splitting accords with this, but of course the difference between the time averages (over the inversion vibration) of J_{ab} and J_{ac} should not be very great so that in itself the evidence from the $-CF_3$ absorption would be inconclusive.

The coupling constants determined are as follows:

		No. of intervening bonds
$\frac{1}{2}(J_{ab} + J_{ac})$	7.7	4
J_{ad}	2.6	5
$\frac{1}{2}(J_{bd} + J_{cd})$	6.5	3
$\frac{1}{2}(J_{bH} + J_{cH})$	3.1	3
J_{dH}	66	2

The compound was prepared by Mr. H. Sutcliffe of this department. Equimolar quantities of CF_3NO and $CF_2:CFH$ had been heated together at 100°C and ca. 8 atm. for 65 hours in a sealed tube; the yield was 87%.
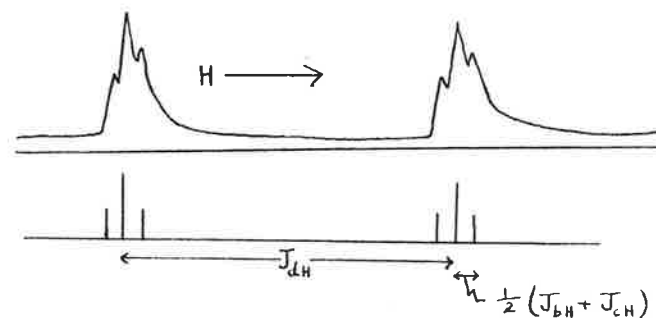

FIG. 2.

J. Lee

The NMR Spectra of Some Fluorocyclohexane Derivatives.

We have just completed a study of some mono- and di-
substituted fluorocyclohexanes and we thought you might be
interested to hear of our findings prior to publication.
A list of the compounds examined is given in Table I and
includes sufficient compounds to yield some information
about the relative importance of the various factors
influencing the shielding of fluorine atoms in such
compounds. Analysis of the spectra of these compounds
was made possible by cataloguing the four nearest neigh-
bours of a given fluorine atom (excluding the fluorine
atom on the same carbon atom as the substituent) paying
due regard to which were neighbours through bonds and through
space. This made it easy to recognise fluorine atoms which
were shielded similarly. By considering inductive effects
through bonds as well as spatial effects (where both the
bulkiness and the electronegativity of the substituent must
be taken into account) all the bands could be assigned and
the following set of empirical rules emerged:-

(a) Proximity to a hydrogen atom through space provides the
    most important shielding effect.

(b) Proximity to a hydrogen atom through bonds is only
    important when (a) is absent, then it is of the same order.

(c) Proximity to a fluorine atom in the CHF group through space
    is important when (a) and (b) are absentand leads to an
    unshielding effect.

2

(d) In the absence of the above factors, the inductive effect
    of one gem fluorine atom on another is important.

(e) Both the inductive effect and the spatial effects are not
    additive.

(f) The difference in chemical shift for two fluorine atoms
    in equatorial and axial positions is less than 20 cycles
    sec^{-1} when other effects are absent. This is to be expected
    because the diamagnetic anisotropic shielding is small from
    C-C and C-F bonds.

In some cases, information about the conformational state of
the isomer was obtained since the spectra could only be
interpreted by assuming one particular conformation. Some
molecules were likewise shown to be rapidly interconverting
Examination of the compounds at different temperatures (-30 to
+150°C) tended to confirm the assignments although the results
were mainly negative.

Interpretation of the spectra was made easier by the presence
of geminal spin-spin interaction which was ~290 cycles sec^{-1} in
all cases and this can now be regarded as a characteristic feature
of fluorocyclohexanes. No other F-F spin-spin interaction
was observed.

This geminal coupling constant (290 cycles sec^{-1}) is
considerably larger than those found in fluorinated cyclo-
propanes (120 cycles sec^{-1}) and cyclobutanes (200 cycles
sec^{-1}) and it should be possible to correlate these values
with the changing bond angles in these compounds.

Table I.

Compound	Conformation.
Undecafluorocyclohexane	Probably fixed; H (1a).
Chloroundecafluorocyclohexane	Fixed: Cl (1e).
Perfluoromethylcyclohexane	Fixed: CF$_3$ (1e).
Cis 1H:2H-Dihydrodecafluoro-cyclohexane	Rapidly interconverting.
Cis 1H:3H-	Fixed: H(1e) H (3e).
Cis 1H:4H-	Rapidly interconverting.
Trans 1H/2H-	Fixed: H (1a) H (2a).
Trans 1H/3H-	Fixed: H (1e) H (3a).

Table II.

Compound	Assignment	Band	Chemical Shift (cycles sec^{-1})
Undecafluorocyclo-hexane	3e,5e	1	1631
		3	1914
	4e,4a	4	1971
	2a,6a	2	1828
		5	2110
I	2e,3a,5a,6e	6	2180
		7	2470
	1e	8	5919
		9	5960
Cis 1H:4H-Dihydrodeca fluorocyclohexane	2',3',5',6'	1	1670
		2	1950
	2,3,5,6	3	2080
		4	2370
II	1,4	5	5940
		6	5980

Atoms marked with a prime (e.g. 2') are trans to the nearest hydrogen atom via the bonds in an interconverting molecule.

4.

The spectra of two typical compounds are shown in fig.1 and the chemical shift data and assignments are given in Table II. The ^{19}F high resolution NMR spectra were obtained at 40 Mc sec^{-1} on the molten pure compounds and also on 50% solutions of the compounds in carbon tetrachloride at room temperature. The chemical shifts were measured relative to trifluoroacetic acid used as an external reference. Fluorine atoms geminal to hydrogen atoms occur at high fields and their absorption bands show a doublet splitting from spin-spin interaction between the hydrogen and fluorine atoms (J_{H-F}=~45 cycles sec^{-1}). The low field pair of doublets in the spectrum of 1H:4H cis-decafluorocyclohexane are typical of an AB system where the coupling constant is large compared with the chemical shift.

Figure 1.
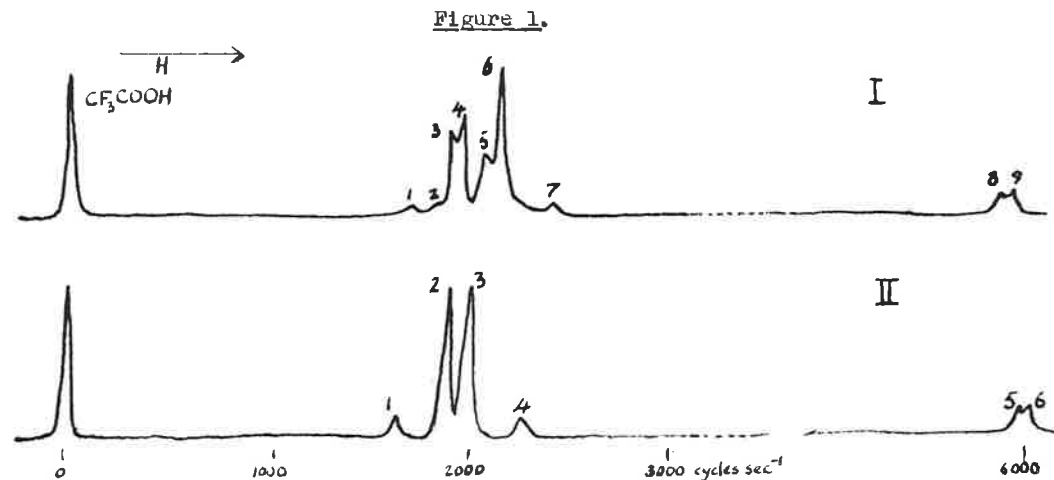
May we say that we agree wholeheartedly with the recommendations on standardisation of spectra made by Shoolery, Johnson and Anderson in MELLONMR No.19.

J. Feeney.

L.H.Sutcliffe.

NMR STUDIES OF HYDROGEN BONDING

I. CARBOXYLIC ACIDS

by Jeff C. Davis, Jr.[1] and Kenneth S. Pitzer

Dept. of Chemistry and Lawrence Radiation Laboratory
University of California, Berkeley

The proton magnetic resonance spectra of formic, acetic, and benzoic acids in benzene have been studied at 60 Mcps in the temperature range 20°- 100° C. Huggins, et. al.,[2] proposed the relation for a monomer - dimer system that

$$\delta = \frac{m}{a} \delta_M + \frac{(a-m)}{a} \delta_D$$

where m is the moles of acid in the monomer form and a the total moles of acid used to make up the solution. The equilibrium constant for such a system is given by

$$K_2 = \frac{X_D}{X_M^2} = \frac{(a-m)(2s\ a\ m)}{4m^2}$$

where X_M and X_D are the mole fractions of the monomer and dimer species in the solution and s is the number of moles of solvent used in preparing the solution.

The association of these acids is too great to permit direct extrapolation of the observed shifts to infinite dilution to obtain the monomer shift δ_M, and at the higher concentrations the presence of polymers greater than the dimer may interfere with selecting a δ_D. However, using previously reported heats of dimerization and equilibrium constants from dielectric constant, cryoscopic, infra-red, and distribution studies m/a and (a-m)/a could be calculated by means of the relation above. Then using the observed shifts and the calculated monomer and dimer weightings, δ_M and δ_D were calculated for every pair of solutions at a given temperature with the first equation above. The results for benzoic acid in benzene are shown in the Figure. Similar behavior was observed for acetic acid. Shifts were calculated for formic acid only at 30°C. since there were no heats of dimerization available.

A striking variation of the monomer shifts from very high fields at 30°C. to about 450 cps at higher temperatures results. Although large errors result in the calculations because of the small amounts of monomer present, it is difficult to ascribe the trend to errors of this sort which should be random. It is suggested that association of the monomer acid with the benzene solvent at the lower temperatures may be the cause of these shifts. Orientation of the carboxyl proton in the face of one or two benzene molecules would produce such a high shielding. Calculations using Johnson and Bovey's tables[3] indicate that a proton along the symmetry axis of the benzene molecule must be within 1.6 Å of the face of the ring to experience the observed shift of ca. 450 cps between the high and low temperature values.

The calculated dimer shifts at 30°C. are -333, -348, and -425 cps to lower field than benzene for formic, acetic, and benzoic acids respectively. This is also the order of increasing hydrogen bond strength.

In the case of formic and acetic acids, the dimer shifts were some 100 cps to lower field than observed for the pure liquid acids. This was also observed by Reeves and Schneider[4] for acetic acid in various solvents. It is suggested that although infra-red frequency shifts indicate considerably stronger hydrogen bonds in the higher polymers (particularly in the crystalline solids) the slight trend of the nmr shifts back toward higher fields may be caused by factors other than a simple electrostatic distortion of the hydrogen electron. In particular, the distance between hydrogen-bonded oxygen atoms may have decreased in the higher polymers to the extent that the unbonded oxygen electrons may contribute measureably to a diamagnetic shielding of the proton. The short O-O distances reported for the crystalline solid acids[5] indicate a much more symmetrical hydrogen bond than in the dimer.

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(2) J. Phys. Chem., 60, 1311 (1956).
(3) J. Chem. Phys., 29, 1012 (1958).
(4) Trans. Faraday Soc., 54, 314 (1958); ibid, 55, 1684 (1959).
(5) Acta Cryst., 11, 484 (1958).
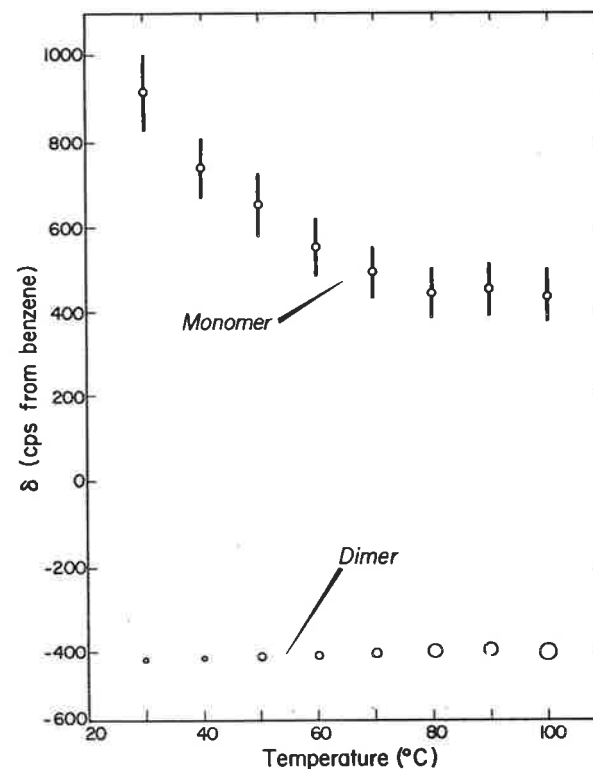
A CORRELATION OF PROTON SHIFTS IN SUBSTITUTED ETHYLENES

WITH GROUP DIPOLE MOMENTS

G.S.Reddy, J.H.Goldstein and Leon Mandell

Mayer and Gutowsky[1] showed that the shielding of the proton
decreases as the number of halogen atoms on the proton-bearing
carbon atom is increased. Also, Bothner-By and Naar-Colin[2]
obtained a linear relation between the shielding of the α-protons
and the dipole moment of the molecule in a series of haloalkanes.
It is expected that a similar relation exists between the proton
shifts and the group dipole moment of the substituent group X in
the series $H_2C = CHX$. We have studied the compounds with X as H,
CH_3, Cl, $C \equiv N$, OCH_3 and C_6H_5. The proton magnetic resonance shifts
in vinyl chloride, vinyl cyanide and methyl vinyl ether[3] were
obtained from their complete analysis in these laboratories; the
others were taken from published data[4]. In the case of vinyl
cyanide and styrene corrections due to diamagnetic anisotropy of
nitrile and phenyl groups on all the protons in these molecules
were estimated. The circles in the graph represent the plot of
the cis proton shifts vs group moments of the group X. The squares
represent that of trans proton shifts. The solid circles and squares
in the case of vinyl cyanide and styrene are the shifts uncorrected
for diamagnetic anisotropy. It is interesting to note that the
shifts of both cis and trans protons in these two compounds lie
on the straight line only after making the necessary corrections
due to diamagnetic anisotropy. The shifts of the β-protons in
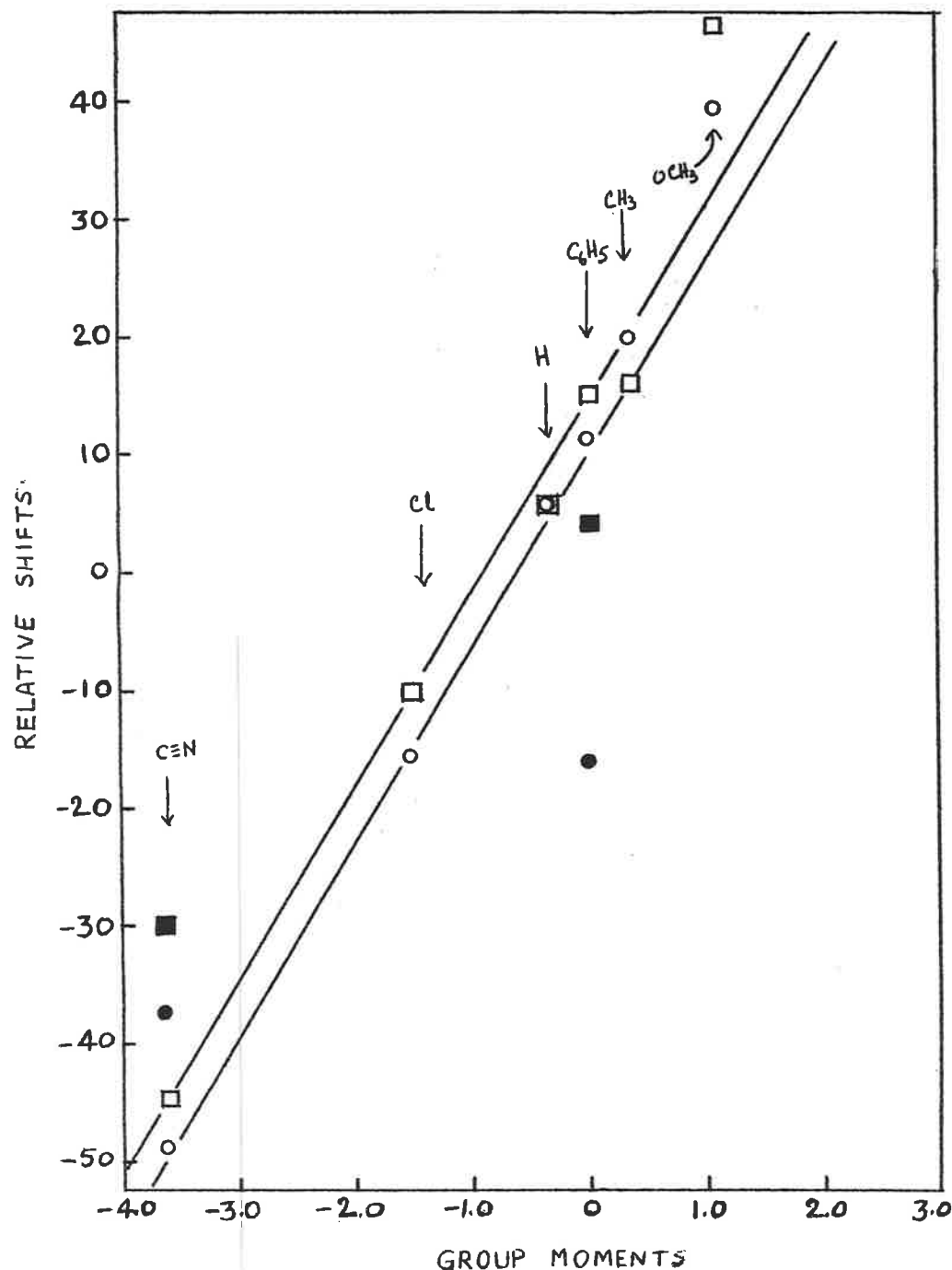methyl vinyl ether are not certain and further work is being

done on the analysis and it is hoped that there will be better
agreement after getting correct values for the shifts in this
compound.

From the graph it is evident that in all the compounds
except propene, cis proton is at lower field than trans proton
to the same extent within experimental error. This suggests
that it is worthwhile checking the assignments in propene made
by previous workers[5].

Details of the analysis, shifts, coupling constants and
anisotropy corrections in all these compounds will be given
in a paper to be published shortly. No attempt has been made
to correlate α-proton shifts since, besides anisotropy, other
effects will be large and difficult to evaluate. Further work
is being done for similar correlations between Hammett's σ-constants
and other group properties in related systems.

References:
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1. L.H.Mayer and H.S.Gutowsky, J.C.P., 57, 481 (1953).

2. A.A.Bothner-By and C.Naar-Colin, J.A.C.S., 80, 1728 (1958).

3. Work is in progress by present authors.

4,5. J.A.Pople, W.G.Schneider and J.H.Bernstein,

   High Resolution Nuclear Magnetic Resonance, McGraw-Hill
   Book Company Inc., New York, N.Y.,1959.

Graph labels: RELATIVE SHIFTS (y-axis), GROUP MOMENTS (x-axis)

Axis values: 40, 30, 20, 10, 0, -10, -20, -30, -40, -50 (y-axis); -4.0, -3.0, -2.0, -1.0, 0, 1.0, 2.0, 3.0 (x-axis)

Data point labels: OCH₃, CH₃, C₆H₅, H, Cl, C≡N

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30th May, 1960.

Dear Barry,

Here at last is my "subscription" to your excellent news letter. I still believe that M.E.L.L.O.N.M.R. is making a very important contribution to the development of our subject and I hope you can continue to obtain contributions to it.

We have now begun to apply to proton spectroscopy the technique of double resonance using a method which Dr. D.W. Turner of our department has developed. The significant feature of his work is the development of rather simple apparatus with which proton-proton spin decoupling can be carried out. This allows spin-spin interaction to be suppressed without introducing spurious resonances from the decoupling radiation, indeed the spectrum obtained can be made to look just like the ordinary spectrum with the exception of the simplification of some multiplet structures.

The effectiveness of double irradiation in aiding assignments in simple proton spectra has of course already been demonstrated by Anderson using separate r.f. generators but the difficulty of constructing and operating two separate transmitters to the required stability in frequency difference did not attract us and we have chosen to generate the decoupling frequency by modulation of that used for observing resonance - the sideband method. To simplify interpretation we required a single sideband only and we have used accordingly a single-sideband suppressed-carrier modulator; this, followed by a linear amplifier, allows the production of a sideband at a much higher power level than the carrier or unwanted sideband. The carrier level at 40-50 dB below the sideband is weak enough to avoid saturation whilst the sideband is strong enough to irradiate effectively a proton resonating within about 10 c/s of it.

The system has the principal advantage that an r.f. phase-sensitive receiver is readily locked on to the carrier before modulation and if an r.f. phase sensitive detector is already used, no modification is required beyond increasing the output filter time constant to remove the strong audio signal at modulation frequency (usually 10-500 c/s). Our modulator is used with the Varian Associates N.M.R. Spectrometer equipped with 56.4 Mc/s Transmitter Receiver and is inserted between the transmitter outlet and the probe. An internal connection already supplies the required r.f. phase.

The block diagram (Fig. 1) summarises the modulation system used. The audio source was a Solartron two-phase audio oscillator. The system is set up by adjustment of the r.f. phase shift units and modulation amplitude controls until a satisfactory rejection of the carrier and unwanted sideband (and harmonies) is obtained. This is carried

out using a single line resonance (water) and diode detector
to show the relative strengths of carrier and sidebands.
The high, or low frequency sideband is then selected at will
by operation of the reversing switch S.   The construction
and adjustment of this equipment will be published in detail
shortly.

A quickly recognisable example of its application is
provided by the ethanol spectrum (Fig. 2) recorded three times
with the decoupling signal having the frequencies (relative
to the carrier) shown.   Here the splitting of the methyl protons
by the methylene and the methylene by the methyl are suppressed
in turn.   Both are suppressed in the same spectrum if modulation
by a single phase oscillator is employed for both upper and
lower sidebands are then generated at once.

A more advanced example is provided by the case of N-methyl
pyrridone (kindly supplied by Dr. J.E. Elvidge).   The spectrum
of the ring protons consists of a triplet at $\tau = 3.85$ (H_6) and
a doublet $\tau = 3.43$ (H_3) both of which show further fine
structure due to long range coupling with other protons.   The
remaining ring protons H_4 and H_5 give rise to a band of complex
structure at $\tau = 2.70$

The spectra in Fig. 3 show in turn the decrease in multi-
plicity which arises when:

1) H_5 is decoupled by irradiation of H_4 and H_6
2) H_3 "   "   "   "   " H_4 " H_5
3) H_4 "   "   "   "   " H_3
4) H_4 and H_6 are decoupled by irradiation of H_5

In 1) and 2) the multiplicity is reduced to a singlet
(apart from residual long range splitting)   In the other two
cases the low field band due to H_4 and H_6 is simplified to two
different ABX systems respectively.

We have already solved several structural problems with
this method and we believe that one of its principal uses,
other than simplification of spin multiplets, is that it some-
times permits the location of resonances which are submerged
in regions of complex absorption.   Chemical shifts between
spin-coupled nuclei can also be accurately measured.

I am sending you a number of reprints under separate cover.

With best wishes,

Yours sincerely,

Lloyd M. Jackman.

Dr. Barry Shapiro,
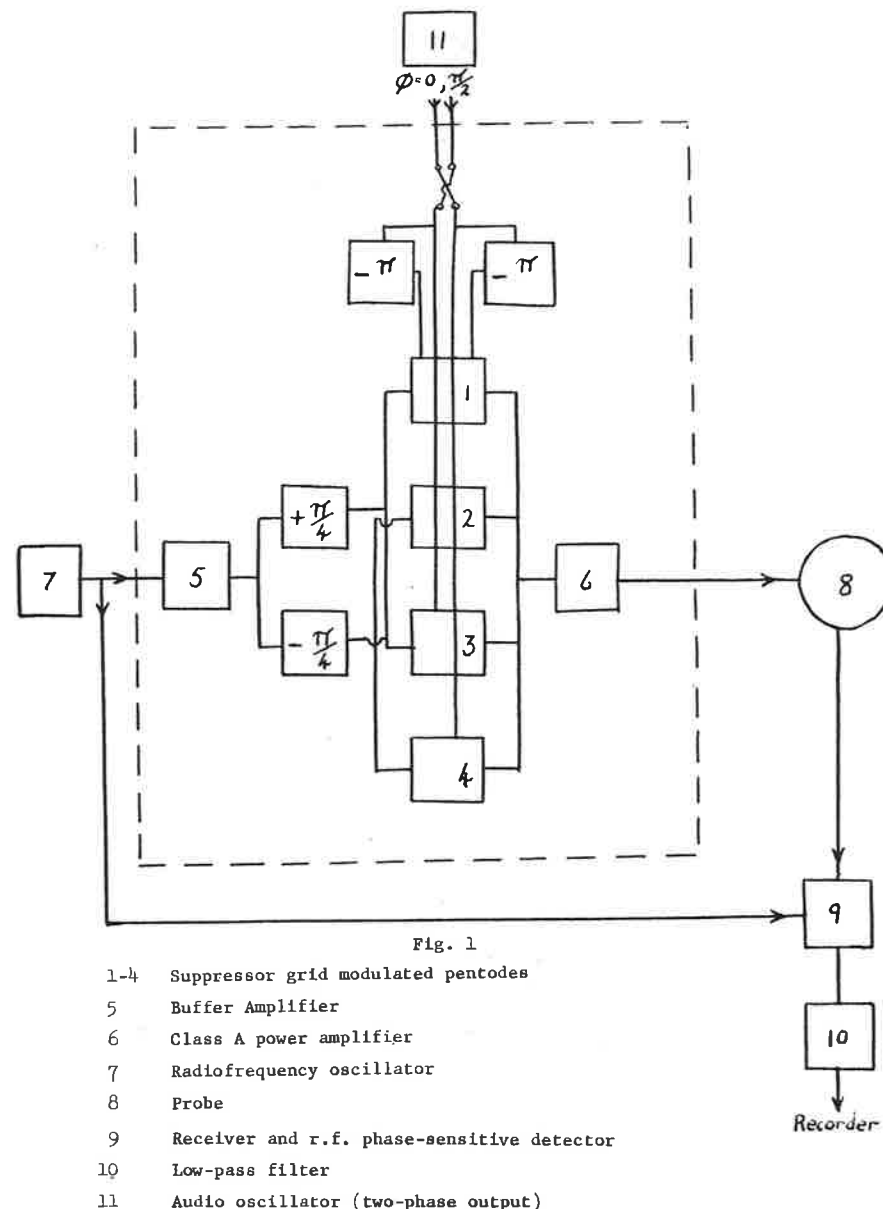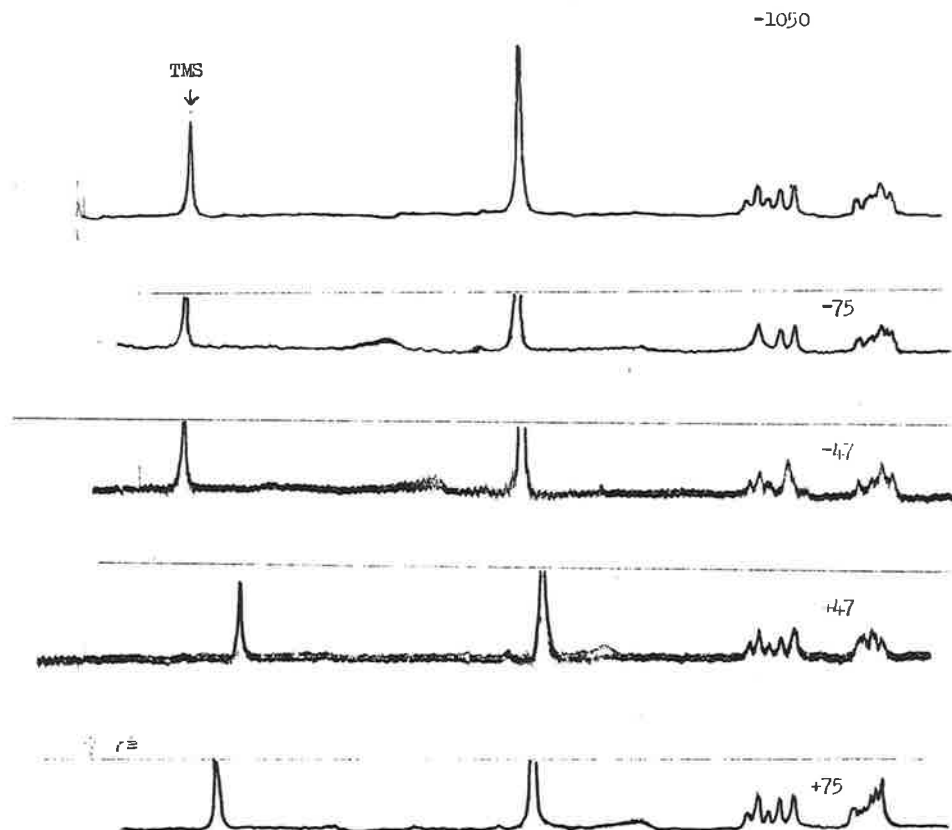Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pa.,
U.S.A.

Fig. 1

1-4	Suppressor grid modulated pentodes
5	Buffer Amplifier
6	Class A power amplifier
7	Radiofrequency oscillator
8	Probe
9	Receiver and r.f. phase-sensitive detector
10	Low-pass filter
11	Audio oscillator (two-phase output)

Fig. 2

Sample Ethanol,   decoupling radiation at:-

+ 1000 c/s

+ 137 c/s

- 137 c/s

Fig. 3.

N-Methyl pyridone
Decoupling frequency (c/s)

-1050

TMS

-75

-47

+47

+75

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