Monthly
  Ecumenical
    Letters from
      Laboratories
        Of
          N-M-R

        No. 8

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

April 27, 1959

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

Dear Aksel:

Herewith are drawings of the magnet cooling-water system designed for us by Mr. S. Shaner of our Physical Plant Department for the use of anyone who might be interested in them.

Briefly stated, our problem was that we have the NMR equipment located on the third floor of a building which has extremely poor regulation of water pressure, particularly in the summertime. On many occasions, operation of the 60 Mc equipment was almost impossible, because of poor heat dissipation. Also, we had occasional pressure drops so large as to cause the Pressurtrol to shut off the magnetic power supply. Added to this, the Pasadena water is normally calcium carbonate saturated which has led to substantial trouble with deposits on the cooling coils.

These difficulties argued for a closed-circuit water-cooling system which might in some localities be serviced by tap water passing through a heat exchanger. However, it is illegal in California to use drinking water for cooling in excess of 5 gallons per minute so that we were forced to either a refrigerative or evaporative cooling scheme to avoid undue water consumption. We chose an evaporative system since it seemed quite clear that refrigeration would be too expensive if sufficient capacity were installed to get through our hottest summer days.

The system design is based on the following method of operation. Heat absorbed by the cooling water in the closed-circuit system is transferred by means of the heat exchanger to an open-circuit system and disposed of in a forced-draft cooling tower. The cooling tower cools the magnet water to a low enough temperature to permit mixing with a stream of hot water so as to obtain a constant temperature supply entering the magnet.

The mixing occurs in two stages; first, through the water blender (item 8 of the enclosed drawing) which discharges water at 82-84° F; second, the control valve (item 2) introduces any necessary additional hot water to raise the final temperature to a set value (± 0.5° F) between 85 and 90° F. A 6 KW immersion heater introduces a constant reliable amount of heat into the system for mixing purposes.

The system (for which a parts list will be supplied for anyone interested)

Dr. Aksel A. Bothner-By   -2-   April 27, 1959

is made of standard commercially available and very rugged control devices suitable for continuous operation. Water is currently supplied to the magnet at 80 psi and 85 ± 0.5° F. The system has been running for about a month now with no maintenance required except for occasional checks on the water level in the expansion tank and servicing of the filter mounted on the magnet.

With the aid of this apparatus, we have diminished the degree of drift in our magnetic field by several orders of magnitude and usually the only adjustment required from day to day for good resolution is a slight manipulation of the field trimmer.

I am not really sure as to whether this degree of water temperature regulation is really required. However, now that we have it, we like it very much and it has certainly solved our biggest operating problem to date.
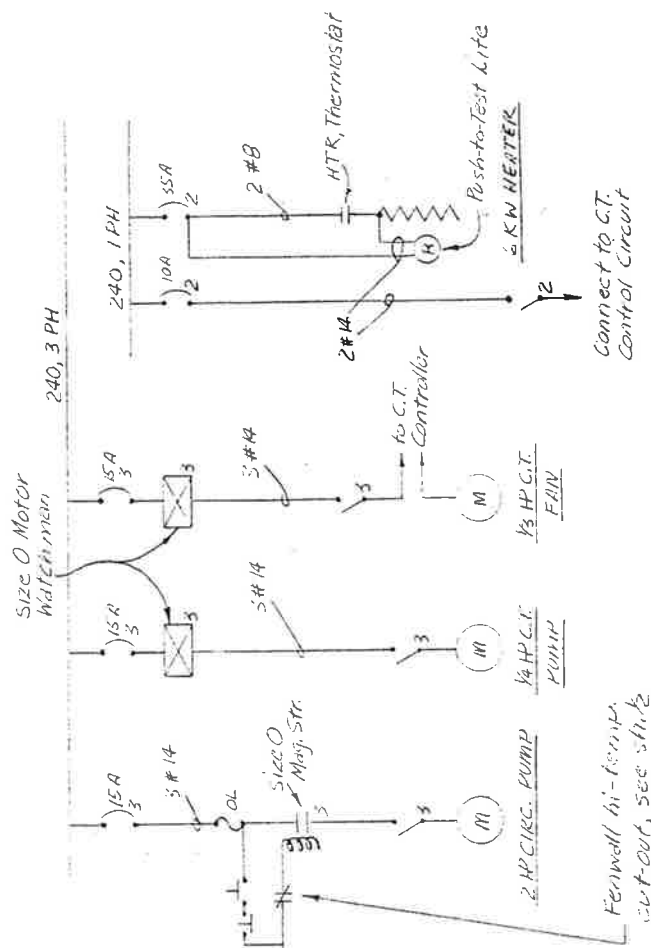
With all good wishes.

Very truly yours,

Jack

John D. Roberts

JDR/eh
encs.

CALIFORNIA INSTITUTE OF TECHNOLOGY
PHYSICAL PLANT DEPT.

SERIAL NO. 689   SH. 2/2
DATE Jan. 13, 1959

240, 1 PH
240, 3 PH

5A / 2
10A / 2

2 #8
2 #14

HTR, Thermostat
Push-to-Test Lite
2 KW HEATER

Connect to C.T. Control Circuit

Size 0 Motor Watchman

15A / 3
3 #14

to C.T. Controller

1/3 HP C.T. FAN (M)
1/4 HP C.T. Pump (M)
2 HP CIRC. PUMP (M)

Size 0 Mag. Str.
OL

Fenwall hi-temp cut-out, see sh. 1/2

C.T. = Cooling tower

JOB TITLE ____ MAGNET COOLING SYSTEM = ELECTRICAL ____
FOR (DEPT.) CHEMISTRY ____ AT (BLDG.) CHURCH LAB ____ RM. NO. 301
ENG W/O ____ JOB W/O 4333 ____ APPROVED E.64
DRAWN H. BAKER   CHECKED S. SHANER   2.

CALIFORNIA INSTITUTE OF TECHNOLOGY
PHYSICAL PLANT DEPT.

SERIAL NO. 689   SH. 1/2
DATE Jan 13, 1959

1. Cooling Tower
2. M & H Control Valve
3. M & H Graduated Relay
4. M & H Immersion Thermostat
5. Heat Exchanger
6. Pump, Cooling Tower
7. Pump, Recirculating (Worthington Regenerative)
8. Sarco MB-DS Blender
9. Fisher Reg & Filter 67FR-TC
10. Fisher Back Press Reg. DR
11. 6 KW Immersion Heater In 3" Brass Pipe
12. Expansion tank - Brass pipe 5"D x 4 ft. lg. with sight gage suitable for 100 psi w.p.
13. Mixing Chamber - see detail
14. 3/4" Bronze bodied relief valve set press 100 psi w.p.

Xa - open to fill system, close for normal operation
Xb - close to fill system, open for normal operation
Xc - open to fill system, close for normal operation
isolating union

with no. 30 hole drilled into wedge or equal
Gauge Cocks
to waste
3/4" GW Fill Line

Detail of 13 Mixing Chamber
4" Brass Pipe
1/4" FPT SPUDS
in →   ← out

Hose Bibb at Low Pt. to Drain System

Note: All piping to be type L copper water tube except cooling tower spray water which should be G.I.

$PI_{1,2}$ 0-160 psi
$PI_{3,4,5}$ 0-30 psi
PI_{3} 0-15 psi
T_F - Fenwall thermostat 17100 set for 110°F to open on temp rise
$TI_{1,2,3,4}$ 20-120°F
Ⓐ Air vent or equal, must not leak
Ⓣ - Immersion thermostat

JOB TITLE ____ MAGNET COOLING SYSTEM = MECHANICAL ____
FOR (DEPT.) CHEMISTRY ____ AT (BLDG.) CHURCH LAB ____ RM. NO. 301
ENG W/O ____ JOB W/O 4333 ____ APPROVED E.64
DRAWN S. Shaner   CHECKED
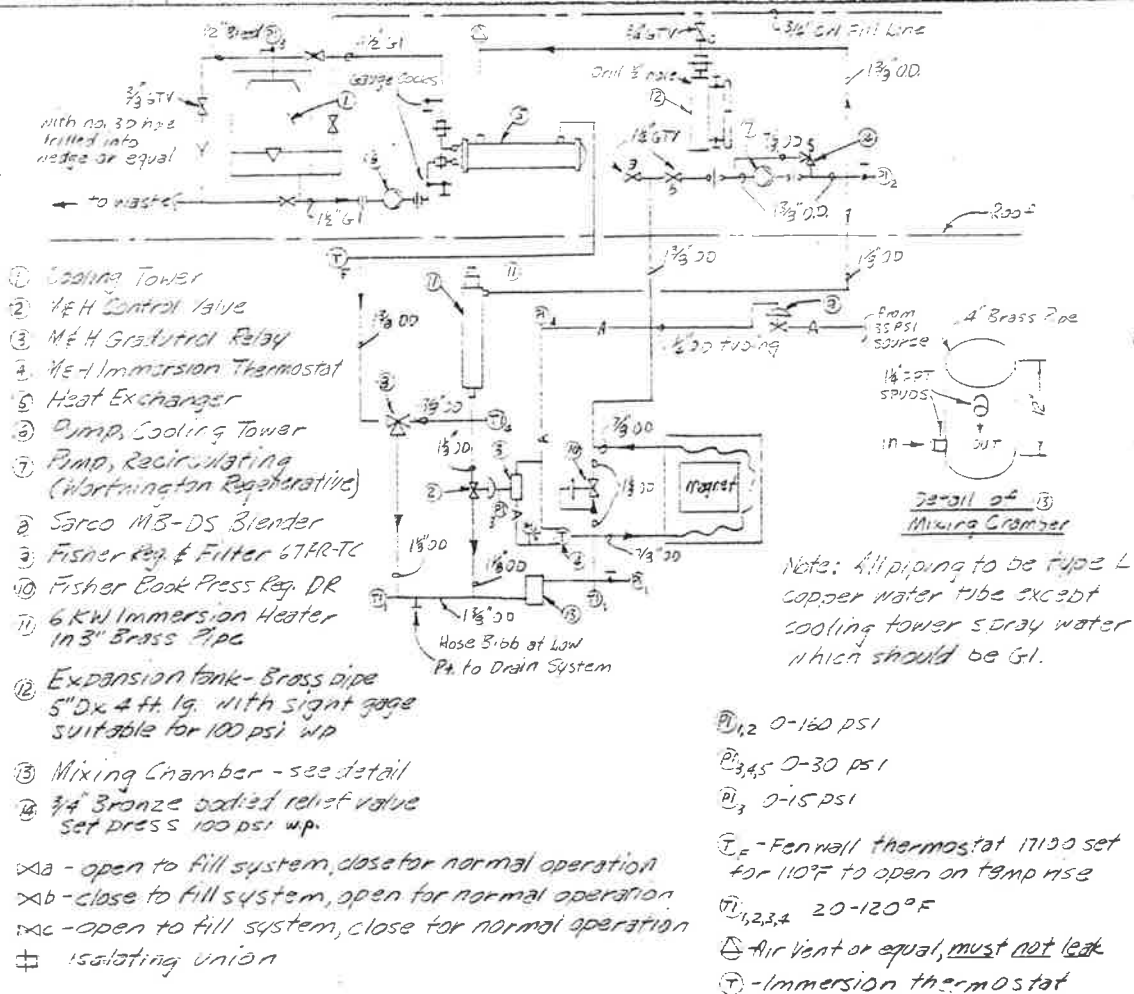
ANGULAR DEPENDENCE OF ELECTRON-COUPLED PROTON INTERACTIONS IN CH$_2$ GROUPS[+]

H. S. Gutowsky, Martin Karplus and D. M. Grant[/]

Noyes Chemical Laboratory, University of Illinois

Urbana, Illinois

Experimental and theoretical studies have been made of the dependence upon HCH angle of the electron coupled proton-proton interactions in CH$_2$ groups. A valence-bond approximation is used in the theoretical treatment which predicts that the coupling constant, A_{gem}^{HH}, decreases from 32 cps to 0 cps for HCH angles of 100° to 125°. For angles greater than 125°, A_{gem}^{HH} is predicted to be negative. Experimental values of A_{gem}^{HH} have been obtained from analyses of the proton magnetic resonance spectra of a number of compounds, including several partially deuterated species. Insofar as the HCH angles are known in these compounds, there is good agreement between the theoretical and experimental coupling constants, especially for angles smaller than 120°, for which A_{gem}^{HH} changes more rapidly with angle. Moreover, a negative value is found experimentally for A_{gem}^{HH} at an HCH angle, in vinyl bromide, which is approximately that at which the theory predicts the coupling to become negative. The substituted ethylenes constitute the largest group of compounds studied experimentally. In them, A_{gem}^{HH} has been found to vary from 3.2 cps to -1.8 cps, while the A_{cis}^{HH} values range from 6.9 cps to 12 cps and the A_{trans}^{HH} from 14.3 cps to 18.4 cps. The various results presented indicate that the value of the coupling constant can serve as a measure of the HCH angle. However, further work is needed to confirm the reliability of the method and investigate the effects of substituent perturbations.
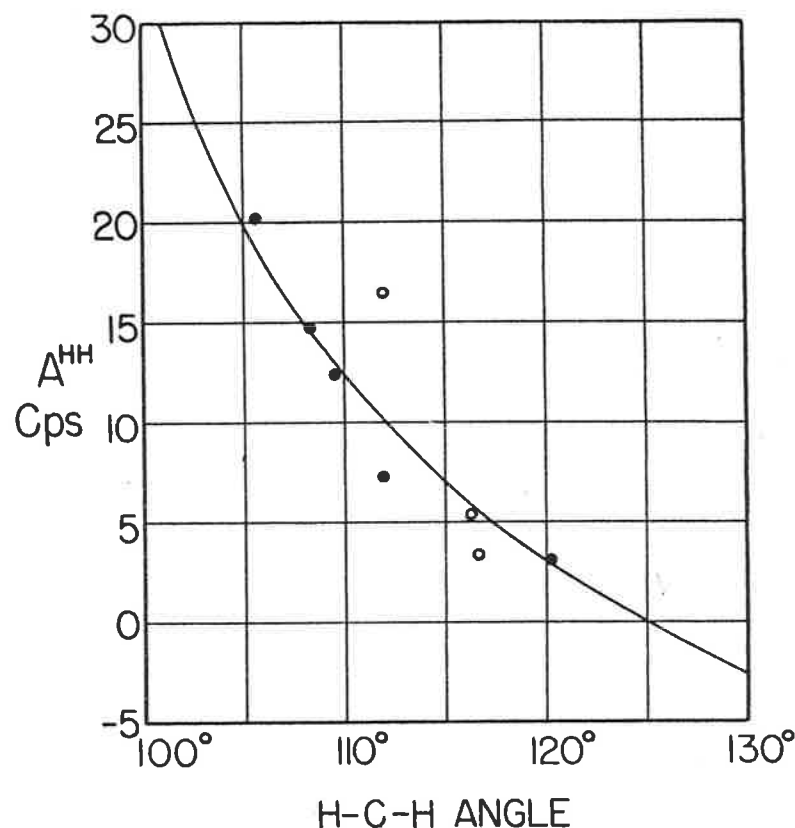

Fig. 10. A comparison of theoretical and experimental values of the H-H coupling constant as a function of the HCH angle. The line represents the results of the theoretical calculations and the points, the experimental data. The three open circles are cases in which the coupling constant was obtained from a substituted form of the compound for which the HCH bond angle was determined. The points, going from the upper left to the lower right, are for the following compounds: (1) malononitrile, (2) β-(p-nitrophenyl)-β-propiolactone, (3) acetone, (4) methane, (5) methylene chloride, (6) propylene oxide and styrene oxide, (7) N-methyl ethylenimine, and (8) vinyl fluoride.

Table III. Summary of H-H coupling constants and HCH bond angles determined experimentally. The bond angles listed for compounds 17 to 20, inclusive, were determined for the unsubstituted parent compound.

Compound	A_{gem}^{HH}	A_{cis}^{HH}	A_{trans}^{HH}	$\angle$ HCH
1. methylene chloride	7.1±0.2 cps	cps	cps	112.0[a] deg.
2. malononitrile	20.3±0.3			105.5[b]
3. acetone	14.9±0.3			108.5[c]
4. methane[10]	12.4±0.6			109.5
5. cyclopentene-3,5-dione	21.5±0.3			
6. trans-cinnamaldehyde			15.6	
7. trans-crotonaldehyde			16.2	
8. 2,3-dibromopropene-1[28]	2.1			
9. 2,3-dimethoxy butadiene	2.2			
10. α-methyl styrene	≲1.5			
11. benzal acetone (cis and trans)[27]		~12	~16.5	
12. methyl (cis and trans) β-cyanoacrylate[27]		11.5	15.0	
13. 3,3-dimethyl 1-butene[28]	1.4[d]	+10.8	+17.5	
14. phenyl vinyl ketone	2.1±0.1	10.8	18.4	
15. vinyl bromide	-1.8±0.1[d]	+6.9	+14.3	
16. vinyl fluoride[30]	(+?)3.2±0.1[d]			120.5[e]
17. styrene oxide[f]	+5.4±0.1[d]	+2.6	+4.0	116.3[g]
18. propylene oxide[f]	5.3±0.1	~9.6	~2.4	116.3[g]
19. β-(p-nitrophenyl)-β-propiolactone[f]	+16.6±0.2[d]	+4.9	+5.9	112[h]
20. N-methyl ethylenimine[12,f]	+3.4 or +2.0[d]	?	+2.0 or +3.4	116.7[i]

(Table III continued)

[a] R. J. Meyers and W. D. Gwinn, J. Chem. Phys. 20, 1420 (1952).

[b] N. Muller and D. E. Pritchard, J. Am. Chem. Soc. 80, 3483 (1953).

[c] J. D. Swalen and C. C. Costain, Symposium on Molecular Spectroscopy, Ohio State University (June, 1958). We thank Dr. Swalen for calling our attention to this value.

[d] Only relative signs of coupling constants were determined from the observed spectra; the absolute signs given were assigned on the basis of theoretical calculations which indicate that the larger H-H coupling constants in hydrocarbons are positive.

[e] B. Bak, D. Christenson, L. Hansen-Hygaard and J. Rastrup-Anderson, Spectrochimica Acta 13, 120 (1958).

[f] The HCH bond angle given is that for the unsubstituted parent compound.

[g] T. E. Turner and J. A. Howe, J. Chem. Phys. 24, 924 (1956); the bond angle given is for ethylene oxide.

[h] N. Kwak, J. H. Goldstein and J. W. Simmons, J. Chem. Phys. 25, 1203 (1956); the bond angle given is for β-propiolactone.

[i] T. E. Turner, V. C. Fiora and W. M. Kendrick, J. Chem. Phys. 23, 1966 (1955); the bond angle given is for ethylenimine.

NATIONAL RESEARCH COUNCIL

CANADA

DIVISION OF PURE CHEMISTRY

OTTAWA 2,

May 13, 1959

Dr. A.A. Bothner-By,
Mellon Institute,
4400 Fifth Avenue,
PITTSBURGH, Pa.,
U.S.A.

Dear Aksel:

I should like to put in some comments on the suggested attempts to dress-up the ordinary δ symbol discussed by Schoolery and Bothner-By, Lauterbur and Shapiro in MELLONMR No. 7.

My first comment is a general plea against loading down this useful symbol too heavily. I think we should remember that published papers in which NMR has been used in a particular investigation are apt to be read by quite a number of chemists and physicists who are not specialists in NMR. It is therefore important that the paper be readable and we should avoid putting our terminology in such a complex code that it is understood only by a comparatively few specialists. Perhaps such a code might be tidier but at the moment it would appear to require a rather complex symbol to satisfy all situations, assuming such a symbol could be agreed upon.

I would go along completely with Jim Shoolery's definition of δ and its sign convention. If this can be agreed upon it would in itself represent some progress. One would not object too strongly to an added subscript or superscript, provided these would always have a unique meaning and could be agreed upon. But this is where the difficulties arise. Actually this whole discussion is really only concerned with chemical shifts in different molecules or in different samples or solutions. When we refer to "internal" chemical shifts in the same molecule there is usually very little ambiguity and for this purpose the shifts between nuclei A and B can be referred to as δ_{AB} or $\delta_A - \delta_B$. In aromatic compounds it is

frequently also convenient to distinguish ortho, meta and para shifts viz: δ_o, δ_m and δ_p. Sometimes the nuclei in the chemical formula are numbered (and here I would endorse Shoolery's suggestion of a "picture" since we are not all organic chemists) and the shifts are identified as δ_1, δ_2, δ_3 etc. Sometimes too the species of nucleus is indicated by a subscript as δ_H, δ_F etc.

When we consider chemical shifts relative to arbitrary reference signals we immediately get into a number of difficulties. In the first place, if the above notation for "intramolecular" chemical shifts is maintained (and it is very useful) we have already used up the subscript, leaving us only a superscript to identify a host of possible conditions, namely

a) What is the reference?
b) Is it internal or external?
c) If external, was it corrected for bulk susceptibility?
d) Is the shift for the pure compound or has it been extrapolated to infinite dilution?

This is a tall order for one little superscript! Putting the chemical formula of the reference in the form of a superscript appears rather clumsy. $\delta^{int.}$ might be confused with "internal" or intramolecular chemical shifts. If $\delta^{ext.}$ is used it still leaves (c) and (d) above unanswered.

While this may sound somewhat discouraging I believe some progress can be made. I think there is some merit in considering a second symbol, as suggested by Shoolery and by Bothner-By et al. One symbol could be used for the primary measured data and another for corrected data. This second symbol could be designed so as to answer questions (c) and (d) above, leaving (a) and (b) to be designated by the first symbol in some suitable manner. This is still not entirely satisfactory, but in any case it is difficult to see how one symbol alone can be used to designate everything that is contemplated.

There may be some advantage to using frequency units for the primary measured data, since this is simply recognizing the laboratory scale. (The comparison with infra-red practice may not be pertinent since in NMR the frequencies are relative only). I think the question of defining a standard state would be difficult and perhaps premature. It is becoming increasingly apparent that solvent effects are rather large, and as suggested by Bothner-By, Lauterbur and Shapiro, the ideal would be the gas state. One could define as a standard environment infinite dilution in CCl_4, but not all substances are soluble therein. Whether or not a suitable correction factor can be arrived at to convert all measurements to such a standard state remains to be seen.

Sincerely yours,

W. G. Schneider

at

May 20, 1959

Dr. Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry:

Here, just under the wire, is my contribution for
MELLONMR. I hope it is what you want, as I should like to
continue my subscription. True, "practical" applications--
i.e., structure determination, seem to have got short shrift,
but it is still very interesting.

These spectra were run to accumulate some information
about the position of strongly intramolecularly hydrogen-
bonded hydroxyl and as part of a series of oxygen heterocycles
of similar type. The shifts which may be achieved by this
type of hydrogen bonding are impressive. The τ values were
determined by measuring the spacing of a 200 cps beat and
assuming linear sweep behavior; so they may be in error by
as much as 2 or 3%.
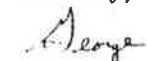
I have not tried to untangle the complex of lines
which are the aryl hydrogens except when the interpretation
appears obvious. In general, though, in those cases in which
the aryl hydrogen peaks are split into two groups, I feel
that this represents the differentiation between the hydrogens
on the electron-poor carbons ortho and para to the carbonyl
(low field) and those on the comparatively electron-rich carbons
ortho and para to the hydroxyl(s). It is true that the hydro-
gens ortho to the carbonyl group are probably lower than those
para, but there does appear to be a transmitted, conjugative
effect as well as a local, inductive one. Incidentally, I
suspect that some of the shift of the hydrogens ortho to a
carbonyl may be due to hydrogen bonding as (i) shows a good
doublet at $\tau = -0.09$, which can reasonably be attributed only
to the hydrogen peri to the carbonyl.

(I)

If this is the sort of material you want, let me know
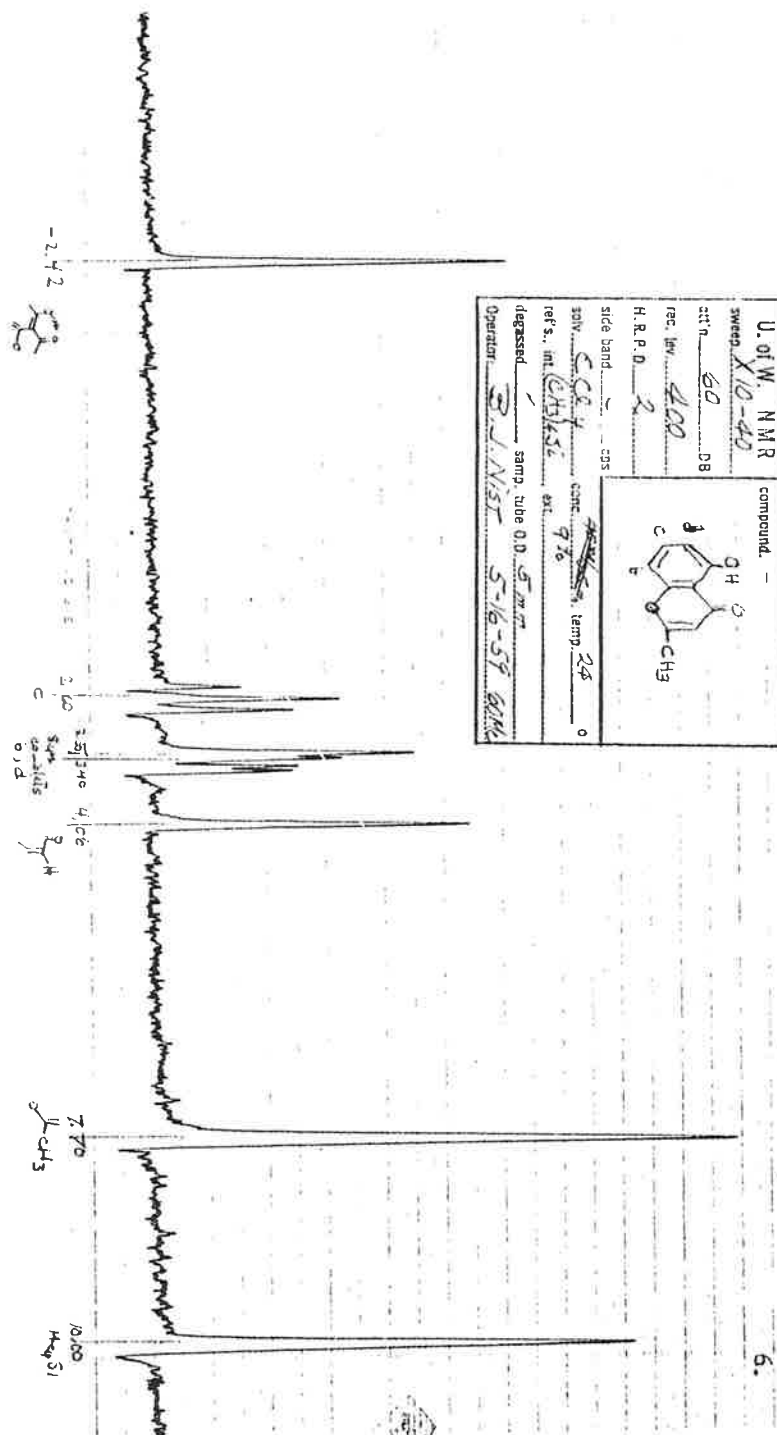and I'll send some more, particularly of mixed oxygen heterocycles.

Best regards to yourself and Aksel. Any chance of
your being out here for the Organic Divisional Meeting?
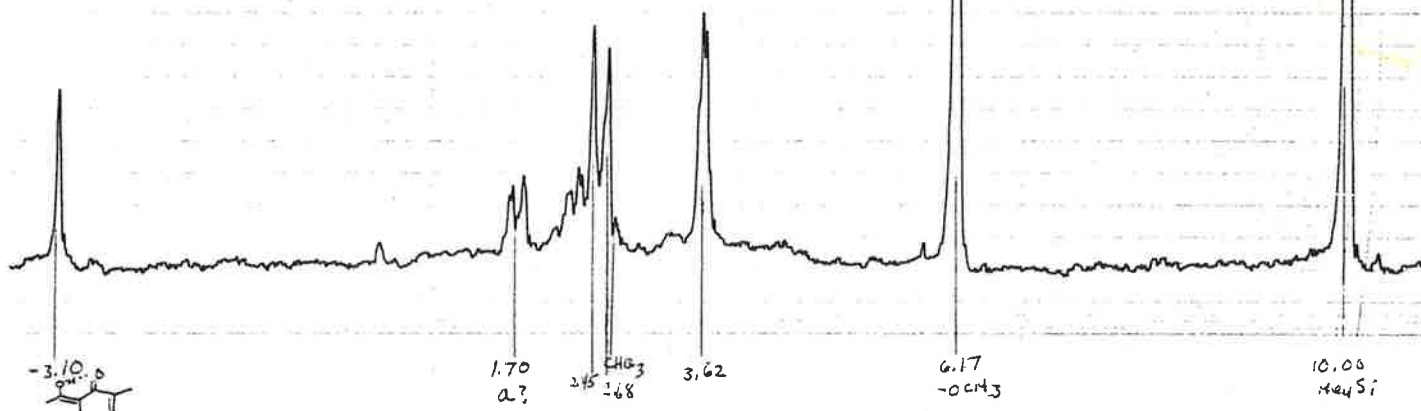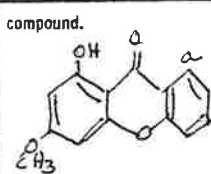
Sincerely,
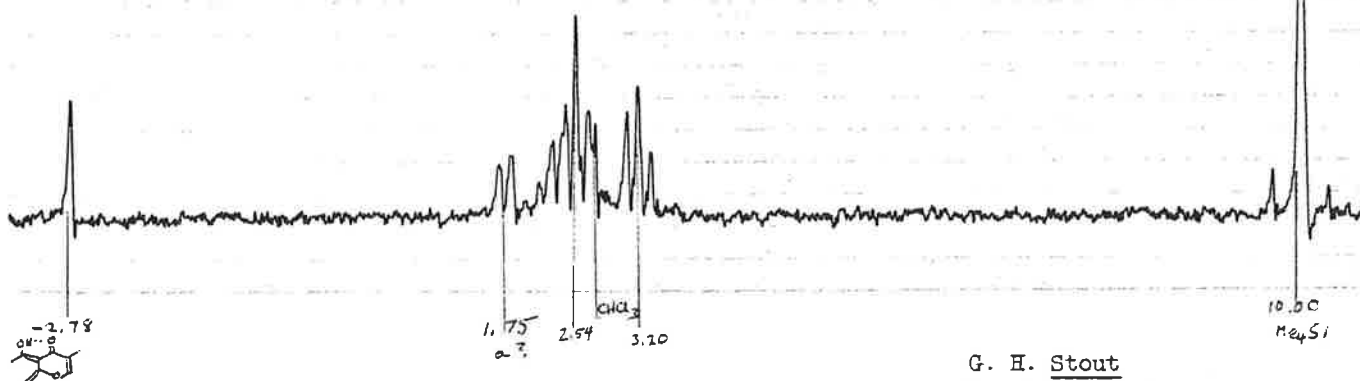
George
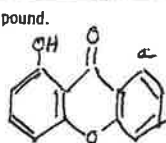
George H. Stout
Assistant Professor

aj

-3.10.0

1.70
a?

2.45 CHG3
      1.68

3.62

6.17
-OCH3

10.00
Me4Si

-2.78

1.75
a?

2.54

CHCl3

3.20

10.00
Me4Si

G. H. Stout
U. of Washington

Top spectrum label box:

U. of W. N M R   compound.

sweep. X10-40

att'n. 60 DB

rec. lev. 400

H.R.P.D. 2

side band 0 cps

solv. CCl₄   conc. /10 %, temp. 24 °

ref's., int. (CH₃)₄Si   ext.

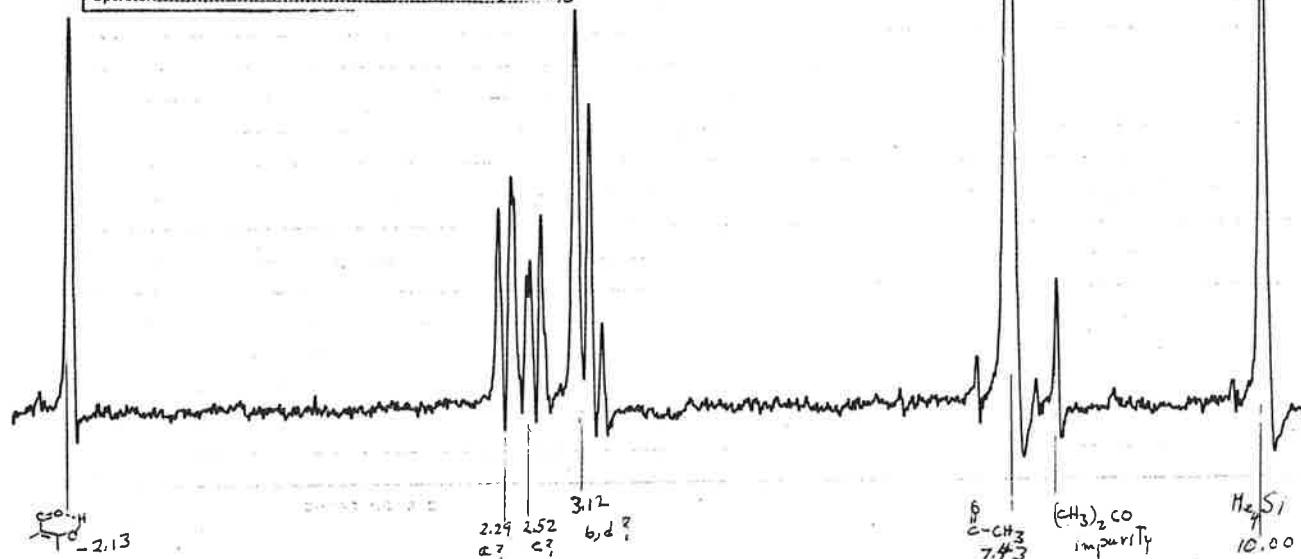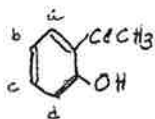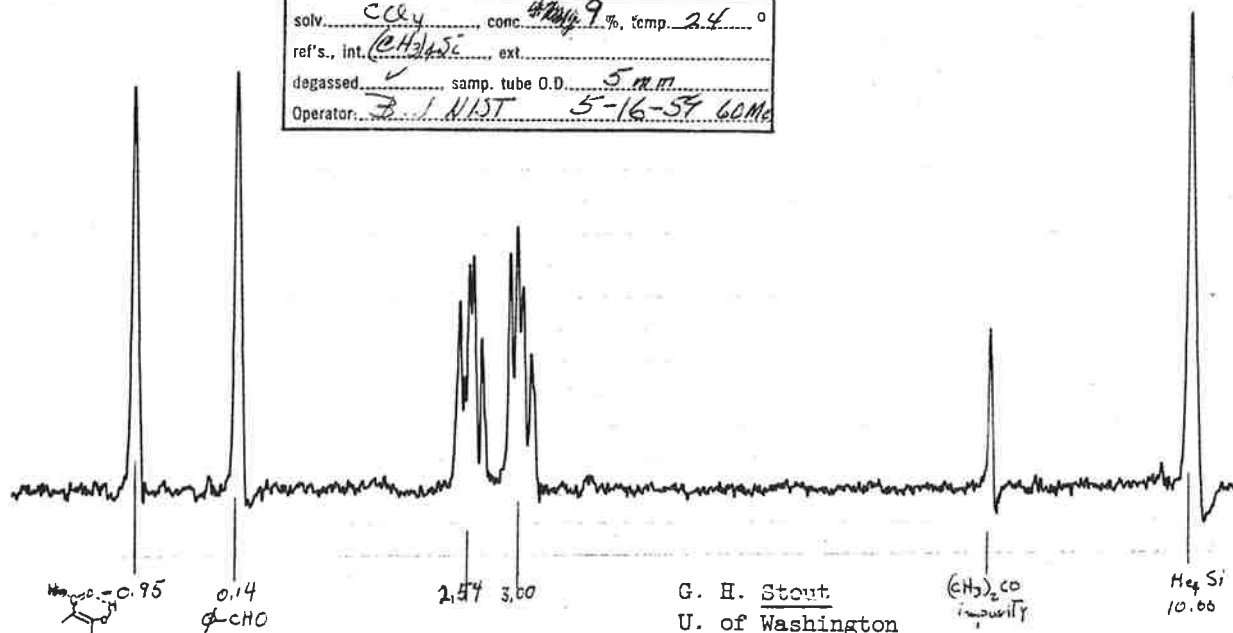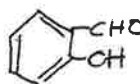degassed ✓   samp. tube O.D. 5 mm

Operator: B. J. NIST 5-16-59 60Hc

Peak labels (top):
-2.13 ... 2.29 a? ... 2.52 c? ... 3.12 b,d? ... 7.43 b c-CH₃ ... (CH₃)₂CO impurity ... Me₄Si 10.00

Bottom spectrum label box:

U. of W. N M R   compound.
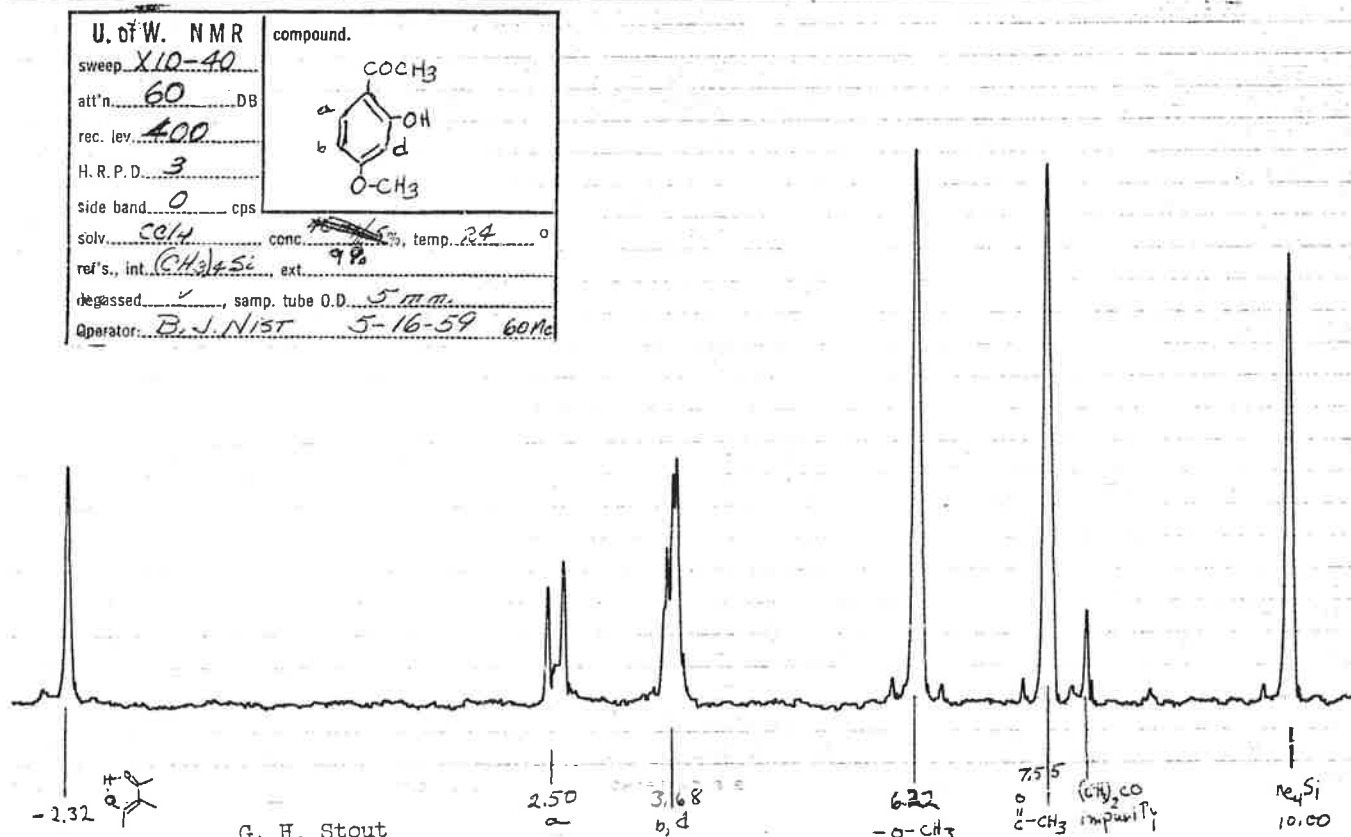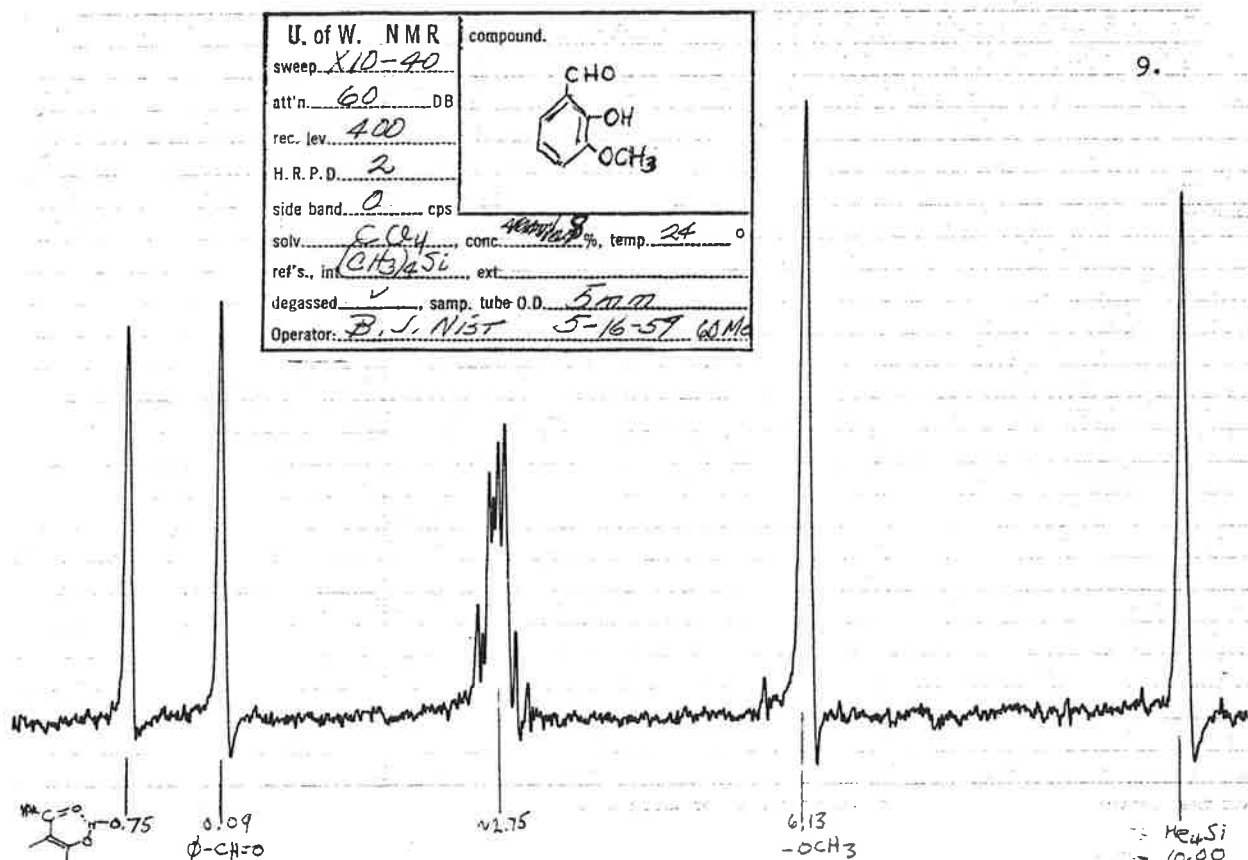
sweep. X10-40

att'n. 60 DB

rec. lev. 400

H.R.P.D. 2

side band 0 cps

solv. CCl₄   conc. 9 %, temp. 24 °

ref's., int. (CH₃)₄Si   ext.

degassed ✓   samp. tube O.D. 5 mm

Operator: B. J. NIST 5-16-59 60Hc

Peak labels (bottom):
-0.95 ... 0.14 φ-CHO ... 2.54 ... 3.00 ... (CH₃)₂CO impurity ... Me₄Si 10.00

G. H. Stout
U. of Washington

U. of W.   N M R   compound.
sweep X10-40
att'n. 60 DB
rec. lev. 400
H.R.P.D. 2
side band 0 cps
solv. CCl4   conc. 40mg/0.4ml 8 %, temp. 24 °
ref's., int. (CH3)4Si   ext.
degassed ✓, samp. tube O.D. 5mm
Operator: B. J. Nist   5-16-59   60Mc

-0.75
0.09
φ-CH=O
~2.75
6.13
-OCH3
Me4Si
10.00

U. of W.   N M R   compound.
sweep X10-40
att'n. 60 DB
rec. lev. 400
H.R.P.D. 3
side band 0 cps
solv. CCl4   conc. 15 %, temp. 24 °
                    9 %
ref's., int. (CH3)4Si   ext.
degassed ✓, samp. tube O.D. 5 mm.
Operator: B. J. Nist   5-16-59   60Mc

-2.32
2.50
a
3.68
b, d
6.22
-o-CH3
7.55
O
‖
C-CH3
(CH3)2CO
impurity
Me4Si
10.00

G. H. Stout
U. of Washington

AMERICAN SOCIETY FOR TESTING MATERIALS

COMMITTEE E-13 ON ABSORPTION SPECTROSCOPY

CHAIRMAN: E. J. ROSENBAUM, SUN OIL CO., MARCUS HOOK, PA.
VICE-CHAIRMAN: L. E. KUENTZEL, WYANDOTTE CHEMICALS CORP., WYANDOTTE, MICH.
SECRETARY: R. F. ROBEY, ESSO RESEARCH AND ENGINEERING CO.,
CHEMICALS RESEARCH DIV., BOX 51, LINDEN, N. J.

Address reply to:

Mr. N. F. Chamberlain
Research and Development Division
Humble Oil & Refining Company
Baytown, Texas

May 21, 1959

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

Dear Aksel:

The thoughtful discussion of nomenclature and referencing procedures which have appeared in MELLONMR will be very helpful to the NMR Subcommittee of ASTM Committee E-13 in formulating standards which will be widely accepted within the shortest time. The need for such standardization is recognized internationally, and we have the unusual opportunity of achieving international agreement on important items in the early stages of the development of NMR. I hope that many more workers in this field will express considered opinions soon.

One thing that must be decided early in the process of setting up nomenclature is just what information the symbols should convey. The variables involved in determining resonance displacements are the nature and concentration of compounds in the sample and in the reference, referencing technique, temperature, operating frequency, isotope observed, and scale units used. It is also desirable to differentiate between displacements of individual peaks and displacements of bands (chemical shifts). It seems unlikely that a single symbol of manageable size can be devised to define all these variables, but it is possible to devise symbols which explicitly define some variables while implicitly specifying values of other variables by definition.

Some displacement symbols which have been proposed and the information they convey are listed below.

Symbol	Information Given by Symbol
$\delta^{int.}_{C_6\bar{H}_6}$ or $\delta^{ext.}_{C_6^{\overline{13}}H_6}$	Referencing method (internal or external). Resonance used to determine scale zero, indicated by bar. Scale, by definition. Parts per million, increasing in direction of increasing shielding. Displacement for bands (chemical shift), by definition. Isotope being studied, indicated by bar.
$\nu^{int.}_{C_6\bar{H}_6}$	Same as above except scale units are cps and displacement is for individual peaks.
$\tau = \delta^{int.}_{Si(C\bar{H}_3)_4} + 10.00$	Same as above. Used to obtain positive displacement values when $SiMe_4$ is used to determine scale zero.
$\sigma = \tau$ when sample is run at < 5% concentration in CCl_4 at approx. 30°C. and $SiMe_4$ concentration is 1% or less.	Referencing method. Resonance determining scale zero. Scale Displacement for bands. Solvent and concentration. Reference compd. concentration. Temperature.

The first symbol, it seems to me, conveys the information one needs to determine whether one set of data is consistent with another set or whether conversion or major correction will be required. For conveying additional information I favor the use of additional statements or numbers following this basic symbol but not necessarily forming a part of it. The parenthetical number or letter following the symbol, with appropriate diagram (as suggested by Shoolery, MELLONMR 7), seems like a good way to designate individual resonance peaks or bands.

I believe that simplified symbols with the complex definitions, such as the last two shown above, are more satisfactory than the complex symbol system proposed by the Mellon group in MELLONMR 7. I also like the idea of defining a standard state such as infinite dilution in CCl_4, but we may have to collect much more information about solvent effects before a satisfactory standard state can be defined. Meanwhile, perhaps it would be good to use the Mellon suggestion of a superscript indicating the solvent to which the infinite dilution data refer. This would make the basic symbol

$$10 + \delta^{CCl_4}_{Si(C\bar{H}_3)_4} (a) \quad \text{for the displacement of resonance band "a" from}$$

($SiMe_4$ - 10) at infinite dilution in CCl_4, which can reduce to the special symbol $\sigma(a)$.

Sincerely,

N. F. Chamberlain

P.S. The monthly bibliographies are very convenient and helpful. Thanks.

NFC

Department of Chemistry,
Imperial College,
London, S.W.7.

22nd May, 1959.

Drs. A.A. Bothner-By and B.L. Shapiro,
Mellon Institute,
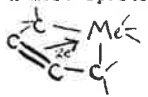4400 Fifth Avenue,
Pittsburgh 18, Pa.

Gentlemen:

We have noticed that the proton resonance spectra of organometallic compounds often cannot be interpreted on the basis of the normal correlation rules. The compounds we have been looking at contain olefine molecules bonded to metal atoms; each olefine group is usually regarded as donating two π-electrons to the metal atom to give the latter an effective inert gas configuration.

In some compounds, such as some ethylene derivatives of platinum, the resonances of the protons on the bonded olefine group appear in about the same region as those on simple olefines, but in others the "olefine"[1] proton resonances appear at higher fields by about 2-6 ppm. An example of this behaviour was found in the compound $(\pi\text{-}C_5H_5)(CO)_2Re$

in which the bonded olefine protons appear about 2 ppm. to a higher field than the non-bonded ones. Another example, shown in the attached diagram, is the norbornadiene derivative of iron tricarbonyl.

In compounds derived from conjugated olefines (cyclopentadiene,[2] cycloheptatriene and butadiene), only some of the "olefine" protons have moved upfield, although all the π-electrons seem to be involved in the bonding. The effect is seen best in the cyclopentadiene and butadiene derivatives, a few of whose spectra are shown. The multiplet structure of the bands can be interpreted to show that it is probably the terminal protons of the group which move upfield. Also, in the iron tricarbonyl derivative of 1:2:3:4-tetraphenyl-butadiene the two terminal protons again appear at a fairly high field (2.38 ppm. on the scale of the diagrams). In both types of compound the metal atom probably lies above the plane of the group, which causes the two protons of the $>CH_2$ group in the cyclopentadiene compounds to be non-equivalent. The two protons of each CH_2 group in the butadiene compound are also probably non-equivalent.

It is tempting to say that the n.m.r. spectra show that these compounds have a structure like this: with two metal-carbon bonds.

However, the infrared spectra don't agree with this. They show the presence of olefine-type C-H bonds but not the lines which would be expected for aliphatic-type C-H bonds at the terminal carbon atoms. The infrared correlations are fairly well established and it seems that the four carbon atoms in the conjugated group are sp^2 hybridised. In contrast to simple olefine molecules the carbon π electrons in olefine-metal complexes are involved in bonding to the metal atom. Work in progress by Dr. L.M. Jackman indicates that the magnetic anisotropy arising from the π electrons produces a paramagnetic contribution to the shift of normal olefine protons, and if this contribution were decreased by bonding to the metal, these proton resonances would appear at higher fields. (A similar effect could explain shifts to higher fields of protons on an aromatic ring when the ring is bonded to metal atoms in sandwich-type structures.)

The separation of the resonances of the conjugated olefine groups into high- and low-field groups may indicate that π electrons are localised over the central atoms of the group, but we can't be sure of this. The shifts cannot be interpreted solely in terms of π electrons, since they depend on the electron circulations in the whole molecule, including the metal orbitals. Even if the C-H bonds were all alike, the magnetic shielding experienced by the terminal protons could be quite different from that at the central ones, depending on the relative orientations of these groups. At present we have few data on the crystal structures of these compounds.

Although the n.m.r. spectra don't tell much about the bonding in these compounds, they have been useful in determining the molecular configuration and the numbers of equivalent protons. For example, in the cobalt compounds the single line (intensity $\equiv 5$) comes from the 5 equivalent protons on the C_5H_5 cyclopentadienyl ring. The triple line at low fields comes from the two equivalent protons H_3 and H_4; each is split into a doublet by the nearest proton of $(H_2 + H_5)$ and again into a doublet by the furthest proton of $(H_2 + H_5)$, the overall splitting being the sum of the two doublet splittings. The rest of the spectrum is simplest when one proton $(H\alpha)$ of the $>CH_2$ group is replaced by a negative substituent whose presence shifts the line from the other proton $(H\beta)$ sufficiently far away from the $(H_2 + H_5)$ lines to allow an "innocent first-order" interpretation to be made.

In the $-CCl_3$ derivative, the $H\beta$ line is split into a triplet by the two equivalent protons H_2 and H_3; in the $-CF_3$ derivative it is further split by the three fluorine nuclei to give a quartet of triplets. The fluorine resonance of this compound is a doublet whose splitting (7.4 ± 0.1 cps) is the same as that in the quartet. The protons $(H_2 + H_5)$ show a quartet line which should be a triple doublet; the overall splitting is the same as the sum of the splittings in the other two groups. In the parent compound, with the C_5H_5 group, the $(H_2 + H_5)$ lines lie close to those of $H\alpha$ and $H\beta$. However, $H\alpha$ is in a different environment to $H\beta$, being closer to the metal atom, and these two protons can be regarded roughly as an AB pair. When $H\alpha$ is replaced by deuterium, the two lines assigned to it disappear and the $H\beta$ line appears at the position calculated for it from an AB pattern.
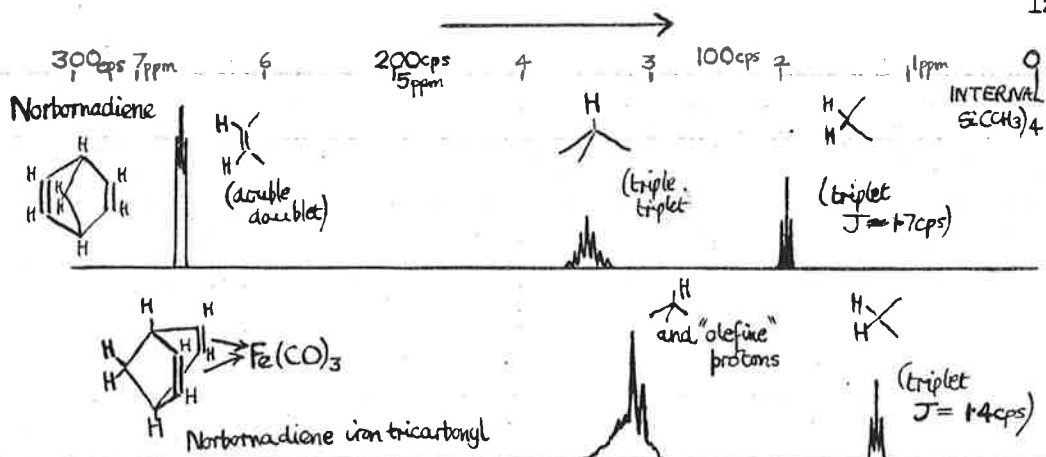
(The iron butadiene tricarbonyl was kindly given to us by Dr. Pauson and the tetraphenyl derivative by the European Research Associates.)
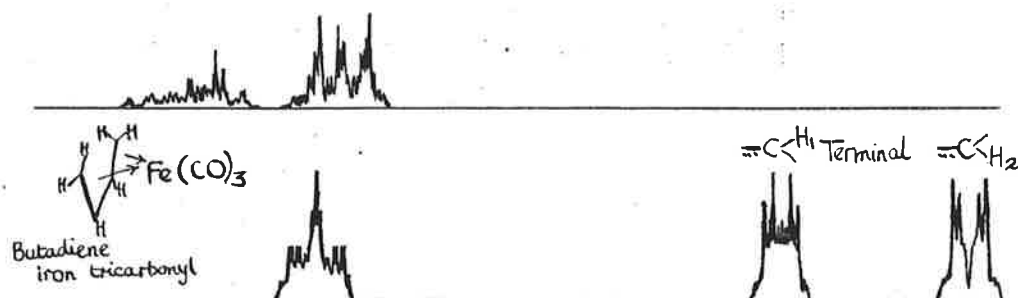
Yours sincerely,

L. Pratt.

1. Green and Wilkinson, J. Chem. Soc., 4314 (1958).
2. Green, Pratt and Wilkinson, J. Chem. Soc. (in the press).
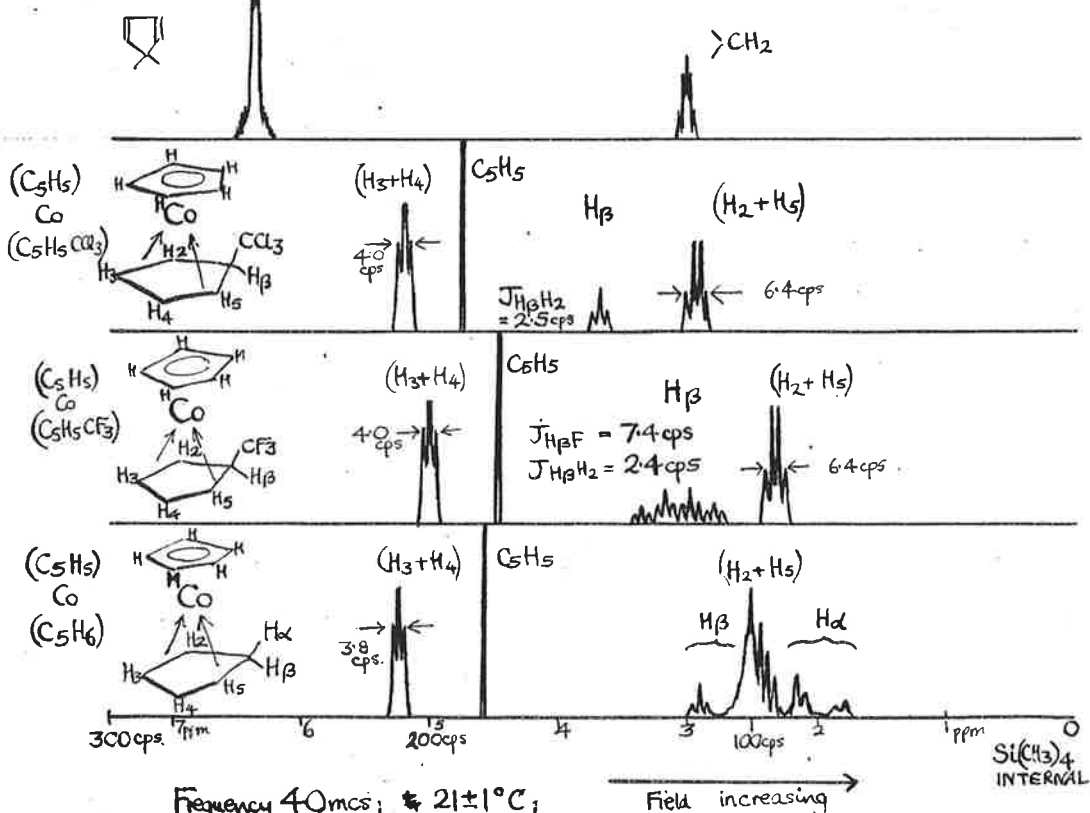
NMR spectra comparison charts for Norbornadiene, Norbornadiene iron tricarbonyl, Butadiene, Butadiene iron tricarbonyl, Cyclopentadiene, and the cobalt cyclopentadienyl complexes.

Frequency 40 mcs; 21±1°C; Field increasing

HIGH RESOLUTION PROTON RESONANCE SPECTRUM
OF THE CH₂ GROUP IN PURE ETHYL ALCOHOL (30.5 MCS)

THEORETICAL
UNLIKE SIGN FOR $J_{CH_3-CH_2}$
AND J_{CH_2-OH}

THEORETICAL
LIKE SIGN FOR $J_{CH_3-CH_2}$
AND J_{CH_2-OH}

RELATIVE INTENSITY

EXPERIMENTAL
SPECTRUM
(J.T. ARNOLD)

FREQUENCY (CPS)
Ref: $\nu_{CH_3} = 0$

MICHIGAN STATE UNIVERSITY EAST LANSING

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

May 25, 1959

Dr. Aksel Bothner-By,
Mellon Institute,
Pittsburgh, Pa.

Dear Aksel:

In view of the central role played by ethyl alcohol in NMR spectroscopy some recent work on the ethanol spectrum carried out by Dr. P. T. Narasimhan in these laboratories may be of interest.

He has treated CH_3CH_2OH as an A_3B_2C spin system, solving the secular equation and obtaining the energy levels and stationary state eigenfunctions as well as the transition frequencies and their relative intensities. Arnold's (Phys. Rev. 102,136(1956)) values of the coupling constants and chemical shifts were employed and the calculations were made both for the case where J_{AB} and J_{BC} have like signs and the case where they have opposite signs. The calculations were programmed for our digital computer MISTIC.

Although the theoretical spectra do not differ much at 30.5 mcs. it can be seen from the figure that the agreement with Arnold's published spectrum is better for the case of like signs than the other case. Since McConnell has predicted positive long-range proton-proton coupling constants from MO theory, and Karplus has found a positive coupling constant for ethane from VB theory, it seems reasonable to suppose that both constants are positive here.

The differences between the spectra calculated in the two cases should, of course, be magnified at a frequency below 30 mcs. and we would therefore like to obtain such a check on the above work. We hoped that some reader of MELLONMR might be able to provide us with a spectrum of pure ethyl alcohol (showing the OH triplet) under high resolution at , say, 10,15 or 20 mcs. If so we would be most grateful and would then repeat our calculations at that frequency.

Yours sincerely,

Max T. Rogers
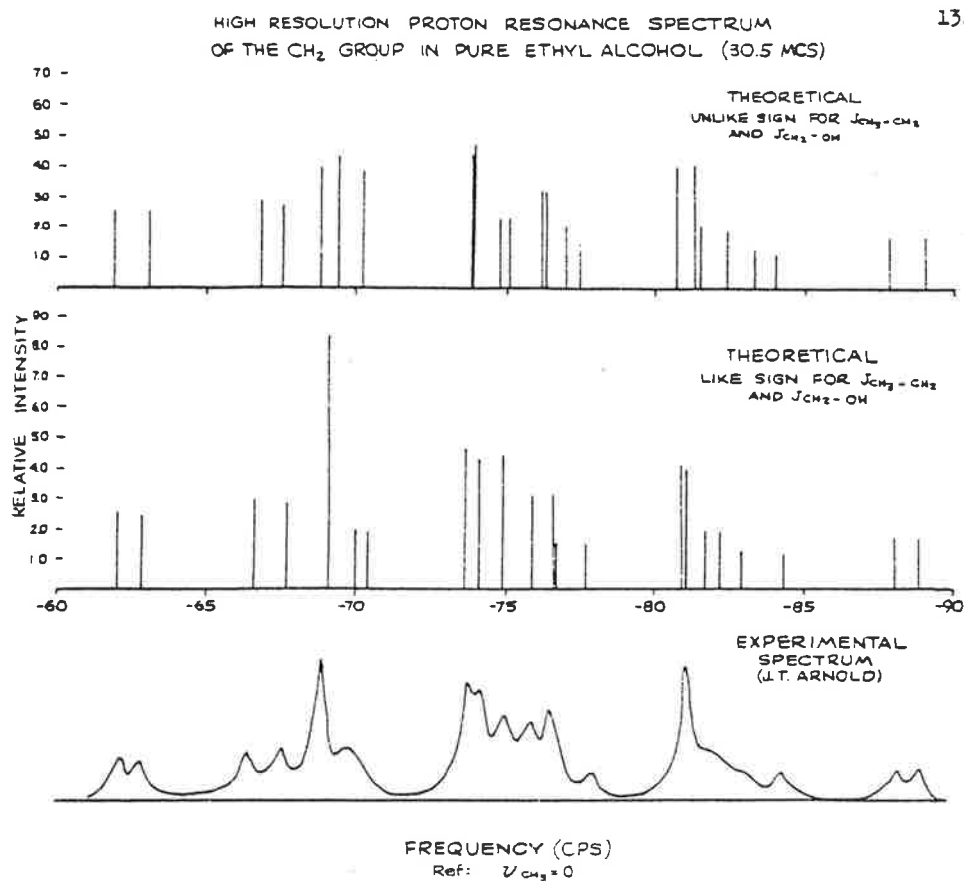
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Preprint Available:

"NMR Spectra of Pentacyclic Triterpenes"
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