13.11.62

Primas

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L aboratories
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Mailed: Oct. 31, 1962

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ohne Lit.

No. 49

DEADLINE FOR NEXT ISSUE
November 26, 1962

Συλλογὴ κατὰ μῆνα ἰδιωτικῶν ἐπιστολῶν ἐκ τῶν ἐργαστηρίων τοῦ NMP.

Τὰ ἀγγέλματα ἐνταῦθα περιληφθέντα μόνον διὰ τόδε πέμπεται, ἵνα ταῦτα ἀναγνῶτε. Οὐδαμῶς ἐπιτρέπεται ταῦτα ἀλλαχοῦ προφέρειν εἰ μὴ ὁ συγγραφεὺς αὐτὸς τῆς ἐπιστολῆς προσομολογῇ, καὶ τὰ εἰσαγγελλόμενα πρέπει ἀναφέρειν ὡς ἥκοντα ἐκ ἰδίας ἐπιστολῆς.

October 1, 1962

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

Dear Dr. Shapiro:

We are using our A-60 instrument for analytical purposes. We hope that you welcome contributions showing how NMR can be used in conjunction with other tools to solve difficult analytical problems.

We were given the problem of detecting and determining 1,2-epoxyoctane in a complex mixture. We were also given as a "standard" a bottle of octylene oxide (K & K Laboratories). A gas chromatograph of the octylene oxide showed it to contain two major compounds. A gas chromatograph of the unknown showed that neither material present in octylene oxide was present in the unknown. Chemical analysis of the unknown showed that an epoxide was present in major amounts.

The unknown's major gas chromatographic peak was trapped. The infra-red spectrum had a C-H stretching vibration at 3060 CM^{-1} which indicated that the compound was a terminal epoxide (Henbest, et al., J. Chem. Soc., 1957, 1459). The NMR spectrum showed that the compound had three hydrogens attached to an epoxy group and that there was one methyl group at the end of a chain of five methylene groups.

δ_{CH_3-} = 0.90 ppm   area = 3 hydrogens

δ_{-CH_2-} = 1.38 ppm   area = 10 hydrogens

δ $\cong$ 2.3 ppm
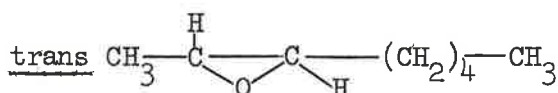 $\cong$ 2.6 ppm   area = 3 hydrogens

(Measured in CCl_4 with TMS internal standard at 60 mcps)

Cleavage of the material with periodic acid gave formaldehyde. This showed that the material was an 1,2-epoxide. We believe that this compound is 1,2-epoxyoctane.

The two major chromatographic components of the octylene oxide were trapped. The NMR spectra of both components indicated that there were two hydrogens per epoxy group, one methyl adjacent to the epoxy group, and one methyl group at the end of a chain of four methylene groups. This suggested that the components were cis and trans 2,3-epoxyoctane. Brownstein (Mellonmr #11, p. 1) has shown that the chemical shift between

and
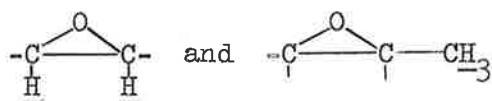
for trans-2,3-epoxybutane is 82.5 cps (at 60 mcps) and for cis-2,3-epoxybutane is 96.7 cps. We found that this chemical shift was 73 cps for component 1 and 95 cps for component 2. Thus, we think that component 1 is trans-2,3-epoxyoctane and component 2 is cis-2,3-epoxyoctane.

trans

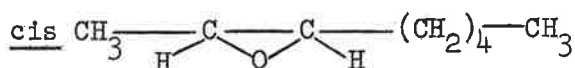$$\delta_{CH_3} = 0.91 \text{ ppm} \qquad \text{area} = 3 \text{ hydrogens}$$

$$\delta_{CH_2} = 1.41 \text{ ppm} \qquad \text{area} = 8 \text{ hydrogens}$$

$$\delta = 1.22 \text{ ppm} \qquad J_{CH_3,H} = 4.9 \text{ cps} \qquad \text{area} = 3 \text{ hydrogens}$$

$$\delta \cong 2.5 \text{ ppm} \qquad \text{area} = 2 \text{ hydrogens}$$

$$\left[\delta \right] - \left[\delta \right] = 73 \text{ cps}$$

$\underline{\text{cis}}$ CH_3—$\overset{\displaystyle C}{\underset{H}{}}$—$O$—$\overset{\displaystyle C}{\underset{H}{}}$—$(CH_2)_4$—$CH_3$

δ_{CH_3} = 0.91 ppm   area = 3 hydrogens

δ_{-CH_2-} = 1.39 ppm   area = 8 hydrogens

δ [CH_3—C—O—C] = 1.19 ppm $J_{CH_3,H}$ = 5.5 cps   area = 3 hydrogens

δ [$-\overset{\displaystyle C}{\underset{H}{}}$—$O$—$\overset{\displaystyle C}{\underset{H}{}}$] $\cong$ 2.8 ppm   area = 2 hydrogens

$$\left[\delta_{-\overset{C}{\underset{H}{}}-O-\overset{C}{\underset{H}{}}}\right] - \left[\delta_{CH_3-C-O-C}\right] = 95 \text{ cps}$$

   The infrared spectra of both compounds did not show any C-H stretch-
ing vibrations above 3000 cm^{-1}. Both compounds were cleaved by periodic
acid to give the odor of acetaldehyde. This shows that the material was an
2,3-epoxide.

Sincerely yours,

Mack C. Harvey

Mack C. Harvey

Ronald Howell

Ronald Howell
Analytical Section
Research Department

MCH:ht

Notes on Computer Programs

<u>NMRIT</u>. I have rewritten subroutine ERROR so as to provide a meaningful measure of the parameter errors. The single iteration following the perturbation of each energy level in turn by 0.001 cps [see J. Chem. Phys. <u>37</u>, 29 (1962)] has been increased to half the number called for by NIT on the control card. Furthermore, the perturbation of each energy level has been reduced from 0.001 cps to 0.0001 cps. It is found that the errors are about what one might expect from the estimated accuracy of the measured line positions. I can supply a listing of this new subroutine to any one who wishes to use it. However, since it is rather expensive to use in terms of computer time if the number of spins is greater than 3 or 4, I recommend that a dummy subroutine be used unless a good measure of the parameter errors is needed.

I have also found that in certain highly mixed spin systems, NMRIT can give an incorrect set of parameters. The vinyl group of acrylic acid is an example of such a case. However, the vinyl group of methyl trivinylsilane appears to be at least as highly mixed a case - but NMRIT gives the correct answer here. This problem is presently being investigated.

<u>PLOT</u>. This program was written to be compatible with our IBM 1401-CALCOMP installation, which is not standard. Prof. C. H. Sederholm at U.C., Berkeley, informs me that he has modified this program for use with the CALCOMP plotter installed according to the IBM recommendations. Further details about the program can be obtained from him.

<u>MARIP1</u>. (Magnetic Resonance Iterative Program No. 1.) This is a program I have written for use with 3, 4, 5 or 6 spins only. In it, revised NMRIT, NMREN1, and PLOT programs have been combined into a single program with an appreciable saving in computer time. Subroutine PLOT can easily be by-passed if a plotted spectrum is not desired or if a plotter is not available. Provision is also made for by-passing subroutine NMREN1 if the energy levels have already been calculated, e.g. by NMREN2. In fact, if two or more spins are equivalent, this is the procedure that is necessary if this program is to be used.

If any one wants to use this program, I can supply a listing.

C. A. Reilly
Shell Development Company
Emeryville, California

NUCLEAR MAGNETIC

NMR
Specialties

RESONANCE SPECIALTIES

145 Greensburg Road

New Kensington, Pa.

Area Code 412
337-7727

October 22, 1962

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

Dear Barry:

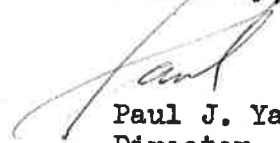Enclosed is a copy of an experiment utilizing our Model PD-60
Homonuclear Spin Decoupler.

Perhaps through the medium of the MELLONMR newsletter this
data could be conveyed to Organic Chemists and NMR Spectroscopists
interested in this field.

We are hopeful that this NMR contribution will entitle us to
be included in the mailing list for MELLONMR.

Sincerely,

Paul J. Yajko
Director

PJY/erb

Enclosure

Proton-Proton Spin Decoupling Experiment with Trans-Crotonaldehyde

A. Undecoupled Spectrum

The spectrum of trans-crotonaldehyde can, to a good approximation, be treated as that of a first order system. The coupling scheme can then be illustrated by diagram 1, the protons being labelled as below;

$$ H (H_A) \quad\quad H (H_k) $$
$$ \diagdown \quad\quad\quad C = O $$
$$ C = C $$
$$ CH_3 (H_x) \quad\quad H (H_b) $$
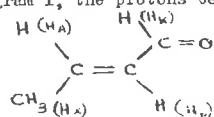
The spectrum of the trans-crotonaldehyde taken in 25 volume percent solution in CCl_4 is shown in spectrum 1; the frequency positions are taken with respect to the center of the aldehyde doublet and are accurate to about 0.5 cps.

The methyl proton line is split into a doublet by H_a, with a spacing J_{ax} = 6.8 cps; each of the doublet components is further split into a smaller doublet by H_b, with spacing J_{bx} - 1.6 cps (diagram 1a; spectrum 1a).

The protons H_a and H_b couple to form an AB type quartet; the spacing between the components of the H_a doublet is equal to J_{ab} = 15.6 cps as is the spacing between the components of the H_b doublet. Each of the two H_b doublet components is further split by H_k into a doublet with spacing J_{bk} = 7.8 cps, to give an overall unsymmetrical quartet; each of these quartet components is further split by coupling with the methyl protons into a quartet with 1,3,3,1 intensity ratio and small spacing J_{bx} = 1.6 cps to yield an overall pattern for the H_b line of four 1,3,3,1 quartets (diagram 1b, spectrum 1b).

Each of the two H_a components is split into a quartet with 1,3,3,1 intensity ratio and spacing J_{ax} = 6.8 cps; the two quartets overlap (diagram 1c, spectrum 1c).

The aldehyde proton, H_k, line is split into a doublet by H_b; the doublet spacing is J_{bk} = 7.8 cps (diagram 1d).

B. Qualitative Description of the Field-Sweep Decoupling Experiment

The field-sweep decoupling experiment can be qualitatively described as follows: Suppose two protons, A and X, (or two groups of equivalent protons) are coupled with a coupling constant J_{ax} much less than the frequency separation of their lines (i.e. much less than their chemical shift difference, $\gamma_a - \gamma_x$, in frequency units). Suppose, furthermore, that the center of the A pattern is being observed at frequency γ_a, field H_a (i.e. the field H_a satisfies the resonance condition $\gamma_a = (1 - \sigma_a) H_a$) and that simultaneously the sample is being irradiated with a sideband at frequency γ_m, (where $\gamma_x \pm \gamma_m \tilde{=} \gamma_a$), such

that the X protons are simultaneously in resonance at field H_a' (i.e. such that $\gamma_x = \frac{\gamma}{2\pi} (1 - \sigma_x) H_a$). Then, if the strength of the irradiating field, $\frac{\gamma}{2\pi} H_2$, H_2 (in frequency units), is much larger than J_{ax}, the A pattern will collapse into a single line.

If the strength of the irradiating field is not much larger than J_{ax} and/or if the irradiating frequency is somewhat off resonance for the X protons, then, in general, the A pattern will not collapse but may even become more complicated. (It should also be noted that satellites may, in principle, be present even when the conditions on the irradiating field strength and frequency are satisfied for systems other than AX_m types.)

If the A proton is coupled to other protons in addition to the X-protons, then, if the conditions on irradiating the X-protons are satisfied, the AX coupling will 'wash out' of the A- pattern and what remains will be the pattern corresponding to the A-protons coupling with all protons other than the X. The required strength of the irradiating field and the appropriate irradiation frequency depend on the magnitude of the coupling constant, JA_x, and on the width of the A pattern. For example, as shown in spectrum 6, if one irradiates with a sideband frequency γ_m = 243 cps such that the center of the methyl line is in resonance as one sweeps through the center of the H_b pattern, then, for the particular decoupling field strength used, the small coupling between methyl and H_b protons (J_{bx} = - 1.6 cps) is washed out as one sweeps over the whole H_b pattern; what remains is the pattern as if H_b coupled with only H_a and H_k, (an unsymmetrical quartet). On the other hand, when the corresponding experiment is tried in sweeping through the H_a pattern, (that is with the irradiating frequency set so that the center of the methyl line is in resonance as the center of the H_a pattern is swept through) (γ_m = 285 cps) then only partial decoupling occurs over the whole H_a pattern, since Jax is larger (6.8 cps) in this case (Spectrum 4b). However, one may still wash out the H_a - methyl coupling by setting the irradiating frequency so that the methyl group is in resonance as each of the doublet components of the A group is swept through; that is, by using an irradiating frequency $_m$ of 285 cps when sweeping through the upfield H_a component and then changing to a sideband frequency of 301 cps when sweeping through the downfield component, as shown in spectrum 4a.

When the width of the pattern to be observed is small, and if the field strength is large enough, then the resonance condition need not be satisfied exactly. For example, as shown in spectrum 5, when the methyl group pattern is observed and the irradiating frequency set to irradiate the center of the H_a, H_b patterns as the center of the methyl pattern is swept, (γ_m = 267 cps)

then both the H_a and H_b couplings are washed out from the methyl pattern; in this case the width of the methyl pattern is smaller (about 7 cps) than that of either the H_a or H_b patterns; (about 16-20 cps); the irradiating field strength was the same as in the above two examples.

One should keep in mind that when the irradiating sideband frequency is kept at a given setting as one sweeps through the field, then the irradiated nuclei will come into resonance at only one particular value of the field and furthermore, other groups of nuclei may in turn be irradiated as one sweeps through the field. Thus, as shown in spectrum 6, portions of the spectrum may become more complicated if, while sweeping through one pattern, another group of nuclei is being irradiated off resonance; for example, as the H_a pattern is being swept through, the methyl protons are being irradiated but are about 50 cps off resonance; as the H_k pattern is being swept through the H_b nuclei are being irradiated and are about 40 cps off resonance; here the sideband frequency is + 273 cps.

C. Decoupling Patterns for Trans-crotonaldehyde

With the above coupling scheme and general remarks about decoupling in mind, one can then interpret the various decoupling patterns observed in the demonstration. (One should note that the above remarks do not generally apply to decoupling experiments with relatively weaker fields--the 'tickling' experiment or experiments involving the determination of coupling constant signs; these were not attempted in this demonstration.)

When the center of the H_b pattern is irradiated at the same time as the H_k line is observed, the H_k doublet is collapsed to a single line (spectrum 2, γ_m = + 204 cps, upper sideband); conversely, when H_k is irradiated, H_b observed, the H_b pattern collapses to the two doublet components of the AB pattern, each component being further split into a 1,3,3,1 quartet (spectrum 3, γ_m = - 204 cps, lower sideband). When the center of the methyl group is irradiated as each H_a doublet component is swept through, the H_a pattern collapses to the AB doublet (spectrum 4a, γ_m = + 285 and + 301 cps, respectively). The methyl quartet collapses to a single line when observed while the center of the H_a - H_b pattern is irradiated (spectrum 5, γ_m = - 267 cps, lower sideband). When the center of methyl pattern is irradiated as the center of the H_b pattern is swept through, the H_b pattern collapses to the unsymmetrical quartet which would be observed if H_b coupled only with H_a and H_k (spectrum 6, γ_m = + 243 cps, upper sideband). Furthermore, at lower irradiating field strengths, each of the four 1,3,3,1 quartets of the H_b pattern can be collapsed separately, corresponding to irradiating the methyl group as one particular quartet group is being swept through (spectrum 7, γ_m = + 234 - 250 cps, respectively, upper sideband).
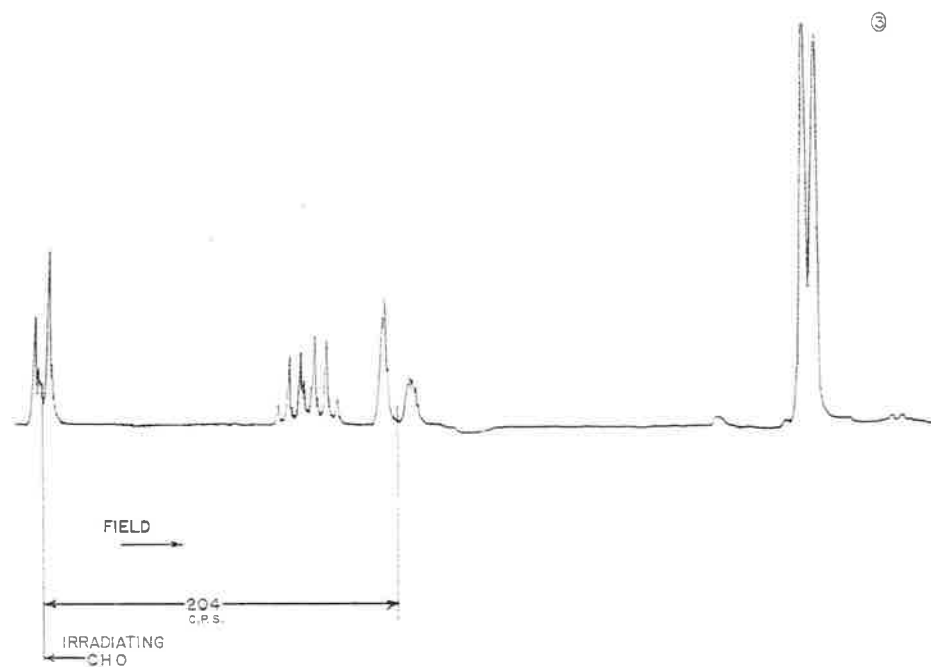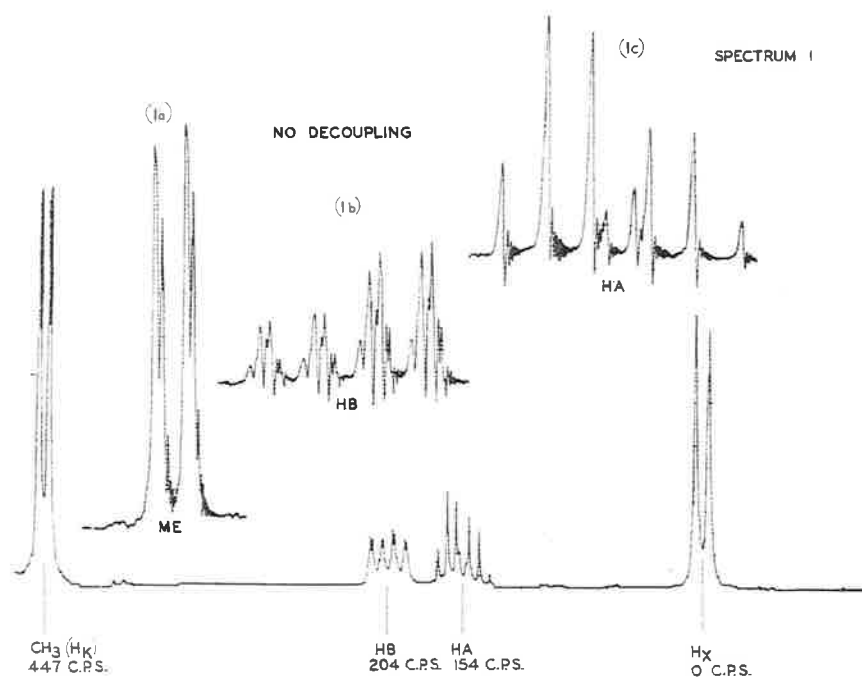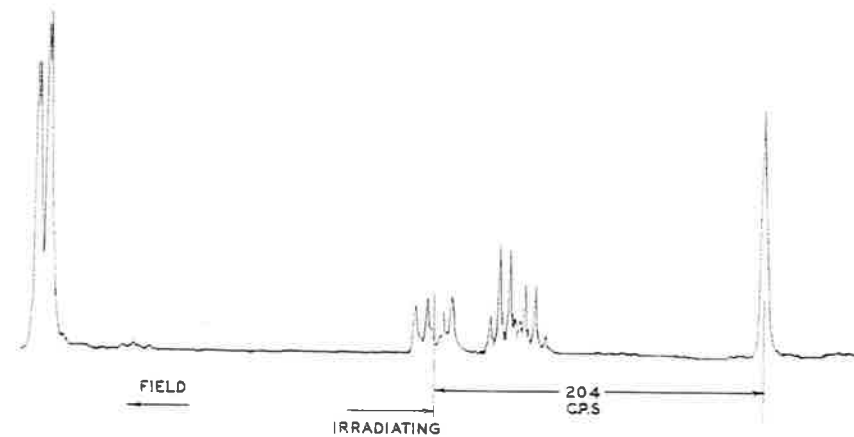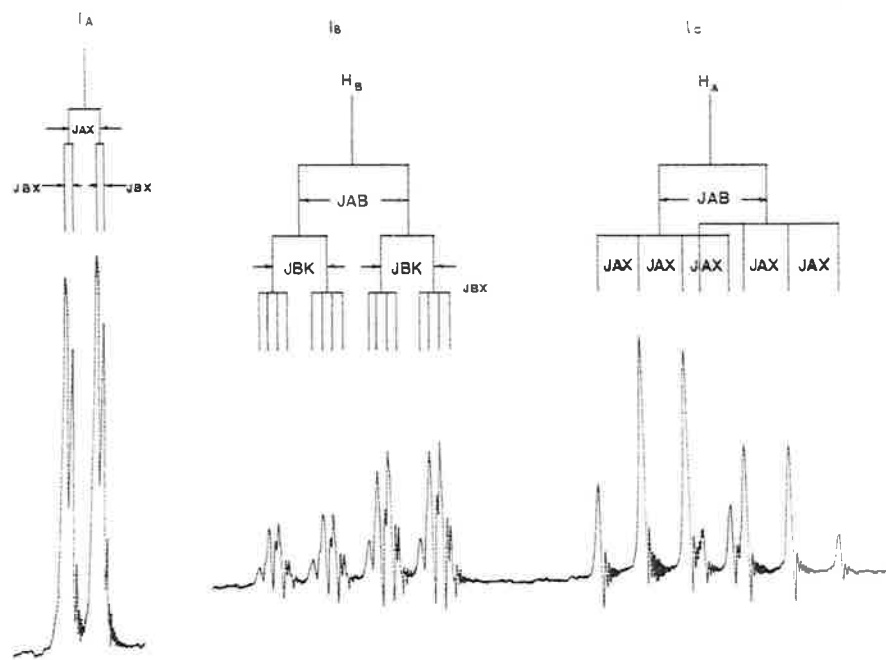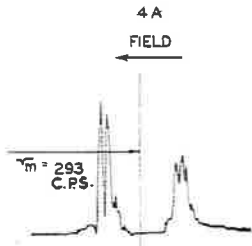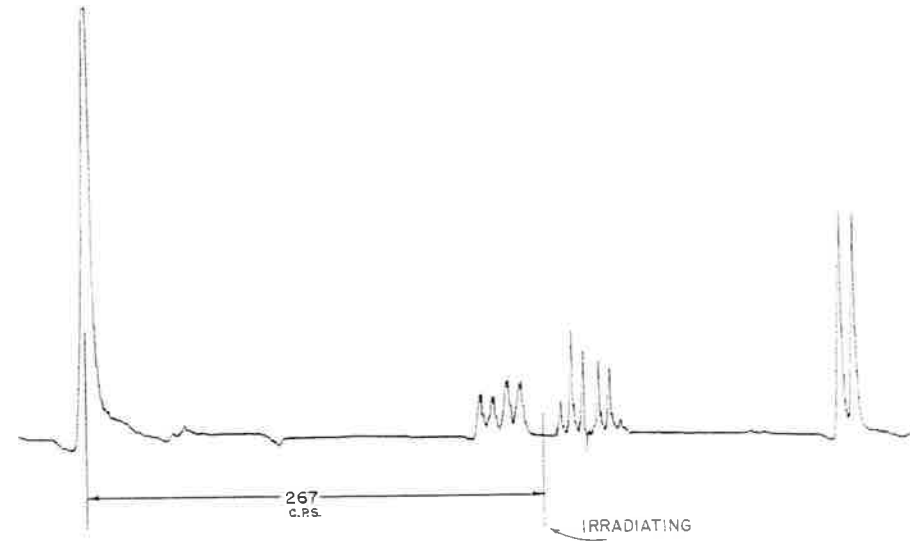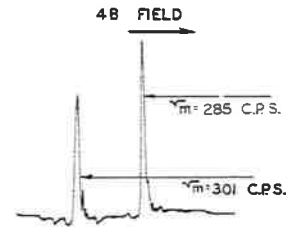
P. J. Yajko and R. J. Kurland

DIAGRAM 1

I_A

J_{AX}

J_{BX} J_{BX}

I_B

H_B

J_{AB}

J_{BK} J_{BK} J_{BX}

I_c

H_A

J_{AB}

J_{AX} J_{AX} J_{AX} J_{AX} J_{AX}

①

CHO DECOUPLED

②

FIELD

204
C.P.S

IRRADIATING

③

SPECTRUM I

(1c)

NO DECOUPLING

(1a)

(1b)

H'A

ME

HB

CH₃ (H_K)
447 C.P.S.

HB
204 C.P.S.

HA
154 C.P.S.

Hx
O C.P.S.

FIELD

204
C.P.S.

IRRADIATING
CHO

4 A   4 B

4 A
FIELD
←——

$\gamma_m = 293$
C.P.S.

4B FIELD
——→

$\gamma_m = 285$ C.P.S.

$\gamma_m = 301$ C.P.S.

267
C.P.S.

IRRADIATING

⑥   SPECTRUM 7

FIELD ——→

252 cps

243
cps

235
c.p.s.

250 cps

242
cps

234
c.p.s.

DECOUPLED

243
C.P.S.

IRRADIATING
CH₃

248 cps

241
cps

233
c.p.s.

No
Decoupling
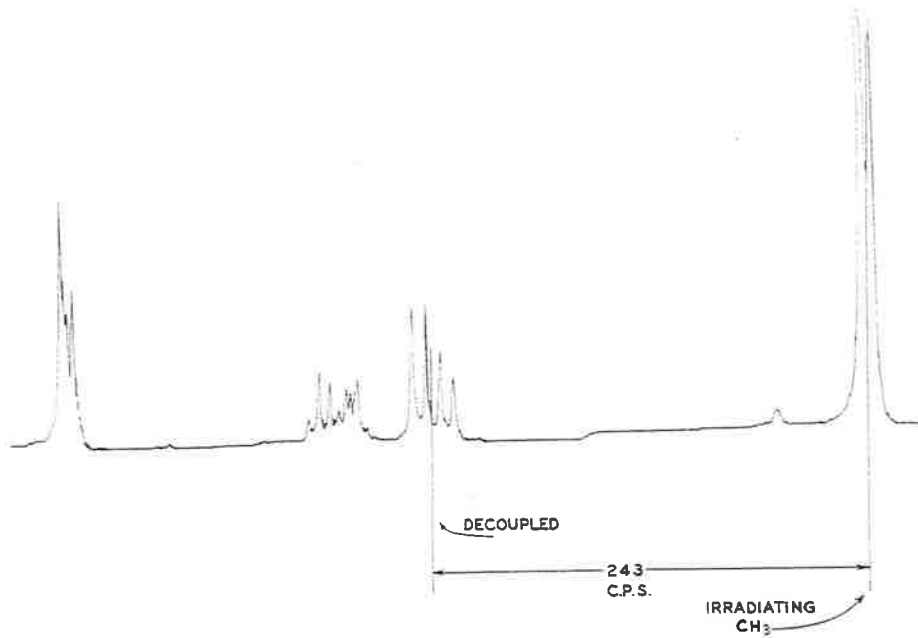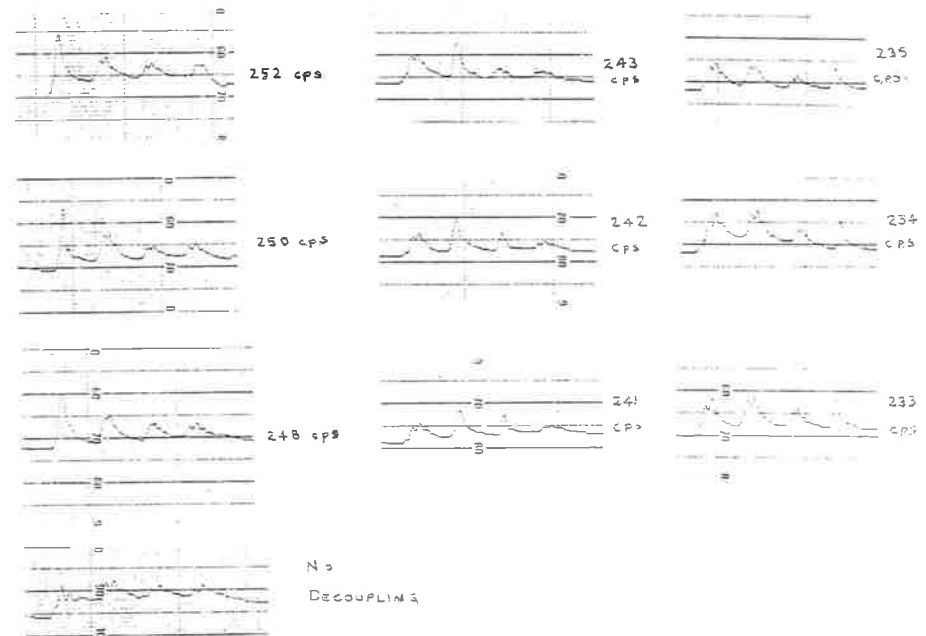
Substituted Pyrrolidone

All spectra were taken on a conventional 60 Mc. spectrometer system with sideband frequencies monitored by a Conn Acoustical Stroboscope ("Acousticon"). Samples were run as approximately 10% wt solutions in $CDCl_3$ (85 mg /1.0 ml $CDCl_3$ for 1; 60 mg /0.4 ml $CDCl_3$ for 2).

1. The undecoupled spectrum (spectrum 1a) of 1 is straightforward; the assignment of lines for the (A) and (K) protons comes from the spectra of a number of other substituted pyrrolidones run in the laboratory. The remaining lines are assigned, then, as given in the table 1. (The equal cis AB and trans AB coupling constants are somewhat surprising, since the molecule is probably planar. The molecule is probably in the anti-form since no low field NH line attributable to an internally H-bonded proton was found, while this low field line (090) has been observed for other similar, presumably "syn", pyrrolidones of this sort).

The decoupling also proceeded straightforwardly and, while not providing any new information about the molecule is a good example of this technique. As indicated, it is possible to decouple proton A from B in several ways in a given sweep; by using the lower sideband (upper sideband suppressed) to irradiate A while observing B (spectrum 1b); by using the upper sideband (suppressing the lower) to irradiate B while observing A (spectrum 1c); or, by switching from one sideband to the other during the sweep, so that A is observed while B is irradiated and then in the same sweep, B is observed while A is irradiated (spectrum 1d). Note that H_2, the irradiating field, is stronger in 1d than in 1b and 1c; the sideband modulating frequency was in all the above 58.2 ops.

1.

H (x)   H(x)
N

(B) H
H
N

(A) H
H
N
O

H (K)   S (L)

85 mg in 1.0 ml $CDCl_3$

Table 1

Assignment (spectrum 1a)

proton		
X	3.81	
K	ca 5.65	$J_{AB} = 6.6$ ops.
A (center)	6.29	
B (center)	7.25	
L (cyclohexyl-L)	ca 8.21	

Captions

Spectrum 1a.	Undecoupled spectrum of 1
Spectrum 1b.	lower sideband; A irradiated B observed
Spectrum 1c.	upper sideband: B irradiated A observed
Spectrum 1d.	lower and upper sidebands: A irradiated, B observed; B irradiated, A observed

R. J. Kurland

SPECTRUM 1a.
←FIELD

TMS

↑ L ↑ ↑ IMP. B ↑ A ↑ K ↑ X

1b.   LOWER SIDEBAND
FIELD →

1b.   LOWER SIDEBAND
← FIELD

↑ X ↑ K ↑ A ↑ B ↑ L   ↑ L ↑ B ↑ A ↑ K ↑ X

1c.   UPPER SIDEBAND
FIELD →

1c.   UPPER SIDEBAND
← FIELD

↑ X ↑ K ↑ A ↑ B ↑ L   ↑ L ↑ B ↑ A ↑ K ↑ X

1d.

UPPER SIDEBAND   LOWER SIDEBAND
← FIELD

1a.

LOWER SIDEBAND   UPPER SIDEBAND
FIELD →

↑ L ↑ B ↑ A ↑ K ↑ X   ↑ X ↑ K ↑ A ↑ B ↑ L

DEPARTMENT OF CHEMISTRY

October 1, 1962.

Dr. Barry Shapiro
Mellon Institute,
Pittsburg, Pennsylvania.

Dear Dr. Shapiro:

    We would like to initiate a new type of contribution, that of "situation wanted," as suggested in MELLONMR # 47.
    We are seeking positions in the area of n.m.r. and/or e.p.r. Industrial, academic, or post-doctoral positions will be entertained. Doctoral work will be completed in the summer of 1963. Have had three to four years experience in various aspects of high-resolution and wide-line n.m.r. Complete details of experience and background will be gladly furnished to any interested parties.
    As graduate students doing n.m.r. research we find your news-letter a valuable aid.

Sincerely yours,

Kenneth D. Lawson

Kermit C. Ramey

Department of Chemistry
University of Florida
Gainesville, Florida

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

October 2, 1962.

Dr. B. L. Shapiro
Department of Chemistry
Mellon Institute
Pittsburgh, Pennsylvania

Dear Barry:

    I read with interest the MELLONMR contribution of C. L. Bumgardner on ^{19}F chemical shifts of aromatic CF_3-groups, especially those para to amino groups.

    In any case, the data available on the properties of CF_3 para to amino seem to indicate that the chemical shifts might well be unusual [JACS, 72, 408 (1950)]. The direction of the effect is not so easily predicted. Contributions of resonance forms such as I

I
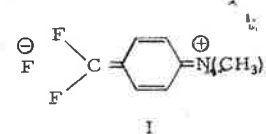
do not perforce lead to net shielding because, while each fluorine is made more like $F^{\ominus}$ in one third of the forms it is made more like F—C= in two thirds of the forms. I don't believe the balance between these effects can be predicted in the present state of the art.

    With all good wishes,

Very truly yours,

Jack

John D. Roberts

JDR:nvl

The Ural Polytechnical Institute
The chair of the Theoretical physics.
Sverdlovsk,USSR.

Dear Dr.Aksel A.Bothner-By!

We have examined the question about the influense of
g-factor anisotropy of the molekules on the linewidth of the
paramagnetic resonance in the solutions.

There are two ordinary mechanisms of the line narrowing in
the solutions: rotational and vibrational random motions.Both
mechanisms does not explain the linewidth of the hyperfine struc-
ture cimponents in the strongly diluted solutions of the organic
free radicals.

There is another mechanism connected with influense of
the g-factor anisotropy of the molecule.

Let us consider the molecule in which one unpaired electron
interractes with one main nucleus (nitrogen) and n protons.
The dispersion of the resonanse frequency connected with the
g-factor anisotropy may be considered as correlation frequensy
that have the order

$$\omega_c \approx \frac{\Delta g}{g}\omega,$$

where ω -the Larmor frequency.If A_p -the hyperfine
structure constant for the protons (in the frequency units),
n- the number of the protons of the molecule,and "extremal
narrowing" condition is fullfiled

$$n\,A_p \ll \omega_c$$

the linewidth of the separate hyperfine structure components is

$$\Delta\omega_m \sim \frac{n A_p^2}{\omega_c}$$

Sinse $n A_p \sim A$,where A -the main hyperfine structure
constant,so $\Delta\omega_m \ll A$ and there is the resolution of the
hyperfine structure.At the week fields the "extremal narrouing"
condition is broken,i.e. $n A_p \gtrsim \omega_c$ and $\Delta\omega_m \sim A$.
At this case the hyperfine structure is not resolved.

For the organic free radicals,for example DPPH, we may
take $A_p \sim A_0$ sec^{-1}, $\frac{\Delta g}{g} \sim 0,01$, $\omega_c \sim 1000$ sec^{-1}
(γ -gyromagnetic ratio),n = 12. We shell have

$$\Delta\omega_m \approx 0,4 \cdot 10^5 \text{ sec}^{-1}$$

At the fields ~ 500 gauss the linewidth of the hyperfine structure
components have the value compared with A and there is no separa-
tion of the hyperfine structure.

This explaines the absence of the hyperfine structure in
the 0,001 M solution of DPPH in the benzene at the field
of 18 gaussthat have been examined in our laboratory
by A.K. Chirkov.

The more detal calculations give the same results.

Sincerely yours

(A.A.Kokin)

26 September 1962

MELLON INSTITUTE
4400 FIFTH AVENUE
PITTSBURGH 13, PA.

October 3, 1962

Dr. B. L. Shapiro
Mellon Institute
Pittsburgh 13, Pa.

Dear Barry:

GEMINAL (F,F) COUPLING CONSTANTS

MelloN-M-R readers may be interested in a comment on published values of geminal (F,F) coupling constants in saturated compounds. For non-cyclic molecules ten values have been measured.[1,2,3] With one exception these all lie in the relatively narrow range 150-175 c/s, in distinct contrast to the variable values of J_{gem}(F,F) in cyclic molecules[4,5] and in unsaturated compounds.[6,7] This apparent anomaly is emphasised by the exception mentioned above, $(CF_3)F_2C.CFlCl$, for which J_{gem} = 270.4 c/s.[3] The explanation seems to be that all the other compounds measured are of the types $ClF_2C.C^x$ and $BrF_2C.C^x$, where the asterisk indicates an asymmetric carbon atom (such asymmetry causes non-equivalence of the geminal fluorine nuclei). It appears that J_{gem} for $XF_2C.C^x$ is sensitive to the nature of X, but replacement of X = Cl by X = Br causes little change. However, X = CF_3 causes an increase of ≈ 110 c/s from X = Cl or Br. This idea is strengthened by ^{19}F resonance measurements made at Cambridge University, England,[8] on the molecule $(SiCl_3)F_2C.CFClH$, with X = $SiCl_3$, for which J_{gem} is as large as 343 c/s, that is about twice the magnitude of most reported values. A similar two-fold increase in J_{gem} has, of course, been observed for cyclic molecules, from ≈ 160 c/s for three-membered rings[4] to ≈ 290 c/s for six-membered ones.[5] The cause of these variations is a matter for speculation — and further experimental work! The size and electronegativity of X do not seem to have consistent effects in the above examples.

The other nuclear magnetic parameters for $(SiCl_3)F_2C.CFClH$ are perhaps worth quoting. The spectrum is of the ABMX type, where X = H and A,B are the geminal fluorine nuclei. With this notation J_{AM} = J_{BM} = 16.8 c/s,

J_{MX} = 48.1 c/s, J_{AX} = 6.6 c/s, J_{BX} = 10.1 c/s (where the resonance of the A nucleus is to low field of the B resonance). These values are not very different from those of $BrF_2C.CFClH$,[1] in particular in the approximate equality of J_{AM} and J_{BM} which is a feature of many 1,2,2 tri-substituted perfluoroethanes and probably indicates that J_g and J_t are not markedly different. The data also indicate that the rotational isomer with Cl and $SiCl_3$ trans to each other is probably the stable one.[8] Chemical shifts were measured for $(SiCl_3)F_2C.CFClH$ in ≈ 50% solution (by volume) in perfluorocyclobutane, using the latter as a secondary internal standard with a ϕ value of 135.5. The results are ϕ_A = 118.8, ϕ_B = 125.2 and ϕ_M = 149.7 (not extrapolated to infinite dilution). It can be seen that the presence of the trichlorosilyl group caused a considerable (≈ 50 p.p.m.) high field shift of the resonances of the geminal fluorine nuclei from their positions for $BrF_2C.CFClH$.[1]

My conclusion is simply that molecules of the type discussed are worthy of further study, in particular to correlate values of J_{gem}(F,F) with structural features. Since I shall be fully occupied with infra-red work for the next year I recommend the topic to anyone interested.

Sincerely yours,

Robin K. Harris.

Robin K. Harris

1. Lee and Sutcliffe, Trans. Far. Soc. 55, 880 (1959).
2. Manatt and Elleman, J.A.C.S. 84, 1305 (1962).
3. Crapo and Sederholm, J.C.P. 33, 1583 (1960).
4. Phillips, J.C.P. 25, 949 (1956).
5. Feeney and Sutcliffe, Trans. Far. Soc. 56, 1559 (1960).
6. McConnell, Reilly and McLean, J.C.P. 24, 479 (1956).
7. Coyle, Stafford and Stone, Spec. Acta 17, 968 (1961).
8. Harris, Ph.D. Thesis, Cambridge University (1962).

Basel, October 4, 1962

Dr. B.L. Shapiro
Mellon Institute
4400 Fifth Ave.
Pittsburgh 13, Pa.
U.S.A.

Dear Barry,

As I mentioned during my visit at the Mellon Institute,
we have recently started to run some more high resolution
D-spectra. Here are a few results:

1. Line width:

We have now measured the line width of acetone - d_6 to be
less than 0,2 cps so that we are sure to have reached the
natural line width in D_2O. It is 0.66 cps. From this value
it is possible to calculate the quadrupole coupling constant
of D in D_2O. Using a translation self-diffusion coefficient
$D=1,85.10^{-5}$ cm^2/sec and a water radius $a=1.74.10^{-8}$ cm, we
obtain

$$\frac{1}{\hbar} eQ \quad \frac{\delta^2 V}{\delta z'^2} \sim 200 \text{ kc/}_S$$

2. Isotope effects:

As an example, I present a D-spectrum of partly deuterated
acetone:
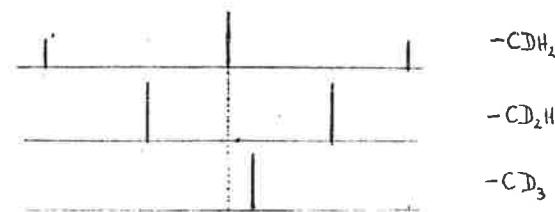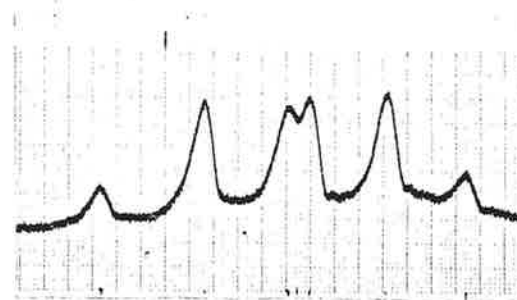
The D-isotope effects are:
- $CDH_2 \rightarrow CD_2H$: $(+ 1,2 \pm 0,1) .10^{-8}$
- $CDH_2 \rightarrow CD_3$: $(+ 2,9 \pm 0,1) .10^{-8}$

$J_{HD} = 2,18 \pm 0,03$ cps

Apparently, the D-isotope effects are in this case of the same order of
magnitude as the H-isotope effects.

$$\left[CH_3 \rightarrow CHD_2 : (+ 3,4 \pm 0,1).10^{-8} \right]$$

3. C^{13}-D- coupling.

A somewhat unexpected result was the C^{13}-D-coupling we observed in
acetone -d_6

$$J_{C^{13}D} = 19,48 \pm 0,05 \text{ cps}$$

This value enables us to join the "$J_{C^{13}H}$ of acetone competition" with
a value of

$$J_{C^{13}H} = 126,8 \pm 0,3 \text{ cps}$$

beeing very well centered in the region published so far (122 cps -
133 cps).

Yours sincerely

Peter

P.D. Dr. P. Diehl

October 10, 1962

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

Dear Dr. Shapiro:

We enjoy and benefit from MELLONMR very much, but are a little disappointed that contributions dealing with purely organic applications of NMR seem to be declining, at least in percentage. Perhaps this is due, at least in part, to the fact that the very rapid recent advances make it difficult for outsiders (i.e. people who are not doing NMR research) to keep up. A couple examples from our own work might demonstrate the importance of these new methods to routine organic work, and will elicit some other examples.

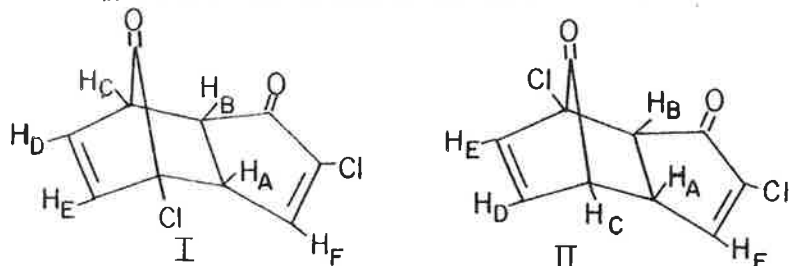(1) Computing of NMR spectra. So far, most of the uses of both the Bothner-By and Reilley-Swalen programs have been to the complete analysis of spectra of small molecules. We were recently interested in determining the structure of the dimer of 2-chlorocyclopentadienone-two structures were reasonable. The crux of the NMR analysis was the

interpretation of the pattern of the very tightly coupled ABC protons of the hydrogens on saturated carbons, since these were further split by the vinyl protons. Reasonable values for coupling constants for both the norbornene and cyclopentenone system were available, and we could make good guesses of chemical shift values directly from the spectrum. We simply put these estimated values for all six protons, first for I and then for II, into FREQINT III and plotted the results.

Dr. B. L. Shapiro
Page Two
October 10, 1962

Comparison with the ABC region of the dimer showed a remarkable similarity between the actual spectrum and that calc. for structure I but quite a different pattern than that predicted for structure II. A slight change in some of the coupling constants gave still a better fit. We therefore adopted structure I as a working hypothesis for a more rigorous proof of structure.

$\delta_{(TMS)}$ cycles/sec.; 60 Mc./sec.
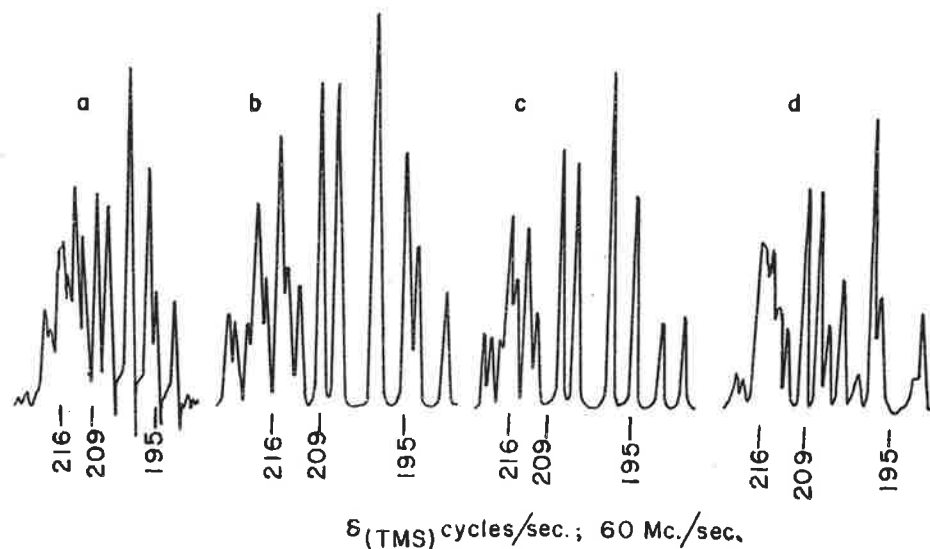
Figure 1. Spectra of 2-chlorocyclopentadienone Dimer. a) actual spectrum of H_A, H_B and H_C. b) computed spectrum for I with following parameters δ_A=209.1, δ_B=194.7, δ_C=217.5, δ_D=385.1, δ_E=374.7, δ_F=449.0; J_{AB}=6.25, J_{BC}=4.85, J_{AF}=2.80, J_{CE}=1.78, J_{CD}=3.98, J_{DE}=7.10. c) computed spectrum for I; δ_A=209.0, δ_B=195.0, δ_C=215.0, δ_D=386.0, δ_E=376.0, δ_F=452.0; J_{AB}=8.00, J_{BC}=4.0, J_{AF}=2.6, J_{CE}=1.0, J_{CD}=3.1, J_{DE}=6.0. d) computed spectrum for II with same parameters as in C, except J_{AC}=4.0 instead of J_{BC}

Dr. B. L. Shapiro
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October 10, 1962

    (2) **Spin decoupling:** Further, even more rigorous evidence for
the structure I could be obtained by spin decoupling experiments.
First the enone hydrogen alone, and then the other two vinyl hydrogens
could be decoupled and the results were in accord with those expected
for structure I. This type of experiment is too familiar to go into
detail, but I would like to mention that here, too, FREQINT can be of
aid, since it is not always obvious just what a tightly coupled spectrum
will look like after the removal of a spin by decoupling. It's a
simple matter, however, to recalculate the spectrum with FREQINT,
removing any desired spins. This can be a big help in interpreting
double resonance experiments.

    (3) **Signs of coupling constants:** I've heard a number of organic
chemists say "So what" when they learn that vicinal and geminal coupling
constants have opposite signs. My own opinion is that perhaps the
physical chemists will end up saying "So what" but organic chemists will
be extremely pleased with this result, since it now gives them a nice
method of identifying the (usually most interesting) unique proton in
ABC or ABX systems. In a system like this   the
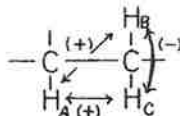
proton H_A is coupled to the other two protons with coupling constants
of the same sign, while each the other two protons has one positive and
one negative coupling constant. Consequently, a determination of relative
signs allow H_A to be determined uniquely. We've found either double
resonance or double quantum experiments to be easy and extremely useful
in this regard..

                    Sincerely,

                    C. H. DePuy

                    R. W. King/CHD

                    L. B. Rodewald

                    G. E. Morris

October 8, 1962

Dr. A. A. Bothner-By
Mellon Institute
44 West Fifth Avenue
Pittsburg 13, Pennsylvania

Dear Dr. Bothner-By:

    During the past several years, I have accumulated a
considerable amount of data relating to the nuclear magnetic
resonance of small ring compounds. Consequently, I am now
planning to tabulate this data into a table which may be
useful to other workers. Therefore I would like to know
if any of the readers of the Mellon letters has any data
which would help to make this summary as complete as possible.
I am especially interested in the data for cyclopropanol,
which happens to be one compound I have not been able to
obtain.

    Copies of this summary may be obtained from me upon
completion in December or January.

                    Sincerely yours,

                    Bernard J. Nist

BJN:ed

49-17

PRINCETON UNIVERSITY
Department of Chemistry
Princeton, New Jersey

Oct. 15, 1962

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

Dear Barry:

Because of the rigid geometry and high symmetry of the adamantane system, we have been interested in analyzing, in collaboration with G.V.D. Tiers and R.D. Nicholas, the nmr spectra of adamantane derivatives, particularly the 1-adamantyl halides. In conjunction with these studies we have examined the 60 mc. spectra of more than 60 acyclic and monocyclic alkyl halides.. A feature of this work is the inclusion of numerous fluorides, for which few chemical shift data have previously been available. (Table I).

Table I.- τ Values for Alkyl Halides

	α-CH	α-CH$_2$	β-CH	β-CH$_2$	β-CH$_3$	γ-CH$_2$	γ-CH$_3$
F	5.28-5.50	5.62-5.89	....	8.14-8.46	8.67-8.76	8.56-8.78	9.01-9.06
Cl	5.80-6.10	6.42-6.73	8.06	8.21-8.37	8.42-8.52	8.45-8.73	8.96-9.99
Br	5.79-5.98	6.60-6.79	8.02	8.05-8.20	8.23-8.32	8.43-8.73	8.45-8.95
I	5.68-5.88	6.81-6.90	8.26	7.93-8.37	8.06-8.14	8.57-8.73	8.41-8.99

Cavananaugh and Dailey (J. Chem. Phys., 34, 1099 (1961) have explained the chemical shifts in a few simple alkyl halides as arising in part from a C-C bond anisotropy shift, and in part from an electronegativity effect. Using their general approach and some of their data, we have derived an empirical equation, simple to use, which successfully predicts the chemical shifts for substituted alkanes. The standard deviation for 44 measurements in alkyl halides is 0.08 P.P.M.; predictions with other functional groups are equally good.

$$\tau_{(any\ CH)} = 9.77 - [Y(9.77 - \tau_{CH_3X}) + \Sigma(C-CX) + \Sigma(C-C)]$$

Where:

$(9.77_{(\tau CH_4)} - \tau CH_3X)$ = the maximum possible electronegativity shift due to the substituent, X.

Y = an electronegativity factor, dependent on first approximation only on structure; it equals 0.93 for α-CH$_2$ in ethyl, 0.90 for α-CH$_2$ in n-propyl and α-CH in isopropyl, 0.20 for β-CH$_3$ groups, 0.04 for γ-CH$_3$ groups, etc.

Σ(C-CX) = the contribution to shielding by the C-CX bonds, varying with X and evaluated from the measured shifts for n-propyl compounds.

Σ(C-C) = the contribution of any other C-C bonds attached to position under consideration; as a first approximation it does not depend on X and has the values 0.65, 0.40 and 0.32 P.P.M. for first, second and third bonds, respectively.

-2-

Although very satisfactory for simple alkyl halides, this equation fails to represent the chemical shifts in the 1-adamantyl halides (Fig. 1). In these halides the β hydrogens become more shielded than the γ in going from the iodide to the fluoride, while the δ-hydrogens, little affected with changes in substituents in other compounds, become more shielded even than the hydrogens of the parent compound, adamantane itself! Of interest also is the alternating character of the direction of shielding. We have at present no satisfactory explanation for this behavior and we welcome comments from your readers.

Fig. 1 - Chemical Shifts in 1-Adamantyl Halides
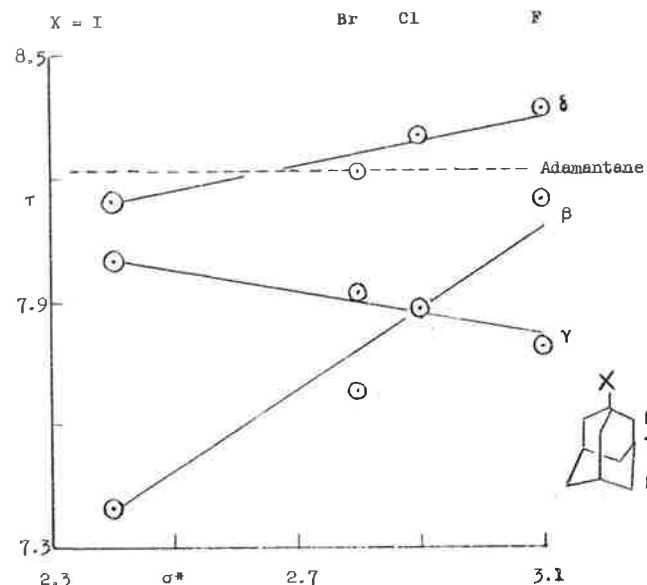
Sincerely yours,

Paul Schleyer

Raymond C. Fort

Division of Physical Chemistry

THE ROYAL INSTITUTE OF TECHNOLOGY

STOCKHOLM 70
SWEDEN

Cable address: Technology

ÅJ/MH

Dr. B.L. Shapiro
Mellon Institute

PITTSBURG, Pennsylvania

USA

Dear Dr. Shapiro:

In no. 46 of MELLON-M-R Scruggs & Li presented an investigation on "NMR Determination of Magnetic Susceptibility". The method used is based upon the fact, that the reference signal in case of external standard will turn into two peaks when the sample spinning is stopped, the separation between the two peaks being proportional to the volume susceptibility of the liquid in the inner tube. Thus the separation n cps can be written

$$n = a \cdot k + b \qquad (1)$$

where k is the volume susceptibility of the sample, and a and b are constants. The values of a and b depend on the dimensions of the coaxial glass tubes and the volume susceptibility of the glass and of the reference substance[1]. Scruggs & Li verified the linear relationship between n and k measuring the separation between the benzene peaks for samples containing four different liquids (water, cyclohexane, carbontetrachloride and methanol) with known volume susceptibility. From the straight line obtained when n is plotted vs k the constants a and b have been determined. The uncertainty of the volume susceptibility values determined using this method is reported to be $0.004 \cdot 10^{-6}$ (c.g.s. units).

The range of susceptibility values covered by the measurements of Scruggs & Li is -0.52 to $-0.72 \cdot 10^{-6}$ (c.g.s. units). I have found it necessary to test the linear relationship between n and k in a wider range of susceptiblity values, the numerically small values being of greatest interest. Using the method described I have tried to verify the linear relationship in the region k = -0.391 to $-1.154 \cdot 10^{-6}$ (c.g.s. units). For each substance I have made ten readings of n, the average of which is plotted in diagram 1. Between each reading the sample is rotated in order to eliminate inhomogeneities in the glass tubes.

I found it somewhat difficult to reproduce the readings of n. The standard deviation was calculated to 6 cps (an average of all substances). Furthermore it is impossible to measure the separation between the peak maxima due to their lack of sharpness. Instead I have used the method described by Scruggs & Li observing the separation at about one fourth of the peak height. However, if the apparent line width increases at low n values due to increasing overlap of the two peaks the plot of n vs k cannot be expected to be linear. This is probably the reason why deviations from the straight line are observed in the region where n passes its minimum.

As can be seen from diagram 1 there are two possible values of k corresponding to each value of n, since

$$n = |a \cdot k + b| \qquad (2)$$

Therefore this method cannot be directly applied, when the susceptibility of the sample is quite unknown. However, through dilution of the sample with a miscible liquid having a susceptibility greater than the greatest k observed (or smaller than the smallest k observed) the proper k value of the sample can be determined.

Yours sincerely,

Åke Johansson

1. C.A. Reilly, H.M. McConnell and R.C. Meisenheimer, Phys.Rev. 98, 264A (1955).
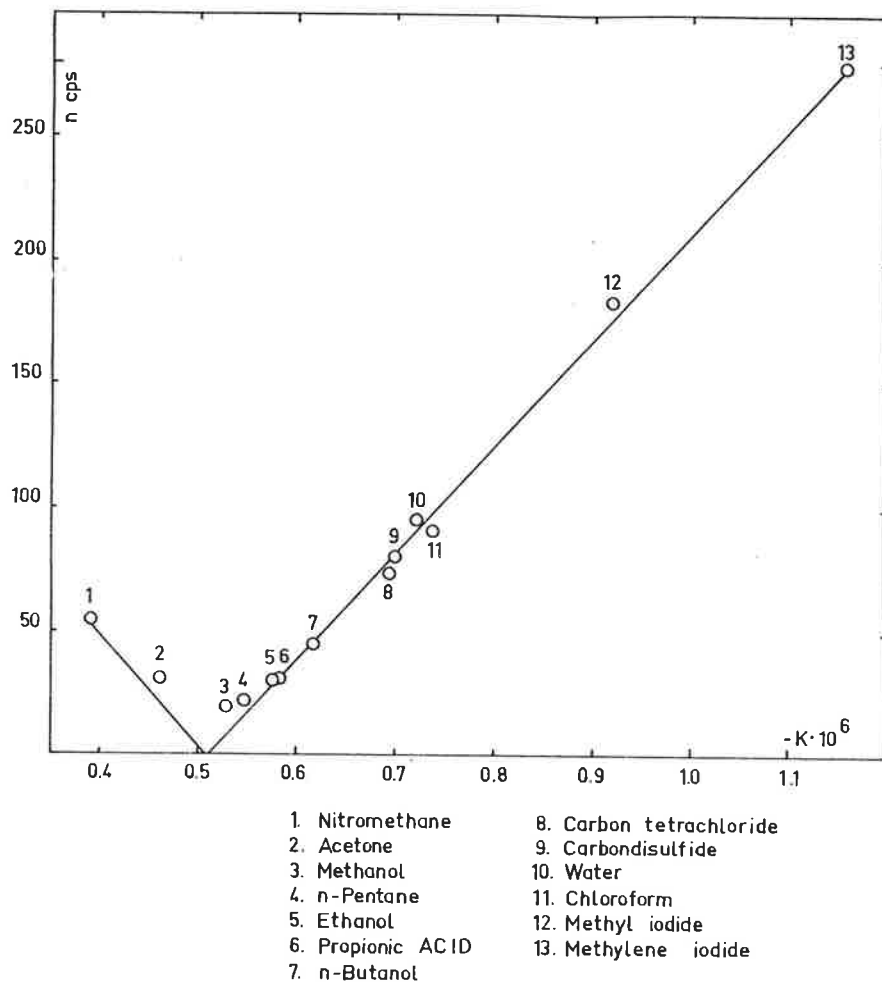
Fig. 1.

1. Nitromethane
2. Acetone
3. Methanol
4. n-Pentane
5. Ethanol
6. Propionic ACID
7. n-Butanol
8. Carbon tetrachloride
9. Carbondisulfide
10. Water
11. Chloroform
12. Methyl iodide
13. Methylene iodide

U.S. ARMY CHEMICAL RESEARCH AND DEVELOPMENT LABORATORIES

Edgewood Arsenal, Maryland

IN REPLY REFER TO

SMUCR-WS(PR)2

Dr. A. A. Bothner-By   15 OCT 1962
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Dr. Bothner-By:

When analyzing mixtures of compounds by nmr to determine the
percentage composition of the mixture, the least detectible concentra-
tion can be important in the accuracy of the determination. We came
across this problem when trying to determine the kinetics of isomeriza-
tion reactions similar to the systox-isosystox study as reported in
J.A.C.S. No. 78 5182 (1956) by N. Muller and J. Goldenson. The relative
areas of the absorption peaks are related to the percent composition of
the mixture. The relative areas were determined by cutting out the
absorption peaks on four or five spectral runs, recorded on a Sanborn
Model 126 Recorder, and weighing the appropriate peaks on an analytical
balance. The P^{31} resonance was observed at 17 mc using 8 mm nmr tubes.
Under these conditions we found the least detectible concentration to
be about 5% for several compounds investigated whose molecular weights
varied from 100 to 250. Consider a mixture of two compounds, A and B,
(6% A and 94% B), each having a single absorption peak, then with the
sensitivity mentioned, it would appear to be a mixture of 1% A and 99% B.
A mixture of 4% A and 96% B would appear to be 100% B. As the concentra-
tion of A is increased the discrepancy will become smaller until a 50 -
50 mixture is reached at which point this error cancels out. As the
concentration of A is increased further the error will favor component
A. This error could cause up to a 10% deviation of the slope of an
isomerization rate plot.

We have developed an equation to conveniently correct for this error.
In this equation it is assumed that a constant area is lost under each
absorption peak and that this area can be related to a percent concentration.
In this equation:

m_i = observed mole percent of ith peak

M_i = true mole percent of ith peak

a_i = measured area of ith peak

a_t = sum of the measured area

A_i = area of ith peak if nmr system were ideal

A_t = sum of the areas of the ideal nmr system

n = total number of absorption peaks

K = the weight of compound not seen in each peak of the nmr spectrum

A_K = the area which would represent K percent on the spectrum

It follows that the observed mole percent is:

$$m_i = 100 \frac{a_i}{a_t}$$

The true mole percent is:

$$M_i = 100 \frac{A_i}{A_t}$$

Since we assume A_K constant for all phosphorus compounds

$$a_i = A_i - A_K$$

$$a_t = A_t - nA_K$$

Using above relationships and the fact that a_t equals 100, we obtain,

$$M_i = a_i(1 - n \frac{A_K}{A_t}) + 100 \frac{A_K}{A_t}$$

Thus for 8 mm nmr tubes which we found have a minumum detectible concentration of 5%

$$A_K = (.05)A_t$$

$$M_i = a_i (1 - n(.05)) + 5$$

and for a two peak system

$$M_i = 0.9 \ a_i + 5$$

Using a 15 mm nmr tube in these analyses, we have found the minumum detectible concentration to be about 1%.

A more detailed report will be published later on.

Yours truly,

HAROLD KLAPPER

CHARLES R. ARNOLD

JOHN F. COTTON

M onthly
E cumenical
L etters from
L aboratories
O f
N - M - R

A monthly collection of informal private letters from laboratories of nmr. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication".

QUEEN MARY COLLEGE
(UNIVERSITY OF LONDON)
MILE END ROAD·E·1
TELEPHONE · ADVANCE 4811
Department of Chemistry

18th October, 1962

Dr. Barry L. Shapiro,
Mellon Institute,
4400, Fifth Avenue,
Pittsburgh, Penn., U.S.A.

Dear Barry,

Here is a first contribution from Queen Mary College. It concerns the notation to be used to concisely describe a multiple resonance experiment. John Baldeschwieler and I, after a discussion with Paul Lauterbur, used a simple notation which has also appeared in Mellonmr (Lauterbur, No.45; Tiers, No.48). The following remarks simply describe and extend this notation.

One can use the normal symbolism with the addition of brackets to indicate which nucleus is being irradiated. Thus $AK\{X\}$ denotes a double resonance in which the A and K transitions are studied while the X transitions are irradiated. Other possibilities are handily given as $\{A\}$ KX and $A\{K\}$ X. A triple resonance in which both the K and X transitions are irradiated would have the symbol $A\{KX\}$. Chemical symbols may be used to specify the nuclei in more detail. Thus $H\{F^{19}\}$ is concisely differenciated from $F^{19}\{H\}$.

For molecules which have more than one nucleus of a given type, subscripts may be used to differenciate these nuclei. The subscripts could, in convenient cases, be the positional numeral, either as used in a conventional molecular formula, or as specified in a structural formula accompanying the spectrum (see below). For unassigned spectra, or in the 'tickling' experiments of Ray Freeman and Wes Anderson (Mellonmr, No.46) in which single transitions are irradiated, the numbers could be used to designate the transitions.

Since it is important to distinguish between fieldswept and frequency swept spectra, one could use different brackets for the two cases, say $\{\ \}$ for field swept and [ ] for frequency swept. Paul Lauterbur has used ( ) for the fieldswept case so it would be essential to keep the confusion minimal by insisting that only [ ] be used for frequency sweep.

Lastly we may add Santonin to the list of molecules in which there is an appreciable proton – proton coupling through five bonds (Freeman and Bhacca, Mellonmr, No.47). The protons involved are labelled (somewhat arbitrarilly) 2 and 3 in the structural formula and the coupling constant is 1.3 ± 0.2 c/s.
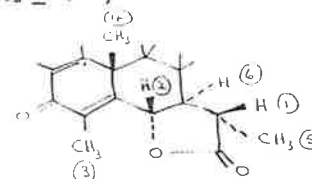
No matter how 'wild' I get I cannot bring myself to draw the requisite diene structures! The assignment, originally due to Professor Corey, was checked by the following experiments: $H_1\{H_5\}$, $H_3\{H_2\}$, $H_2\{H_6\}$. The last experiment was a hidden proton experiment and served to measure the shift of H_6. The assignment was further supported by a study of β–Santonin (visualised by interchanging $CH_3(5)$ and H_1) which also have the long range splitting. Other epimers were studied but so far I gave not yet analysed the spectra. The work was done at Harvard with John Baldeschwieler.

Yours sincerely,

Ed Randall

Ed Randall

EWR/JLC

The University of Sydney

SYDNEY, N.S.W.

IN REPLY PLEASE QUOTE: AVR:jk

Department of Organic Chemistry,

22nd October, 1962.

Dr. B.L. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13,
Pennsylvania, U.S.A.

Dear Dr. Shapiro,

The value of NMR in assisting the structure determination of quinoline alkaloids has been demonstrated by Goodwin, Shoolery and Johnson for the case of lunacrine (JACS, 1959, 81, 3065). I have done an NMR survey of this class of natural products and several correlations emerge which will be useful for structural work on new compounds in future. These will be reported in the Australian Journal of Chemistry. Organic chemists face a general problem in this series in deciding whether the side chain at C-3 (see formulae on spectra) is cyclized to the C-2 oxygen (giving a 4-quinolone) or to the C-4 oxygen (giving a 2-quinolone). Previous methods of choosing between the "linear" or "angular" fusion of the rings (4-quinolone or 2-quinolone respectively) have involved extensive degradative work or syntheses to provide model chromophores etc.

A secure and rapid distinction is now available in the NMR spectrum. As noted in the lunacrine paper, the signal from H-5 is shifted downfield from the other aromatic proton signals because of its proximity to the C-4 carbonyl group. The deshielding of H-5 by the C-4 oxygen would be expected to be reduced when this oxygen is present as an ether link such as

- 2 -

happens when the compound in question belongs to the angular series. The NMR survey confirms this prediction and it is illustrated here in the spectra of the new alkaloid ifflaiamine (linear rings) and N-methyltetrahydroflindersine, a derivative of the naturally occurring angular compound flindersine. The H-5 signal in ifflaiamine is separated from the centre of the band for the aromatic protons by 60 cps, whereas this distance in the flindersine derivative is only 36 cps. The magnitude of these separations changes when the homocyclic ring is substituted (many compounds have alkoxy groups on this ring) but for the same substitution pattern, the difference between the values for linear and angular isomers is always about 25 cps.

The impact of NMR on this class of alkaloids has been dramatic. The structure of flindersine was established around 1955 in this Department by classical methods involving some four man-years of work. The structure of ifflaiamine can be written just from NMR spectra.

Our A-60 arrived in August in time to be displayed at the ANZAAS conference by Varian's Roy Johnson. It has a variable temperature probe operating from -110 to +200°C and we are still learning to drive the thing. The internal geometry of this probe differs from the standard models and it seems to be somewhat more difficult to attain maximum performance. I will be interested to compare operating characteristics with others who have this hot and cold probe.

Yours sincerely,

Alex. Robertson.

Dr. A.V. Robertson

H (5)

56 cps

H (6,7,8)

CHCl₃

N-METHYLDIHYDROFLINDERSINE IN CDCl₃

HIGH GAIN SPECTRUM

N-Me

(Me)

H (5)

J ortho 8cps

J meta 2cps

60 cps

H (6,7,8)

CHCl₃

IFLAIAMINE IN CDCl₃

HIGH GAIN SPECTRUM

22nd October, 1962.

Please address reply to

Dear Dr. Shapiro,

When installing our Varian A60 spectrometer, we experienced some difficulty in deciding on suitable British-made voltage stabilisers and other ancillary equipment, since at that time there were only two spectrometers available in this country. Details of the equipment that we eventually purchased after useful discussions with Professor G.W. Kenner and Dr. R. Abraham at Liverpool University and Professor B. Lythgoe and Dr. P.R. Brook at Leeds University and has given satisfactory service during the last three months may interest other N.M.R. tyros in this part of the world.

The A60 spectrometer is installed together with two Perkin-Elmer model 21 spectrophotometers in a 13' x 11' room maintained at 20-21°C. by a Temkon "series N" air-conditioner (Temperature Ltd., London, S.W.6). The three spectrometers and a spectropolarimeter incorporating a xenon arc are fed through a TS-3 voltage stabiliser (32 amp., 7.36 nominal K.V.A., response speed 40 v./sec.; Claude Lyons Ltd., Hoddesdon, Herts.); this stabiliser is of the motor-driven Variac type.

The magnet coils are cooled by distilled water, which is cycled by a small pump (Type B15; Mono Pumps Ltd., London), fitted with a pressure relief valve, through a domestic calorifier (a 36" x 15" vertical cylinder containing a coil of 24 ft. of 1" I.D. 18 S.W.G. copper tube) as heat-exchanger; the calorifier is cooled with mains water. Provision has also been made for circulating mains water directly through the magnet in an emergency; the change-over can be made without switching off the magnet. Flow indicators are inserted in the mains water and distilled water lines; copper piping is used throughout; this system is similar to that operating at Liverpool University. Green algae grow rapidly in the distilled water system. We are attempting to suppress them by adding 100 p.p.m. of streptomycin sulphate.

Compressed air for the spinner is supplied by a Compton diaphragm pump (Series 4, ECC4; Dawson, MacDonald and Dawson Ltd., Ashbourne, Derbyshire) used in conjunction with a pressure tank (2 cu.ft. capacity) and a pressure switch (Type HP1; Londex Ltd., London, S.E.20) operating at about 30 p.s.i. with a differential of 3 p.s.i. The compressor pump, although a model recommended by the manufacturers as especially quiet, proved too noisy, and we have been forced to move it from the instrument room. We would therefore recommend that a water-cooled pump enclosed in a sound-proof box should be used when the pump has to be in the room with the instrument.

Yours sincerely,

J.H. Chapman   G.F.H. Green   J.E. Page
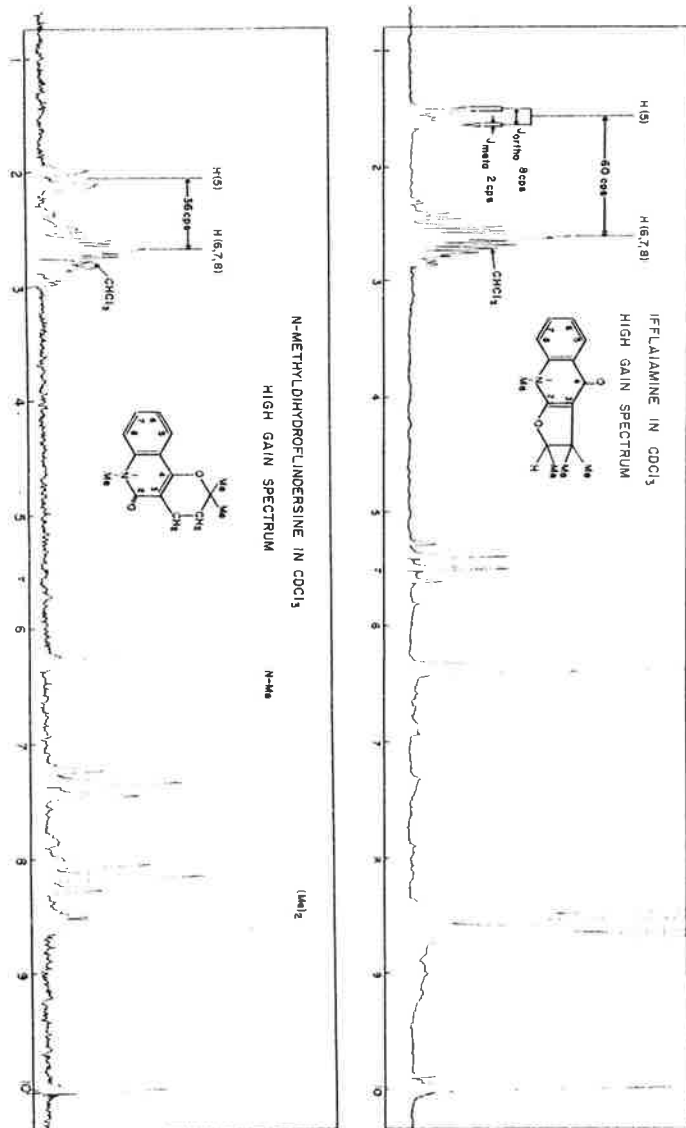
October 22, 1962

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

Dear Dr. Shapiro:

Some Comments on the Letter of Bommer and Primas (No. 48)

Theoretical calculations of nuclear magnetic double resonance behavior
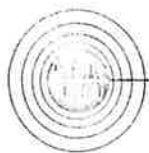are already proving a useful aid to the experimentalist, and any improvements
are only to be welcomed. However before embarking on a rigorous general
calculation, it is perhaps advisable to consider rather carefully the aims of
double resonance experiments, so that the new information may be extracted in
the most economical manner. Professor Primas[1] has raised the question of the
double resonance theory of strongly-coupled systems, and mentioned some
calculations of his own which cover this case, quoting by way of example a
formula for the exact decoupling condition for an AB system[2]. While there is
nothing new to be learnt from the very simple spin systems such as an AB
molecule, the more complex strongly-coupled cases have so many additional
parameters that a general mathematical treatment becomes exceedingly difficult.
One solution is to treat each particular example separately, solving the
double resonance Hamiltonian numerically on a computer. This has been used to
find relative signs of spin coupling constants in a situation where the analysis
method is not applicable[3]. Our own philosophy has been to abandon "spin
decoupling" for strongly-coupled molecules in favor of double irradiation with
a very weak perturbing radiofrequency field ("tickling"), where H_2 is so weak
that only one transition is affected at a time. A general treatment of these
experiments is very much simpler, and the physics of the method can be
described in terms of some very simple rules, the most important being that
transitions are split if they have an energy level in common with the
irradiated transition[4].

(R. Freeman and W. A. Anderson)

The method can be used to construct an energy level diagram from
observed transition frequencies, and this is a big step towards the analysis
of a complex spectrum. A related application is the determination of relative
signs of spin coupling constants in spectra of intermediate complexity. The
principle is the same as that of the spin decoupling method, but in practice
the range of applicability is greatly improved. A third possibility is to
trace out spectra that are obscured, either by overlying resonances or
because of low inherent sensitivity. The investigating frequency may be set
on the peak of a certain transition, and any transitions which have a common
energy level may then be examined by sweeping the perturbing radiofrequency
through the obscured region. We have been able to record C^{13} spectra in this
way by monitoring coupled proton lines, and similar experiments have been
performed by Baker[5].

The versatility of the technique is such that for complex spectra
there seems to be no point in ever reverting to the strong radiofrequency
fields of spin decoupling experiments.

Yours sincerely,

R. Freeman, W. A. Anderson
Instrument Division

1. Bommer and Primas, Newsletter No. 48, p.23.
2. It is interesting to note that if one were to take the frequency of the
   center of each doublet as ω_A and ω_B, then this expression is identical
   with that obtained for the weakly-coupled case -- in this sense the AB
   spectrum behaves like an AX.
3. Rao and Baldeschwieler, J.Chem.Phys., to be published.
4. Newsletter No. 46; R. Freeman and W. A. Anderson, Summer Symposium on
   High Resolution N.M.R., Boulder, Colorado, July 1962; J.Chem.Phys.(Nov.1962).
5. Baker, J.Chem.Phys. 37, 911, (1962).

ZÜRICH, October 23, 1962
Universitätstrasse
Tel. (051) 32 73 30

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

Dear Dr. Shapiro,

the intensity sum rules valid in high resolution
magnetic proton-resonance:

$$(1) \qquad \sum_{\ell} I_{ij}^{m-1} - \sum_{k} I_{jk}^{m} = 2m \qquad \begin{array}{l} (m = \text{magnetic} \\ \quad\text{quantum number}) \end{array}$$

which were published some months ago by G. Gioumousis and
J.D. Swalen (1) are very useful to find the correct coordi-
nation of the spectral lines to the scheme of transitions.
If we denote the vector of the total angular momentum by
$F = (F_1, F_2, F_3)$, then the intensity I_{ij}^{m-1} is defined by

$$(2) \qquad I_{ij}^{m-1} = \left| \left\langle m-1, i \,\middle|\, F_- \,\middle|\, m, j \right\rangle \right|^2$$

where: $F_- = F_1 - iF_2 = (F_1 + iF_2)^+ = (F_+)^+$

Now new relations of a similar type have been found, which
can be helpful for the same purpose.

If we write the hamiltonian in the form:

$$(3) \qquad H = Z + S$$

wherein Z denotes the so-called Zeeman-term and S describes
the spin-spin coupling, then the following formula can easily
be derived:

$$(4) \qquad Z = \left[\left[H, F_+ \right], F_- \right]$$

From the form of the matrix of Z in the basis of the product-
functions $\alpha\alpha\beta\alpha$...etc., it is well-known, that:

$$(5) \qquad \mathrm{Tr}_m(Z) + \mathrm{Tr}_{-m}(Z) = 0$$

wherein $\mathrm{Tr}_m(\ )$ denotes the trace in the eigen-space of F_3 to
the eigenvalue m. If we substitute (4) in (5) and express the
whole equation in the eigenbasis of H, we obtain:

$$(6) \quad \sum_i \left\{ \sum_k \left(\gamma_{ki}^{m-1} I_{ki}^{m-1} - \gamma_{ik}^{-m} I_{ik}^{-m} \right) + \sum_j \left(\gamma_{ji}^{-(m+1)} I_{ji}^{-(m+1)} - \gamma_{ij}^{m} I_{ij}^{m} \right) \right\} = 0$$

Herein γ_{ki}^{m-1} denotes the frequency, which belongs to the transition
$|m-1, k\rangle \rightarrow |m, i\rangle$. (6) represents a system of $\langle n \rangle$ independent
relations between the frequencies and the intensities of the
spectrum, where n denotes the number of protons and:

$$\langle n \rangle = \begin{cases} n/2 & \text{if n is even} \\ n-1/2 & \text{if n is odd} \end{cases}$$

In the case of a three-proton system the scheme of transitions
has the form:
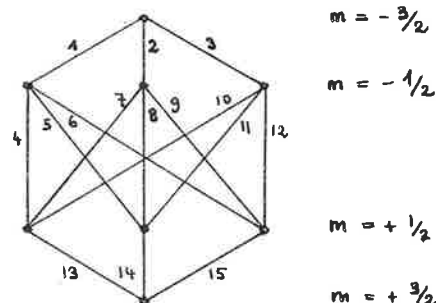
In this special case there exists only one independent equation
of the type of (6), which has the form:

$$(7) \qquad \gamma_1 I_1 + \gamma_2 I_2 + \gamma_3 I_3 = \gamma_{13} I_{13} + \gamma_{14} I_{14} + \gamma_{15} I_{15}$$

Herein the numeration of the frequencies and intensities agrees
with that of the transitions in the above scheme.

Formula (4) has still another remarkable aspect.
It allows namely to base a numerical analysis of nmr-spectras
on it. But to this consequences of formula (4) I shall come
back in my next letter.

(1) G. Gioumousis and J.D. Swalen, JCP 36, 2077 (1962)

Yours sincerely

H. Kummer

H. Kummer

49-26

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