20.3.64

Premas

Monthly Ecumenical Letters from Laboratories Of N-M-R

Illinois Institute of Technology

N-M-R Newsletter

No. 65

Tickling

El. Field

M onthly   I llinois
    E cumenical   I nstitute of
        L etters from   ———>   T echnology
            L aboratories
            O f   N - M - R
          N - M - R   N ewsletter

Please remember that all correspondence, contributions, etc.,
should now be sent to the following address:

> Associate Professor B. L. Shapiro
> Department of Chemistry
> Illinois Institute of Technology
> Technology Center
> Chicago, Illinois 60616.

Deadline Date: It will now be necessary to both advance our
deadline date a few days and to observe it more rigorously than in the
past. Our new deadline date will now be approximately the 20th of each
month, the exact date to appear on the previous month's issue. The
deadline date for the March issue will be Thursday, March 19, and all
material must be in my hands by that date to make the IIT NMRN No. 66.

* * * * * * * * * * *

Contributors are reminded to please submit all material on
8-1/2 x 11" paper, to avoid the use of blue ink, and generally to insure
legibility and at least a modicum of esthetic appeal by sending in copy
which is very black on white paper to give our cameras a fighting chance.
Further, figures, graphs, etc., which are already copies will look rather
fuzzy if reproduced again, so remember our offer to return originals at
your request.

BLS

UNIVERSITY OF DURHAM

TELEPHONE DURHAM 3541-8

CHEMISTRY DEPARTMENT,
SCIENCE LABORATORIES,
SOUTH ROAD,
DURHAM CITY,

JWE/LR

20th January, 1964.
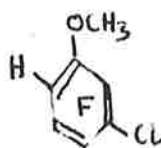
Dear Professor Shapiro,

nmr work in Durham is progressing along two major lines: (1) collaboration with our group of fluorine chemists in determining the structure of fluoro-organic compounds, and (2) more fundamental investigations of F^{19} chemical shifts and coupling constants. Under the first category I have two items which might interest readers of the newsletter.

(a) It seems a good rule that the methyl protons in an OCH_3 group attached to a fluorinated benzene ring couple with any ortho F^{19} nuclei to the extent of about 1 cycle sec.$^{-1}$ We have noted this coupling in many aromatic compounds, such as
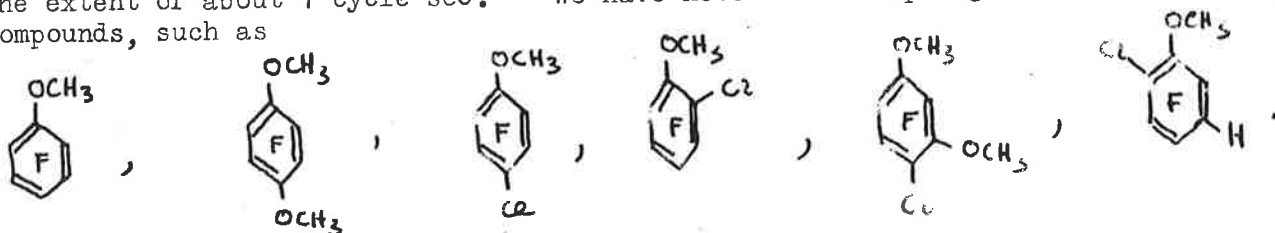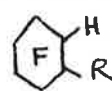
However, we have found one exception to the rule, namely

The H^1 and F^{19} spectra of the pure liquid were examined and there is definitely no OCH_3-F coupling. Our first reaction was to doubt that there is an OCH_3 group present, but the analysis, infra-red spectrum and method of preparation all point to the structure shown. I would be interested to hear of any other apparent exceptions to the OCH_3-F coupling rule.

(b) For some time now we have been trying to establish the conformations of compounds of the type   from their H^1 and F^{19} spectra. It would help us emormously to have a double resonance spectrum, both H-F and F-F decoupling, and I would be delighted to hear from anyone who could run such spectra for us, perhaps in exchange for samples of fluorine-containing compounds?

As a more euphonious title for the newsletter, I suggest NMR-NOISE, being NMR News Of Illinois (Institute of Technology) Serving Everyone.

Yours sincerely,

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago 16,
Illinois, U.S.A.

Jim Emsley.

Jim Emsley

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.
January 23, 1964

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

Dear Barry:

We have recently considered the cross correlation of dipole-dipole interactions in relaxation problems.

An important assumption that is frequently invoked in the assignment of NMR spectra using relaxation effects is that the probability of relaxation between spin states of different symmetry is zero, or at least negligible in comparison with relaxation probabilities among states of the same symmetry (1-3).

1. K. F. Kuhlmann and J. D. Baldeschwieler, J. Am. Chem. Soc. 85 1010 (1963).

2. R. Kaiser, J. Chem. Phys. 39, 2435 (1963).

3. G. W. Flynn and J. D. Baldeschwieler, J. Chem. Phys. 38, 226 (1963).

It is thus important to determine whether a mechanism can, in fact, contribute to relaxation between states of different symmetry. Recent calculations (4-6) of the contribution of internal dipole-

4. P. S. Hubbard, Phys. Rev. 109, 1153 (1958); 111, 1746 (E) (1958).

5. G. W. Kattawar and M. Eisner, Phys. Rev. 126, 1054 (1962).

6. P. S. Hubbard, Phys. Rev. 128, 650 (1962).

Page 2

dipole interactions to the relaxation in specific systems
indicate that the effect of cross-correlation of different
dipole-dipole interactions can be neglected. We would like
to point out that in the calculation of the contribution of
the internal dipole-dipole interactions to relaxation between
states of different symmetry, the tempting approximation to
neglect cross terms gives incorrect results.

In the notation of Redfield (7), the correlation function
(8) is:

$$G_{\alpha\beta\alpha'\beta'}(\tau) = \overline{\langle\alpha|\mathscr{H}'(t)|\beta\rangle\langle\alpha'|\mathscr{H}'(t+\tau)|\beta'\rangle^*} \tag{1}$$

where $\mathscr{H}'(t)$ is a random perturbation expressed in the basis
$|\alpha\rangle$ of eigenfunctions of the time-independent Hamiltonian.

7. A. G. Redfield, IBM J. of Res. and Dev., 1, 19 (1957).

8. A. Abragam, "The Principles of Nuclear Magnetism", (Oxford
    University Press, London, 1961), Chap. 8.

The dipole-dipole interaction Hamiltonian is:

$$\mathscr{H}'(t) = \sum_N \sum_m F^{(m)*}(\theta_N, \phi_N) A_N^{(m)} \tag{2}$$

where the subscript N refers to a distinct pair of spins I_N
and S_N,

$$A_N^{\pm 2} = I_N^{\pm} S_N^{\pm}$$

$$A_N^{\pm 1} = \mp (I_N^{\pm} S_N^{z} + I_N^{z} S_N^{\pm})$$

$$A_N^{0} = \left(\frac{2}{3}\right)^{1/2} \left(I_N^{z} S_N^{z} - \frac{1}{4}\left[I_N^{+} S_N^{-} + I_N^{-} S_N^{+}\right]\right)$$

$$F^{(m)}(\theta_N, \phi_N) = -\left(\frac{6\pi}{5}\right)^{1/2} \hbar \gamma_{I_N} \gamma_{S_N} r_N^{-3} Y_{(2)}^{(m)}(\theta_N, \phi_N)$$

with r_N the fixed distance between the Nth pair of spins, θ_N,

Page 3

ϕ_N the polar and azimuthal angles specifying the orientation of the vector $\underset{\sim}{r}_N$ relative to the laboratory coordinate system, and $Y_{(2)}^{(m)}(\Theta_N, \phi_N)$ the normalized rank two spherical harmonics. The time dependence of $\mathcal{H}'(t)$ enters implicity through the variation of the angles $\Theta_1, \phi_1; \Theta_2, \phi_2; \cdots \Theta_N, \phi_N$. due to the molecular Brownian motion. These angles are not indepentent, but are related in a complicated way by the molecular geometry. However, if $F^{(m)*}(\Theta_N, \phi_N)$ is transformed to molecule-fixed coordinates (9),

9. M. E. Rose, "Elementary Theory of Angular Momentum", (John Wiley and Sons, Inc., New York, 1958), Chap. 4.

$$\mathcal{H}'(t) = \sum_N \sum_m \sum_{m'} F^{(m')*}(\Theta_N', \phi_N') D_{m'm}^{(2)}(\Omega) A_N^{(m)}$$

(3)

The angles Θ_N' and ϕ_N' are independent of time, and the time dependence enters implicity through the independent Eulerian angles $\alpha, \beta, \gamma = \Omega$ which relate laboratory and molecule coordinates. Assuming isotropic motion governed by a diffusion equation, the correlation functions become (6,8)

$$G_{\alpha\beta\alpha'\beta'}(\tau) = \left[e^{-|\tau|/\tau_c} / 8\pi^2 \right] \sum_{NN'mm'\mu\mu'} \int D_{m'm}^{(2)}(\Omega) D_{\mu'\mu}^{(2)*}(\Omega) d\Omega$$

(4)

$$\times F^{(m')*}(\Theta_N', \phi_N') F^{(\mu')}(\Theta_{N'}, \phi_{N'}') \langle \alpha | A_N^{(m)} | \beta \rangle \langle \alpha' | A_{N'}^{(\mu)} | \beta' \rangle^*$$

$$= \sum_{NN'} e^{-|\tau|/\tau_c} g_{NN'} \sum_m \langle \alpha | A_N^{(m)} | \beta \rangle \langle \alpha' | A_{N'}^{(m)} | \beta' \rangle^*$$

where we have used

$$\int D_{m'm}^{(2)}(\Omega) D_{\mu'\mu}^{(2)*}(\Omega) d\Omega = (8\pi^2/5) \delta_{m\mu} \delta_{m'\mu'}$$

The factor

$$g_{NN'} = \sum_m F^{(m)*}(\Theta_N', \phi_N') F^{(m)}(\Theta_{N'}', \phi_{N'}')$$

is reduced to

$$(3/20) \hbar^2 \gamma_{SN} \gamma_{IN} \gamma_{SN'} \gamma_{SN'} r_N^{-3} r_{N'}^{-3} (3\cos^2 \psi_{NN'} - 1)$$

where $\psi_{NN'}$ is the angle between $\underset{\sim}{r}_N$ and $\underset{\sim}{r}_{N'}$, by the spherical harmonic addition theorem. The magnitudes of the cross

Page 4

correlation terms thus depend upon the angles $\psi_{NN'}$.

It is apparent that the relaxation probability between states of different symmetry, W_{ab}, will be very sensitive to the magnitudes of the cross-correlation terms. For example in the molecule <u>trans</u> 1, 2-difluoroethylene where r_N and $r_{N'}$ connecting fluorine and hydrogen atoms are parallel, W_{ab} between states of symmetry A_g and B_u is rigorously zero when the cross-correlation terms are properly considered. However, if the cross-correlation terms are neglected, W_{ab} is simply proportional to

$$\sum_N \sum_m \gamma_{IN}^2 \gamma_{SN}^2 r_N^{-6} |\langle a | A_N^{(m)} | b \rangle|^2 .$$

Since each term in this sum is positive and the $A_N^{(m)}$ operators can connect states of A_g and B_u symmetry, W_{ab} in this approximation is not zero.

Yours very truly,

Jospeh H. Noggle

Karl F. Kuhlmann

John D. Baldeschwieler

JDB:ms

BRADFORD INSTITUTE OF TECHNOLOGY
BRADFORD 7
ENGLAND
DEPARTMENT OF CHEMICAL TECHNOLOGY

Head of Department :
R. L. ELLIOTT, B.Sc., PH.D.(LONDON),
F.R.I.C., F.T.I., F.S.D.C.

Telephone :
BRADFORD 28837

Our Ref : RLE/DWJ/SMG

24th January,1964.

Your Ref :

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

Dear Dr. Shapiro,

M.E.L.L.O.N.M.R. readers might be interested to know that a
short introductory course in "Interpretation of high-resolution N.M.R.
spectra", with accompanying programme of lectures and spectra interpretation,
sessions, will be held at the Bradford Institute of Technology, England,
from 29th April to 1st May, 1964.

Application for places (course fee £2 5s. 0d.) should be made
to the Registrar of the Institute.

Yours sincerely,

D. W. Jones.

DEPARTMENT OF CHEMICAL TECHNOLOGY

Interpretation of High-Resolution N.M.R. Spectra

A Special Short Course.

Wednesday, 29th April.

2.10 p.m.	Opening of the course - Dr. E. G. Edwards (Principal, Institute of Technology, Bradford).
2.15 - 3.15 p.m.	Introduction to N.M.R. Spectra - Dr. D. W. Jones (Institute of Technology, Bradford).
3.15 - 3.30 p.m.	Questions and discussion.
4.00 - 5.00 p.m.	N.M.R. Instrumentation. Mr. R. F. Warren (Univ. of Manchester)
5.00 - 5.15 p.m.	Questions and discussion.

Thursday, 30th April.

9.15 a.m.	Applications in Organic Chemistry - Dr. P. R. Brook (University of Leeds).
10.15 - 10.30 a.m.	Questions and discussion
11.00 - 12.30 p.m.	Spectra Interpretation Session I.
2.15 p.m.	Spin-spin Splitting and Stereochemistry - Dr. C. N. Banwell (University of Sussex).
3.15 - 3.30 p.m.	Questions and discussion
4.00 - 5.30 p.m.	Spectra Interpretation Session II.

Friday, 1st May.

9.15 a.m.	Spin-decoupling and Sign Determination - Dr. K. A. McLauchlan (N.P.L., Teddington).
10.15 - 10.30 a.m.	Questions and discussion
11.00 - 12.00 noon	Calculation of High-resolution Spectra - Dr. J. W. Emsley (University of Durham).
12.00 - 12.15 p.m.	Questions and discussion
2.15 p.m.	Applications in Inorganic Chemistry - Dr. J. A. S. Smith (University of Leeds).
3.15 - 3.30 p.m.	Questions and discussion.

P.D.Dr.W.v.Philipsborn   January 24, 1964
Organisch-chemisches Institut
der Universität Zürich

Prof. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Ill.

" Allylic and homoallylic proton-proton coupling via heteroatoms "

Dear Professor Shapiro:

In the recent literature one can find considerable interest in
the magnitude, sign, angular dependance and mechanism of allylic
and homoallylic proton-proton coupling [1]. Although most cases
are confined to interactions via a carbon skeleton there are also
systems reported in which one sp^2 - carbon atom is replaced by
heteroatoms, for instance oxygen [2] or nitrogen [3,4].

$$H-\overset{|}{\underset{|}{C}}-\overset{|}{C}=X-\overset{|}{\underset{|}{C}}-H \qquad X = C, O, N$$
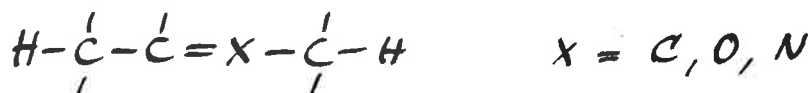
We now wish to report such data from a pair of new compounds
showing an interesting long range proton-proton coupling via
oxygen atoms. These couplings across four and five bonds respect-
ively can be rationalized in terms of allylic and homoallylic
interactions if one assumes that the polar mesomeric structures
contribute to the groundstate of the respective molecules I and II;
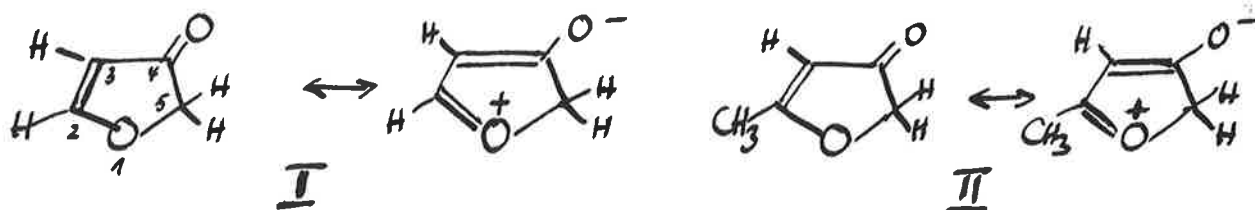
$J_{CH_2-H(2)} = 0.8 \pm 0.1$ cps $J_{CH_2-CH_3} = 0.8 \pm 0.1$ cps

The signs of these constants expected to be opposite remain to
be determined. I is the long sought for " β-hydroxyfuran " recently
synthesized [5] and II was described in (2).

Bearing in mind that both compounds are in fact vinylogous lactones and exhibit such chemical behaviour [2] these results are not too surprising. They could then be taken as evidence that allylic and homoallylic couplings are of the same magnitude even if one sp^2 - carbon atom is replaced by an oxonium atom. It is however interesting to note that there is no measurable interaction between the H-3 and the H-5 protons as might be concluded from this picture. Since the contact-δ,π-interactions assumed to dominate these couplings should be proportional to η_π^2 [6] this would indicate a smaller π -bond order η for the 3,4- than for the 1,2- bond. The influence of the oxygen atom in 4-position may also be considered but allylic and homoallylic coupling in heterocyclic vinylethers was recently reported to be normal [7].

Analogous homoallylic couplings were found across nitrogen in the system [3]
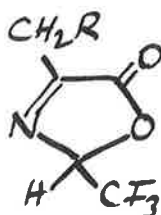
$J_{CH_2-H} = 1.4-2.5$ cps,

depending upon the nature of the substituent R and presently under investigation.

---

1) For references consult: J.T.Pinhey & S.Sternhell, Tetrahedron Letters 1963, 275 ; S.Sternhell, Mellonmr 61-4 .
2) R.E.Rosenkranz, K.Allner, R.Good, W.v.Philipsborn & C.H.Eugster Helv.chim.Act. 46, 1259 (1963).
3) F.Weygand, W.v.Philipsborn et al., full paper in preparation.
4) M.A.Weinberger & R.Greenhalgh, Mellonmr 52-9 .
5) C.H.Eugster, A.Hofmann & W.v.Philipsborn, forthcoming paper.
6) H.M. McConnell, J.Chem.Phys. 24, 460 (1956) .
7) D.Gagnaire & E.Payo-Subiza, Bull.Soc.Chim. 1963, 2623 .

Wishing you the best for the New Year, your new position in Chicago and our Newsletter,

Yours sincerely,

W.v.Philipsborn

SHELL DEVELOPMENT COMPANY

A DIVISION OF SHELL OIL COMPANY

EMERYVILLE, CALIFORNIA

January 29, 1964

AIRMAIL

Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Dear Barry:

H^1, F^{19}, and P^{31} SPECTRA OF SOME METAL CARBONYL COMPLEXES

Before leaving Mellon Institute, we prepared (in collaboration with Dr. W. R. Cullen of the University of British Columbia) a number of complexes containing terminal or bridging $-As(CF_3)_2$ groups. The H^1 and F^{19} n.m.r. spectra of these complexes may be of interest to some of your readers.

Complex[a]	τ	ϕ^{*}[b]
$[C_5H_5Fe\{As(CF_3)_2\}(CO)_2]$[c]	5.08	+42.16
$[C_5H_5Mo\{As(CF_3)_2\}(CO)_3]$[c]	4.52	+40.45
$[C_5H_5Fe\{As(CF_3)_2\}(CO)]_2$ (trans-isomer)[d]	5.43	+48.57
(cis-isomer)[d]	5.43	+46.15, 51.38[e]
$[C_5H_5Mo\{As(CF_3)_2\}(CO)_2]_2$[d]	4.44	+46.29
$[Mn\{As(CF_3)_2\}(CO)_4]_2$[d]	–	+45.84
$[Fe\{As(CF_3)_2\}(NO)_2]_2$[d]	–	+43.52

a) CCl_3F used as solvent. b) Measured at 56.4 Mc. c) Contains terminal $-As(CF_3)_2$ group. d) Contains bridging $-As(CF_3)_2$ groups. e) Quartets with J_{FF^1} 6.6 c.p.s.

One of the main points of interest is that the gem-trifluoromethyl groups in cis-$[C_5H_5Fe\{As(CF_3)_2\}(CO)]_2$ have different chemical shifts owing to molecular asymmetry. The observed J_{FF^1} is similar to that found in the C^{13} satellite spectrum of $(CF_3)_2AsCl$ (R.K.Harris, J. Mol. Spect., 10, 309; 1963).

Dr. B. L. Shapiro   - 2 -   January 29, 1964

This may also be a good place to record the P^{31} spectra of some related $-P(CH_3)_2$ bridged complexes. (We are indebted to Drs. M. M. Crutchfield and C. F. Callis for these data).

Complex	Chemical Shift[a]	Solvent
$[Fe\{P(CH_3)_2\}(CO)_3]_2$	-116.5	$CHCl_3$
$[Cr\{P(CH_3)_2\}(CO)_4]_2$	-245.0	$CHCl_3$
$[(C_5H_5)_2Fe_2H\{P(CH_3)_2\}(CO)_2]$	-163.5	C_6H_6

a) p.p.m., relative to external H_3PO_4, measured at 24.3 Mc.

With best wishes,

R. G. Hayter

RGH/jfn

RESEARCH LABORATORIES

GENERAL MOTORS CORPORATION

January 31, 1964

Associate Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Dear Barry:

To renew my IITNMRN subscription I am writing concerning several matters.

For the interest of wide line enthusiasts I have a few preprints of a paper entitled "Modulation Effects in Magnetic Resonance—Widths and Amplitudes for Lorentzian and Gaussian Lines" which has been accepted for publication in J. App. Phys. I have enclosed a copy of the preprint.

———————

Mr. B. W. Joseph and I have found that we can use the Varian V3521A integrator (in the external mode) quite conveniently to integrate the derivative wide line signals from the V4270A Output Control Unit. A few minor modifications must be made. Since the output of the V4270A is balanced while the input to V3521A (J401) has one side grounded, one must obtain the signal to be integrated from pin 2 of V703 (12AY7) of the V4270A rather than from the output itself. This cuts down the signal strength by a factor of 2 or so but this effect is unimportant in view of the gain in S/N through the use of the integrator. A small DC unbalance between pin 2 of V703 and ground causes a steady drift of the integrator, but this is eliminated by use of the following circuit:

Dr. B. L. Shapiro
Page 2.

To J401 of V3521A

BNC "T"

To pin 2 of V703 in V4270A
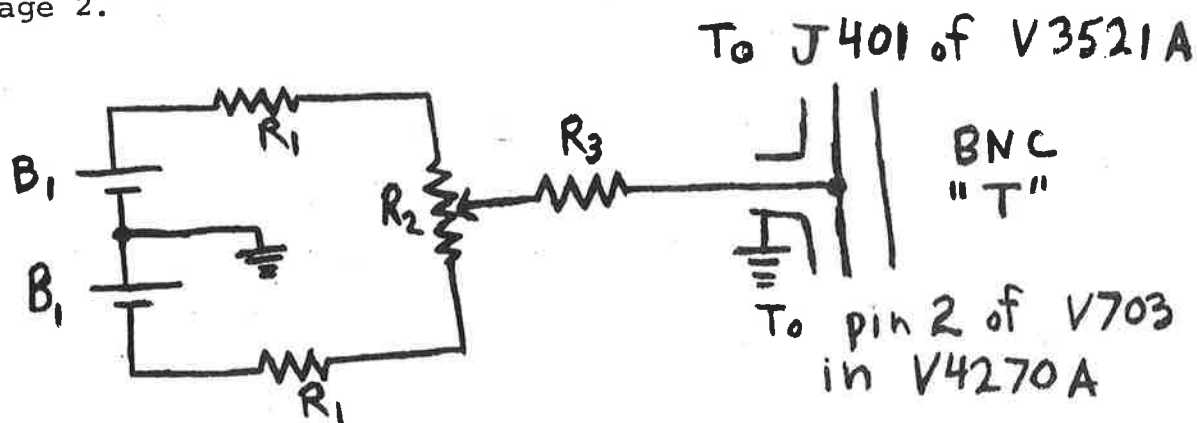
B_1 = Type 1R Hg cell
R_1 = 56K, R_2 = 10K, R_3 = 6.8M

It is quite easy to add a BNC connector to the V4270A in order to make the connection to pin 2 of V703. The initial unbalance is so small ($\sim 0.01v$) that use of the above circuit does not visibly affect the operation of V4270A. After the integrator is balanced initially the unbalance due to V4270A can be bucked out by adjustment of R_2. It is quite easy to record both inte-grated derivative and derivative simultaneously. Such simultaneous recordings are reproduced below.

Area = 1

Area = 235
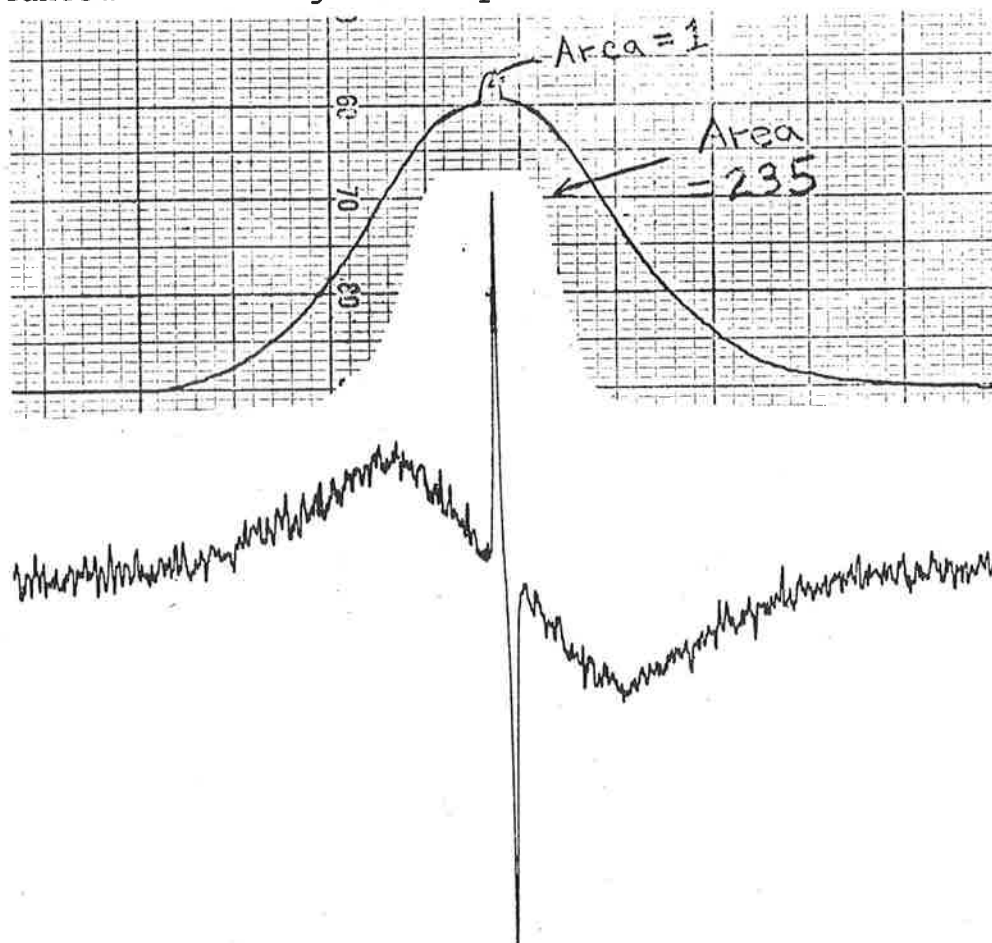
Dr. B. L. Shapiro
Page 3.

It can be seen that one of the benefits to be gained is an improved signal to noise ratio. It can be seen from the tracings that the integral allows one to estimate intensities of the components of the lines from their relative areas. (The ratio of the areas, of course, is independent of modulation amplitude even if one component is over modulated. This follows from Andrew, Phys. Rev. 91, 425(1953). Another benefit is the esthetic one of actually being able to see the physically "real" quantity, the line shape function for χ'' (or for χ' if one tunes to the dispersion mode) rather than its derivative. It is of course equally easy to obtain the second moment graphically from either g(H) or $\frac{dg}{dH}$.

A small item which may eliminate MELLONMR readers' pen cleaning chores for the Varian recorders is the use of a device which we call a "humidity cell". This is simply a covered dish of water with a receptacle to hold the recorder pen. The high humidity in the cell keeps the ink in the pen from drying, and thus the pen remains unclogged.
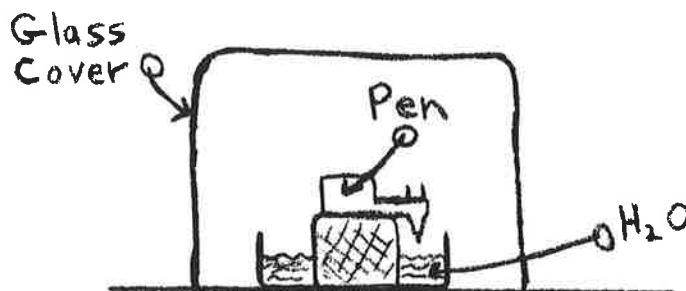
Now for a high resolution PMR item. In the October 15, 1963, J. Chem. Phys. (p.2031) I presented results on J_{XCH} for $X Me_4$ compounds and generalized an idea of Karabatsos et al {J. Phys. Chem. 65, 1657 (1961)} to calculate effective nuclear charge Z^*_{NMR} assuming the Fermi contact term to dominate using the relation

$$J_{XCH} = \frac{\alpha^2}{\alpha^2_H} \frac{\Delta E_H}{\Delta E_X} \frac{1}{n^3} \frac{(Z_X^*)^3}{(Z_H^*)^3} \frac{g_X}{g_H} J_{HCH} \qquad 1)$$

where α^2 is the s-character of the X-orbital in the X-C bond. ($\alpha^2 = 0.25$ for XMe_4). A rough correlation of $(J/g)_X$ with n^3 was taken as evidence supporting the dominance of the Fermi term since $Z_X^* \sim n^2 \left(\frac{a_o}{r_m}\right)$.

Dr. B. L. Shapiro
Page 4.

Since then I have extended the use of the equation to $HgMe_2$ ($\alpha^2 = 0.50$); $(Me_3PtI)_4$ ($\alpha^2 = 0.25$); $(Me_4P)^+Cl^-$ ($\alpha^2 = 0.25$); and $TlMe_3$ ($\alpha^2 = 0.33$) (X is underlined). A logarithmic plot of the resulting Z^*_{NMR} versus the true nuclear charge Z for these four compounds, plus five Me_4X, and CH_2OOH, and methane is shown in the attached figure. The correlation seems remarkable. I feel that the correlation tends to support the idea of the dominance of the Fermi term. High values of Z* for heavy atoms could be due to dipole-dipole coupling which Schneider and Buckingham {Diss. Far. Soc. No. 34, 147 (1962)} say can be sizeable. Both dipole-dipole and Fermi terms go as $(Z^*/n)^3$.

If one assumes the validity of the Z^*_{NMR} plot, one can compute α^2 from known J_{XCH} values (for covalent bonding). For instance, using $J_{PCH} = 2.7$ cps in PMe_3 {Whitesides et. al, J. Am. Chem. Soc. 85, 2665 (1963)} we get $\alpha^2 = 0.05$, a reasonable value since one expects p-bonding. Also for $TeMe_2$ Klose { Z. Naturforsch 16A, 528 (1961)} gives $J_{TeCH} = 20.7$ cps. This yields $\alpha^2 = 0.14$, a quite reasonable value since the C-Te-C bond angle is expected to be around 100°.

A fuller account of this will appear shortly in a letter to J. Chem. Phys.

If one attempts to compute α^2 values for F from J_{FCH} one gets (for CH_3F) {Muller and Carr, J. Phys. Chem. 67, 112 (1963)} $\alpha^2 = 0.33$, much too high (one expects $\alpha^2 \sim 0.05$). Perhaps the discrepancy is due to ionic contributions to J.

An extension to J_{XCY} would be

$$J_{XCY} = \frac{W_Y}{W_H} \cdot J_{XCH} = \frac{W_Y}{W_H} \cdot \frac{W_X}{W_H} J_{HCH}$$

where $W_X = \dfrac{\alpha_X^2 \, norm_X \, (Z_X^*)^3 \, g_X}{\Delta E_x}$

and $\dfrac{norm_X}{norm_H} = \dfrac{1}{n_X^3}$.

It is worth noting that this equation agrees with the statement of Schneider and Buckingham {loc. cit} that J_{XY} is proportional

to $\left(\dfrac{Z_X^*}{n_X}\right)^3 \left(\dfrac{Z_Y^*}{n_Y}\right)^3 \dfrac{\gamma_X \gamma_Y}{\gamma_H^2}$.

Dr. B. L. Shapiro
Page 5.

The only data I know of to test this equation are J_{FCC} in CF_3CH_2Br (= 38.5 cps) {Muller and Carr, loc. cit.} and J_{FCS_n} in $(CH_3)_2 Sn(C_2F_4H)_2$ (=251 cps) {Reeves and Wells, Can J. Chem. <u>41</u>, 2698 (1963)}. These values yield $\alpha^2(Z_F^*)^3$ = 86 and $\alpha^2(Z_F^*)^3$ = 35 respectively. The fact that the two results are off only by a factor of 2 is satisfying, but use of $Z_{NMR}^* = 4.6$ from the plot gives α^2 = 0.87 and 0.36 respectively. These values are high, no doubt due to ionic contributions which we expect to be large because of the multiple fluorines. It would be of interest to test equation 2) for some J_{XCY} where only covalent bonds are present.

A final possible extension of the equation is an obvious one to the case J_{XQY} (if one wishes to get really wild). Drake and Jolly {U.S. At. En. Comm. Report U CRL-10422 (1962) ——— Chem. Abst. <u>58</u> 2042a (1963)} give J_{PSiH} = 16.2 cps in SiH_3PH_2. Using J_{HSiH} from Ebsworth and Turner {J. Chem. Phys. <u>36</u>, 2628 (1962)} and $(Z_P^*)_{NMR}$ = 6.23 we get α^2 = 1.5, obviously incorrect. Because of p-bonding in phosphine we expect $\alpha^2 \approx$ 0. However, Ebsworth and Turner point out that their results for J_{HSiH} depart radically from the theory of Gutowsky et. al. {J. Chem. Phys. <u>31</u>, 1278 (1958)} upon which equation 1) rests, so that the failure of the extension to J_{PSiH} is not surprising. Ebsworth and Turner indicate that the discrepancy of the J_{HSiH} results may be due to the contribution of d orbitals of silicon. It would appear that an extension to J_{XQH} is likely to be unsuccessful for most Q.

———————

I should like to point out an apparent discrepancy in the Varian Table of Nuclear Properties. This occurs for the Sn isotopes (all I=1/2) in that the ratio of their quoted NMR frequencies does not agree with the ratios of the magnetic moments (μ). In the table the ratio of the frequencies in 10 kg for $Sn^{115}/Sn^{117}/Sn^{119}$ is 13.22/15.77/15.87 (a ratio 0.834/0.994/1.000) whereas the quoted μ values are 0.9132/0.9949/1.0409 (a ratio 0.877/0.956/1.000). In my paper on J_{XCH}, the J_{SnCH} values are in the ratio 0.878/0.957/ 1.000, in agreement with the μ values.
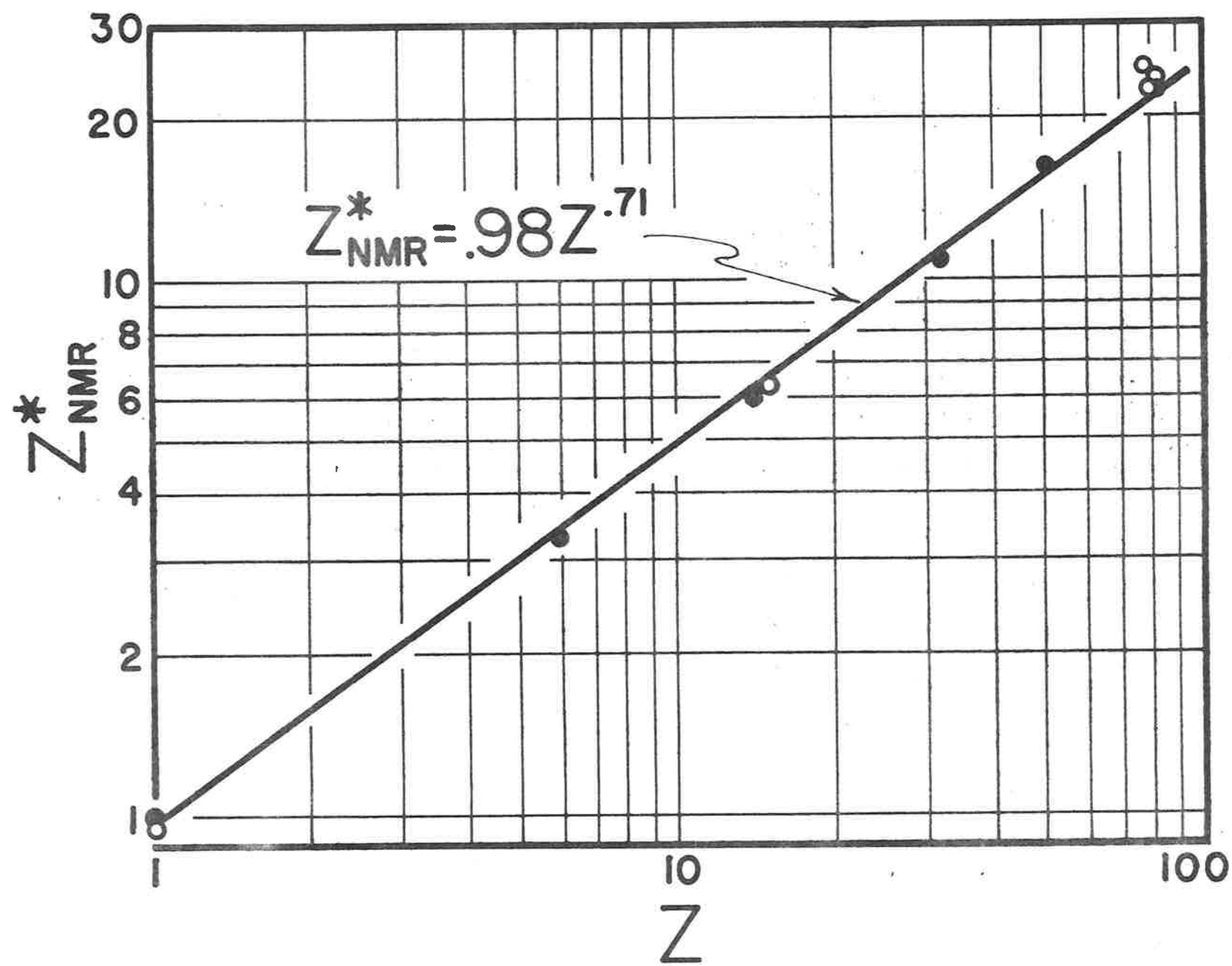
I hope this letter is not too lengthy. If it is feel free to edit out any of the five sections separated by ——— . We could then submit the edited portions at a later time.

Yours truly,

George

George W. Smith
Physics Department

GWS/vf
Enclosures

$$Z^*_{NMR} = .98Z^{.71}$$

Department of Chemistry
Kobe, University
Kobe, Japan

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago 16, Illinois

Dear Professor Shapiro:

In need of C-halogen bond anisotropies, we attempted to make an estimate of their orders of magnitude from Spieseck and Schneider's data.[1] If we take anisotropy shifts σ_{anis} to be the deviations from the linear relations between the proton chemical shifts of alkyl-X compounds and the electronegativity of X, and locate the center of anisotropy at the halogen nucleus, the required anisotropies $\Delta\chi$ are as given in the Table. As can be seen from the Table, the discrepancies in required anisotropy for the α proton shifts and β proton shifts are considerable and the anisotropies seem to be too large compared with the diamagnetic susceptibilities of halogen negative ions. The discrepancies become even more prominent as the center of anisotropy is moved towards the midpoint of the C-X bond. One could obtain negative $\Delta\chi$ values consistent for the α and β protons by locating the center of anisotropy near the carbon atom. However, this may not represent the actual situation, since then the dipole approximation may break down particularly for the α protons.

In contrast to reference 1, Reddy and Goldstein[2] deduced negative σ_{anis} values from correlations between C^{13}-H coupling constants and proton chemical shifts. It is felt, however, there is some doubt about the simple correlations between coupling constants and chemical shifts.

Zürcher[3] pointed out the use of the Gans-Mrowkwa equations in determining magnetic anisotropies. According to this method, one obtains $\Delta\chi_{C-Cl} = +0.86 \times 10^{-6}$ and $\Delta\chi_{C-Br} = +1.00 \times 10^{-6}$[4] using Denbigh's electron polarizability data.

The above inconsistencies and conflicts deduced from the NMR data suggest that great care should be exercised in estimating magnetic anisotropies from NMR spectroscopic data. Generally NMR tends to exagerate the anisotropy effects compared with other methods.

Yours sincerely,

A. Saika

A. Saika

1) Spieseck and Schneider, J. Chem. Phys. 35, 722(1961).
2) Reddy and Goldstein, J. Chem. Phys. 38, 2736(1963).
3) Zürcher, J. Chem. Phys. 37, 2421(1963).
4) Denbigh, Trans. Fared Soc. 36, 936(1940)

TABLE. Anisotropy shifts and required halogen bond anisotropies in alkyl halides.

	σ_{anis} p.p.m.	$\Delta\chi$ $10^{-6} cm^3 mole^{-1}$	
CH_3Cl	-0.80	13.8	
CH_3Br	-0.85	16.5	
CH_3I	-1.01	23.1	
CH_3CH_2Cl	-0.87	14.4	
CH_3CH_2Br	-1.07	20.3	
CH_3CH_2I	-1.41	33.8	
CH_3CH_2Cl	-0.39	37.8	(staggered)
		49.3	(eclipsed)
CH_3CH_2Br	-0.61	51.7	(staggered)
		59.9	(eclipsed)
CH_3CH_2I	-0.88	76.3	(staggered)
		88.6	(eclipsed)

UNIVERSITY OF PITTSBURGH

PITTSBURGH 13, PENNSYLVANIA

DEPARTMENT OF CHEMISTRY

February 4, 1964

Dr. Aksel A. Bothner-By
Mellon Institute

Dear Aksel:

Two Bond Phosphorus-Proton Couplings in Phosphonium Salts

We have recently examined the spectra of a number of phosphonium salts in collaboration with Irving Borowitz of Lehigh University in an attempt to distinguish between alternative O- and C-phosphonium structures. Since the knowledge of P-C-H coupling constants would provide a convenient method for identifying the C-phosphonium structures, we have obtained the spectra of a number of representative phosphonium salts in which unequivocal assignments of J_{P-C-H} can be made.

The spectra were taken on an A-60 spectrometer with 10%-saturated solutions in deuterated chloroform; TMS was used as an internal reference. The coupling constants were obtained from the 50 c.p.s. sweep width.

| | $[R_3PR']^+$ | Chemical Shift | |
R	R'	(τ scale)	J_{P-C-H} (C.P.S.)
C_6H_5	$CH_2C_6H_5$	4.72	14.1
	$CH_2C_6H_4OCH_3$-p	4.86	13.4
	$CH_2C_6H_4COOCH_3$-p	4.27	15.5
	$CH_2C_6H_4Cl$-p	4.26	14.7
	CH_2COOH	----*	13.5
	$CH_2COOC_2H_5$	4.58	14.5
	$CH_2COOCH_2C_6H_5$	4.25	14.0
	CH_3	6.75	13.9
$n-C_4H_9$	$CH_2C_6H_5$	5.68	15.4
	CH_2COOH	6.14	12.7

*Recorded in D_2O.

Only three salts of those examined have shown J_{P-C-H} values significantly outside the relatively narrow range cited above. A J_{P-C-H} (P-CH$_2$-N) value of 6.0 c.p.s. (in DMSO-d$_6$) is observed for:

$$[(NCCH_2CH_2)_3PCH_2N(CHO)CH_3]^+$$

In two cyclic phosphonium salts provided by L. D. Quin of Duke University, J_{P-C-H} values of ca. 10 c.p.s. have been observed for coupling with ring methylenes.
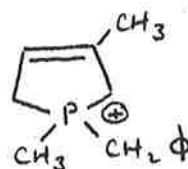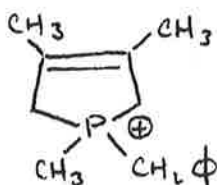
J_{P-C-H}			
	(methylene)	10.5	10.3
	(methyl)	14.3	14.4
	(benzyl)	16.8	16.5

We are currently extending this range of phosphonium salts and hope to publish our results in the near future.

Sincerely,

Claibourne E. Griffin

Myra Gordon

The Indirect Observation of NMR Spectra

(E. B. Whipple, Union Carbide Research Laboratories)

Double resonance techniques can be used to obtain the information available in a region of an NMR spectrum whose direct observation is impractical, e.g., the Xe^{129} spectra of xenon fluorides.[1] The simple description of the splittings which was given in that work, while sufficient for the purpose at hand, applies only to frequency swept experiments and ignores secondary complications due to different effective sweep rates[2] and general Overhauser effects.[3]

A field sweep experiment which passes simultaneously through the frequencies of two connected, nondegenerate transitions is described by the condition $\Omega = k\Delta$ or $\Omega^* = k\Delta$, depending on whether the energy levels are in the $\Lambda = 0$ or $\Lambda = 2$ arrangements[3] ($k = |\gamma_1||\gamma_2|$). The Bohr condition is satisfied when

$$\omega_2 = \omega_{rs} \overset{+}{} h_{rs}/2\sqrt{k(k-1)}$$

for $\Lambda = 0$, or

$$\omega_2 = \omega_{rs} \overset{+}{} h_{rs}/2\sqrt{k(k+1)}$$

for $\Lambda = 2$. The ratio of the splittings is hence $\left\{|\gamma_1 + \gamma_2|/|\gamma_1 - \gamma_2|\right\}^{1/2}$, and the intensities of the components are proportional to

$$L = 1/2(1 - \frac{1}{2k-1}) \qquad\qquad (\Lambda = 0)$$

$$L = 1/2(1 + \frac{1}{2k+1}) \qquad\qquad (\Lambda = 2).$$

In addition, a population enhancement is generally associated with the $\Lambda = 2$ arrangement and a dimunition with the $\Lambda = 0$ arrangement. The details can

become quite complicated, but a simple estimate of the population factor made by assuming independent relaxation and complete saturation of the tickled line is $(1 \pm |2k|^{-1})$.

The limiting behavior for $\gamma_1 > \gamma_2$ reduces to the simple argument we applied to the xenon fluorides, but with k = -3.38 they are a rather poor approximation of this case. Another case of general interest is the homonuclear field sweep with k = 1; here one can satisfy the Bohr condition only for the Λ = 2 arrangement, and the intensities of the components are about equal to that of the unsplit line. Cases with k < 1 are of little practical importance.

To illustrate something in between, the low-field F^{19} line (normalized intensity = 12) in PF_3 vapor is shown below with simultaneous irradiation of the second lowest frequency line in the P^{31} spectrum. One of the outer F^{19} quartet transitions is unaffected, and one is split according to Λ = 0. The inner quartet and two degenerate doublet transitions are all split according to Λ = 2 with k = 2.324, we therefore expect a quintet with a splitting ratio of 1.58 and intensity ratio of (3/2 x 0.363):(3 x 0.588):3:1.764:1.045. Including the population factors estimated as above, the intensities become 0.86:4.29:3:4.29:0.86.
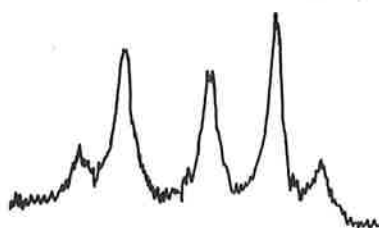
PF_3, Field Sweep
ν_1 = 56.446 660 m.c.
ν_2 = 24.284 145 m.c.

1. T. H. Brown, E. B. Whipple, and P. H. Verdier, J. Chem. Phys. 38, 3029 (1963).

2. R. Freeman and W. A. Anderson, J. Chem. Phys. 37, 2053 (1962).

3. R. Kaiser, J. Chem. Phys. 39, 2435 (1963).

THE UNIVERSITY OF LIVERPOOL
DEPARTMENT OF ORGANIC CHEMISTRY

FROM PROFESSOR A. R. BATTERSBY

THE ROBERT ROBINSON LABORATORIES,
OXFORD STREET,
LIVERPOOL 7.
TELEPHONE: ROYAL 6022

Assoc. Prof. B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,   3rd February, 1964
Technology Center,
Chicago 16,
Illinois.

Dear Dr. Shapiro,

Here is my first subscription to I.I.T.N.M.R.N.

As part of an investigation into the Proton Resonance Spectra of some proline derivatives in strong acid and alkaline solutions,[1] we measured a number of proposed internal reference compounds for aqueous solutions in neutral, acid (3 N DCl) and alkaline (3 N NaOD) solutions. Our results, expressed on the τ' scale proposed by Tiers (MELLON 16, 1) are shown in the Table, together with the results of Tiers in neutral and 5% sulphuric acid solutions, shown in brackets. It can be seen that the two sets of results for the neutral solutions and those for the alkaline solutions are all in excellent agreement (our experimental error is ca. $\pm$ .005 p.p.m.). However, the acid τ' values do vary. We find a constant difference between the τ' values in D_2O and DCl (except for dimethylsulphoxide which protonates in acid solution and therefore is not a satisfactory internal reference), shown in column 4. Our explanation of this constant difference is that the DSS exists as the undissociated acid in these strongly acid solutions (PKa of methane sulphonic acid is ca. 0) and thus the chemical shift of the methyl peaks changes by 0.030 p.p.m. compared to the sodium salt. In support of this, no further change was observed in 5 N acid. Thus our conclusions are that any of the above compounds (except dimethyl-sulphoxide) are satisfactory reference compounds in acid and alkaline solutions, (although there is ᵕ doubt about the use of tert-butanol with aromatic solutes[2]), and that if the τ' scale is to be used, for accurate comparisons of chemical shifts in strong acid and neutral solutions, one adds 0.030 to the acid values.

/ cont.

Changing the subject, I was interested in Dr. Manatt's letter (MELLON, 63, 12) as we have also had some troubles due to the A-60 temperature probe not being positioned correctly in the magnet gap. (In our case the field was too dished to be corrected by the curvature potentiometer). We checked the homogeniety of the control sample by first maximising the homogeniety controls in the normal manner (on ADJUST) and then interchanging leads J203 and J303 and observing the control sample signal directly (on OPERATE) without changing the homogeniety control settings.

Whilst on the topic of the A-60 temperature probe, we find that the magnet (or something) goes over cycled on cooling and under cycled on heating – so much so that if the curvature potentiometer isn't in the middle of its range at room temperature it is liable to go off its range at either high or low temperatures. Also, we would like to go to much lower temperatures than the guaranteed -60ºC, I would be interested to know how many MELLON readers have run the A-60 probe at -90ºC without damage.

With best wishes,

Yours sincerely,

R. J. Abraham.

[1] R.J. Abraham and W.A. Thomas, J.Chem.Soc., (submitted)

[2] Jones, Katritsky and Sheppard, J, 2576, 1962.

Table 1.

Proton Chemical Shifts (τ') of Reference Compounds
in Acid, Neutral and Alkaline Solutions

Sample	Acid	Neutral	Alkaline	$\tau'(D_2O) - \tau'(DCl)$
DSS [2]	10.000	10.000	10.000	0.000
Tert.butanol	8.735	8.769	8.763	0.034
Acetonitrile	7.911(7.934)	7.941(7.946)	- [1]	0.030
Acetone	7.760	7.784(7.777)	- [1]	0.024
Dimethylsulphoxide	7.188	7.290(7.285)	7.281	0.102
$Me_4N^+ Br^-$	6.795(6.794)	6.822(6.824)	6.825	0.027
Dioxan	6.238(6.249	6.257(6.251)	6.253	0.025

[1] Exchanges in alkaline solution.

[2] Sodium 3-trimethylsilylpropanesulphonate.

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

FOOD AND DRUG ADMINISTRATION

WASHINGTON, D.C. 20204

January 31, 1964

Assoc. Prof. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Dear Barry:

Let me report on the 60 mc spectrum of 1-methyl-1-cyano-3-isopropyl idenecyclobutane. The proton spins may be described as an $A_2B_2M_6X_3$ system or, if transannular coupling is neglected, as an $(AB)_2M_6X_3$ system.

In band $\underline{A}$, X_3 (methyl) gives a single peak and M_6 (isopropylidene) a quintet with the highest-field component merged with the X_3 peak. In band $\underline{B}$ the four peaks of the $(AB)_2$ pattern (ring protons) are split into septuplets, of sorts, by M_6. The fact that the bands are not exactly symmetrical may be, e.g., due to second-order effects, transannular coupling with the ring protons, and to J_{AM} and J_{BM} not being equal.

At any rate, rough parameters for this molecule are:

τ_A	τ_B	τ_M	τ_X	J_{AB}	$J_{(AB)M}$
6.93	7.37	8.40	8.45 ppm	$|15.5|$	$|2.0|$ cps

The features of potential interest in this spectrum are the following.

1. There is no appreciable coupling between methyl and ring protons.

2. There is a sizable coupling of about 2 cps between the iso-propylidene and the ring protons. We have observed this kind of long-range coupling in a number of similar molecules.

3. A geminal coupling constant is obtained for protons bonded directly to atoms of a four-membered ring. Its magnitude is comparable to those observed earlier in four-membered rings[1] and falls in the range predicted[2] for geminal protons with one adjacent π-bond. In view of several as yet unknown aspects of four-membered rings, such as geometry and type of
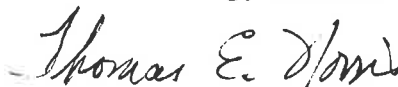
bonding, this latter fact may be fortuitous.

We are indebted to Dr. H. N. Cripps of DuPont Company for samples of the above-mentioned and similar compounds.

Best wishes for continued success with the NMR Newsletter at your and its new location.

Sincerely yours,

Ernest Lustig, Chemist

Thomas E. Norris, Chemist

Division of Food
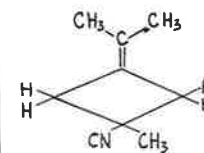Bureau of Biological and Physical Sciences

Enclosure

REFERENCES

(1) See e.g., H.S. Gutowsky, M. Karplus and D.M. Grant, J. Chem. Phys. 31, 1278 (1959); J.K. Williams, D.W. Wiley and B.C. McCusick, J. Am. Chem. Soc. 84, 2210 (1962); E. Lustig, J. Chem. Phys. 37, 2527 (1962); K.L. Servis and J.D. Roberts, J. Phys. Chem. 67, 2885 (1963).

(2) M. Barfield and D.M. Grant, J. Am. Chem. Soc. 85, 1899 (1963).
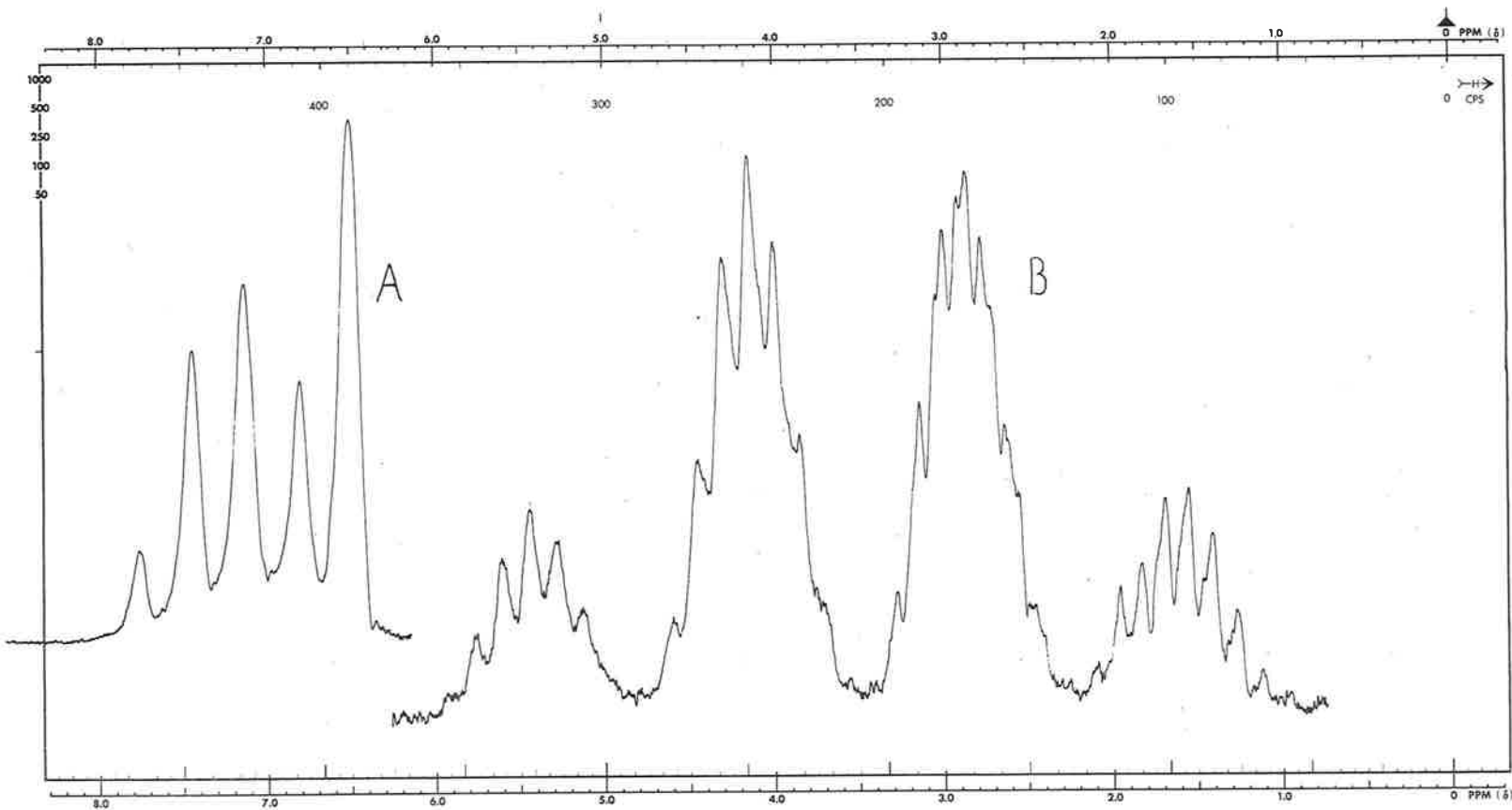
February 6, 1964

Dr. Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

<u>On Binding Site of N-methylacetamide.</u>

Dear Dr. Shapiro:

Thank you for your letter of January 20, addressed to
Dr. Norman C. Li, mentioning that it is time for a contribution
to MELLONMA. Since Dr. Li is on his way to Formosa to be a
Visiting Professor at National Tsing Hua University for the
spring semester, he has asked me to write you.

In order to determine whether the coordination site in
N-methylacetamide (NMA) is the carbonyl oxygen or the nitrogen,
we have studied the change in proton spectra of solutions of NMA
on adding metal ions. The principle is that if the site is the
carbonyl oxygen, then the effect of metal would be greater on
the CH_3CO rather than on the $N-CH_3$. Relative to benzene as
external reference, solutions of 0.75 M NMA in 99.8% D_2O at room
temperature exhibit a HDO signal at 1.88 ppm, and two signals
at 3.85 and 4.58 ppm all upfield from benzene. These are
ascribed to $N-CH_3$ and CH_3CO protons, respectively. D_2O was used
as solvent to reduce the obscuring resonance of H_2O. However,
exchange of the labile NH proton in NMA with solvent and the H_2O
present in 99.8% deuterium oxide, introduce sufficient protons
to give a HDO resonance. In the presence of 10^{-3} M $MnSO_4$, the
HDO line is broadened to the extent that it becomes unobservable,
while the signals at 3.85 and 4.58 ppm are broadened by about 17
and 22%, respectively.

For the purpose of demonstrating a greater effect of metal
ion on the proton spectra of NMA, we carried out experiments
using methanol as solvent at $-10°$. Tetramethylsilane (TMS) was
used as internal reference and signals are downfield from it.
Fig. 1 and 2 show the results obtained, the signals at $\delta = -1.92$
and -2.70 ppm are ascribed to the CH_3CO and $N-CH_3$ protons,
respectively. It is seen that the presence of a paramagnetic
metal ion exerts a greated broadening effect on the $\delta = -1.92$ ppm
signal than on the -2.70 ppm signal. The presence of the
diamagnetic zinc ion causes the -1.92 ppm signal to move downfield
to a greater extent than the -2.70 ppm signal. The effects of
paramagnetic and diamagnetic metal ions therefore point to

DUQUESNE UNIVERSITY
PITTSBURGH 19, PA.

conclution that the carbonyl oxygen, rather than the nitrogen, in NMA is the coordination site to these metal ions. This is the first experimental evidence of the binding site in NMA toward Cu(II) and zinc ions.

Dr. Li has asked me to send you his best wishes for your new position at IIT.

Sincerely yours,

Sung Mao Wang

NMA + 0.005 M Cu

− 2.70   − 1.92

NMA + 0.012 M Cu

NMA + 0.025 M Cu

δ, P.P.m.

NMA

-2.70   -1.92   0

NMA · Zn

-276   -2.05   0

δ, P.P.m.

2
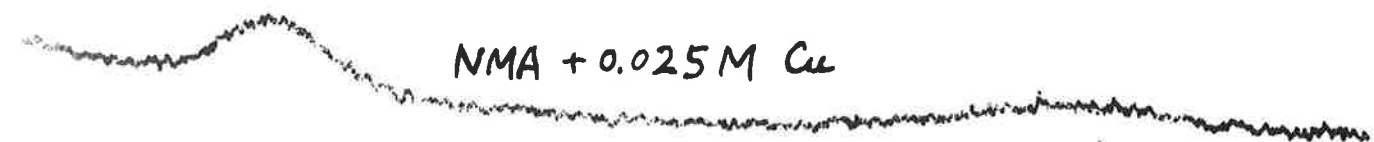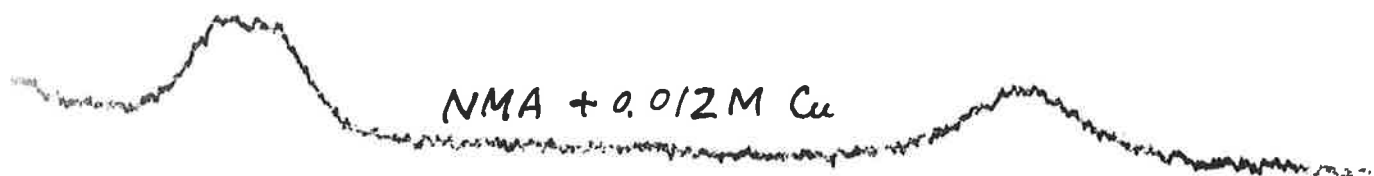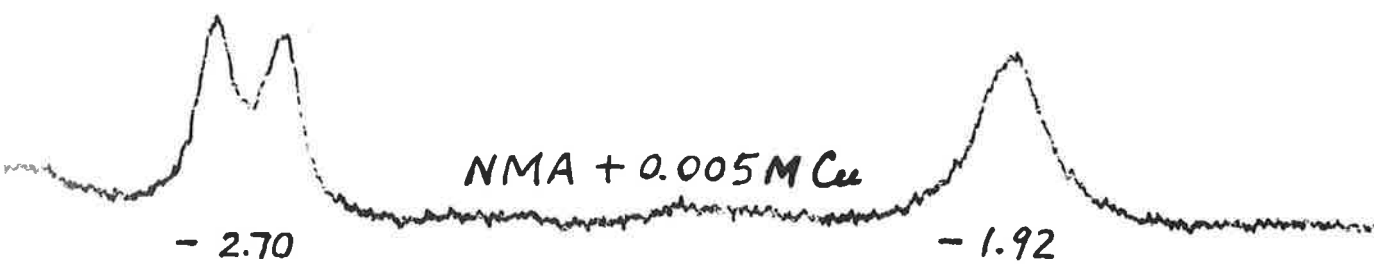
DOW CHEMICAL OF CANADA, LIMITED

SARNIA, ONTARIO

February 12, 1964

Assoc. Prof. B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

Dear Dr. Shapiro:

N.M.R. of N,N-Dimethylformamide
Lewis Acid Adducts

Recently we have investigated some interesting complexes of dimethylformamide with Lewis acids and would like to submit our results.

Several complexes of the type $D.M.F.:MX_n$ and $2 D.M.F.:MX_n$ have been prepared in a solution of 2-nitropropane. Their N.M.R. spectra were recorded on an A-60 spectrometer at room temperature. The chemical shifts of the methyl protons (C and D) were measured relative to the second band of the nitropropane septuplet (E) (see Fig. 1 for $D.M.F.:BF_3$). Shifts were determined on the 100 cycle sweep width except in the few cases where the shift was greater than 100 c.p.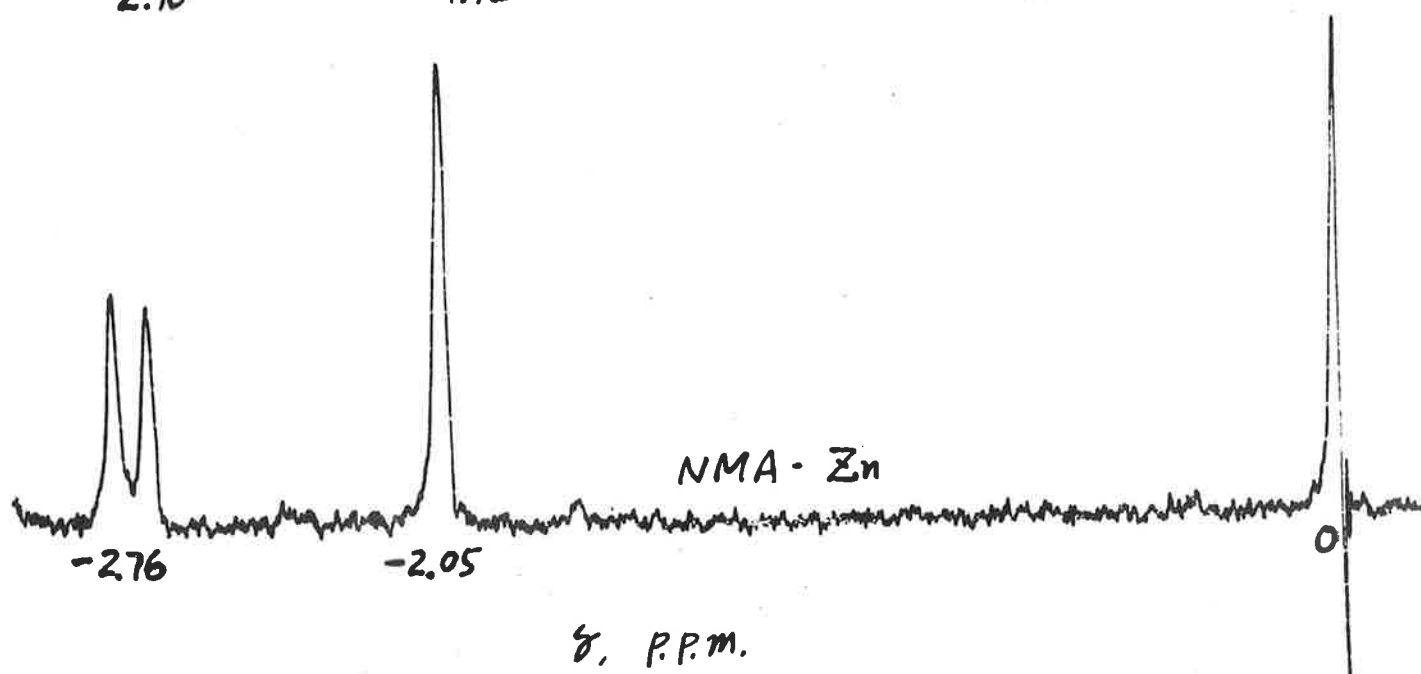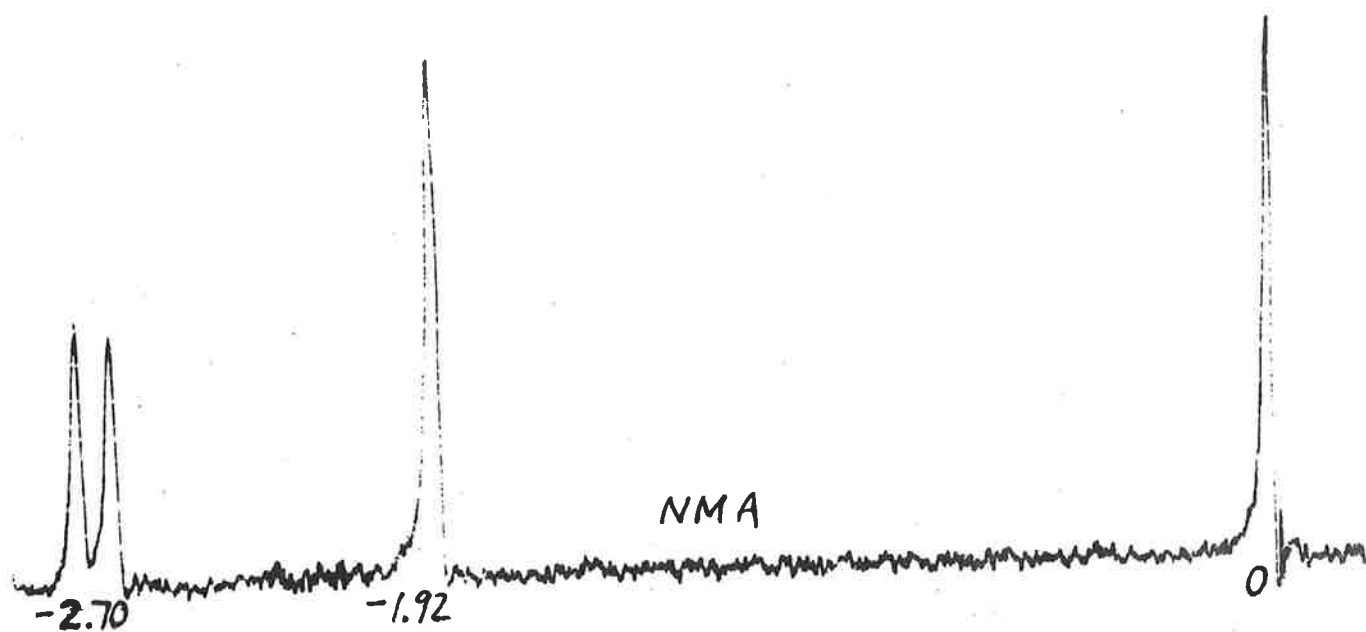s. and then measurement was on the 250 cycle sweep width. The aldehyde shifts (F) were measured relative to tetramethyl silane (A). (See Table I).
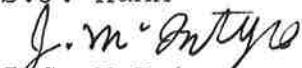
The spectra obtained support co-ordination on the carbonyl oxygen rather than on the nitrogen atom. Co-ordination on the nitrogen would destroy the conjugated structure of dimethylformamide and the methyl protons would then become equivalent (1). Relative strengths of the Lewis acids may be assigned from the shifts of the methyl groups. A comparison of this order with that obtained for Lewis acids by Cook (2) by I.R. methods shows general agreement.

A complete report on this subject will be published later.

References:

1. G. Fraenkel and C. Niemann, Proc.Nat.Acad.Sci., U.S.A. 44, 688 (1958).
2. D. Cook, Can.J.Chem. 41, 522 (1962).

Sincerely,

S.J. Kuhn

J.S. McIntyre

/ss

TABLE I

PROTON SHIFTS OF D.M.F. LEWIS ACID COMPLEXES
IN 2-NITROPROPANE

Complex	Cis Methyl[a,b]	Trans Methyl[a,b]	Aldehyde[c]
D.M.F.	102	94	474
$ZnCl_2.2D.M.F.$	91	82	487
$SnI_4.2D.M.F.$	89	79	483
$InCl_3.1D.M.F.$	87	77	493
$ZnCl_2.1D.M.F.$	85	75	489
$ZrBr_4.2D.M.F.$	84	75	503
$BiCl_3.1D.M.F.$	82	69	507
$TiCl_4.2D.M.F.$	78	69	518
$SnCl_4.2D.M.F.$	80	69	500
$SnBr_4.2D.M.F.$	80	68	502
$BF_3.1D.M.F.$	78	68	487
$TiCl_4.1D.M.F.$	75	65	512
$PF_5.1D.M.F.$	75	64	502
$AlCl_3.1D.M.F.$	74	64	493
$AsF_5.1D.M.F.$	72	60	507
$SbF_5.1D.M.F.$	70	60	505
$BCl_3.1D.M.F.$	68	57	506
$SbCl_5.1D.M.F.$	68	56	519

a) Shifts in c.p.s. upfield from second peak in nitropropane septuplet.
b) Cis or trans with respect to aldehyde proton.
c) Shifts in c.p.s. from tetramethyl silane.
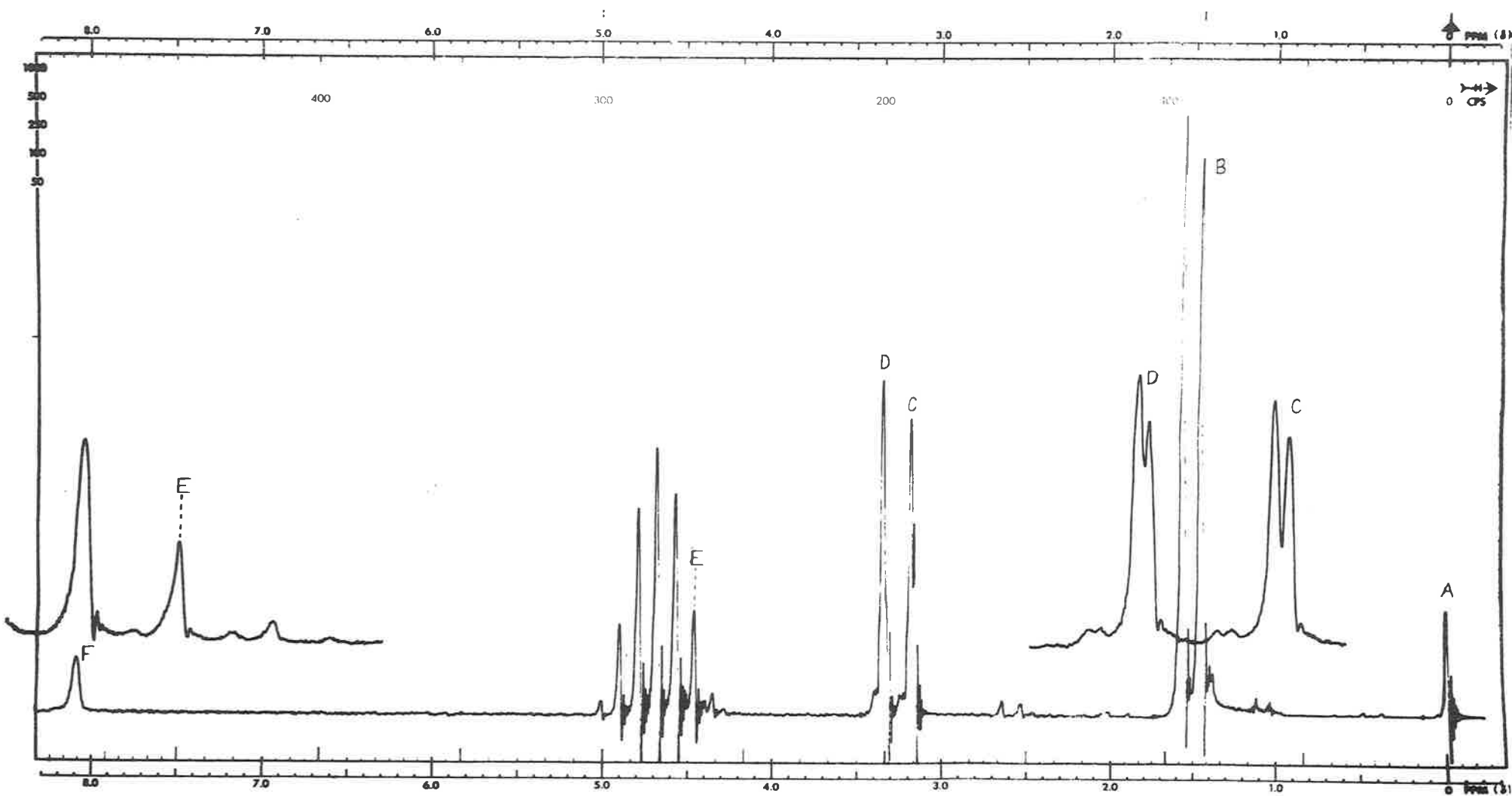
ROHM & HAAS COMPANY

REDSTONE ARSENAL   RESEARCH DIVISION

HUNTSVILLE, ALABAMA 35807
February 12, 1964

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Professor Shapiro:

      I am sorry that I nearly let my subscription lapse.
We have found MELLO-NMR very useful in our work and
expect to find IITNMRN just as useful. We hope the following
bit of information is of enough interest to get us back in your
good graces.

      We are still working with tetrafluorohydrazine. As
you may recall the F^{19} nuclear magnetic resonance spectrum
of N_2F_4 was reported[1] to consist of a single broad unresolved
band at a field of approximately -55.6ϕ. Recently it has been
shown[2] that when N_2F_4 is dissolved in perfluoro-2,3-dimethylhexane
at room temperature a triplet n.m.r. spectrum is observed in
which the N^{14}-F^{19} coupling constant is $\sim$117 cps.

      We now would like to report on the F^{19} n.m.r. spectrum
of N_2F_4 in solution in NF_3 at low temperatures (-180° to -155°C.).
At these low temperatures rotation around the N-N bond appears
to be hindered to the extent that a fairly complex spectrum appears.
It appears to consist of a singlet superimposed on a quartet (Fig. 1).
While it is difficult to show it in an illustration, there is evidence
that the spectra are even more complex than this. We hope to carry
out a more detailed study of this phenomena using double resonance
techniques.
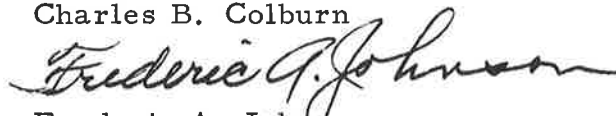
Professor B. L. Shapiro   -2-   February 11, 1964

        We would like to acknowledge early conversations on this matter with Dr. S. Frank.

                         Sincerely yours,

                         Charles B. Colburn

                         Frederic A. Johnson

                         Carolyn Haney

Enclosures: 1

[1] C. B. Colburn in Advances in Fluorine Chemistry, Vol. 3 Butterworths (Washington) 1963 p. 96.
[2] Raymond Ettinger and Charles B. Colburn, Inorganic Chemistry 2, 1311 (1963).
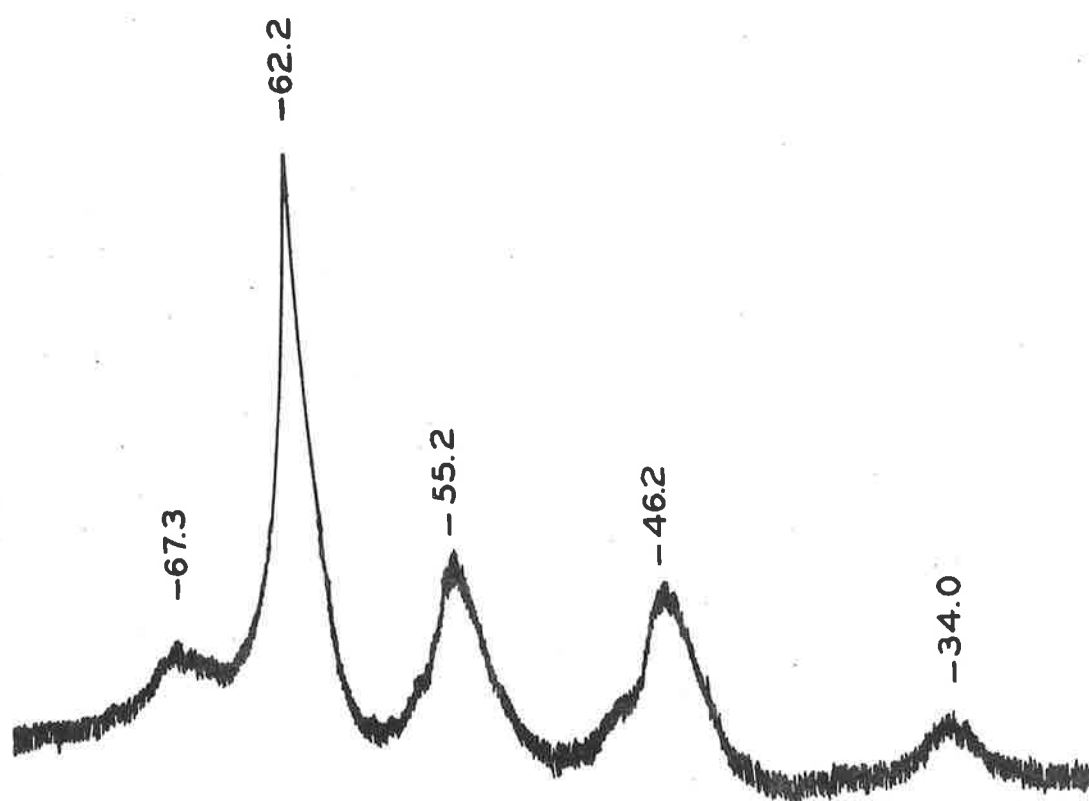
Fig. 1 F^{19} NMR SPECTRUM OF N$_2$ F$_4$ AT -157°C.

THE ROCKEFELLER INSTITUTE

A Graduate University and Research Center

NEW YORK 21, NEW YORK

February 11, 1964

Dr. B. L. Shapiro
Illinois Institute of Technology
Chicago 16, Illinois

Dear Barry:

Best of luck on your new job, or should I say welcome to academia, whatever you decide the new name of this newsletter should be!

I just wanted to report the interpretation of some experimental data that I have been waiting a couple of years for. The data are the chemical shift differences between axial and equatorial fluorine atoms in mono- and gem-di-fluorinated cyclohexanes. Bovey and colleagues have shown $\sigma_{ax} - \sigma_{eq} = 2o.5 \times 10^{-6}$ in fluorocyclohexane while Roberts and colleagues have shown $\sigma_{ax} - \sigma_{eq} = 14.5 \times 10^{-6}$ in 1,1-difluorocyclohexane. The data of Thomas et al. and Tiers which give $\sigma_{ax} - \sigma_{eq} = -21 \times 10^{-6}$ for CHF in multi-fluorinated (α, β positions) cyclohexanes and $\sigma_{ax} - \sigma_{eq} = -18.2 \times 10^{-6}$ for CF_2 in perfluorocyclohexane. When these results are combined, following my ideas of intramolecular electric fields ~~to give~~ using a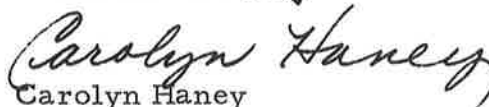 value for the difference in the dipole moments of CH and CF bonds taken from CH_3F ~~which~~ (arbitrarily assuming H = C), then gives

$$|\mu_{CF}| = 1.0D, \ 0.9D \qquad F \ negative$$

$$|\mu_{CH}| = 0.8D, \ 0.9D \qquad H \ positive$$

for the determinations. One obtains also k_E the constant for the linear electric field effect

$$k_E = 2.5 \times 10^{-10} esu \ (CF), 1.95 \times 10^{-10} esu \ (CF_2).$$

Note that it is considerably different for the two bonds. It is also positive whereas a simple-minded calculation

2 -- Dr. Shapiro

based on the expression of Karplus and Das gives the same
magnitude but of opposite sign. The sign agrees with
that determined by Bernstein et al. for CF_4 but is con-
siderably larger in magnitude. The above procedure con-
tains numerous simplifications, most of which seem rea-
sonable -- there is no effect presently understood of
sufficient magnitude to account for these shifts other
than the electric field effect, which gives an unexpectedly
large value of $|\mu_{CH}|$ An interaction stronger than the
Van der Waals interaction between fluorines could affect
the interpretation of the perfluoro- data (the Van der
Waals effect at worst would change these by 2-3ppm) but
there seems to be little that could affect the mono- and
di-fluoro-derivatives. This confirms what I argued in
an "errata and further comments" in JCP that even in hy-
drogen-containg molecules the electric field shift is
very significant.

I also want to thank those readers for the comments
evinced by my "sounding off" in a recent MelloNMR, even
though I have been lax about responding to them.

Yours sincerely,

Jeremy I. Musher

JIM/sm

המכניון - מכון מכוולוני לישראל

UNION — ISRAEL INSTITUTE OF TECHNOLOGY

המחלקה לכימיה
DEPARTMENT OF CHEMISTRY

10 February, 1964

Professor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Ill.
U.S.A.

Dear Professor Shapiro:

 Enclosed please find our contribution to IITNMRN,
(excellent name !).

Helix Coil Transitions in Poly-L-Glutamic Acid

$$\begin{bmatrix} {}^5COOH \\ {}^4CH_2 \\ {}^3CH_2 \\ NH-{}^2CH-{}^1CO \end{bmatrix}_n$$
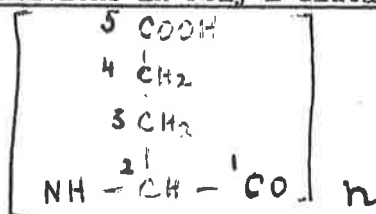
 It is known, principally from optical rotation measurements,
that poly-l-glutamic acid (P-L-GA) in aqueous solutions can be in
either the helix or the coil form. The transition is induced by
changing the hydrogen ion concentration. Below pH~5 the helix is
predominant whereas above it the shape of the molecule is that of
a random coil. Transition is very sharp and occurs within a few
tenths of a pH unit. We observed this transition in the nmr
spectra and this communication reports some of the results.

-2-

Because of the low sensitivity of the nmr method we had to use rather high P-L-GA concentrations - about 40 mg/ml. The P-L-GA sample had a degree of polymerization of about 120. Since the water and -CH- resonances overlap we lyophylized our solutions in D_2O thus replacing most of the exchangeable hydrogens with D_2O. The pH was adjusted by adding small quantities of DCl or NaOD and measuring the "pH" with a combined glass-calomel electrode. Above pH 5 the -CH- resonance consists of a "triplet" - namely three almost equispaced distinct, rather sharp lines with intensity "ratio" of approximately 1 - 2 - 1. The -CH- resonance is not a true spin-spin triplet because of the non-equivalence of the two protons in the (3) -CH_2- group and ~~because~~ because of the strong coupling between the (3) and (4) CH_2's. At pH 5 a sudden change occurs - each of the "triplet" components broadens giving the CH resonance an appearance of a single broad line. The $(CH_2)_2$ resonance appears throughout the pH range studied (from pH 10 to pH 4.7) as a broad multiplet and does not change much in appearance - no detailed structure is observed. At pH 4.7, slightly below the transition point, the compound precipitates.

The sudden change in the appearance of the -CH- resonance is not due to bulk viscosity change or to effects associated with the N-D exchange - both possibilities were checked and eliminated. We thus believe that the broadening of the -CH- resonance is associated with sudden restriction of motion of the -CH- segment relative to its neighbours. Such a change is to be expected in a random coil to helix transition.

Another interesting observation is the behaviour of the
chemical shift of the -CH- "triplet". It was measured relative
to tetramethyl ammonium and remains constant down to pH 5 where
it abruptly changes. The chemical shift of the $-CH_2-$ resonance,
can not be measured very exactly but seems to change monotonously
with pH down to the precipitation point. Contrary to glutamic
acid, where CH_2 lines are sharp, the side chains in ~~PLGA~~ P-L-GA seem to
be strongly hindered in both helix and coil form.

Yours sincerely,

A. Loewenstein

A. Loewenstein

H. Gilboa

H. Gilboa

for / A. Berger (Biophysics Dept.
A. Loewenstein   Weizmann Institute,
Rehovot).

INSTITUT FÜR ORGANISCHE CHEMIE DER TECHNISCHEN HOCHSCHULE BRAUNSCHWEIG

PROF. DR. H. H. INHOFFEN

SCHLEINITZSTRASSE
Telefon 308 11 · Apparat 225

Asst. Professor B.L. Shapiro,   14th. February '64
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago,Illinois 60616.

Dear Professor Shapiro,

        Thank you very much indeed for your
recent letter and the enclosures concerning the policy of
your News Letter. We are very pleased that you are able to
add the name of this Institute to the News Letter mailing
list and hope that the following contribution on the
reduction products of octaethylporphin will serve as our
first subscription.

        Two products have been obtained by
the diimide reduction of the Sn^{IV} complex of octaethyl-
porphin,I. Analyses indicated that these compounds were
the di- and tetrahydro- derivatives of the starting material.
The dihydro- compound was formulated as the chlorin II and,
on the basis of its U.V. spectrum,the tetrahydro- compound
was suspected to be III rather than IV.

(I)   (II)
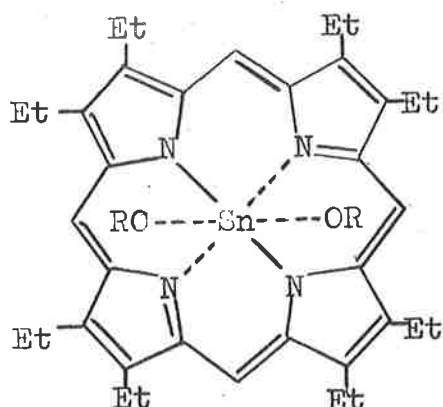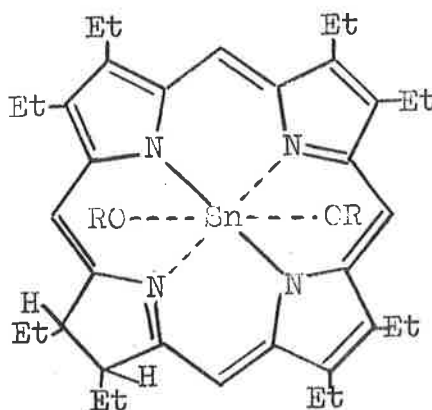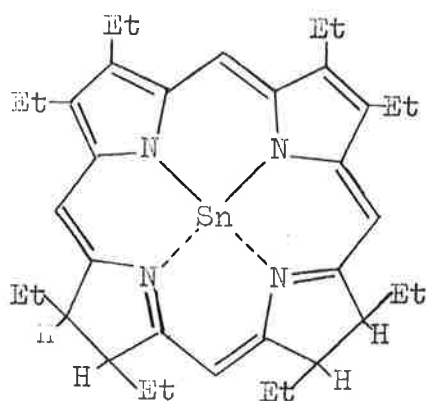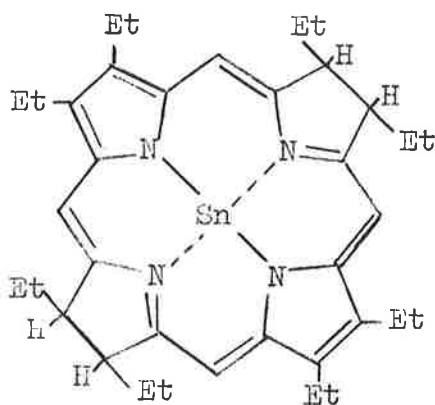
(III)   (IV)

These structural assignments are supported
by the accompanying n.m.r. spectra, which give us a direct
indication of the symmetry of our compounds. The molecular
symmetry is most clearly shown by a study of the respective
methine bridge proton signals, which are easily identifiable
at low fields.

The simple spectrum of the starting material
I (R = Ac-) shows it to be a completely symmetrical
molecule, and the two equal intensity methine proton lines
(τ= 1.15 & 0.20 ; area ratio 2:2) in the spectrum of the
dihydro- product are as expected for II (R = Ac-). The
spectrum of the tetrahydro- product shows three methine
proton signals (τ= 2.75 , 2.11 & 1.94 ; area ratio 1:2:1)
in agreement with its formulation as III, rather than the
single line which would be expected if the structure were
IV.

It is interesting to note the high field
position of the acetate methyl group in the spectra of I
(R=Ac-;τ=11.58) and II (R=Ac-;τ= 10.77). A similar, expected
high field position for the protons of the anionic res-
idue of I is observed when R=CH_3CH_2CO- (multiplet;τ= 11.4)
and when R= H.CO- (sharp singlet;τ=7.96) also.

Wishing you every success at I.I.T.,
Yours sincerely,

(H.H.Imhoffen) (H.Parnemann) (R.G.Foster)

(i.V.)

3.

All spectra measured as solutions in CDCl$_3$

Compound I
(R = Ac-)

Offset 200 cps.

t.m.s.

Dihydro- product.
(R=Ac-)

t.m.s.

Offset 150 cps.

Tetrahydro- product.

t.m.s.

Offset 200 cps.
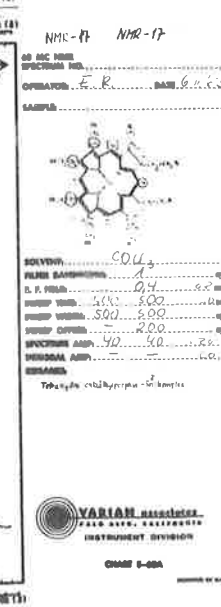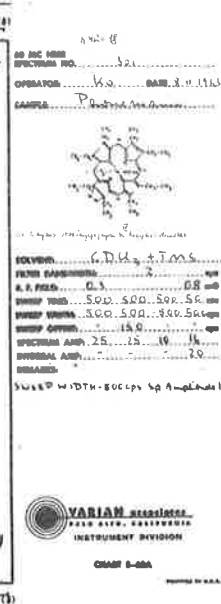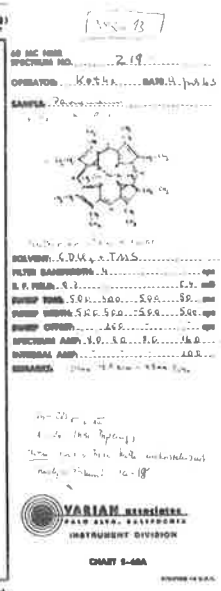
QUEEN MARY COLLEGE
(UNIVERSITY OF LONDON)
MILE END ROAD · E·1
TELEPHONE · ADVANCE 4811

Magnetic Resonance Group
Department of Physics

Dr. B. L. Shapiro,   17th January 1964.
Mellon Institute,
4400, Fifth Avenue,
Pittsburgh 13,
Pennsylvania.

Dear Dr. Shapiro,
          I would like to describe a high temperature accessory for a
Varian DP-60 probe head, hoping that this will qualify this laboratory for
Mellon Letters.
          Previous work done on this subject has been confined to a
modification of the Varian probe insert (1,2) rather than a complete redesigning
of the variable temperature accessory.
          The maximum sample temperature available with the accessory
is 330°C and any temperature up to this limit can be kept stable to within half
a degree. The temperature difference between the site of the receiver coil and
the thermocouple end, which is a distance of some 7mm, is never greater than
two degrees. Asample spinning mechanism is not incorporated so that only the
larger chemical shifts and spin lattice relaxation times can be measured. Since
many of our samples are enclosed organic liquids, pressures of fifty atmospheres
or more may be developed in the glass sample tube, making spinning very risky
anyway.
          Air, the heat exchanging medium, is forced through the system
at 3p.s.i. and passes through the heater coil three times. A heater power of
80 watts is required for a sample temperature of 330°C. An essential feature is
a device for rotating the receiver coil when the sample is hot to allow optimum
balance of r.f. leakage. A large radio frequency field is used for relaxation
time measurements (eg. by Adiabatic Fast Passage,3), so this facility is very
neccessary. As the receiver coil is cemented directly on to the sample tube
(with a high temperature strain gauge cement, Brimor type U529),a much improved
filling factor over the usual high resolution probe is achieved.

                                         Yours sincerely,

                                         Daryll K. Green.
                                         Daryll K. Green.

References
1. Schneider,W.G.,Bernstein,H.J.and Pople,J.A., J. Chem. Phys. 28, 601, (1958)
2. Shoolery,J.N. and Roberts,J.D., Rev. Sci. Instr., 28, 61, (1957)
3. Powles,J.G., Berichte der Bunsengesellscaft fur physikalische Chemie,
                                         67, 328, (1963)

— 2 —

AIR

275 %

VAPOUR

H

TOLUENE AT 304°C

BASE OF PROBE

TOP OF PROBE

ALUMINIUM

TEFLON

Telephone : Bristol 24161 Ext. 311

F. G. A. STONE, Sc.D.
Professor of Inorganic Chemistry
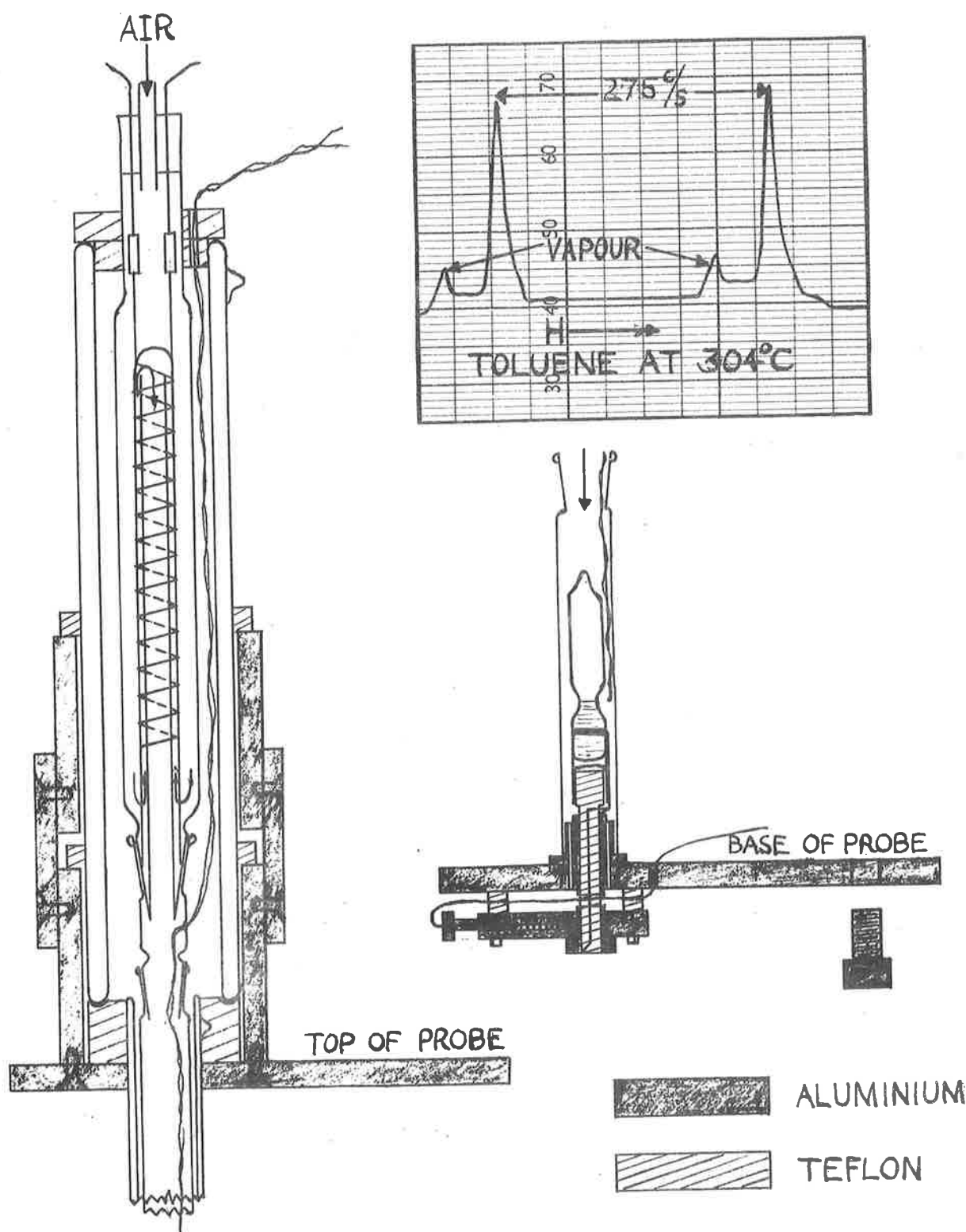
UNIVERSITY OF BRISTOL,
DEPARTMENT OF INORGANIC CHEMISTRY,
THE SCHOOL OF CHEMISTRY,
BRISTOL 8
ENGLAND.

FGAS/445

17th February, 1964.

Professor Bernard L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago 16,
ILLINOIS,
U. S. A.

Dear Barry,

At Bristol we are continuing our studies on
fluorocarbon derivatives of metals and the new compounds prepared
present a number of structural problems.

Of interest to us at the moment is the addition
of alkylmetal carbonyls and hydridometal carbonyls to chlorotrifluoro-
ethylene and other substituted fluoroethylenes. Of some importance is
the direction of addition across the double bonds. In several instances
the isomeric character of the products has been established by F^{19} n.m.r.
studies. Thus Fig. 1 shows the spectrum of a product obtained by John
Wilford from the reaction between methylmanganese pentacarbonyl and chloro-
trifluoroethylene. Chemical shifts and the overall appearance of the
spectrum show that the complex formed is $CH_3CF_2CFClMn(CO)_5$ rather than
$CH_3CFClCF_2Mn(CO)_5$. The doublet at 78.2 p.p.m. must be due to a single
fluorine atom. Moreover, it must be bonded to the carbon atom linked
directly with the manganese atom, since it is the absorption at lowest
field (Pitcher, Buckingham and Stone, J. Chem. Phys., 36, 124 (1962)). The
doublet splitting represents coupling with a fluorine atom on an adjacent
carbon. The absence of further splitting shows that the methyl group is
not bound to the same carbon atom. The other resonances, in the form of
an AB pattern, must be assigned to a β-CF_2 group. They are split into
two sets of quartets by the expected coupling with the adjacent methyl
group. The pair of quartets centred at 81.6 p.p.m. are further split
(13.0 c.p.s.) by coupling with the α-fluorine atom. Non-equivalence of
the fluorine atoms of the CF_2 group occurs because the adjacent carbon

Professor B. L. Shapiro   -2-   17th February, 1964.

atom of the $CFClMn(CO)_5$ group has three different groups bonded to it
(Pople, Mol.Phys., 1, 1 (1958)).

The pattern of the absorptions centred at 53.1 and
114.8 p.p.m. in Fig. 2 also corresponds to CF_2 groups with non-equivalent
fluorine atoms. This spectrum assisted our work by showing that a mixture
of $HCFClCF_2Mn(CO)_5$ and $HCF_2CFClMn(CO)_5$ can be obtained from $HMn(CO)_5$ and
$CF_2:CFCl$ by using low olefin concentrations. Under different reaction
conditions we had previously obtained only one of the possible isomers.
The spectrum (Fig 2) led us to separate the isomers and characterise
them completely. In both isomers the CF_2 group is bonded to an asym-
metric carbon atom. The low-field shift of the bands centred at 53.1 p.p.m.
establish that they are due to the CF_2 group bound to the manganese atom.

I am indebted to Mr. A. J. R. Bourn for measuring the
fluorine n.m.r. spectra. Will you please note my new address.

Yours sincerely,

Gordon

FGAS:scb
Enclosure:

$$CH_3Mn(CO)_5 + CF_2{:}CFCl \xrightarrow[\text{25° in pentane}]{\text{ultraviolet light at}} CH_3CF_2{\cdot}CFCl{\cdot}Mn(CO)_5$$

30% yield. White crystals.
m.p. 53–54°

^{19}F SPECTRUM

$CH_3CF_2{\cdot}CFCl{\cdot}Mn(CO)_5$
β $\quad$ α

H →

$J_{H-F_\beta} = 18\ \text{c.p.s.}$

$J_{F-F(gem)} = 249{\cdot}5\ \text{c.p.s.}$

CCl$_3$F
Standard

78·2 $\qquad$ 81·6 $\qquad\qquad\qquad$ 93·6 $\qquad$ p.p.m.
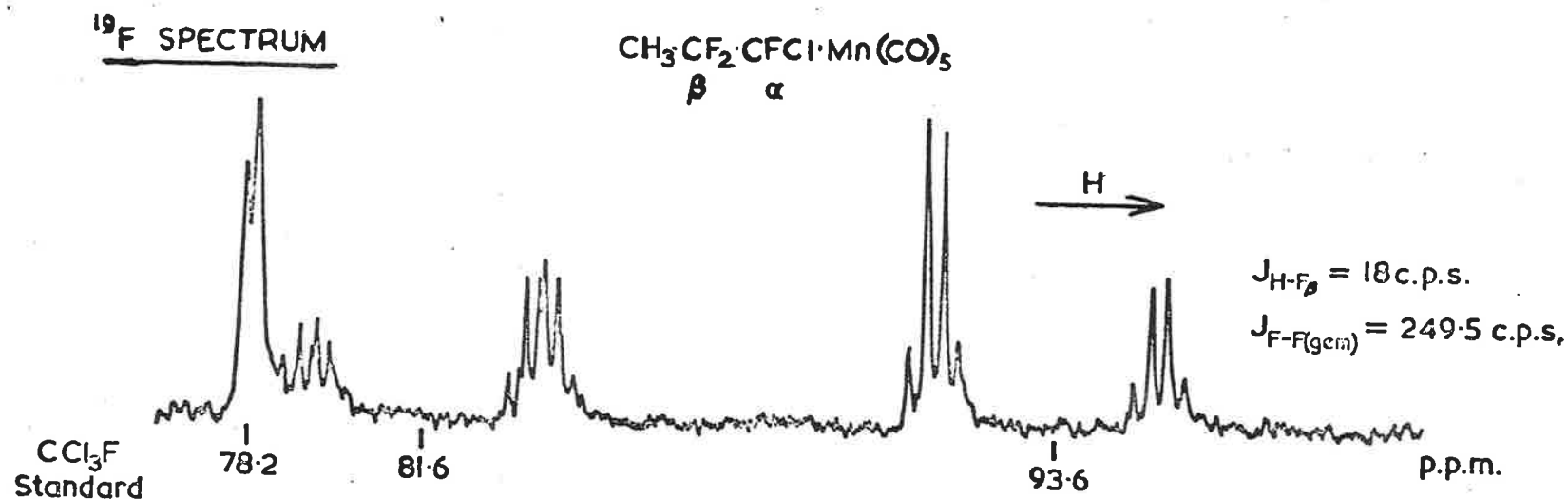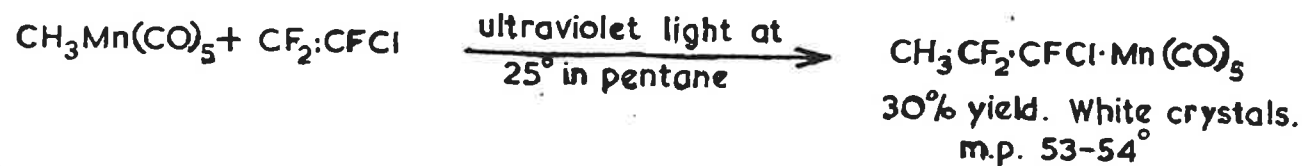
^1H SPECTRUM

A triplet with each line of triplet split into a doublet.

J_{H-F_β}, 18·4 c.p.s. and J_{H-F_α}, 2·0 c.p.s.

FIG. 1

^{19}F NUCLEAR MAGNETIC RESONANCE SPECTRA OF A MIXTURE OF $HCFCl \cdot CF_2 \cdot Mn(CO)_5$ AND $HCF_2 \cdot CFCl \cdot Mn(CO)_5$ FROM MANGANESE PENTACARBONYL HYDRIDE AND CHLOROTRIFLUOROETHYLENE AT 2 ATM.
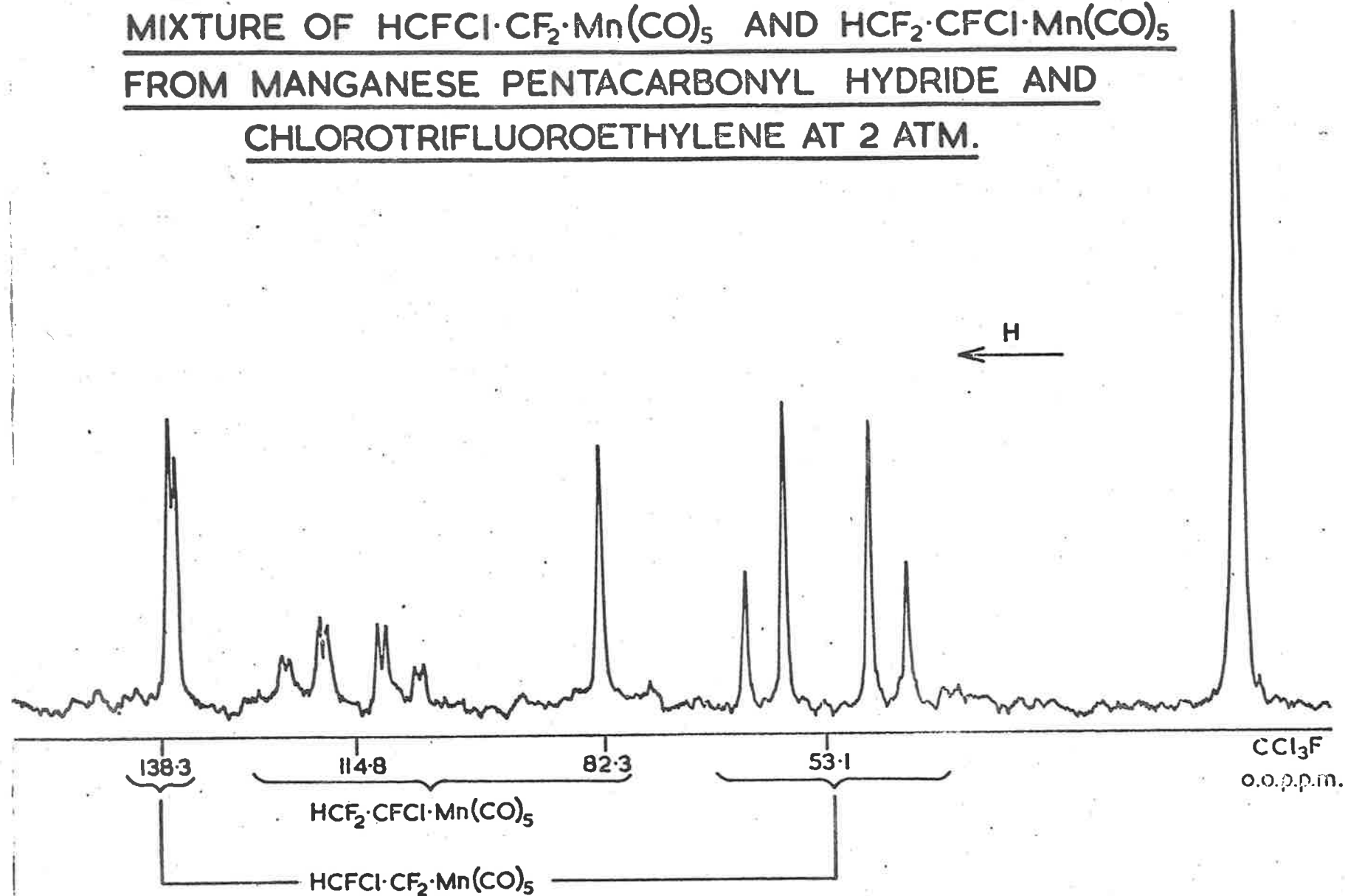
Fig 2.

UNION CARBIDE CHEMICALS COMPANY

DIVISION OF UNION CARBIDE CORPORATION

P.O. BOX 8361 SOUTH CHARLESTON 3, W. VA

RESEARCH AND DEVELOPMENT

February 18, 1964

Assoc. Prof. B. L. Shapiro
Dept. of Chemistry
Illinois Institute of Technology
Technology Center
Chicago (16), Illinois

Dear Barry:

Congratulations and best wishes for your new job, and also a hearty vote of thanks for keeping alive your NMR newsletter in the process....... As you're well aware, I have some boat-rocking thoughts about the most appropriate name for your newsletter, but we can resume that argument later. Meanwhile, on to more pressing matters, such as my subscription renewal.

I read with interest the work reported by Dr. R. Freymann (MELLONMR <u>58</u>, 54) on the NMR of gases under pressure. In particular, he reported that a pyrex glass tube, 5.0 mm o.d. and 2.0 mm i.d., could withstand internal gas pressure of nearly 250 atmospheres (3600 psi) before rupture.

Since NMR Specialties, Inc. of New Kensington, Pa., sells precision glass NMR sample tubes having about these same dimensions (Size A: Precision Semi-Micro NMR Sample Tube; o.d. 0.196" and i.d. 0.080"; $1.90 each) we have ventured to use these tubes to retain liquids far above their normal boiling temperatures. One application has been to make readily usable certain interesting but ordinarily inconvenient or inappropriate solvents for NMR studies; these might include SO_2, CO_2, NH_3, Cl_2, H_2S, NO_2, PH_3, methyl ether, phosgene, ethane, cyanogen, acetylene, etc., at room temperature - or more conventional solvents at quite high temperatures.

Assoc. Prof. B. L. Shapiro   - Page Two -   February 18, 1964

In our work, we have never approached the 3000 psi range of pressures. However, we have exceeded 1000 psi without mishap - provided that the tube is carefully sealed with a torch, the vicinity of the seal then being "flame annealed" to relieve strains in the glass. Caution suggests that the entire tube should be annealed overnight in a glass oven prior to filling and sealing; however, we have on occasion gotten along without doing so, simply using the tubes as received. The lower end of the tubes must be kept in dry-ice (or liquid nitrogen), of course, during the sealing operation to reduce the internal pressure of the contents to permissibly low values. (If liquid nitrogen is used, beware of condensing liquid oxygen into the sample!)

In conclusion, I guarantee nothing. But if one has a little nerve, this is one very simple route to some interesting liquids for NMR study, or for solvents in NMR work, etc., using conventional NMR spectrometers.

Sincerely,

Charlie

Charles W. Wilson III

CWW/jdm

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

19th February, 1964.

Professor B.L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Centre,
Chicago, Ill.,
U.S.A.

Dear Barry,

We have continued to find letters very relevant to our own work in Mellonmr. Tony Bourn's work on amides is in thesis form and will soon be appearing in the literature. Work not mentioned previously concerns N-phenylformamide-N^{15}, N-methylformanilide, N-ethylformamide. The spectrum of N-phenylformamide-N^{15} is shown (CIS and TRANS refers to phenyl with respect to the C=O group). The assignment is based on that made by Charlie Krabeck and John Baldeschwieler for the N^{14} molecule when I worked with them on amides, and is checked by the J N^{15}-H's compared with other N^{15} substituted amides (Mellonmr No. 56). 64% ± 4% exists as the isomer with the phenyl CIS to the carbonyl. In N-methylformanilide-N^{14} more than 96% exists in this CIS form (J(H-Me) = 0.4 ± 0.1 c/s). This can be contrasted with the cases studied by LaPlanch and Rogers in which the bulkier of the two alkyl groups on the nitrogen was CIS to the formyl proton.

In N-methylformamide-N^{15} although we see lines in the region expected for the isomer with the methyl CIS to the formyl proton, these lines have the wrong structure. We conclude that there is less than 3% of this form present. We do find for N-ethylformamide 15% ± 2% of the isomer with the ethyl CIS to the formyl proton (cf. Mellonmr No. 61). The spectrum of the methylene protons, because of overlap, appears as a quintet, collapsing to a quartet at 160° C when the NH exchanges.

We have looked at our N-H couplings in amides and at values in the literature for NH_3, NH_4^+, pyridimium ion and pyrrole in the light of s characters in the N-H bond deduced from known structures. We get a fair correlation except for pyrrole. Should we suspect

(i) value for J   (ii) structural data - planar molecule; $\stackrel{\frown}{CNC}$ = 105° ± 4°
(iii) hybridisation theory to get a^2 from structural data (a^2 = 0.6)
(iv) J coupling theory?

Incidentally, we have been deterred from ENDOR work by the following quotation from Rudyard Kipling:

> Oh, the road to En-dor is the oldest road
> And the craziest road of all!
> Straight it runs to the Witch's abode
> As it did in the days of Saul.
> And nothing has changed of the sorrow in store
> For such as go down on the road to En-dor!

Yours sincerely,

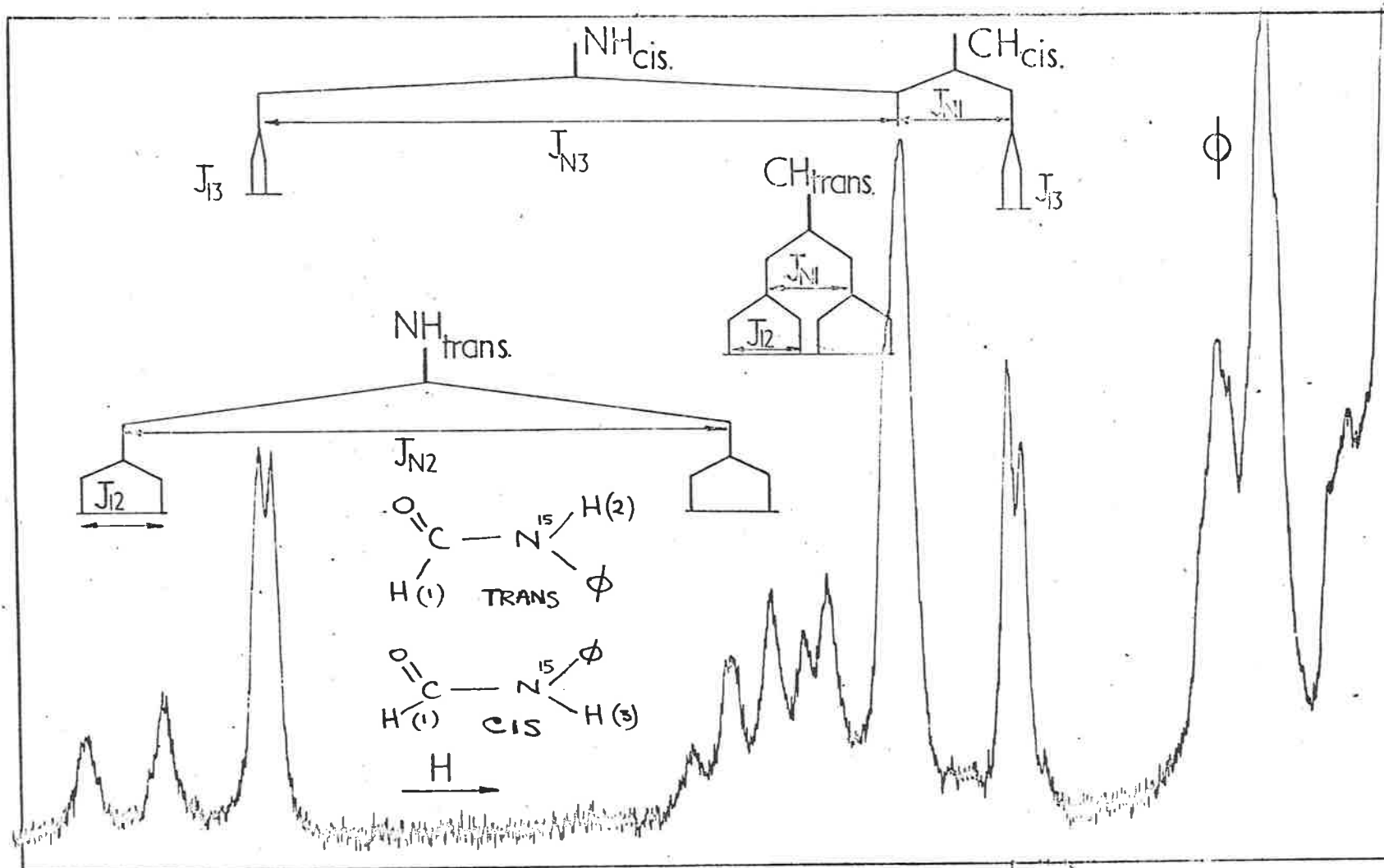Ed Randall.

Edward W. Randall

Fig. 27.

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE
WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
800 BUCHANAN STREET, ALBANY 10, CALIFORNIA

February 24, 1964

AIRMAIL

Professor B. L. Shapiro
Dept. of Chemistry
Illinois Institute of Technology
Technology Center
Chicago, Illinois 60616

Dear Barry:

I thought some of your readers might be interested in the circuitry
we have developed to connect a 1024 CAT to our A-60.

The attached diagram shows the various circuits that are required
as well as the interconnecting cables. Ground currents caused us
a good deal of trouble, and for that reason we have tried to be
very explicite in showing common and shield connections.

Since the sweep potentiometer in the A-60 would very soon fail if
it were used for many overnight experiments, we generate externally
an equivalent minus one volt ramp by means of a Miller integrator
and then feed this voltage to the lead normally connected to the
slidewire. This is one of the three minor changes in the A-60
circuitry that is required. We designed the sweep around the Dymec
amplifier because its current output is sufficient for all the A-60
sweep ranges, although with the single dividing network of the
amplifier output only one range (we use 500 cps.) can be accurately
calibrated. The sweep is initiated by having the address overflow
pulse from the CAT (a connector was added on the front panel) discharge
the integrating capacitor via a sensitive relay. The A-60 offset con-
trols are adjusted so that the sweep always begins a few cycles above
TMS and sweeps downfield. When TMS is reached, the address trigger
level control has been adjusted so that the CAT cycle is initiated.
We are now using a sweep time of 256 seconds for a 512 cps. sweep.
We have had absolutely no trouble with this method of sweeping once
we found how to connect and shield the source voltage for the integrator
(top L. H. circuit).

With the output of the A-60 connected as shown, the CAT converter
will not be overloaded as long as the signal level meter remains on
scale, and full scale on the A-60 recorder corresponds to roughly one-
half the maximum arithmetic analog output voltage. In order to obtain
this performance another minor change in the A-60 was made at TB802
as shown at the bottom right hand side of the diagram.

Five switches have to be reset in going from accumulate to readout
besides the function switch on the CAT. Possibly they could be
combined in a single multideck assembly, but we experienced so much
trouble at the beginning with ground loops that we preferred to keep
them separate. Switch S1 determines whether the amplifier circuitry
performs as an integrator (in count) or as an inverting amplifier
with a gain of roughly thirty in readout and standby. The A-60
amplifier is not used for this purpose because the overall gain of
the amplifier-recorder combination as normally connected is insuf-
ficient for readout of the arithmetic analog voltage. Incidentally,
the manual shorting switch, S2, across the integrating capacitor is
very useful when the sweep ramp is being adjusted.

The three-way switch, S3, in the "ramp adjust" circuit determines the
DC voltage fed to the input of the amplifier: zero volts in "off",
a maximum of 300 uv. for the ramp generator, and a zero offset of up
to 100 mv. in readout (the maximum analog voltage is 70 mv.) The
function of S4 is obvious.

The routing switch, S5, is used to feed the amplifier output to the
sweep coils in count, to the recorder, in readout, and to both these
units in the range-adjust position. Recording provides a convenient
means of adjusting the sweep rate and checking stability and linearity
of the integrator. With improper grounding the ramp output will not
hold up at all levels when the source voltage is removed. The normal
and fast switches on the A-60 provide a very convenient means for
checking the sensitivity of the integrating circuit to line transients.
We observe no deflection with a 0.3 volt meter across the output. One
further means for isolating the integrator is now being used which
was omitted from the diagram: a small isolation transformer at the
AC input to the amplifier. We obtain slightly better stability against
transients when it is used.

The only mechanical modifications to the A-60 is the DPDT toggle, S6,
and the sweep input jack which we installed on the right hand side
of the recorder cover. With S6 set in "normal sweep" and S4 set on
"A-60 normal-count", the spectrometer is completely disconnected from
the CAT circuitry.
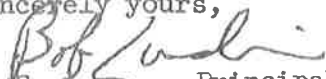
We are now in the process of finishing a modulation sideband unit which
will provide a side band signal to trigger the CAT at any point in the
spectrum and then automatically turn-off the modulation. We will gladly
supply the diagram to anyone interested.

In order to maintain the temperature within the A-60 console as constant
as possible, we disconnected the blower from the standby switch so that
it remains on while the recorder is shut off during the count period.
The switch on the zero control cannot be used since it disconnects the
DC amplifier from the phase detector output.

Enclosure

R. H. Elsken, Elect.Eng.
Wool and Mohair Laboratory

Sincerely yours,

R. E. Lundin, Principal Chemist
Wool and Mohair Laboratory

A-60—CAT
COMBINATION
WITH
ELECTRONIC SWEEP
FOR A-60
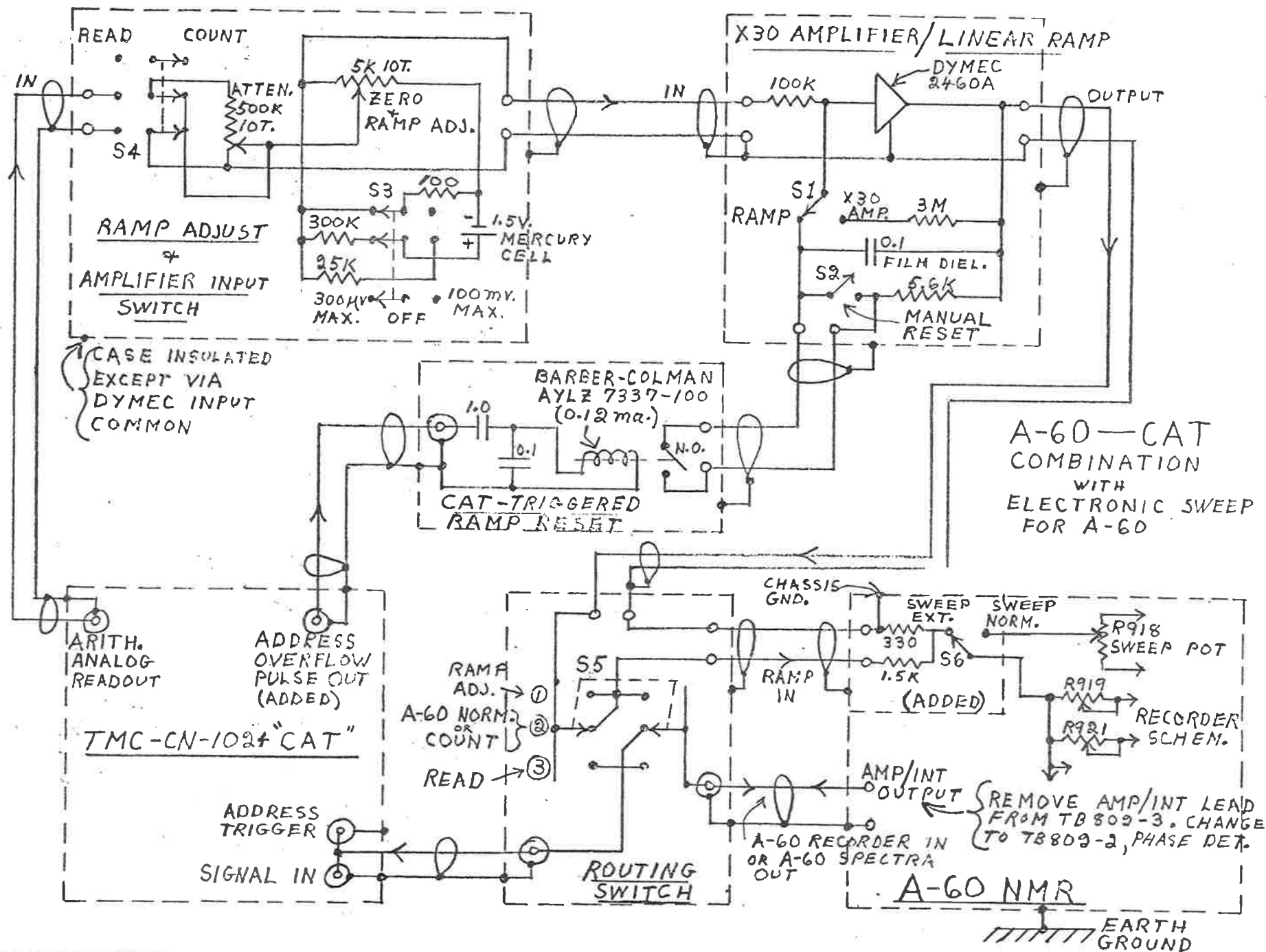
PROFESSOR DR. F. BOHLMANN

ORGANISCH-CHEMISCHES INSTITUT

TECHNISCHE UNIVERSITÄT BERLIN

1 Berlin 12, den   11.2.64

Straße des 17. Juni Nr. 115

Fernruf: 32 51 81 / 252

Dr. L. Shapiro

Mellon Institue

4400 Fifth Avenue

Pittburgh 13   PA

Dear Dr. Shapiro,

       I think it is time to send a contribution from our
Institute. We have done a lot of work in structure determination of natural
occuring acetylenic compounds. It turns out that we need only 2 - 5 mg.
As an example which may be of interest to the readers I whish to represent
the data for the two cis-trans isomeric thioethers I and II :
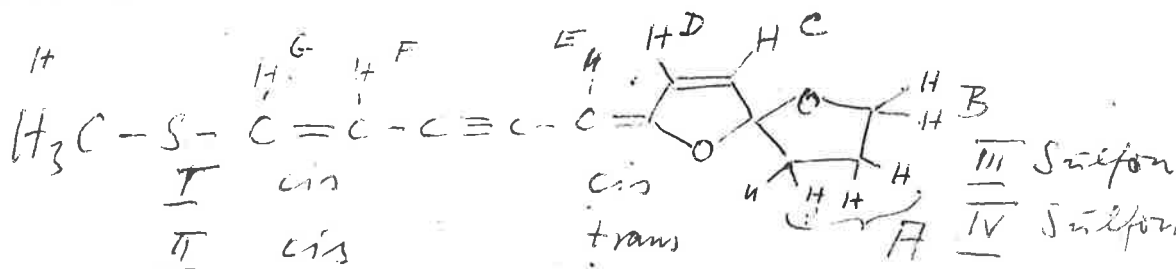
For the elucidation of the structures double resonance was very helpful.
On irridation of $\omega_1 - \omega_2$ (78 C/S) on the signals of III at 3,64 and 3,52
the octett at 4,88 collapses to a doublett and the opposit irridation
gives a doublett and a singlett at 3,64 and 3,52. The irridation of $\omega_1 - \omega_2$
(120 C/S) on the signals at 2,89 gives a quartett at 4,88 and the opposit
irridation gives a simple doublett at 2,89, which clearly demonstrates the
presence of an ABX-system in which X is coupled with a further proton.
Together with other results the only possible structures are 1 and II for
the isomers. It is perhaps of interest that the resolution of the olefinic
signals of II (d 3,75 (1) and 3,72 (1) were only possible at high dilution
(0,2 %).

Sincerely yours,

_

N m r – signals of I – IV in

(measured with the Varian DP 60 (in CCl_4)

	A	B	C	D	E	F	G	H
I	m 7,9 (4)	m 6,0 (2)	dd 3,22 (1) $J_{CD}= 5,5$ $J_{CE}= 0,6$	dd 3,91 (1) $J_{CD}=5,5$ $J_{DE}=1,9$	ddd 5,03 (1) $J_{CE}=0,6$ $J_{DE}=1,9$ $J_{EF}=2,7$	dd 4,45 (1) $J_{EF}=2,7$ $J_{FG}=9,8$	d 3,77 (1) $J_{FG}=9,8$	s 7,68 (3)
I	m 7,95(4)	m 6,1 (2)	d 3,75 (1) $J_{CD}=5,6$	dd 3,97(1) $J_{CD}=5,6$ $J_{DE}=0,7$	dd 5,35(1) $J_{DE}=0,7$ $J_{EF}=2,6$	dd 4,4(1) $J_{EF}=2,6$ $J_{FG}=9,9$	d 3,72 $J_{FG}=9,9$	s 7,66 (3)
II	m 7,85 (4)	m 5,95(2)	dd 2,89(1) $J_{CD}=5,6$ $J_{CE}=0,6$	dd 3,64(1) $J_{CD}=5,6$ $J_{DE}= 1,7$	ddd 4,88(1) $J_{CE}=0,6$ $J_{DE}=1,7$ $J_{EF}=2,8$	m 3,52 (2)		s 6,93 (3)
V	m 7,85(4)	m 5,9(2)	3,62 (2)		d 5,20(1) $J_{EF}=2,5$	m 3,42 (2)		s 6,76 (3)

"Hydrogen Bonding Effects Studied by PMR and IR Spectroscopy
and the π-Electron Distribution in Methoxy Derivatives of
Salicylaldehyde and o-Hydroxyacetophenone"
S. Forsén and B. Akermark
Acta Chem. Scand. 17, 1907 (1963)

"On the Analysis of the A_2B_2 Spectrum of the 1,3-Dioxolane
Ring in 3-Bromo-2-thiophene Aldehyde Ethylene Acetal"
B. Mathiasson
Acta Chem. Scand. 17, 2133 (1963)

"Hydrogen Nuclear Magnetic Resonance Chemical Shift Correla-
tion Charts for Organic Compounds"
M. W. Dietrich and R. E. Keller
Anal. Chem. 36, 258 (1964)

"The Conformation of 1,4-Cyclohexanedione and the Two Isomer-
ic 1,4-Dithiane-1,4-Dioxides"
C. Y. Chen and R. J. W. Le Fèvre
Australian J. Chem. 16, 917 (1963)

"The Stereochemistry of Rings A and B in 6-Substituted
Δ^4-3-Oxosteroids: A Study of H^1 Allylic Spin-Spin
Coupling in Systems with Defined Geometry"
D. J. Collins, J. J. Hobbs and S. Sternhell
Australian J. Chem. 16, 1030 (1963)

"The Analysis of the Proton Magnetic Resonance Spectra of
Heteroaromatic Systems"
P. J. Black and M. L. Heffernan
Australian J. Chem. 16, 1051 (1963)

"The Proton Magnetic Resonance Spectrum of Rimuene"
R. M. Carman
Australian J. Chem. 16, 1104 (1963)

"Proton Magnetic Resonance Spectra of Nitronaphthalenes
in Dimethylacetamide Solution"
P. R. Wells and P. G. E. Alcorn
Australian J. Chem. 16, 1108 (1963)

"Interaction entre Systèmes de Spins par l'Intermédiaire du
Réseau"
J. Henry
Bull. Classe Sci. Acad. Roy. Belg. 697 (1963)

"N.M.R. Experiments on Ketals. Part. I. Reaction Heat and
Entropy of the Methyl Ketal Formation of Cyclohexanone,
Cyclopentanone and Cyclobutanone"
M. Anteunis, F. Alderweireldt and M. Acke
Bull. Soc. Chim. Belg. 72, 797 (1963)

"Résonance Magnétique Nucléaire de Produits Naturels. VII.
Nouvelles Données Sur les Dérivés Flavoniques"
J. Massicot, J.-P. Marthe et S. Heitz
Bull. Soc. Chim. France 2712 (1963)

"Études Stéréochimiques en Série Tétrahydrofurannique. IV.
Diméthoxy-2,5 Dihydro-2,5 Furannes cis et trans. Confor-
mation de Dérivés Tétrahydrofuranniques"
D. Gagnaire et P. Vottero
Bull. Soc. Chim. France 2779 (1963)

"Étude des Spectres de Résonance Magnétique Nucléaire des
Phényl-Chloro-Stannanes et des Phényl-Chloro-Silanes"
J.-C. Maire et F. Hemmert
Bull. Soc. Chim. France 2785 (1963)

"Structure de la Phyllalbine. Application de la Résonance
Magnétique Nucléaire et de la Spectrométrie de Masse à
l'Étude des dérivés du Tropane"
J. Parello, P. Longevialle, W. Vetter et J. A. McCloskey
Bull. Soc. Chim. France 2787 (1963)

"Structure de la Técostanine: Alcaloïde du Tecoma Stans Juss.
(3e mémoire). Monoterpénoïdes (2e mémoire)"
Y. Hammouda, M. Plat et J. Le Men
Bull. Soc. Chim. France 2802 (1963)

"Sur la Técostidine: Nouvel Alcaloïde du Tecoma Stans Juss.
(4e Mémoire). Monoterpénoïde (4e Mémoire)"
Y. Hammouda et J. LeMen
Bull. Soc. Chim. France 2901 (1963)

"Reaktionen mit Chlormethylen-cyclohexan"
H. Günther und A. A. Bothner-By
Chem. Ber. 96, 3112 (1963)

"Die Acidität olefinischer Wasserstoffatome von gespannten
Cycloalkenen"
G. Schröder
Chem. Ber. 96, 3178 (1963)

"Über Kumulene, XVI. Ausweichreaktionen bei Versuchen zur
Darstellung von Pentatetraenen"
R. Kuhn und B. Schulz
Chem. Ber. 96, 3200 (1963)

"Metall-π-Komplexe des Rutheniums und Osmiums mit 6- und
8-gliedrigen cyclischen Oligoolefinen"
E. O. Fischer und J. Müller
Chem. Ber. 96, 3217 (1963)

"Tetrakis(dimethylamino)-äthylen, VI. Das Octamethyl-oxa-
midinium-Kation"
N. Wiberg und J. W. Buchler
Chem. Ber. 96, 3223 (1963)

"Spektroskopische Untersuchungen an organometallischen
Verbindungen, XXV. Protonenmagnetische Resonanzspektren
von Triphenylstannan, Diphenylstannan und Monophenylstannan"
E. Amberger, H. P. Fritz, C. G. Kreiter und M.-R. Kula
Chem. Ber. 96, 3270 (1963)

"Reaktionen von Nitrosaminen mit Elektrophilen, II.
Nitrosamin-Additionsverbindungen"
A. Schmidpeter
Chem. Ber. 96, 3275 (1963)

"Substitutions- und Additionsreaktionen an silylierten
Acetylenen"
L. Birkofer, A. Ritter und H. Uhlenbrauck
Chem. Ber. 96, 3280 (1963)

"Alkychlorcarbene, I. Intramolekulare Reaktionen von
Alkychlorcarbenen"
W. Kirmse und B.-G. v. Bülow
Chem. Ber. 96, 3316 (1963)

"Strukturaufklärung und Synthese einer Thiophenverbindung
aus Chrysanthemum frutescens L."
E. Winterfeldt
Chem. Ber. 96, 3349 (1963)

"Die thermische Zersetzung des Trimethyl-Δ^2-bicyclo[3.1.0]
hexenyl-(6)-ammoniumhydroxyds"
B. Föhlisch
Chem. Ber. 97, 88 (1964)

"Zur Kenntnis der Trialkylsiloxy-aluminiumdihalogenide"
H. Schmidbaur, H. Hussek und F. Schindler
Chem. Ber. 97, 255 (1964)

"Die NMR-Spektren der Hexamethylheterosilmethylene"
H. Schmidbaur
Chem. Ber. 97, 270 (1964)

"The Preparation of a Pentasilacyclooctane"
H. Gilman and S. Inoue
Chem. Ind. 74 (1964)

"6-S-Acetyl-5-deoxy-1,2-O-isopropylidene-6-thio-α-D-xylo-
hexofuranose: Photocatalysed Addition of Thiolacetic Acid
to an Unsaturated Sugar"
D. Horton and W. N. Turner
Chem. Ind. 76 (1964)

"Concentration Dependence of the N.M.R. Spectra of Indoles"
M. G. Reinecke, H. W. Johnson, Jr. and J. F. Sebastian
Chem. Ind. 151 (1964)

"Polarisation Nucléaire par Rotation du Champ Magnétique"
J. Combrisson, J. Ezratty et A. Abragam
Compt. Rend. 257, 3860 (1963)

"Spectrographe Autodyne à Discrimination de Fréquence Pour
l'Étude de la Dispersion en Résonance Magnetique"
R. Reimann
Compt. Rend. 257, 3863 (1963)

"Mesure du Produit $T_1 T_2$ des Temps de Relaxation d'un Charbon
en Fonction de la Température à la Fréquence de 34,6 GHz.
Calcul de T_1"
J. Conard
Compt. Rend. 257, 4160 (1963)

"The Synthesis and Reactions of Some Thienyl Furans"
D. J. Klinke
Dissertation Abstr. 24, 2273 (1963)

"Part A. Carbonium Ion Rearrangements in the Reaction of
t-Amyl Chloride with Aluminum Chloride."
"Part B. N.M.R. Studies of Stereoisomerism in Some Carbonyl
Derivatives"
F. M. Vane
Dissertation Abstr. 24, 2277 (1963)

"Energy Transfer in Unimolecular Gas Reactions & Nuclear
Magnetic Resonance Studies of Hydrogen Bonding of Pyrazoles
and Imidazoles"
N. C. Hung
Dissertation Abstr. 24, 2287 (1963)

"Protonenresonanzspektren alkylsubstituierter Azulene und
ihrer konjugaten Säuren"
D. Meuche, B. B. Molloy, D. H. Reid und E. Heilbronner
Helv. Chim. Acta 46, 2483 (1963)

"Über die Chemie des Vitamins E. 5. Mitteilung. Die Syn-
these von rac. all-trans-ζ_1- und -ε-Tocopherol"
P. Schudel, H. Mayer, J. Metzger, R. Ruegg und O. Isler
Helv. Chim. Acta 46, 2517 (1963)

"Welkstoffe und Antibiotika. 29. Mitteilung. Synthese von
2,4-Dimethoxy-6-hydroxy-9,10-dihydrophenanthren"
E. Hardegger, N. Rigassi, J. Seres, Ch. Egli, P. Müller und
K. O. Fitzi
Helv. Chim. Acta 46, 2543 (1963)

"Über Protonenresonanz-Spektren von Pteridinen III. Zur
Struktur von 9-Acetonylxanthopterin und Erythropterin"
W. von Philipsborn, H. Stierlin und W. Traber
Helv. Chim. Acta 46, 2592 (1963)

"Über Pterinchemie. 8. Mitteilung. Struktur und Protonen-
resonanz-Spektren einiger Xanthopterinderivate"
L. Merlini, W. von Philipsborn und M. Viscontini
Helv. Chim. Acta 46, 2597 (1963)

"Über die Stereochemie der cyclischen Additionsprodukte
von Butadiendioxid mit Hydrazinen"
W. Koch und Hch. Zollinger
Helv. Chim. Acta 46, 2697 (1963)

"Zur Kenntnis ätherischer Öle. 4. Mitteilung. Zur Kenntnis
des sog. «destillierten» Limetten-Öls (Citrus medica, L.,
var. acida, BRANDIS; Citrus aurantifolia, SWINGLE)"
E. sz. Kováts
Helv. Chim. Acta 46, 2705 (1963)

"Ein neues Verfahren zur Herstellung von 21-Desoxy-aldosteron
und 21-Desoxy-17-iso-aldosteron"
J. Schmidlin und A. Wettstein
Helv. Chim. Acta 46, 2799 (1963)

"Cycloheptatrien-1,6-dicarbonsäure und Bicyclo-[4,1,0]-2,4-
heptadien-1,6-dicarbonsäureanhydrid"
R. Darms, T. Threlfall, M. Pesaro und A. Eschenmoser
Helv. Chim. Acta 46, 2893 (1963)

"Das Eindeutigkeitsproblem in der Hochauflösenden Protonen-
resonanzspektroskopie"
H. Kummer
Helv. Phys. Acta 36, 901 (1963)

"Solvent Effect on Magnetic Susceptibility of Liquid Binary
Systems"
S. K. K. Jatkar, V. S. Jatkar and A. J. Mukhedkar
Indian J. Chem. 1, 465 (1963)

"LCAO-MO Charge Distribution and Proton Nuclear Magnetic Res-
onance Shifts in Transition Metal Hydride Complexes"
L. L. Lohr, Jr. and W. N. Lipscomb
Inorg. Chem. 3, 22 (1964)

"The Paramagnetic Influence of Hexaaquochromium(III) Ion in
Aqueous Perchlorate Solutions"
M. Alei, Jr.
Inorg. Chem. 3, 44 (1964)

"Systematics of Mössbauer Isomer Shifts of Iron-Organic
Compounds"
R. H. Herber, R. B. King and G. K. Wertheim
Inorg. Chem. 3, 101 (1964)

"Exchange on Triply Connected Arsenic of the Substituents:
Methoxyl, Dimethylamino, and the Halogens"
K. Moedritzer and J. R. Van Wazer
Inorg. Chem. 3, 139 (1964)

"Chemistry of Boranes. VII. Octachlorononaborane-9 and its
Salts"
J. A. Forstner, T. E. Haas and E. L. Muetterties
Inorg. Chem. 3, 155 (1964)

"Positional and cis-trans Isomeric Dimethylaminotriphospho-
nitriles. The Use of H^1 Nuclear Magnetic Resonance in
Configurational Analysis"
C. T. Ford, F. E. Dickson and I. I. Bezman
Inorg. Chem. 3, 177 (1964)

"Nuclear Magnetic Resonance Studies of $P_2O_3Cl_2F_2$ and Its
Reorganization Products"
M. M. Crutchfield, C. F. Callis and J. R. Van Wazer
Inorg. Chem. 3, 280 (1964)

"Preparation of an Acyl Fluoride from an O-Fluorosulfate;
Some New O-Fluorosulfates"
M. Lustig and J. K. Ruff
Inorg. Chem. 3, 287 (1964)

"Structure of Sodium Ethylenediaminetetraacetic Acid in
Aqueous Solution"
J. E. Tackett and D. T. Sawyer
Inorg. Chem. 3, 304 (1964)

"Formation and Hydroboration of an Olefinic Sugar"
H. Arzoumanian, E. M. Acton and L. Goodman
J. Am. Chem. Soc. 86, 74 (1964)

"Synthesis of Hypophosphite Esters from Orthocarbonyl Com-
pounds"
S. J. Fitch
J. Am. Chem. Soc. 86, 61 (1964)

"Restricted Rotation in Aromatic Aldehydes"
F. A. L. Anet and M. Ahmad
J. Am. Chem. Soc. 86, 119 (1964)

"Olefin Coordination Compounds of Rhodium: The Barrier to
  Rotation of Coordinated Ethylene and the Mechanism of
  Olefin Exchange"
R. Cramer
J. Am. Chem. Soc. 86, 217 (1964)

"The Addition of the Trichloromethyl Radical to ω-Phenyl-
  alkenes"
M. M. Martin and G. J. Gleicher
J. Am. Chem. Soc. 86, 238 (1964)

"Oxymercuration of Olefins. II. cis- and trans-Oxymercura-
  tion of Bicyclo[2.2.2]oct-2-ene"
T. G. Traylor
J. Am. Chem. Soc. 86, 244 (1964)

"The Pentalenyl Dianion"
T. J. Katz, M. Rosenberger and R. K. O'Hara
J. Am. Chem. Soc. 86, 249 (1964)

"Mass Spectrometry in Structural and Stereochemical Problems.
  XXXV. Mass Spectrometric Fragmentation and Hydrogen Trans-
  fer Reactions in 16-Keto Steroids. A Novel Synthesis of
  Side Chain Labeled Cholestanes"
C. Beard, J. M. Wilson, H. Budzikiewicz and C. Djerassi
J. Am. Chem. Soc. 86, 269 (1964)

"The Existence of Sulfenes"
J. F. King and T. Durst
J. Am. Chem. Soc. 86, 287 (1964)

"Total Syntheses of Diterpenes and Diterpene Alkaloids.
  IV. Garryine"
S. Masamune
J. Am. Chem. Soc. 86, 290 (1964)

"Total Syntheses of Diterpenes and Diterpene Alkaloids.
  V. Atisine"
S. Masamune
J. Am. Chem. Soc. 86, 291 (1964)

"Intramolecular Ligand Exchange in Seven-Coordinate Structures"
E. L. Muetterties and K. J. Packer
J. Am. Chem. Soc. 86, 293 (1964)

"Preparation of Tris(trimethylsilyl)- and Tris(trimethyl-
  stannyl)amines"
W. L. Lehn
J. Am. Chem. Soc. 86, 305 (1964)

"Determination of Nuclear Quadrupole Coupling Constants from
  Nuclear Magnetic Resonances in Polycrystalline Solids"
P. A. Casabella
J. Chem. Phys. 40, 149 (1964)

"On Imaginary Solutions to Three-Spin Spectra"
J. R. Cavanaugh
J. Chem. Phys. 40, 248 (1964)

"Density Matrix Description of Nuclear Magnetic Double Res-
  onance"
J. D. Baldeschwieler
J. Chem. Phys. 40, 459 (1964)

"Nuclear Magnetic Resonance Study of Interlayer Water in
  Hydrated Layer Silicates"
J. Graham, G. F. Walker and G. W. West
J. Chem. Phys. 40, 540 (1964)

"Use of Field-Sweep Double Resonance in the Unambiguous
  Analysis of Three-Spin Spectra"
E. B. Whipple and Y. Chiang
J. Chem. Phys. 40, 713 (1964)

"Nuclear Magnetic Resonance and Molecular Field Approxima-
  tion in $KCoF_3$"
T. Tsang
J. Chem. Phys. 40, 729 (1964)

"Oxygen-17 Nuclear Magnetic Resonance in Paramagnetic MnO
  and CoO"
D. E. O'Reilly and T. Tsang
J. Chem. Phys. 40, 734 (1964)

"Effect of Molecular Shape on Nuclear Magnetic Relaxation.
  II. Quadrupole Relaxation"
H. Shimizu
J. Chem. Phys. 40, 754 (1964)

"Étude par Résonance Magnétique Protonique des Actions Inter-
  moléculaires Entre L'Acide Orthophosphorique et des Sol-
  vants Organiques"
C. Dorémieux-Morin et G. Martin
J. Chim. Phys. 60, 1341 (1963)

"Relative Signs of H—H, H—F, and F—F Coupling Constants
  by Nuclear Magnetic Double Resonance"
M. Barfield and J. D. Baldeschwieler
J. Mol. Spectr. 12, 23 (1964)

"Proton Magnetic Resonance Studies of Butadiene-1,3 and
  Some of its Derivatives"
R. T. Hobgood, Jr. and J. H. Goldstein
J. Mol. Spectr. 12, 76 (1964)

"α-Fluorinated Ethers. I. Aryl Fluoroalkyl Ethers"
W. A. Sheppard
J. Org. Chem. 29, 1 (1964)

"α-Fluorinated Ethers. II. Alkyl Fluoralkyl Ethers"
P. E. Aldrich and W. A. Sheppard
J. Org. Chem. 29, 11 (1964)

"Macrocyclic Diterpene Hydroxy Ethers from Tobacco and Cigar-
  ette Smoke"
R. L. Rowland, A. Rodgman, J. N. Schumacher, D. L. Roberts,
  L. C. Cook and W. E. Walker, Jr.
J. Org. Chem. 29, 16 (1964)

"The Synthesis of C-15 β-Substituted Estra-1,3,5(10)-trienes.
  I. "
E. W. Cantrall, R. Littell and S. Bernstein
J. Org. Chem. 29, 64 (1964)

"Photodimerization of $\Delta^{4,6}$-Diene-3-keto Steroids"
M. B. Rubin, G. E. Hipps and D. Glover
J. Org. Chem. 29, 68 (1964)

"Perhydroindanone Derivatives. IV. The 1,1a,4,4a-Tetrahydro-
  fluoren-9-one System"
H. O. House and R. G. Carlson
J. Org. Chem. 29, 74 (1964)

"Highly Substituted Aromatics. The Synthesis and Nuclear
  Magnetic Resonance Spectrum of 2,4,6-Tri-t-butyl-3-fluoro-
  phenol"
B. Rickborn, D. A. May and A. A. Thelen
J. Org. Chem. 29, 91 (1964)

"Electrophilic Substitution of 4a-Methyl-1,3,9-triphenyl-
  4aH-fluorene"
H. W. Moore and H. R. Snyder
J. Org. Chem. 29, 97 (1964)

"Hydrogenolyses with Chloroaluminum Hydrides. III. Allylic
 Alcohols"
J. H. Brewster and H. O. Bayer
J. Org. Chem. 29, 116 (1964)

"Dehydration of Alcohols, Diols and Related Compounds in
 Dimethyl Sulfoxide"
V. J. Traynelis, W. L. Hergenrother, H. T. Hanson and J. A.
 Valicenti
J. Org. Chem. 29, 123 (1964)

"Chemistry of Isocyanic Acid. III. Reaction of Isocyanic
 Acid with Olefins"
F. W. Hoover and H. S. Rothrock
J. Org. Chem. 29, 143 (1964)

"The Reaction of Fenton's Reagent with Phenoxyacetic Acid
 and Some Halogen-Substituted Phenoxyacetic Acids"
R. F. Brown, S. E. Jamison, U. K. Pandit, J. Pinkus,
 G. R. White and H. P. Braendlin
J. Org. Chem. 29, 146 (1964)

"Polyfunctional Aliphatic Compounds. V. The Cyclization
 of Dinitriles by Halogen Acids. A New Synthesis of Imida-
 zoles"
F. Johnson and W. A. Nasutavicus
J. Org. Chem. 29, 153 (1964)

"The Synthesis of 1α-Methylhydrocortisone and 1α-Methyl-
 cortisone Acetate"
W. J. Wechter
J. Org. Chem. 29, 163 (1964)

"On the Stereochemistry of Conjugate Addition. II. Hydro-
 cyanation of 1-Acetyl-$\Delta^{1,8}$-hydrindene"
W. L. Meyer and J. F. Wolfe
J. Org. Chem. 29, 170 (1964)

"The Cyanoethylation of Indene and Related Reactions"
H. Dressler and R. J. Kurland
J. Org. Chem. 29, 175 (1964)

"Reaction of Indole Derivatives with Thionyl and Sulfuryl
 Chlorides"
J. Szmuszkovicz
J. Org. Chem. 29, 178 (1964)

"Baeyer-Villiger Oxidation of syn-7-Chloronorcamphor and
 syn-7-Bromonorcamphor"
R. R. Sauers and J. A. Beisler
J. Org. Chem. 29, 210 (1964)

"Pyrano[2,3-d]- and Pyrido[2,3-d]pyrimidines"
H. C. Scarborough
J. Org. Chem. 29, 219 (1964)

"Decomposition of Dimethyl Sulfoxide Aided by Ethylene Glycol,
 Acetamide, and Related Compounds"
V. J. Traynelis and W. L. Hergenrother
J. Org. Chem. 29, 221 (1964)

"Heterocyclic Derivatives of 3-Aminopropanethiol"
E. Campaigne and P. K. Nargund
J. Org. Chem. 29, 224 (1964)

"The Preparation of (2,2-Dicarbethoxypropyl)-ethoxydimethyl-
 silane"
H. Gilman and W. H. Atwell
J. Org. Chem. 29, 237 (1964)

"Dibromination of Adamantane"
G. L. Baughman
J. Org. Chem. 29, 238 (1964)

"A 1,3,5-Dioxazine"
B. Loev, K. M. Snader and M. F. Kormendy
J. Org. Chem. 29, 245 (1964)

"Analysis of the Structure of Dehydro-D-glucosazone by
 Nuclear Magnetic Resonance and by Comparison of Its
 Optical Isomers"
L. Mester and E. Moczar
J. Org. Chem. 29, 247 (1964)

"Addition of Acetaldehyde to Fluoroethylenes"
E. R. Bissell and D. B. Fields
J. Org. Chem. 29, 249 (1964)

"Some Isomers of Chloroiodotrifluoroethane"
E. R. Bissell
J. Org. Chem. 29, 252 (1964)

"The Stability of Cyclopropyllithium in Diethyl Ether and in
 Tetrahydrofuran"
D. Seyferth and H. M. Cohen
J. Organometal. Chem. 1, 15 (1963)

"Pentaalkylsiloxalane"
H. Schmidbaur
J. Organometal. Chem. 1, 28 (1963)

"Studies on Some Alkyl and Olefin Complexes of Iron and
 Manganese"
M. L. H. Green and P. L. I. Nagy
J. Organometal. Chem. 1, 58 (1963)

"Spektroskopische Untersuchungen an Organometallischen Verbin-
 dungen. XIX. PMR-Spektren Einiger Azulenium-Derivate und
 Azulenium-Chrom-Cyclopentadienyl-Komplexe"
H. P. Fritz und C. G. Kreiter
J. Organometal. Chem. 1, 70 (1963)

"Studies on an Iron-σ-Propargyl Complex"
J.K. P. Ariyaratne and M. L. H. Green
J. Organometal. Chem. 1, 90 (1963)

"The Isomeric 1-Propenyllithium Reagents: their NMR Spectra
 and the Stereochemistry of their Formation by the Direct
 Reaction and by the Transmetalation Reaction"
D. Seyferth and L. G. Vaughan
J. Organometal. Chem. 1, 201 (1963)

"Études Récentes de la Structure de Quelques Minéraux a
 l'Aide de la Résonance Magnétique Nucléaire"
M. Harmelin
J. Phys. Radium 24, 753 (1963)

"Thermal Degradation of N-Substituted Polycarbamates"
E. Dyer and R. J. Hammond
J. Polymer Sci. A2,1 (1964)

"Proton Magnetic Resonance in Cupric Formate Tetrahydrate,
 $Cu(HCO_2)_2 \cdot 4H_2O$"
H. Kiriyama
Mem. Inst. Sci. Ind. Res., Osaka Univ. 20, 133 (1963)

"Nuclear Magnetic Resonance in Alloys"
N. Bloembergen
Metallic Solid Solutions, Chapt. XIV, pp.1-15
J. Friedel and A. Guinier, Ed.
W. A. Benjamin, Inc. 1963

"Nuclear Magnetic Resonance in Chromium-Vanadium Alloys"
L. E. Drain
Metallic Solid Solutions, Chapt. XXXI, pp.1-12
J. Friedel and A. Guinier, Ed.
W. A. Benjamin, Inc. 1963

"Theoretical Calculation of N.M.R. Spectral Line Shapes"
M. Suzuki and R. Kubo
Mol. Phys. 7, 201 (1964)

"Proton Nuclear Magnetic Relaxation in Antiferromagnetic
   $CuCl_2 \cdot 2H_2O$"
H. Benoit et J. P. Renard
Phys. Letters 8, 32 (1964)

"Longitudinal Spin Relaxation in Solid He[3]"
S. R. Hartmann
Phys. Rev. 133, A17 (1964)

"Nuclear Magnetic Relaxation in NaCl at High Temperatures"
M. Eisenstadt
Phys. Rev. 133, A191 (1964)

"Ytterbium NMR:Yb[171] Nuclear Moment and Yb Metal Knight
   Shift"
A. C. Gossard and V. Jaccarino and J. H. Wernick
Phys. Rev. 133, A881 (1964)

"The Investigation of Polyacetaldehyde Structure by High
   Resolution Nuclear Magnetic Resonance"
J. Brandrup and M. Goodman
Polymer Letters 2, 123 (1964)

"The Structure and Dual Reactivity of N-Ethyleneiminocarbin-
   ols"
R. G. Kostyanovskii and V. F. Bystrov
Proc. Acad. Sci. USSR, Chem. Sect. (English Transl.) 148,
   97 (1963)

"The Structure of 2-Aminothiazoline"
Yu. N. Sheinker, E. M. Peresleni, A. I. Kol'tsov, N. M.
   Bazhenov and M. V. Vol'kenshtein
Proc. Acad. Sci. USSR, Chem. Sect. (English. Transl.) 148,
   133 (1963)

"Investigation of the Hydrogen Bond by the NMR Method. Effect
   of Steric Hindrances on the Hydrogen Bond in Diorthoalkyl-
   phenols"
V.F.Bystrov, K.M.Dyumaev, V.P.Lezina and G.A.Nikiforov
Proc. Acad. Sci. USSR, Chem. Sect. (English Transl.) 148,
   139 (1963)

"The Nature of H-Bonds in Systems with π-Electrons and
   their Effect on Proton Magnetic Resonance"
D. N. Shigorin, N. N. Shapet'ko, A. P. Skoldinov and G. S.
   Ryagchikova
Proc. Acad. Sci. USSR, Phys. Chem. Sect. (English Transl.)
   148, 147 (1963)

"Nuclear Magnetic Relaxation and the Magnetic Properties of
   V-Cr Alloys"
J. Butterworth
Proc. Phys. Soc. 83, 71 (1964)

"Spin-change Cross Sections Between Hydrogen Atoms"
A. Dalgarno and R. J. W. Henry
Proc. Phys. Soc. 83, 157 (1964)

"Constitution of Rifamycins"
V. Prelog
Pure Appl. Chem. 7, 551 (1963)

"Bromowanie k,5-Naftyrydyny W Dymiacym Kwasie Siarkowym"
W. Czuba
Roczniki Chem. 37, 1589 (1963)

"The Structure of Securinine"
C. Shu-Feng, X Jing-Xi and L. Xiao-Tian
Sci. Sinica (Peking) 12, 1525 (1963)

"Temperature Dependence of the Spin-Lattice Relaxation Time
   of V^{4+} in TiO_2"
G. M. Zverev
Soviet Phys. JETP (English Transl.) 17, 1251 (1963)

"Anomalous Resonance Spin Flip of a Particle in a Magnetic
   Field"
Kh. A. Simonyan and Yu. F. Orlov
Soviet Phys. JETP (English Transl.) 18, 123 (1964)

"Nuclear Magnetic Resonance in Ferromagnetic Substances"
L. L. Buishvili and N. P. Giorgadze
Soviet Phys. Solid State (English Transl.) 5, 1322 (1964)

"A Study of the Protonation of Quinoline by Proton Magnetic
   Resonance"
E. Krakower and L. W. Reeves
Spectrochim. Acta 20, 71 (1964)

"The Stereochemistry and Absolute Configuration of Narcotine"
A. R. Battersby and H. Spencer
Tetrahedron Letters 11 (1964)

"4-Methylpyrimidine N-Oxides"
M. Ogata, H. Watanabe, K. Tori and H. Kano
Tetrahedron Letters 19 (1964)

"The Structure of Phaseolin"
D. R. Perrin
Tetrahedron Letters 29 (1964)

"The Synthesis, Nuclear Magnetic Resonance and Ultraviolet
   Spectrum of 2,4,6-Tri-T-Butyltoluene"
W. A. Gibbons and H. Fischer
Tetrahedron Letters 43 (1964)

"Synthesis and Properties of 3,4-Di-t-Butylphenol"
A. W. Burgstahler, M. O. Abdel-Rahman and P.-L. Chien
Tetrahedron Letters 61 (1964)

"Ketones from "Mayur Pankhi" : Some New Cuparene-Based
   Sesquiterpenoids"
G. L. Chetty and S. Dev
Tetrahedron Letters 73 (1964)

"Structures of Nobiline and Dendrobine"
S. Yamamura and Y. Hirata
Tetrahedron Letters 79 (1964)

"A Simple Method for the Preparation of β-Tetralone-3-
   Carboxylates"
S. W. Pelletier and P. C. Parthasarathy
Tetrahedron Letters 103 (1964)

"Ion Pairs in the Rearrangement of Trityl 2-Methylbenzene-
   sulfinate"
D. Darwish and E. A. Preston
Tetrahedron Letters 113 (1964)

"Cycloartocarpin"
P. M. Nair, A. V. Rama Rao and K. Venkataraman
Tetrahedron Letters 125 (1964)

"Alkaloids from Nuphar Luteum . Part III. A New Alkaloid -
   Neothiobinupharidine. Spectroscopic Studies on the
   Structure of Thiobinupharidine and Neothiobinupharidine"
O. Achmatowicz and J. T. Wróbel
Tetrahedron Letters 129 (1964)

"Synthesis and Cyclodimerization of Stable 1-t-Alkylamino-
   2,3-Epoxypropanes; Related Sterically Promoted Eight-
   Membered Ring Closures"
V. R. Gaertner
Tetrahedron Letters, 141 (1964)

"The Mechanism of the Reduction of Pyridinium Ions by Sodium
   Borohydride, II.
P. S. Anderson and R. E. Lyle
Tetrahedron Letters 153 (1964)

"Thermische Spaltung Von 7,7-Dimethoxy-Bicycloheptadien-
  [2:2:1] -Derivaten, Ein Weg Zum Tetramethoxy-Äthylen"
R. W. Hoffmann und H. Häuser
Tetrahedron Letters 197 (1964)

"Zur Elektrophilen Substitution von Enaminen"
H. Metzger
Tetrahedron Letters 203 (1964)

"Conformational Analysis of Δ^5-3-Keto-Steroids and their
  4,4-Dimethyl Derivatives"
M. Gorodetsky and Y. Mazur
Tetrahedron Letters, 227 (1964)

"Interactions Spin-Spin Nucleaires III. Couplage Spin-Spin
  a "Longue Distance" $^4J_{HH}$ Entre Protons"
A. Rassat, C. W. Jefford, J. M. Lehn et B. Waegell
Tetrahedron Letters 233 (1964)

"Bis-(Alkylthio)-Carbenes"
D. M. Lemal and E. H. Benitt
Tetrahedron Letters 245 (1964)

"A Novel Photochemical Addition Reaction of 3 β-Acetoxypreg-
  na-5,16-Dien-20-One"
I. A. Williams and P. Bladon
Tetrahedron Letters 257 (1964)

"A Simple Method for the Preparation of Bicyclo [2.2.2] -
  Octane Systems from Methyl Vinyl Ketone Derivatives"
K. Morita and Z. Suzuki
Tetrahedron Letters 263 (1964)

"Structure of Linderene"
K. Takeda and M. Ikuta
Tetrahedron Letters 277 (1964)

"Isomere des Voacamins: Voacamidin, Conodurin und Conoduramin"
U. Renner und H. Fritz
Tetrahedron Letters 283 (1964)

" π -Allylic Complexes from Allene"
R. G. Schultz
Tetrahedron Letters 301 (1964)

"High-Resolution N.M.R. Spectra in Electric Fields"
A. D. Buckingham and J. A. Pople
Trans. Faraday Soc. 59, 2421 (1963)

"Nuclear Magnetic Resonance Spectra of Cyclic Fluorocarbons.
  Part I. ^{19}F Spectra of Fluorocyclohexanes"
J. Homer and L. F. Thomas
Trans. Faraday Soc. 59, 2431 (1963)

"Proton Transfer Between Methanol and Ortho-Chlorophenol"
E. Krakower and L. W. Reeves
Trans. Faraday Soc. 59, 2528 (1963)

"Umsetzung von Nitrilen mit Dimethyl-oxo-sulfonium-methylid"
H. König und H. Metzger
Z. Naturforschg. 18b, 976 (1963)

"Über Stabile Schwefelylide"
H. Metzger und H. König
Z. Naturforschg. 18b, 987 (1963)