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Jones
  Announcement of a Course: "Interpretation of High-Resolution N.M.R. Spectra"

v. Philippborn
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Lundin, Elsken
  Circuitry for Use of a 1024 Gate with the A-60; Concerning A-60 Console Temperature Constancy

Bohmann
  Structure Determination of Naturally Occurring Acetylenic Compounds
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.

A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication".
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 fluorinated organic compounds, and (2) more fundamental investigations of F19 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 OCH3 group attached to a fluorinated benzene ring couple with any ortho F19 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 and F19 spectra of the pure liquid were examined and there is definitely no OCH3-F coupling. Our first reaction was to doubt that there is an OCH3 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 OCH3-F coupling rule.

(b) For some time now we have been trying to establish the conformations of compounds of the type \( \text{CH}_2 \text{F} \) from their H and F19 spectra. It would help us enormously 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.

JWE/LR

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).

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-

The 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:

$$G_{\alpha \beta \gamma \delta} (t) = \langle \alpha | \psi (t) \rangle \langle \alpha | \psi (t) \rangle$$

where \( \psi (t) \) is a random perturbation expressed in the basis \( \{ \psi \} \) of eigenfunctions of the time-independent Hamiltonian.


The dipole-dipole interaction Hamiltonian is:

$$\mathcal{H} (t) = \sum_{N} \sum_{m} \mathcal{F}^{(m)} \alpha \beta \gamma \delta \mathcal{A}_{N}^{(m)}$$

where the subscript \( N \) refers to a distinct pair of spins \( \mathcal{I}_{N} \) and \( \mathcal{S}_{N} \):

$$\mathcal{A}_{N}^{\pm \pm} = \mathcal{I}_{N}^{\pm} \mathcal{S}_{N}^{\pm}$$

$$\mathcal{A}_{N}^{\pm \mp} = \mp \frac{1}{2} (\mathcal{I}_{N}^{\pm} \mathcal{S}_{N}^{\mp} + \mathcal{I}_{N}^{\mp} \mathcal{S}_{N}^{\pm})$$

$$\mathcal{A}_{N}^{0} = \lambda_{N}^{0} (\mathcal{I}_{N}^{+} \mathcal{S}_{N}^{-} - \mathcal{I}_{N}^{-} \mathcal{S}_{N}^{+})$$

$$\mathcal{F}^{(m)} (\theta_{N}) = -\left( \frac{\hbar}{\gamma} \right) \mathcal{Y}_{N} \mathcal{Y}_{N}^{\prime} \mathcal{F}_{N}^{(m)} (\theta_{N}, \phi_{N})$$

with \( r_{N} \) the fixed distance between the \( N \)th pair of spins, \( \theta_{N} \).
\( \phi_N \) the polar and azimuthal angles specifying the orientation of the vector \( \mathbf{r} \) relative to the laboratory coordinate system, and \( Y_{\ell m}^{(m)}(\theta_N, \phi_N) \) the normalized rank two spherical harmonics. The time dependence of \( \psi(t) \) enters implicitly through the variation of the angles \( \sigma, \phi; \sigma, \theta; \ldots \sigma, \phi \) due to the molecular Brownian motion. These angles are not independent, but are related in a complicated way by the molecular geometry. However, if \( F^{(m)}(\Theta, \Phi) \) is transformed to molecule-fixed coordinates (9).


\[
\psi(t) = \sum_N \sum_m \sum_{m'} F^{(m)}(\Theta, \Phi) D^{(2)}_{mm'}(J, L) A^{(m)}_N
\]

The angles \( \Theta_N \) and \( \Phi_N \) are independent of time, and the time dependence enters implicitly through the independent Eulerian angles \( \alpha, \beta, \gamma \) which relate laboratory and molecule coordinates. Assuming isotropic motion governed by a diffusion equation, the correlation functions become (6, 8)

\[
G_{\alpha \beta \gamma}^{(2)}(z) = \left[ \frac{e^{-r^2/2\sigma^2}}{\sqrt{2\pi \sigma^2}} \right] \sum_{NN'} \sum_{mm'} \sum_{m''} \int D^{(2)}_{mm'}(r, \sigma) D^{(2)}_{m'm''}(\sigma, \rho) \cdot \cdot \cdot
\]

where we have used

\[
\int D^{(2)}_{mm'}(r, \sigma) D^{(2)}_{m'm''}(\sigma, \rho) \cdot \cdot \cdot = (3\pi^{-1/2}) \sum_{m''} \sum_{m''}
\]

The factor

\[
\mathcal{F}_{NN'} = \sum_{m} F^{(m)}(\Theta, \Phi) F^{(m)}(\Theta', \Phi')
\]

is reduced to

\[
(3\pi) \frac{1}{2} Y_N \sum Y_N Y_N Y_N Y_N r_N^{-3} c_N^{-3} (3 \cos^2 \Theta_N - 1)
\]

where \( \Theta_N \) is the angle between \( \Theta_N \) and \( \Theta_N' \), by the spherical harmonic addition theorem. The magnitudes of the cross
correlation terms thus depend upon the angles $\varphi_{NN'}$.

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 trans 1, 2-difluoroethylene where $\mathcal{Z}_N$ and $\mathcal{Z}_N'$ 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

$$\sum_N \mathcal{Z}_N \mathcal{Y}_N \mathcal{V}_N \mathcal{R}_N^{-1} \left| \left\langle \alpha | A_N^{-1} \alpha \rightangle \right|^2.$$  

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,

Joseph H. Noggle
Karl F. Kuhlmann
John D. Baldeschwieler

JDB:ms
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. Od.) 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. M. 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 (S.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.
"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 dependence 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\(^3\).\(^4\).

\[
\begin{align*}
H-C-C-x-C-H \quad x = C, O, N
\end{align*}
\]

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 respectively 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;

\[
\begin{align*}
I & \quad J_{CH_2-H(2)} = 0.8 \pm 0.1 \text{ cps} \\
\quad & \quad J_{CH_2-CH_3} = 0.8 \pm 0.1 \text{ cps}
\end{align*}
\]

The signs of these constants expected to be opposite remain to be determined. I is the long sought for \(\beta\)-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 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$\pi$-interactions assumed to dominate these couplings should be proportional to $\eta^2$ this would indicate a smaller $\pi$-bond order $\eta$ 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 vinyl ethers was recently reported to be normal.

Analogous homoallylic couplings were found across nitrogen in the system

![Chemical structure](image)

$J_{\text{CH}_2-H} = 1.4-2.5$ cps, depending upon the nature of the substituent R and presently under investigation.

---

4) M.A.Weinberger & H.Greenhalgh, MellonMr 52-9.

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

Yours sincerely,

W.v.Philipsborn
AIRMAL

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

Dear Barry:

H¹, F¹⁸, and P³¹ 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(CF₃)₂ groups. The H¹ and
F¹⁸ n.m.r. spectra of these complexes may be of interest to some of your
readers.

<table>
<thead>
<tr>
<th>Complex</th>
<th>τ</th>
<th>J_FF†</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅H₅Fe{As(CF₃)₂}(CO)₂</td>
<td>5.06</td>
<td>+42.16</td>
</tr>
<tr>
<td>C₅H₅Mo{As(CF₃)₂}(CO)₃</td>
<td>4.52</td>
<td>+40.45</td>
</tr>
<tr>
<td>C₅H₅Fe{As(CF₃)₂}(CO)₂ (trans-isomer)</td>
<td>5.43</td>
<td>+48.57</td>
</tr>
<tr>
<td>C₅H₅Fe{As(CF₃)₂}(CO)₂ (cis-isomer)</td>
<td>5.43</td>
<td>+46.15, 51.38⁵</td>
</tr>
<tr>
<td>C₅H₅Mo{As(CF₃)₂}(CO)₂</td>
<td>4.44</td>
<td>+46.29</td>
</tr>
<tr>
<td>Mn{As(CF₃)₂}(CO)₄</td>
<td>-</td>
<td>+45.84</td>
</tr>
<tr>
<td>Fe{As(CF₃)₂}(NO)₂</td>
<td>-</td>
<td>+43.52</td>
</tr>
</tbody>
</table>

a) CCl₃F used as solvent. b) Measured at 56.4 Mc. c) Contains terminal
-As(CF₃)₂ group. d) Contains bridging -As(CF₃)₂ groups. e) Quartets with
J_FF† 6.6 c.p.s.

One of the main points of interest is that the gem-trifluoromethyl
groups in cis-[C₅H₅Fe{As(CF₃)₂}(CO)]₂ have different chemical shifts owing
to molecular asymmetry. The observed J_FF† is similar to that found in the
C¹³ satellite spectrum of (CF₃)₂AsCl (R.K. Harris, J. Mol. Spect., 10,
309; 1963).
Dr. B. L. Shapiro

January 29, 1964

This may also be a good place to record the $^{31}$P spectra of some related $-\text{P(CH}_3\text{)_2}$ bridged complexes. (We are indebted to Drs. M. M. Crutchfield and C. F. Callis for these data).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Chemical Shift$^a$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe}{\text{P(CH}_3\text{)_2}}{\text{CO}}_3}^2_2$</td>
<td>-116.5</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>$[\text{Cr}{\text{P(CH}_3\text{)_2}}{\text{CO}}_4}_2$</td>
<td>-245.0</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>$[(\text{C}_5\text{H}_5\text{)}_2\text{Fe}_2\text{H}{\text{P(CH}_3\text{)_2}}{\text{CO}}_2$</td>
<td>-163.5</td>
<td>C$_2$H$_6$</td>
</tr>
</tbody>
</table>

$^a$ p.p.m., relative to external H$_3$PO$_4$, measured at 24.5 Mc.

With best wishes,

R. G. Hayter

RGH/jfn
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:
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 (~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 R2. It is quite easy to record both integrated derivative and derivative simultaneously. Such simultaneous recordings are reproduced below.

\[ R_1 = 56K, \quad R_2 = 10K, \quad R_3 = 6.8M \]

\( B_1 = \text{Type 1R Hg cell} \)
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 X (or for X' 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 dg

A small item which may eliminate MELLO-NMR 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 XMe_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

\[ J_{XCH} = \frac{\alpha^2}{\alpha^2 + \Delta E_H} \frac{\Delta E_X}{\Delta E} \frac{1}{n^3} \frac{(Z_{X^*})^3}{(Z_{H^*})^3} \frac{g_X}{g_H} J_{HCH} \]

where \( \alpha^2 \) 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 \( Z_{X^*} \sim n^2 \left( \frac{g}{r_m} \right) \).
Since then I have extended the use of the equation to 
\[ \text{HgMe}_2 (\alpha^2 = 0.50); (\text{Me}_3\text{P})_4 (\alpha^2 = 0.25); (\text{Me}_4\text{P})^+\text{Cl}^- (\alpha^2 = 0.25); \]
and \( \text{TlMe}_3 (\alpha^2 = 0.33) \) (X is underlined). A logarithmic plot of the resulting \( Z_{\text{NMR}}^* \) versus the true nuclear charge \( Z \) for these four compounds, plus five \( \text{Me}_4\text{X} \), and \( \text{CH}_2\text{DOH} \), 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 \( Z_{\text{NMR}}^* \) plot, one can compute \( \alpha^2 \) from known \( J_{\text{XCH}} \) values (for covalent bonding). For instance, using \( J_{\text{CHCH}} = 2.7 \) cps in \( \text{PMe}_3 \) \{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 \( \text{TeMe}_2 \) Klose \{Z. Naturforch 16A, 528 (1961)\} gives \( J_{\text{TeCH}} = 20.7 \) 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 \( \alpha^2 \) values for \( \text{F} \) from \( J_{\text{FCH}} \) one gets \{Muller and Carr, J. Phys. Chem. 67, 112 (1963)\} \( \alpha^2 = 0.33 \), much too high (one expects \( \alpha^2 \approx 0.05 \)). Perhaps the discrepancy is due to ionic contributions to \( J \).

An extension to \( J_{\text{XY}} \) would be

\[
J_{\text{XY}} = \frac{w_Y}{w_X} \cdot J_{\text{XCH}} = \frac{w_Y}{w_X} \cdot \frac{w_X}{w_H} \cdot J_{\text{HCH}}
\]

where

\[
\alpha^2 = \frac{\Delta E_X}{\text{norm}_X (Z_X^*)^3 g_X}
\]

and

\[
\frac{\text{norm}_X}{\text{norm}_H} = \frac{1}{n_X^3}
\]

It is worth noting that this equation agrees with the statement of Schneider and Buckingham \{loc. cit\} that \( J_{\text{XY}} \) is proportional to \( \left( \frac{Z_X^*}{n_X} \right)^3 \left( \frac{Z_Y^*}{n_Y} \right)^3 \frac{y_X}{y_Y^2} \).
The only data I know of to test this equation are $J_{\text{FCC}}$ in CF$_3$CH$_2$Br (= 38.5 cps) \{Muller and Carr, loc. cit.\} and $J_{\text{PCb}}$ in (CH$_3$)$_2$Sn(CF$_3$H)$_2$ (= 251 cps) \{Reeves and Wells, Can J. Chem. 41, 2698 (1963)\}. These values yield $\alpha^2(Z_p^*)^3 = 86$ and $\alpha^2(Z_p^*)^3 = 35$ respectively. The fact that the two results are off only by a factor of 2 is satisfying, but use of $Z_{\text{NMR}}^* = 4.6$ from the plot gives $\alpha^2 = 0.87$ 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 $J_{\text{XCY}}$ where only covalent bonds are present.

A final possible extension of the equation is an obvious one to the case $J_{\text{XCY}}$ (if one wishes to get really wild). Drake and Jolly \{U. S. At. En. Comm. Report U CRL-10422 (1962)\} Chem. Abst. 58 2042a (1963) give $J_{\text{PSiH}} = 16.2$ cps in SiH$_3$PH$_2$. Using $J_{\text{HSiH}}$ from Ebsworth and Turner \{J. Chem. Phys. 36, 2628 (1962)\} and $(Z_p^*)_{\text{NMR}} = 6.23$ we get $\alpha^2 = 1.5$, obviously incorrect. Because of p-bonding in phosphine we expect $\alpha^2 \leq 0$. However, Ebsworth and Turner point out that their results for $J_{\text{HSiH}}$ depart radically from the theory of Gutowsky et. al. \{J. Chem. Phys. 31, 1278 (1959)\} upon which equation 1) rests, so that the failure of the extension to $J_{\text{PSiH}}$ is not surprising. Ebsworth and Turner indicate that the discrepancy of the $J_{\text{HSiH}}$ results may be due to the contribution of d orbitals of silicon. It would appear that an extension to $J_{\text{XCH}}$ 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 $\text{Sn}_5$ isotopes (all I=1/2) in that the ratio of their quoted NMR frequencies does not agree with the ratios of the magnetic moments ($\mu$). In the table the ratio of the frequencies in 10 kg for $\text{Sn}^{115}/\text{Sn}^{117}/\text{Sn}^{119}$ is 13.22/15.77/15.87 (a ratio 0.834/0.994/1.000) whereas the quoted $\mu$ values are 0.9132/0.9949/1.0409 (a ratio 0.877/0.956/1.000). In my paper on $J_{\text{XCH}}$, the $J_{\text{SnCH}}$ values are in the ratio 0.878/0.957/1.000, in agreement with the $\mu$ 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 W. Smith
Physics Department

GWS/vf
Enclosures
$Z_{\text{NMR}}^{*} = 0.98Z^{0.71}$
Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago 15, 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. If we take anisotropy shifts $\Delta_{\text{anis}}$ to be the deviations from the linear relations between the proton chemical shifts of alkyl-$\Lambda$ compounds and the electronegativity of $\Lambda$, 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 $\alpha$ proton shifts and $\beta$ 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-$\Lambda$ bond. One could obtain negative $\Delta \chi$ values consistent for the $\alpha$ and $\beta$ 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 $\alpha$ protons.

In contrast to reference 1, Reddy and Goldstein deduced negative $\Delta_{\text{anis}}$ values from correlations between $^{13}$C-$H$ 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 pointed out the use of the Gans-Mrowka equations in determining magnetic anisotropies. According to this method, one obtains $\Delta \chi_{C-CB} = +0.86 \times 10^{-6}$ and $\Delta \chi_{C-Br} = +1.00 \times 10^{-6}$ using Wenbigh'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 exaggerate the anisotropy effects compared with other methods.

Yours sincerely,

A. Saika

4) Denbigh, Trans. Farad Soc. 36, 936 (1940)

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

<table>
<thead>
<tr>
<th></th>
<th>$\Delta \chi$</th>
<th>p.p.m.</th>
<th>$10^{-6}$ cm$^3$ mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$Cl</td>
<td>-0.80</td>
<td>13.8</td>
<td></td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>-0.85</td>
<td>16.5</td>
<td></td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>-1.01</td>
<td>23.1</td>
<td></td>
</tr>
<tr>
<td>CH$_2$CH$_2$Cl</td>
<td>-0.87</td>
<td>14.4</td>
<td></td>
</tr>
<tr>
<td>CH$_2$CH$_2$Br</td>
<td>-1.07</td>
<td>20.3</td>
<td></td>
</tr>
<tr>
<td>CH$_2$CH$_2$I</td>
<td>-1.41</td>
<td>33.0</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH$_2$Cl</td>
<td>-0.39</td>
<td>37.0 (staggered)</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH$_2$Br</td>
<td>-0.61</td>
<td>51.7 (eclipsed)</td>
<td></td>
</tr>
<tr>
<td>CH$_3$CH$_2$I</td>
<td>-0.88</td>
<td>70.3 (staggered)</td>
<td></td>
</tr>
</tbody>
</table>
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 C- 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 $J_{\text{P-C-H}}$ 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.

<table>
<thead>
<tr>
<th>$[R_2PR']^+$</th>
<th>Chemical Shift ($\tau$ scale)</th>
<th>$J_{\text{P-C-H}}$ (C.P.S.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$C$_6$H$_5$</td>
<td>4.72</td>
<td>14.1</td>
</tr>
<tr>
<td>CH$_2$C$_6$H$_4$COCH$_3$-p</td>
<td>4.86</td>
<td>13.4</td>
</tr>
<tr>
<td>CH$_2$C$_6$H$_4$COOCH$_3$-p</td>
<td>4.27</td>
<td>15.5</td>
</tr>
<tr>
<td>CH$_2$C$_6$H$_4$Cl-p</td>
<td>4.26</td>
<td>14.7</td>
</tr>
<tr>
<td>CH$_2$COOH</td>
<td></td>
<td>13.5</td>
</tr>
<tr>
<td>CH$_2$COOC$_2$H$_5$</td>
<td>4.58</td>
<td>14.5</td>
</tr>
<tr>
<td>CH$_2$COOCH$_2$C$_6$H$_5$</td>
<td>4.25</td>
<td>14.0</td>
</tr>
<tr>
<td>CH$_3$</td>
<td></td>
<td>13.9</td>
</tr>
<tr>
<td>n-C$_6$H$_9$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$C$_6$H$_5$</td>
<td>5.68</td>
<td>15.4</td>
</tr>
<tr>
<td>CH$_2$COOH</td>
<td>6.14</td>
<td>12.7</td>
</tr>
</tbody>
</table>

*Recorded in D$_2$O.
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:

\[ [(\text{NCCH}_{2}\text{CH}_{2})_{2}P\text{CH}_{2}N(\text{CHO})\text{CH}_{2}]^{+} \]

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.

\[ \begin{align*}
\text{J}_{P-C-H} & \quad \text{(methylene)} \quad 10.5 \\
\text{J}_{P-C-H} & \quad \text{(methyl)} \quad 14.3 \\
\text{J}_{P-C-H} & \quad \text{(benzyl)} \quad 16.8
\end{align*} \]

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

Sincerely,

Clay

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

$$\omega_2 = \omega_{rs} + \frac{\hbar_{rs}}{2\sqrt{k(k-1)}}$$

for $\Lambda = 0$, or

$$\omega_2 = \omega_{rs} + \frac{\hbar_{rs}}{2\sqrt{k(k+1)}}$$

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

$$L = \frac{1}{2}(1 - \frac{1}{2k-1})$$  \hspace{1cm} (\Lambda = 0)$$

$$L = \frac{1}{2}(1 + \frac{1}{2k+1})$$  \hspace{1cm} (\Lambda = 2).$$

In addition, a population enhancement is generally associated with the $\Lambda = 2$ arrangement and a diminution 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 \(1 + \frac{1}{2k} \approx -1\).

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 \(A = 2\) 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\(^{21}\) spectrum. One of the outer F\(^{19}\) quartet transitions is unaffected, and one is split according to \(A = 0\). The inner quartet and two degenerate doublet transitions are all split according to \(A = 2\) with \(k = 2.32\), we therefore expect a quintet with a splitting ratio of 1.58 and intensity ratio of \((3/2 \times 0.363):(3 \times 0.588):5:1.764:1.045\). Including the population factors estimated as above, the intensities become 0.86:4.29:3:4.29:0.86.

\[P_{F_3}^2, \text{field sweep} \]
\[\nu_1 = 56,446,460 \text{ m.c.} \]
\[\nu_2 = 24,284,145 \text{ m.c.} \]

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, we measured a number of proposed internal reference compounds for aqueous solutions in neutral, acid (3 N DCI) and alkaline (3 N NaOD) solutions. Our results, expressed on the \( \gamma' \) scale proposed by Tiers (MELLON 10, 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 \( \gamma' \) values do vary. We find a constant difference between the \( \gamma' \) values in D_2O and DCI (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 dimethylsulphoxide) are satisfactory reference compounds in acid and alkaline solutions, (although there is doubt about the use of tert-butanol with aromatic solutes), and that if the \( \gamma' \) 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 -60°C, I would be interested to know how many MELLON readers have run the A-60 probe at -90°C without damage.

With best wishes,

Yours sincerely,

R. J. Abraham.

### Table 1.
Proton Chemical Shifts ($\gamma'$) of Reference Compounds in Acid, Neutral and Alkaline Solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acid  ($\gamma'$)</th>
<th>Neutral ($\gamma'$)</th>
<th>Alkaline ($\gamma'_{(D_2O)} - \gamma'(DCl)$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSS $^2$</td>
<td>10.000</td>
<td>10.000</td>
<td>10.000</td>
</tr>
<tr>
<td>Tert. butanol</td>
<td>8.735</td>
<td>8.769</td>
<td>8.763</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>7.911 (7.934)</td>
<td>7.941 (7.946)</td>
<td>- $^1$</td>
</tr>
<tr>
<td>Acetone</td>
<td>7.780</td>
<td>7.784 (7.777)</td>
<td>- $^1$</td>
</tr>
<tr>
<td>Dimethylsulphoxide</td>
<td>7.188</td>
<td>7.290 (7.285)</td>
<td>7.281</td>
</tr>
<tr>
<td>$^{+}$Me$_4$N$^-$ Br</td>
<td>6.795 (6.794)</td>
<td>6.822 (6.824)</td>
<td>6.825</td>
</tr>
<tr>
<td>Dioxan</td>
<td>6.238 (6.249)</td>
<td>6.257 (6.251)</td>
<td>6.253</td>
</tr>
</tbody>
</table>

$^1$ Exchanges in alkaline solution.

$^2$ Sodium 3-trimethylsilylpropanesulphonate.
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-isopropylidenecyclobutane. The proton spins may be described as an $A_2B_2M_3X_3$ system or, if transannular coupling is neglected, as an $(AB)_2M_3X_3$ system.

In band $A$, $X_3$ (methyl) gives a single peak and $M_3$ (isopropylidene) a quintet with the highest-field component merged with the $X_3$ peak. In band $B$ the four peaks of the $(AB)_2$ pattern (ring protons) are split into septuplets, of sorts, by $M_3$. 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:

$\begin{array}{cccccc}
\tau_A & \tau_B & \tau_M & \tau_X & J_{AB} & J_{(AB)M} \\
6.93 & 7.37 & 8.40 & 8.45 & 15.5 & 2.0 \\
\end{array}$

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 isopropylidene 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 and falls in the range predicted for geminal protons with one adjacent \( \pi \)-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


February 6, 1964

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

On Binding Site of N-methylacetamide.

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 MellonXMA. 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 CH₃CO rather than on the N-CH₃. Relative to benzene as external reference, solutions of 0.75 M NMA in 99.8% D₂O at room temperature exhibit a HDO signal at 1.58 ppm, and two signals at 3.85 and 4.58 ppm all upfield from benzene. These are ascribed to N-CH₃ and CH₃CO protons, respectively. D₂O was used as solvent to reduce the obscuring resonance of H₂O. However, exchange of the labile NH proton in NMA with solvent and the H₂O present in 99.8% deuterium oxide, introduce sufficient protons to give a HDO resonance. In the presence of 10⁻³ M MnSO₄, 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°C. Tetramethyldilane (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 CH₃CO and N-CH₃ protons, respectively. It is seen that the presence of a paramagnetic metal ion exerts a greater 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
conclusion 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

-2.70

-1.92

0

NMA - Zn

-2.76

-2.05

0

δ, ppm.
DO\,V 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-Dimethylformamid e
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 and 2 D.M.F.:MX 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.:BF3). 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 their measurement was on
the 250 cycle sweep width. The aldehyde shifts (F) were measured rela-
tive 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 pro-
tons 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:

Sincerely,

S.J. Kuhn
J.S. McIntyre

EXECUTIVE OFFICES: SARNIA • SALES OFFICES: VANCOUVER, CALGARY, WINNIPEG, TORONTO, MONTREAL, SAINT JOH N • CABLE ADDRESS: “DOWCAN”
<table>
<thead>
<tr>
<th>Complex</th>
<th>Cis Methyl&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>Trans Methyl&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>Aldehyde&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.M.F.</td>
<td>102</td>
<td>94</td>
<td>474</td>
</tr>
<tr>
<td>ZnCl₂·2D.M.F.</td>
<td>91</td>
<td>82</td>
<td>487</td>
</tr>
<tr>
<td>SnI₄·2D.M.F.</td>
<td>89</td>
<td>79</td>
<td>483</td>
</tr>
<tr>
<td>InCl₃·1D.M.F.</td>
<td>87</td>
<td>77</td>
<td>493</td>
</tr>
<tr>
<td>ZnCl₂·1D.M.F.</td>
<td>85</td>
<td>75</td>
<td>489</td>
</tr>
<tr>
<td>ZrBr₄·2D.M.F.</td>
<td>84</td>
<td>75</td>
<td>503</td>
</tr>
<tr>
<td>BiCl₃·1D.M.F.</td>
<td>82</td>
<td>69</td>
<td>507</td>
</tr>
<tr>
<td>TiCl₄·2D.M.F.</td>
<td>78</td>
<td>69</td>
<td>518</td>
</tr>
<tr>
<td>SnCl₄·2D.M.F.</td>
<td>80</td>
<td>69</td>
<td>500</td>
</tr>
<tr>
<td>SnBr₄·2D.M.F.</td>
<td>80</td>
<td>68</td>
<td>502</td>
</tr>
<tr>
<td>BF₃·1D.M.F.</td>
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<td>68</td>
<td>487</td>
</tr>
<tr>
<td>TiCl₄·1D.M.F.</td>
<td>75</td>
<td>65</td>
<td>512</td>
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<tr>
<td>PF₅·1D.M.F.</td>
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<tr>
<td>AlCl₃·1D.M.F.</td>
<td>74</td>
<td>64</td>
<td>493</td>
</tr>
<tr>
<td>AsF₅·1D.M.F.</td>
<td>72</td>
<td>60</td>
<td>507</td>
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<tr>
<td>SbF₅·1D.M.F.</td>
<td>70</td>
<td>60</td>
<td>505</td>
</tr>
<tr>
<td>BCl₃·1D.M.F.</td>
<td>68</td>
<td>57</td>
<td>506</td>
</tr>
<tr>
<td>SbCl₅·1D.M.F.</td>
<td>68</td>
<td>56</td>
<td>519</td>
</tr>
</tbody>
</table>

<sup>a</sup> Shifts in c.p.s. upfield from second peak in nitropropane septuplet.

<sup>b</sup> Cis or trans with respect to aldehyde proton.

<sup>c</sup> Shifts in c.p.s. from tetramethyl silane.

Contribution No. 116
Exploratory Research Laboratory
Dow Chemical of Canada, Limited
Sarnia, Ontario, Canada
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 IIITNMRN 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$_2$F$_4$ was reported$^1$ to consist of a single broad unresolved band at a field of approximately -55.6$^\circ$. Recently it has been shown$^2$ that when N$_2$F$_4$ 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 ~117 cps.

We now would like to report on the F$^{19}$ n.m.r. spectrum of N$_2$F$_4$ in solution in NF$_3$ at low temperatures (-180$^\circ$ to -155$^\circ$ 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.
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

Fig. 1 $^{19}F$ NMR SPECTRUM OF $N_2F_4$ AT $-157^\circ C$. 
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 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 $\Delta \sigma_{ax} - \Delta \sigma_{eq} = 20.5 \times 10^{-6}$ in fluorocyclohexane while Roberts and colleagues have shown $\Delta \sigma_{ax} - \Delta \sigma_{eq} = 14.5 \times 10^{-6}$ in 1,1-difluorocyclohexane. The data of Thomas et al. and Tiers which give $\Delta \sigma_{ax} - \Delta \sigma_{eq} = -21 \times 10^{-6}$ for CHF in multi-fluorinated ($\alpha$, $\beta$ positions) cyclohexanes and $\Delta \sigma_{ax} - \Delta \sigma_{eq} = -18.2 \times 10^{-6}$ for CF2 in perfluorocyclohexane. When these results are combined, following my ideas of intramolecular electric fields to give a value for the difference in the dipole moments of CH and CF bonds taken from CH3F which (arbitrarily assuming H = C) then gives

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

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

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

$$k_E = 2.5 \times 10^{-10} \text{esu (CF)}; 1.95 \times 10^{-10} \text{esu (CF2)}.$$ 

Note that it is considerably different for the two bonds. It is also positive whereas a simple-minded calculation...
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 CF₄ but is considerably larger in magnitude. The above procedure contains numerous simplifications, most of which seem reasonable -- 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 $|\mu_{\text{CH}_2}|$. 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 2-3 ppm) 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 hydrogen-containing 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
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!).

\[
\text{Helix Coil Transitions in Poly-L-Glutamic Acid}
\]

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.
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 lyophilized our solutions in D$_2$O thus replacing most of the exchangeable hydrogens with E$_2$O. 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 equipspaced 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 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 -CH₂- resonance, can not be measured very exactly but seems to change monotonously with pH down to the precipitation point. Contrary to glutamic acid, where CH₂ lines are sharp, the side chains in GLAA seem to be strongly hindered in both helix and coil form.

Yours sincerely,

A. Loewenstein

H. Gilboa

for A. Berger (Biophysics Dept., Weizmann Institute, Rehovot).
Asst. Professor B.I. 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° complex of octaethylporphin, 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.
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 (\(\tau = 1.15 \& 0.20\); 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 (\(\tau = 2.75, 2.11 \& 1.94\); 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-; \(\tau = 11.58\)) and II (R = Ac-; \(\tau = 10.77\)). A similar, expected high field position for the protons of the anionic residue of I is observed when R = CH\(_2\)CH\(_2\)CO- (multiplet; \(\tau = 11.4\)) and when R = H, CO- (sharp singlet; \(\tau = 7.96\)) also.

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

\(\text{(H.H. Dihoffen) (H. Parnemann) (R.G. Foster)}\)
3.

All spectra measured as solutions in CDCl₃

**Compound I**
(\( R = \text{Ac}^- \))

Offset 200 cps.

**Dihydro-product**
(\( R = \text{Ac}^- \))

Offset 150 cps.

**Tetrahydro-product**

Offset 200 cps.
Dr. B. L. Shapiro,
Mellon Institute,
4400, Fifth Avenue,
Pittsburgh 13,
Pennsylvania.

Dear Dr. Shapiro,

I would like to describe a high temperature accessory for a Varian DF-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. A sample 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 necessary. 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,

Daryl K. Green

References
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 chlorotrifluoroethylene 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\textsuperscript{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 chlorotrifluoroethylene. Chemical shifts and the overall appearance of the spectrum show that the complex formed is C\textsubscript{3}H\textsubscript{2}CF\textsubscript{2}CFClMn(CO)\textsubscript{5} rather than C\textsubscript{3}H\textsubscript{2}CFClCF\textsubscript{2}Mn(CO)\textsubscript{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 \(\beta\)-CF\textsubscript{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 \(\alpha\)-fluorine atom. Non-equivalence of the fluorine atoms of the CF\textsubscript{2} group occurs because the adjacent carbon
Professor B. L. Shapiro -2- 17th February, 1964.

atom of the CFC1Mn(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 CF2 groups with non-equivalent fluorine atoms. This spectrum assisted our work by showing that a mixture of HCFClCF2Mn(CO)5 and HCF2CFC1Mn(CO)5 can be obtained from HMn(CO)5 and CF2: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 CF2 group is bonded to an asymmetric carbon atom. The low-field shift of the bands centred at 53.1 p.p.m. establish that they are due to the CF2 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,

[Signature]

FEAS:scb
Enclosure:
\[ \text{CH}_3\text{Mn(CO)}_5 + \text{CF}_2\text{CFCI} \xrightarrow{\text{ultraviolet light at 25° in pentane}} \text{CH}_3\text{CF}_2\text{CFCI}\cdot\text{Mn(CO)}_5 \]

30% yield. White crystals.

m.p. 53-54°

\[ ^{19}\text{F SPECTRUM} \quad \text{CH}_3\text{CF}_2\text{CFCI}\cdot\text{Mn(CO)}_5 \]

\[ ^{1}H \text{ SPECTRUM} \]

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

\[ J_{\text{H-F}_\beta} = 18\text{ c.p.s.} \quad \text{and} \quad J_{\text{H-F}_\alpha} = 2\cdot0\text{ c.p.s.} \quad F_{16}, I \]
\( ^{19}F \) NUCLEAR MAGNETIC RESONANCE SPECTRA OF A MIXTURE OF HCFCI-\( CF_2 \)-Mn(\( CO \))\(_5 \) AND HCF\(_2\)-CFCl-Mn(\( CO \))\(_5 \) FROM MANGANESE PENTACARBONYL HYDRIDE AND CHLOROTRIFLUOROETHYLENE AT 2 ATM.

\[ \begin{align*}
138.3 & \quad HCF_2-\text{Cl}-\text{Mn}(\text{CO})_5 \\
114.8 & \quad \text{H}_{2}\text{C}-\text{F}-\text{C}-\text{H}-(\text{CO})_5 \\
82.3 & \quad \text{Mn}(\text{CO})_5 \\
53.1 & \quad \text{CCl}_3\text{F} \\
\end{align*} \]
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 (MELLOMNMR 58, 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 SO₂, CO₂, NH₃, Cl₂, H₂S, NO₂, PH₃, methyl ether, phosgene, ethane, cyanogen, acetylene, etc., at room temperature - or more conventional solvents at quite high temperatures.
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
Dear Barry,

We have continued to find letters very relevant to our own work in X-ray. 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-15N, N-methylformanilide, N-ethylformamide. The spectrum of N-phenylformamide-15N is shown (cis and trans refers to phenyl with respect to the C=O group). The assignment is based on that made by Charlie Kraheck and John Suliceschieler for the N7 molecule when I worked with them on amides, and is checked by the J(h-h) of the other N15 substituted amides (Kollman No. 56). 696 ± 15 exists as the isomer with the phenyl cis to the carbonyl. In N-methylformanilide-13C more than 96% exists in this cis form (J(N=H) = 0.4 ± 0.1 c/s). This can be contrasted with the cases studied by LaPlace and Rogers in which the bulkier of the two alkyl groups on the nitrogen was cis to the formyl proton.

In N-methylformanilide-15N 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-ethylformanilide 15N ± 2% of the isomer with the ethyl cis to the formyl proton (cf. Kollman 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 NH3, NH4+, pyridinium ion and pyrrole in the light of a 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; C6H5 = 10° ± 4°
(iii) hybridisation theory to get a2 from structural data (a2 = 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 Sh-hor is the oldest road
And the croisiest road of all.
Straight it runs to the Witch's above.
As it did in the ways of Saul.
And nothing has changed of the sorrow in store
For such as go down on the road to Sh-hor!

Yours sincerely,

Edward W. Randall
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 explicit 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 controls 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 react 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 SI 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 insufficient 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

Sincerely yours,

R. E. Lundin, Principal Chemist
Wool and Mohair Laboratory
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 occurring acetylenic compounds. It turns out that we need only 2 - 5 mg.

As an example which may be of interest to the readers I wish 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 irradiation 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 doublet and the opposit irradiation gives a doublett and a singlet at 3.64 and 3.52. The irradiation of $\omega_1 - \omega_2$ (120 C/S) on the signals at 2.89 gives a quartett at 4.88 and the opposit irradiation gives a simple doublett at 2.89, which clearly demonstrates the presence of an AABX-system in which X is coupled with a further proton. Together with other results the only possible structures are I 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 CCl₄)

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