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Deadline Dates: No. 89: 18 February 1966
No. 90: 18 March 1966

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".
13th December, 1965.

Professor B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
CHICAGO,
Illinois 60616, U.S.A.

Title: **Spectral Parameters for isoquinoline.**

Dear Barry,

I have now become accustomed again to standing on my head; many of us here in Australia would like to see more people from the Northern Hemisphere trying this exercise. Seriously however, I found my recent visit to the States very enjoyable and rewarding in a number of ways.

One of the problems that we tried some time ago, and put aside for a rainy day, was that of unravelling the closely coupled system, isoquinoline. We only required chemical shift data for our own particular purposes but we were also interested in the patterns of coupling values in these sorts of systems. We were able to make a bit more progress on the problem when we had a second look at it. The spectra of the pure liquid, the solution in CCl₄ and also acetone were examined and the parameters were extracted using an iterative computer programme of the Reilly–Swalen type. The acetone results were not too satisfactory, mainly because we could not assign enough transitions. However we were able to get moderately accurate estimates of the chemical shifts. We used field-sweep spin decoupling in order to determine the approximate chemical shifts of protons 4, 5, 7 and 8. The results obtained are set out below:
Table: Chemical Shifts and coupling constants (c/s) for isoquinoline.

<table>
<thead>
<tr>
<th></th>
<th>Isoquinoline</th>
<th>Isoquinoline</th>
<th>Isoquinoline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pure liquid</td>
<td>0.063g/ml in</td>
<td>0.050 g/ml in</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>acetone</td>
</tr>
<tr>
<td>( \tau_1 )</td>
<td>0.553</td>
<td>0.856</td>
<td>0.71</td>
</tr>
<tr>
<td>( \tau_3 )</td>
<td>1.233</td>
<td>1.550</td>
<td>1.49</td>
</tr>
<tr>
<td>( \tau_4 )</td>
<td>2.515</td>
<td>2.501</td>
<td>2.26</td>
</tr>
<tr>
<td>( \tau_5 )</td>
<td>2.427</td>
<td>2.295</td>
<td>2.08</td>
</tr>
<tr>
<td>( \tau_6 )</td>
<td>2.542</td>
<td>2.433</td>
<td>2.26</td>
</tr>
<tr>
<td>( \tau_7 )</td>
<td>2.632</td>
<td>2.508</td>
<td>2.34</td>
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<tr>
<td>( \tau_8 )</td>
<td>2.264</td>
<td>2.137</td>
<td>1.92</td>
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<td>( J_{13} )</td>
<td>( \sim 0 )</td>
<td>( \sim 0 )</td>
<td></td>
</tr>
<tr>
<td>( J_{15} )</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td></td>
</tr>
<tr>
<td>( J_{34} )</td>
<td>5.8</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>( J_{48} )</td>
<td>( \sim 0.8 )</td>
<td>( \sim 0.8 )</td>
<td></td>
</tr>
<tr>
<td>( J_{56} )</td>
<td>8.62</td>
<td>8.68</td>
<td></td>
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<tr>
<td>( J_{57} )</td>
<td>0.88</td>
<td>1.07</td>
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<tr>
<td>( J_{58} )</td>
<td>0.82</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>( J_{67} )</td>
<td>7.02</td>
<td>6.99</td>
<td></td>
</tr>
<tr>
<td>( J_{68} )</td>
<td>1.09</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>( J_{78} )</td>
<td>8.39</td>
<td>8.21</td>
<td></td>
</tr>
</tbody>
</table>

The spectra and those calculated with the above parameters are shown in Figures 1 and 2. We have also compared in Figure 3, the proton shifts in the pure liquid and acetone with those obtained in CCl<sub>4</sub>. An effect rather similar to that found in quinoline (P.J. Black and M.L. Heffernan, Aust. J. Chem., 17, 558, (1964)) was noticed wherein a specific influence seems to be operating at the protons closest to the heteroatom, particularly in the case of the pure liquid. The protons more distant from the heteroatom seem to undergo only a more general shift, presumably arising from reaction field effects. However, like a lot of "effects" in NMR, they may proceed from a multiplicity of causes!

Best wishes,

Peter J. Black*  
Michael L. Heffernan

* Present address:
Department of Chemistry,  
University of British Columbia,  
Vancouver 8,  
B.C., Canada.
Figure 1 (a) Experimental and (b) Calculated spectrum of isoquinoline as pure liquid at 100 Mc/s
Figure 2 (a) Experimental and (b) Calculated spectrum of isoquinoline (0.063 g/ml in CCl₄) at 100 Mc/s
Figure 3. Shifts of ring protons in isoquinoline relative to their positions in CCl₄ solution; Δ acetone solution; ○ pure liquid.
Selective Deshielding of Aromatic Protons in some Nitro Acetanilides

Dear Barry:

We have examined several nitro acetanilides on our A-60 spectrometer and find that certain o-nitroacetanilides exhibit signals at unusually low field for the aromatic proton adjacent to the acetamido group and for the amido proton itself. Our results are summarized in the Table.

![Chemical structures of nitroacetanilides](attachment:image.png)

**TABLE**

<table>
<thead>
<tr>
<th></th>
<th>$\tau$ Values</th>
<th></th>
<th>$\tau$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{CDCl}_3, 30^\circ$</td>
<td>$\text{CH}_3\text{CN, 70}^\circ$</td>
<td>$\text{CH}_3\text{CN, 70}^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\text{H-3}$</td>
<td>$\text{H-6}$</td>
<td>$\text{NH}$</td>
</tr>
<tr>
<td>Ia 2-nitroacetanilide</td>
<td>1.80</td>
<td>1.23</td>
<td>-0.29</td>
</tr>
<tr>
<td>Ib 4-methyl-2-nitroacetanilide</td>
<td>1.95</td>
<td>1.31</td>
<td>-0.25</td>
</tr>
<tr>
<td>Ic 5-methoxy-2-nitroacetanilide</td>
<td>1.83</td>
<td>1.58</td>
<td>-0.75</td>
</tr>
<tr>
<td>II 3-nitroacetanilide</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>III 4-nitroacetanilide</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

* insufficient solubility in deuteriochloroform

The splitting patterns in the substituted nitroacetanilides Ib and Ic permit unambiguous assignment of the aromatic proton signals. In both compounds the H-6 proton resonance appears consistently at lower field than the H-3, in acetonitrile
as well as in chloroform-d. For o-nitroacetanilide itself (Ia) the assignment of the pair of doublets at lower field to the H-6 proton and the pair of doublets at 1.87 to the H-3 proton follows logically.

We believe that the resonance of H-6 at low field results from intramolecular hydrogen-bonding in o-nitroacetanilides, already demonstrated by infra-red and ultraviolet spectral studies. Such hydrogen-bonding might be expected to favor the conformation (IV), in which the N-H and C=O groups have the trans relation typical of acyclic amides. In this conformation the H-6 proton should experience the strong deshielding effect resulting from the particular proximity of the carbonyl group. This conclusion is supported by the following evidence:

1. The appearance of the broad N-H signal in compounds Ia, b and c at lower field than is normal for simple anilides, confirming the existence of intramolecular hydrogen-bonding.

2. The entirely normal behavior of 3-nitroacetanilide (II) and 4-nitroacetanilide (III) which exhibit N-H and aromatic proton resonances at positions expected in the absence of intramolecular hydrogen-bonding.

3. The unusual solvent sensitivity of the H-6 resonance in the o-nitroacetanilides (Ia-c), which is reasonable if the polar solvent acetonitrile at 70° is effective in breaking down some of the intramolecular hydrogen-bonding present in chloroform solution. The reduction in population of molecules having conformation (IV) would diminish the net deshielding effect of the carbonyl group on the H-6 proton and also lead to the observed upfield solvent shift of the N-H proton.

4. The resonance of the amido proton in Ic appears at lower field than the equivalent protons in Ia and Ib by about 0.5-0.7 ppm. The solvent dependence of this amido proton as well as of H-6 is less in Ic than in Ia and Ib, all of which can be explained by stronger intramolecular hydrogen-bonding in Ic owing to increased electron density of the nitro-oxygens under the influence of the para methoxy group.

Further systems in which related intramolecular hydrogen-bonding is likely are currently under study.

We wish to thank Mrs. Patricia Morrison and Mr. Martin Mach for valuable assistance in the determination of the spectra.

Sincerely,

[Signature]

James R. Bartels-Keith
Ronald F. W. Ciecich

1. Relevant coupling constants lay within the ranges 7.5-10.0 c./sec. for J_{HH(ortho)} and 1.5-3.0 c./sec. for J_{HH(meta)}.


Professor Bernard Shapiro  
Illinois Institute of Technology  
Chicago, Illinois, 60616

Dear Barry:

Since mailing in our communication on "Selective Deshielding of Aromatic Protons in some Nitroacetanilides" we noticed the letter of Dr. Sternhell in the January 1965 issue of IITNMRN, No. 76, page 2. We regret having missed this previously and would like to note at this time Dr. Sternhell's prior reporting of the phenomenon that we came upon independently.

Of some relevance also is the letter of Dr. Anteus in the March 1965 issue, No. 78, page 31.

With best wishes for the New Year.

Sincerely,

POLAROID CORPORATION

James Bartels-Keith

Ronald F. Cieciuch
January 3, 1966

Dr. Barry Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois  60616

Dear Dr. Shapiro:

I hope this brief note will serve as notification of my new address and also to keep my subscription to IITNMR going. I'm finally getting settled and trying to put the A-60 here to good use.

The last few months I was still at Texas we were doing some C\textsuperscript{13} work and were using a NDC-800 Enhancetron which was available to improve S/N. Since several people voiced an interest in the use of such computers, especially on instruments besides the A-60, I've included a circuit diagram of the trigger we used to correlate the magnetic field sweep of our DP-60 with the Enhancetron memory storage. Part (a) of the circuit utilizes the V-4352 linear sweep flyback to trigger the Enhancetron storage while (b) provides a suitable trigger signal if the S/N of a peak in the spectrum exceeds 3/1. A little care is required to adjust memory sweep and field sweep times but both modes have been used to advantage. We also found Jim Shooling's 2000 c.p.s. sideband, direct absorption technique very successfully with 12 mm OD spinning samples that were plugged to prevent a vortex. A number of metal carbonyls, prepared in vacuum, were observed this way.

I hope I'll be able to report on some of our other work in the near future.

Sincerely yours,

Jeff C. Davis, Jr.  
Associate Professor

JCD:sdd
Output from V-4352 Sweep Unit to Scope Horizontal

T₁ - Chicago - Stancor PA-8421
T₂ - Chicago - Stancor P-6469
SW₂ = S.P.S.I.
Input from Spectrometer (Integrator)

Output to Enhancetron Trigger

Q - Q_e = 2N1308
P_1 - P_2 - P_3 BNC Connectors
Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Professor Shapiro:

May I submit an example of deceiving simplicity in a PMR-spectrum and, by doing so, restore my good standing on the mailing list.

One of our colleagues obtained a product from a Michael-addition of nitromethane to an unsaturated ketone:

$$\begin{align*}
\text{R}'' & \quad \text{H} \quad \text{CH}_2\text{-NO}_2 \\
\text{CH}_2\text{-NO}_2 & \quad \text{H} \quad \text{R}''
\end{align*}$$

We expected this product to have structure A. The observed signals at about 4.6 ppm (Fig. 1) obviously have neither the features expected for an "equivalent methylene group" nor the usual pattern for a "nonequivalent methylene group." Who will blame me for looking for unusual and fancy structures which were compatible with the observed facts.

When the spectrum of the compound which was obtained from the corresponding reaction with nitroethane (B) showed a doublet for the methyl group, I began to calculate. To my surprise I found that this observed pattern could be readily interpreted as an ABX\textsuperscript{1}\textsuperscript{-}case:

$$\begin{align*}
\gamma_0 & = 4.1 \text{ cps, } J_{AC} = 12.3; J_{AC} = -11.65; J_{BC} = -3.45.  \\
\text{Transition} & \quad \text{Calculated} & \quad \text{Observed} & \quad \text{Intensity (Calc.)}  \\
1 & 284.9 & 286 & 0.17  \\
2 & 291.1 & -- & 0  \\
3 & 272.6 & 273.2 & 1.83  \\
4 & 278.8 & 278.8 & 2.0  \\
5 & 270.0 & 270.8 & 1.83  \\
6 & 278.9 & 278.8 & 2.0  \\
7 & 257.7 & 258 & 0.17  \\
8 & 266.5 & -- & 0
\end{align*}$$

\textsuperscript{1} The number of the transitions corresponds to Pople, Schneider, Bernstein "High-resolution NMR" p.134.

The presence of the weak lines 1 and 7 was confirmed by a "mouse-track." (Fig. 2)

Sincerely yours,

R. K. Kullig
December 30, 1965

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

Dear Barry,

N.M.R. of 1,4-dichalcogenocyclohexanes

I won't blame anybody if I hear of complaints about our chosen title; this is simply the result of applying nomenclature rules without regard for phonetics.

We have characterized a series of 1,4-diheterocyclohexanes of the group VI elements (provided to us by Professor J.D. McCullough of these laboratories) in anticipation of their use as ligands in transition metal complexes (of which such an application has already appeared in the literature). The symmetrical derivatives, 1,4-X,X', display a single sharp line (half-intensity band width 0.5 cps). The unsymmetrical derivatives, 1,4-X,0', show two groups of lines for which a typical spectrum is given in Fig. 1; the protons in the unsymmetrical derivative 1,4-S,Se were very nearly equivalent.

Each of the lines on spectra similar to that shown on Fig. 1 is actually a closely spaced doublet (line width at half-intensity, 0.9 cps; TMS at these conditions, 0.3 cps). These spectra were analyzed essentially by the procedure outlined in a recent report of spectra of other 1,4-diheterocyclohexanes. Our calculations were performed on the improved JNMRT-NMRIN programs of Reilly and Swalen. The data on the present compounds and some previously determined compounds is presented in Table 1.

Satellites arising from magnetically active hetero-atoms are satisfactorily resolved for coupling to α-protons and less well separated for β-coupling. 13C coupling constant was found to depend mainly on the heteroatom attached to a particular methylene group (α) and very little on the other heteroatom (β) in the molecule, when it was different than α. The chemical shift of the protons, strongly dependent on the α-hetero atom, also show some significant dependence on the β-hetero atom (when different than α).

The spectra show that these compounds are rapidly equilibrating chair forms at temperature of investigation (30°). No change was observed in the spectrum of selenoxane from +170 to -70 °C, in marked contrast to behavior noted for 4,5-tetradeuter-1,2-dithiane, and the substituted thioxanes recently reported in IITNMR.

References listed bottom of Table 1

Sincerely yours,

Herbert Kaesz
Associate Professor

M.L. Maddox and

CC: Prof. J.D. McCullough, U.C.L.A.
Table 1
Proton Magnetic Resonance Data (Varian A-60) on 1,4-dichalcogenocyclohexanes.

<table>
<thead>
<tr>
<th>X</th>
<th>X'</th>
<th>δ CH₂</th>
<th>δ CH₁</th>
<th>ΔJ gem</th>
<th>J₁,₃</th>
<th>J₁,₄</th>
<th>J₁₃C-H</th>
<th>c.p.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>O (2)</td>
<td>6.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>138.0</td>
</tr>
<tr>
<td>S</td>
<td>S</td>
<td>7.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>140.0</td>
</tr>
<tr>
<td>Se</td>
<td>Se*</td>
<td>7.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>S (2)</td>
<td>6.12</td>
<td>7.43</td>
<td>1.97</td>
<td>2.65</td>
<td>7.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>S</td>
<td>6.13</td>
<td>7.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>Se*</td>
<td>6.00</td>
<td>7.38</td>
<td>1.74</td>
<td>2.75</td>
<td>7.35</td>
<td>142.0</td>
<td>140.0</td>
</tr>
<tr>
<td>O</td>
<td>Te</td>
<td>5.98</td>
<td>7.31</td>
<td>1.63</td>
<td>2.95</td>
<td>7.49</td>
<td>142.0</td>
<td>139.5</td>
</tr>
<tr>
<td>S</td>
<td>Se**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*) J(Se-C-H) 11.60
# " " ±14.0 J(Se-C-C-H) ± 5.2 |
** ) " " 11.0 |
") J(Te-C-H) ± 29.5 J(Te-C-C-H) ± 9.6 |

References
Figure 1: M.L. Maddox and H.D. Kaesz

Te(CH₂CH₂)₂O
Neat/HMDSO

Relative Intensity

250  200  150

C.P.S.

Frequency
Dear Barry,

The enclosed communication summarizes results we have obtained recently for cyclic dienes and trienes. The compounds studied were of interest in connection with our investigations of cyclodecapentaenes and oxepines and the synthetic work of Prof. E. Vogel and his group.

The complete analysis of the spectra clearly shows, that the different appearance of diene- and triene-system, mentioned earlier (IIT-NMR-Newsletter 76-20 ) is due mainly to the different size of the parameter $N$ in diene- and triene-type AA'BB'-spectra and speculations about the influence of the double bond anisotropy on chemical shifts are not necessary in this case.

Sincerely yours,

H. Günther

H.-H. Hinrichs
_H-NMR-Spektren cyclischer Diene und Triene [1]_

Von Dr. H. Günther und Dipl.-Chem. H. H. Hinrichs
Institut für Organische Chemie der Universität Köln


Die Gegenüberstellung läßt charakteristische Unterschiede zwischen den Kopplungskonstanten beider Systeme erkennen: J_Dien_12 < J_Trien_12 ; J_Dien_13 > J_Trien_13 ; J_Dien_34 > J_Trien_34 . Die Analyse des Spektrums erlaubt danach in fraglichen Fällen (z.B. bei Norcaradien-Cycloheptatrien Valenztautomerien) eine eindeutige Strukturzuordnung. Der Parameter N (= J_13 + J_14) beträgt für die untersuchten Diene ca. 10 Hz, für die Triene dagegen nur ca. 6 Hz. Da N in vielen Fällen dem Spektrum direkt entnommen werden kann [10], ist ein Hinweis auf das Vorliegen der einen oder anderen Struktur auch auf einfache Weise erhältlich.

### T A B E L L E 1 [7]

A) Parameter im Cyclohexadien-(1,3)-System

<table>
<thead>
<tr>
<th></th>
<th>( \nu_0 \delta )</th>
<th>( J_{12} )</th>
<th>( J_{13}=J_{24} )</th>
<th>( J_{14}=J_{23} )</th>
<th>( J_{34} )</th>
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<tr>
<td>(1)</td>
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<td>5.41</td>
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<td>0.88</td>
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<td>9.51</td>
<td>0.75</td>
<td>0.96</td>
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<tr>
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<td>9.55</td>
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<td>0.88</td>
</tr>
<tr>
<td>(4)</td>
<td>25.51</td>
<td>5.48</td>
<td>9.71</td>
<td>0.72</td>
<td>1.09</td>
</tr>
<tr>
<td>(5)</td>
<td>21.65</td>
<td>5.94</td>
<td>9.25</td>
<td>0.58</td>
<td>1.31</td>
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</table>

B) Parameter im Cycloheptatrien-(1,3,5)-System

<table>
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<tr>
<th></th>
<th>( \nu_0 \delta )</th>
<th>( J_{12} )</th>
<th>( J_{13}=J_{24} )</th>
<th>( J_{14}=J_{23} )</th>
<th>( J_{34} )</th>
</tr>
</thead>
<tbody>
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<td>27.54</td>
<td>11.20</td>
<td>5.39</td>
<td>0.73</td>
<td>-0.20</td>
</tr>
<tr>
<td>(7)</td>
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<td>11.04</td>
<td>5.58</td>
<td>0.68</td>
<td>-0.12 [2],[8]</td>
</tr>
<tr>
<td>(8)</td>
<td>35.74</td>
<td>11.44</td>
<td>5.43</td>
<td>0.65</td>
<td>-0.03</td>
</tr>
<tr>
<td>(9)</td>
<td>27.62</td>
<td>9.68</td>
<td>6.80</td>
<td>0.73</td>
<td>-0.16 [9]</td>
</tr>
</tbody>
</table>

[7] Alle Werte in Hz; Spektren wurden, wenn nicht anders vermerkt, in \( \text{CCl}_4 \) (1 molar bzw. 20 Vol%) mit einem Varian A 60 Spectrometer bei 60 MHz aufgenommen.


[8] In CS₂ aufgenommen.


Dear Barry:

I've noticed that I seem to be in disagreement with the Kowalewskis on the values of couplings to the aldehyde proton in some p-substituted benzaldehydes (compare Kowalewski and Kowalewski, J. Chem. Phys. 37, 1009, to Martin and Dailey, ibid., 37, 2594). Bob Green, a student of mine, has been studying some unsaturated aldehydes on the HA100 with the idea of getting some conformational energy barriers, etc., and we hereby present our best values:

![Diagram of molecule]

<table>
<thead>
<tr>
<th>Substituents &amp; positions</th>
<th>Observable couplings, c.p.s. at 32°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 - Cl</td>
<td>( J_{A3} = J_{A5} = 0.42 \pm 0.02 )</td>
</tr>
<tr>
<td>4 - Br</td>
<td>( J_{A3} = J_{A5} = 0.31 \pm 0.03 )</td>
</tr>
<tr>
<td>3 - Cl, 4 - Cl</td>
<td>( J_{A5} = 0.35 \pm 0.03 )</td>
</tr>
<tr>
<td>2 - Cl, 4 - Cl</td>
<td>( J_{A3} = J_{A5} = 0.78 \pm 0.05 )</td>
</tr>
<tr>
<td></td>
<td>(these become unequal at low temperature)</td>
</tr>
<tr>
<td>4 - ( N(CH_3)_2 )</td>
<td>( J_{A2} = 0.2 \pm 0.1 )</td>
</tr>
<tr>
<td></td>
<td>( J_{A3} = 0.42 \pm 0.05 )</td>
</tr>
</tbody>
</table>

This last molecule shows evidence of an eight-bond aldehyde to N-methyl coupling, as shown in the accompanying spectra of the CHO proton. The increase in sharpness when the N-methyls are irradiated is evidence of a coupling of perhaps 0.01 or 0.02 c.p.s. It's reproducible; we've checked the possibility of its being second-order splitting via the ring protons, or an obscure dynamic
effect; we think it is a real coupling.

We've been breaking off the locking piece of the pressure caps for the V4333 variable-temperature probe with alarming ease, and have replaced the bottom section with aluminum, as shown in the accompanying diagram.

We have found the reports of the experience of other laboratories with the HA100 and its associated equipment to be immensely valuable.

Many thanks.

Sincerely,

J.S. Martin

Suggested Titles: Benzaldehyde couplings; another long one; V4333 pressure cap modification.

Enclosures: 2 diagrams
Aldehyde signal at 60 mc.
PRESSURE CAP MODIFICATION FOR
VARIAN V 4333
Variable Temperature Probe

![Diagram of Pressure Cap Modification](image)
Long-range couplings with protons on Nitrogen

Dear Professor Shapiro,

We have observed rather unusual long-range couplings between protons on Nitrogen 3 and on Carbon 5 in compounds I a - d. 1)

These couplings \( J_{35} \) are of the same magnitude as the allylic couplings \( J_{15} \) in I a - c and somewhat larger than \( J_{75} \) in I a, I c, and I d. The coupling constants are listed together with \( \tau \)-values of the olefinic protons in the following table. 2)

---

1. Dr. H. Fritz
   c/o J.R. Geigy S.A.
   Basle 21 (Switzerland)
   20th December, 1965

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

---

<table>
<thead>
<tr>
<th>Comp.</th>
<th>X</th>
<th>R</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>I a</td>
<td>0</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>I b</td>
<td>0</td>
<td>H</td>
<td>Br</td>
</tr>
<tr>
<td>I c</td>
<td>S</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>I d</td>
<td>S</td>
<td>CH₃</td>
<td>H</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Comp.</th>
<th>( \tau )</th>
<th>( J_{35} )</th>
<th>( J_{15} )</th>
<th>( J_{75} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I a</td>
<td>5.66</td>
<td>1.6</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td>I b</td>
<td>5.13</td>
<td>1.5</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>I c</td>
<td>5.50</td>
<td>2.0</td>
<td>2.0</td>
<td>1.3</td>
</tr>
<tr>
<td>I d</td>
<td>5.28</td>
<td>2.6</td>
<td>-</td>
<td>1.3</td>
</tr>
</tbody>
</table>
In I b and I d the J-values can directly be read from the line spacings of the olefinic proton signals and verified by decoupling experiments.

In I a and I c the olefinic proton resonances are unresolved multiplets which upon irradiation at the position of the allylic CH₃ signal become triplets with splittings of 1.6 and 2.0 cps respectively.

After shaking the solutions with a drop of aqueous 1 n NaOD all couplings with NH vanish, resulting in a quartet for the olefinic proton in I a, I c and I d and a singulet in I b.

Yours sincerely,

1) The compounds were synthesized by Prof. Zigeuner, University of Graz, Austria. We are grateful to him for permission to report the above results prior to publication of his synthetic work.

2) The NMR-spectra were recorded on a HA-100 Spectrometer in approximately 5 % (w/v) solutions in CDCl₃. Spin-decoupling experiments were performed in the frequency-sweep mode.
Asymmetry Effects in α,β-Epoxypophosphonates

In a number of cases, the observed doubling of proton resonances in \(-\text{P}(\text{O})(\text{OR})_2\) groups has been attributed to the presence of an asymmetric center in the molecule. A chemical shift difference of ca. 4 c.p.s. between the pairs of O-methyl doublets has been reported in a phosphonate \([\text{RR'C}^\ast \text{HP}(\text{O})(\text{CCH}_3)_2]\) by Ramirezc. A similar chemical shift difference has been reported by Bentrude for a phosphate system \([\text{RR'C}^\ast \text{OP}(\text{O})(\text{CCH}_3)_2]\). The methyl protons and the interacting asymmetric centers are separated by four and five bonds, respectively, in these examples.

We have recently examined the spectra of a number of α,β-epoxypophosphonates and have observed similar asymmetry effects. In both the cis- (I) and trans- (II) epoxides, the 0-methyl proton signals appear as pairs of doublets. The chemical shift difference between the doublets reflects the stereochemistry of the particular isomer, 7.2 c.p.s. in I and 1.6 c.p.s. in II. The doubling is not a result of restricted rotation since the spectra of I and II are unchanged over the range -30 to 125°. The same asymmetry effects are apparent in the methylene resonances of the ethyl analogs of I and II, although the assignment of chemical shift differences is difficult because of the complexity of the methylene multiplets.

Compounds I and II possess two asymmetric centers, four and five bonds removed from the methyl protons. In order to determine which of these centers is responsible for the doubling phenomenon, the spectrum of III was examined. Two doublets with a 1.0 c.p.s. separation were observed for the O-methyl protons of III indicating, for this system at least, that the longer range five bond interaction is the more important. A similar lack of attenuation with distance of asymmetry induced nonequivalence has been observed by Roberts in alkyl benzenes.

The spectra of these compounds are also solvent sensitive. While I, II and III showed doubled 0-methyl resonances in \(\text{CCl}_4\) solution, nonequivalence is not observed in the spectra of neat samples. A study of these nonequivalence and solvent effects is continuing in this and other rigid systems.
\[ \begin{align*}
\text{I} & \quad \text{II} \\
\tau_B & \quad 6.72 \quad 6.97 \\
\tau_{\text{CH}_3} & \quad 6.70, 6.58 \quad 6.25, 6.22 \\
J_{AB} & \quad 4.5 \quad 2.3 \\
J_{PB} & \quad 27.4 \quad 30.2 \\
J_{\text{PCH}_3} & \quad 10.5, 10.5 \quad 10.3, 10.3
\end{align*} \]

\[ \begin{align*}
\text{III} \\
\tau_{\text{OCH}_3} & \quad 6.27, 6.25 \\
\tau_A & \quad 7.67 \\
\tau_{\text{CCH}_3} & \quad 8.57, 8.55 \\
J_{\text{PCH}_3} & \quad 10.3, 10.3 \\
J_{PA} & \quad 25.8 \\
J_{\text{PCCCH}_3} & \quad 10.2, 7.7
\end{align*} \]

Best regards,

Clay \hspace{2cm} W. E. Byrne

C. E. Griffin \hspace{2cm} W. E. Byrne

Ramakrishna Churi \hspace{2cm} Mike Wilkinson

R. H. Churi \hspace{2cm} M. P. Williamson
Dear Barry,

We have noted previously on the basis of some scattered data\(^1\) that in systems of type (I) the transoid allylic coupling constants (i.e., \(J_{AX}\)) appear to be larger than the cisoid allylic coupling constants (i.e., \(J_{BX}\)) which is the opposite of what is generally, but not always \(^2,\,^3\) found in acyclic systems. We have now examined compounds (II)-(V) and find the trend confirmed. Numbers are \(5\) in c/s ex TMS for a 2% solution in \(\text{CCl}_4\). While we intend to look at many more structures before considering this rule established, a tentative explanation can already be proposed:

The trend towards larger cisoid allylic coupling constants has been rationalised\(^2\) on the basis of a contribution by a positive interaction carried through the sigma framework\(^4,\,^5\) which is at a maximum for the \(W\)-configuration, i.e. in the allylic cases for the transoid configuration with the allylic angle \(= 0^\circ\) (c.f. VI). In systems with vinylic protons exocyclic (i.e. I), the allylic angle cannot approach \(0^\circ\) and hence this contribution is suppressed.

With best regards,

Yours sincerely,

\[\text{G. P. Newsoroff}\]

\[\text{S. Sternhell}\]

---

2. Rottendorf, Sternhell and Wilmshurst, \textit{ibid}., 18, 1759 (1965)
(I) $J_{\text{allylic}} = 1.78 \text{ c/s}$

(II) $J_{\text{allylic}} = 1.78 \text{ c/s}$

(III) $J_{\text{allylic}} = 1.35 \text{ c/s}$

(IV) $J_{\text{allylic}} = 1.95 \text{ c/s}$

(V) $J_{\text{allylic}} = 1.7 \text{ c/s}$

(VI)
January 6, 1966

Professor Barry Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois

Dear Dr. Shapiro:

In a series of investigations of NMR spectra of peptides containing a glycine residue, we have observed in several cases magnetic non-equivalence of the two protons of glycine. Thus the signal of the CH2 protons shows an AB-type pattern with a gem-coupling constant of 16-17 c.p.s. Among glycylamino acids so far investigated, only glycyl-L-phenylalanine and glycyl-L-tryptophan show this splitting. On the other hand, among aminoacetylglycines, the zwitterion forms of almost all peptides which have an α-asymmetric carbon atom in the aminoacyl group show the splitting. An aromatic group or a bulky alkyl group attached to the α-carbon increases the splitting. Although L-alanylglycine and L-leucylglycine show the splitting, L-alanylglycylglycine and L-leucylglycyl-L-leucine do not. The chemical shift difference between the two CH2 protons is dependent on temperature and ionic strength. As temperature or concentration of LiCl increases, the chemical shift difference decreases by up to 30%.

Sincerely yours,

Oleg Jardetzky
Asao Nakamura

Enclosure
<table>
<thead>
<tr>
<th>Peptide</th>
<th>Cation</th>
<th>Zwitterion</th>
<th>Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycyl-L-alanine</td>
<td>231.4</td>
<td>228.8</td>
<td>199.3</td>
</tr>
<tr>
<td>Glycyl-L-valine</td>
<td>233.7</td>
<td>232.6</td>
<td>201.3</td>
</tr>
<tr>
<td>Glycyl-L-leucine</td>
<td>232.3</td>
<td>229.9</td>
<td>199.4</td>
</tr>
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<td>Glycyl-L-isoleucine</td>
<td>233.5</td>
<td>231.7</td>
<td>200.8</td>
</tr>
<tr>
<td>Glycyl-L-methionine</td>
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<td>230.7</td>
<td>201.2</td>
</tr>
<tr>
<td>Glycyl-L-serine</td>
<td>234.8</td>
<td>233.8</td>
<td>202.1</td>
</tr>
<tr>
<td>Glycyl-L-proline</td>
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<td>236.8</td>
<td>206.2</td>
</tr>
<tr>
<td>Glycyl-L-aspartic acid</td>
<td>232.5</td>
<td>230.9&lt;sup&gt;1&lt;/sup&gt;, 228.9&lt;sup&gt;2&lt;/sup&gt;</td>
<td>199.4</td>
</tr>
<tr>
<td>Glycyl-L-glutamic acid</td>
<td>233.2</td>
<td>230.7&lt;sup&gt;3&lt;/sup&gt;, 230.2&lt;sup&gt;4&lt;/sup&gt;</td>
<td>200.1</td>
</tr>
<tr>
<td>Glycyl-L-lysine</td>
<td>233.0</td>
<td>233.5&lt;sup&gt;5&lt;/sup&gt;</td>
<td>206.9&lt;sup&gt;6&lt;/sup&gt;, 200.3</td>
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<tr>
<td>Glycyl-L-histidine</td>
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<td>230.1&lt;sup&gt;7&lt;/sup&gt;, 220.4&lt;sup&gt;8&lt;/sup&gt;</td>
<td>196.3</td>
</tr>
<tr>
<td>Glycyl-L-tryptophan</td>
<td>227.4&lt;sup&gt;9&lt;/sup&gt;</td>
<td>*</td>
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<tr>
<td>Glycyl-L-phenylalanine</td>
<td>226.5</td>
<td>227.1</td>
<td>192.9</td>
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<tr>
<td>Glycyl-( \beta )-alanine</td>
<td>226.9</td>
<td>220.3</td>
<td>196.6</td>
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<td>L-Valylglucose</td>
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<td>226.7</td>
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<td>L-Leucylglucose</td>
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<tr>
<td>L-Serylglucose</td>
<td>245.5</td>
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<td>L-Prolylglycine</td>
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<td>L-Hydroxyprolylglycine</td>
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<td>228.3</td>
<td>225.8</td>
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<tr>
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<td>228.2&lt;sup&gt;9&lt;/sup&gt;, 226.3&lt;sup&gt;10&lt;/sup&gt;</td>
<td>225.9</td>
</tr>
<tr>
<td>L-Histidylyglucose</td>
<td>240.2&lt;sup&gt;11&lt;/sup&gt;</td>
<td>221.7&lt;sup&gt;11&lt;/sup&gt;, 226.3&lt;sup&gt;12&lt;/sup&gt;</td>
<td>223.1</td>
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<td>L-Phenylalanylglucose</td>
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<td>223.4</td>
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<td>L-Tyrosylglycine</td>
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<td>213.3</td>
<td>217.3</td>
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<tr>
<td>( \beta )-Alanylglucose</td>
<td>241.0</td>
<td>214.2</td>
<td>219.4</td>
</tr>
</tbody>
</table>

1) \( \text{pD} 3.61 \), 2) \( \text{pD} 6.94 \), 3) \( \text{pD} 3.79 \), 4) \( \text{pD} 6.85 \), 5) \( \text{pD} 3.59 \), 6) \( \text{pD} 8.47 \), 7) \( \text{pD} 4.80 \), 8) \( \text{pD} 7.60 \), 9) \( \text{pD} 5.88 \), 10) \( \text{pD} 9.58 \), 11) \( \text{pD} 4.11 \), 12) \( \text{pD} 6.61 \). * Solubility is not enough for the measurement.
FROM

PROFESSOR GEOFFREY ALLEN
PROFESSOR OF CHEMICAL PHYSICS
TELEPHONE: ARDwick 3333

Professor B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago, 60616,
U.S.A.

Dear Professor Shapiro,

We report a study of coupling constants and chemical shifts in a series of mono-substituted pentachloro triphosphonitrile rings \( \text{N}_3\text{P}_3\text{Cl}_5 Y \), where \( Y = \text{F}, \text{OMe}, \text{OEt}, \text{OPr}^1, \text{OCH}_2\text{CF}_3, \text{NMe}_2 \). The spectra belong to the class \( \text{AB}_2 R \) or \( \text{AB}_2 R X \) where \( A \) and \( B \) represent the \( 3\text{P} \) nuclei and \( R \) and \( X \) are the magnetic nuclei in the substituent \( Y \). A program written in Atlas Autocode was used to compute trial spectra. The results are summarised below.

\[
\begin{array}{cccccccc}
Y & -\text{F} & -\text{OCH}_2\text{CF}_3 & -\text{OCH}_3 & -\text{OCH}_2\text{CH}_3 & -\text{OCH}(\text{CH}_3)_2 & -\text{H} & -\text{N}(\text{CH}_3)_2 \\
\delta_A \text{ p.p.m.} & 14.4 & 16.5 & 16.7 & 13.6 & 12.6 & 19.6 & 22.7 \\
\delta_B \text{ p.p.m.} & 23.0 & 22.7 & 22.5 & 21.3 & 21.7 & 19.6 & 20.6 \\
J_{AB} \text{ c/s} & \pm 78.3 & 66.2 & 63.3 & 63.3 & 62.7 & - & 49.7 \\
J_{AR} \text{ c/s} & \pm 1012 & 10.5 & 16.5 & 10.2 & 11.3 & - & 18.3 \\
\delta_A^+ \text{ p.p.m.} & - & 4.58 & 3.84 & - & 4.76 & - & 2.68 \\
\delta_B^+ \text{ p.p.m.} & - & - & - & 1.42 & 1.42 & - & - \\
\end{array}
\]

* downfield from \( \text{H}_3\text{PO}_4 \)

+ downfield from T.M.S. \( \delta_A - \alpha \text{protons, } \delta_B - \beta \text{protons in } Y \)

For \( \text{N}_3\text{P}_3\text{Cl}_5\text{F} \) \( J_{BR} = \pm 11 \text{ c/s} \)
The line-widths of the $^{31}\text{P}$ spectra were too great to allow the $^{31}\text{P} - \beta$ proton coupling constants to be measured ($J_{Ax} < 1 \text{ c/s and } J_{Bx} = 0 \text{ c/s}$).

In the fluoroderivative $J_{AB}$ and $J_{BR}$ have opposite signs to $J_{AR}$. The relative signs could not be determined with confidence for the other compounds. This may be due in part to a variation in line-width in the observed spectra causing poor agreement with the calculated spectra (which assume a constant line-width) for the contours of overlapping multiplets. There is a variation in line-width in the spectra of the monofluoro compound also but it is not troublesome because each line is discrete. The variation is consistent with a relaxation mechanism in which the efficiency of relaxation depends on the $F_z$ value for the transition.

Broadly speaking the magnitudes of $\delta_A - \delta_B$ and $J_{AB}$ increase with increasing electron withdrawing power of the group Y.

We are extremely grateful to Dr. H. Verenkamp of the University of Munich for providing us with excellent $^{31}\text{P}$ spectra at 40 mc/s.

Yours sincerely,


G. Allen,
F. Heatley,

Short title: N.M.R. spectra of monosubstituted chloro triphosphonitriles.
Dear Professor Shapiro,

I enclose the following communication, which will, I hope, serve as my first subscription to the Newsletter:

We have been using a Hewlett Packard 3440A digital voltmeter with our A.60 for the measurement of integrals and have developed a method of operating the voltmeter from the A.60.

The conversion of the voltmeter is simple. A switch is fitted on the front panel above the sample rate knob and a miniature jack plug on the rear panel to carry the switch leads to the A.60. A double pole single throw relay is mounted inside the case close to the sample rate potentiometer, the circuit being modified as follows:

![Ramp Generator Circuit Fig. 5/14.](image-url)
The -35V used to switch the relay is obtained from the power supply of the voltmeter. The A.60 is connected via the external equipment switch of the spectrometer. The switch $S_1$ is used to switch the digital voltmeter back to its normal operation when required.

When $S_1$ is connected to the relay, the voltmeter is on 'hold' until the normal sweep switch of the A60 is operated. On releasing the sweep switch, the voltmeter holds the integral voltage enabling this to be easily read.

Yours faithfully,

A.A. Wagland.
December 13, 1965

Corrosion Inhibitors in A-60 Cooling Systems

The pump troubles which accompanied the use of chromate corrosion inhibitor in the recirculated water cooling system of an A-60 spectrometer, as outlined by C. A. Hirt in IITNMR Newsletter 86-34, are very similar to problems we have encountered. We have found the use of corrosion inhibitors necessary to the satisfactory operation of our A-60 magnet, however, and have studied the problem enough to find a workable solution.

The direct cause of the pump failures appears to be a gelatinous deposit which forms under the seals and behind the carbon vanes. This deposit first opens the seals to permit leakage, and finally restricts the sliding action of the vanes so as to cause excessive wear and rapid loss of pressure. This deposit is slightly water soluble and can be washed away by running fresh, uninhibited distilled water through the system for a few hours. It is detectable in the water by its dark cloudy appearance, so that washing should be repeated until the circulated water stays sparkling clear.

Changing to a gear pump which uses glass-filled teflon and metal gears reduces the rate of pump wear, but does not stop the leakage past the seals. Control of the problem requires elimination of the deposit.
Composition of the deposit has not been determined, but it was thought to be produced by attack of the basic (pH about 8) inhibitor solution on the rubber hoses used in the system. Accordingly, the long hoses were replaced with 1/2-inch copper tubing and a new chromate inhibitor solution which is buffered to a pH of about 6 and has a lower concentration of chromate was used. The short pieces of rubber tubing used inside the heat exchanger housing were not changed.

These modifications have eliminated the pump problems while still controlling magnet cooling system fouling. The circulating water stays sparkling clear, and inhibitor concentration can be estimated from the intensity of the yellow color. Our cooling system has operated without difficulty for 5 months since these changes were made.

The inhibitor recommended by our Mr. R. V. Comeaux is prepared as a concentrate with the following composition:

- 33% Cr$\text{VI}_4$, added as Na$_2$Cr$_2$O$_7$
- 5% Zn$^{++}$, added as ZnSO$_4$
- 5% PO$_4$$^-$, added as Na$_3$PO$_4$

Buffered if necessary by adding NaHCO$_3$. We have not found this necessary.

One cc of this concentrate is added to each 5 gallons of circulating distilled water in the system initially. The yellow color fades slowly due to reduction of six-valent chromium, making it necessary to withdraw about one gallon/week and replenish with the fresh inhibitor solution (1cc/5 gal). This replacement procedure replenishes the inhibitor while removing the undesirable reduced products.

N. F. Chamberlain
Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry,

'Transient Nutations in Nuclear Magnetic Double Resonance'

If a strong radiofrequency field, adjusted to resonance for a given nmr line, is suddenly switched to a high level $H_1$ well above saturation, a transient oscillation of the kind described by Torrey$^1$ may be observed. This corresponds to a nutational motion of the magnetization vector, that is to say a precession about $H_1$ in the rotating frame of reference. For exact resonance, and if

$$\gamma H_1 \lambda \gg \frac{1}{T_1}, \frac{1}{T_2}, \frac{1}{T_2^*},$$

the detected mode signal oscillates with a frequency

$$\Omega = \gamma H_1 \lambda$$

where $\lambda$ is the matrix element of the line in question, and decays through spin-spin and spin-lattice relaxation with a time constant

$$\frac{1}{T} = \frac{1}{2} \left[ \frac{1}{T_1} + \frac{1}{T_2} \right]$$

The strong field $H_1$ overrides the dephasing effects of spatial inhomogeneity in $H_o$.

Among other applications, we have been exploiting this phenomenon in double resonance. In an internally locked proton spectrometer$^2$, a saturating rf field $\omega_1$ is held at exact resonance for a chosen line $\omega_{pq}$ of a complex spectrum while a second rf field $\omega_2$ of about the same strength is swept through the entire spectrum at such a rate that the adiabatic fast passage conditions are approximated:

$$\gamma H_2 \lambda \gg \frac{1}{H_2 \lambda} \frac{dH_o}{dt} \gg \frac{1}{T_1}, \frac{1}{T_2}$$

(Note that the matrix element $\lambda$ may vary considerably from line to line.)

As $\omega_2$ sweeps through a typical line and inverts the spin populations of the two energy levels, one observes one of three possible effects:

(a) If the line does not terminate on the levels $p$ or $q$ (for example, $\omega_{sr}$), there is no appreciable change in the signal carried at $\omega_1$. 

\[\begin{align*}
\text{P} & \quad \text{Q} \\
\text{q} & \quad \text{s} \\
\text{r} & \\
\end{align*}\]
(b) If $\omega_2$ sweeps through a connected transition that bears a 'progressive' relation to $\omega_{pq}$ (for example, $\omega_{qr}$), excess population is pumped into the lower level q (or out of the upper level p) and excites a transient 'Torrey oscillation' at the spectrometer frequency $\omega_1$, very similar to that observed when $H_1$ is suddenly switched on.

(c) If $\omega_2$ sweeps through a regressive connected transition (for example, $\omega_{ps}$), excess population is transferred into the upper level p (or out of the lower level q) leaving the net magnetization vector aligned temporarily along the negative Z axis. Precession about $H_1$ therefore carries it first into the negative Y direction; that is to say, the transient oscillation starts out in the negative sense.

We believe that this technique draws such a clear distinction between progressive and regressive connected transitions that it may be preferred over 'spin tickling' for the assignment of transitions of complex spectra to the appropriate energy level diagram. An illustrative example is provided by the ABC spectrum of 2-chlorothiophene where line 3 has been monitored by $\omega_1$ and transient nutations detected as $\omega_2$ is swept through the connected transitions 5 and 14 (progressive) and 1, 7, 8, and 12 (regressive). Note that the weak matrix element of the 'combination' line 1 can be compensated by increasing $H_2$ as in inset (d).

A more detailed discussion may be found in preprints of an article submitted to J.C.P. (obtainable by writing to R. F.). Would you please add Jim Ferretti to your mailing list and credit this letter as his first subscription?

Yours sincerely,

James A. Ferretti
Istituto Chimico
Universitá di Napoli
Via Mezzocannone 4
Naples, Italy


2Home-made conversion of HR 60.
J. A. Ferretti and R. Freeman
Dear Doctor Shapiro:

Quadrupole - versus Hexadecapole - relaxation in GeH₄

When we first measured the proton nmr spectrum of GeH₄ [Zeitschrift f. Naturf. 19a 139 (1964)] we noticed that the satellite lines due to a coupling with the germanium isotope Ge⁷³ (Spin ⁹/₂; 7.6% abundance) were not of equal width. See Fig. 1. This we explain as due to a different life-time of the Ge in its spin-states. We now remeasured these satellite lines very carefully and the spectra at -60°C are given in Fig. 2. For a strict tetraeder the relaxation due to the quadrupole-moment of the Ge⁷³ would be exactly zero.

In case of a lorentzian shaped line the line width is given by:

\[
\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{T_m'}
\]

where \(\frac{1}{T_2'}\) is due to the dipole-dipole relaxation of the protons which in case of negligible slow relaxation of the Ge⁷³ dominates the line width. In case of any higher multipole-interaction with components \(Q_i\) the other term \(\frac{1}{T_m'}\), might become dominant and may be evaluated for the state \(m'\) considered by summing the transition probabilities \(P_{m',m''}\) over all other states \(m''\).

\[
\frac{1}{T_m'} = \sum_{i,m''} Q_i \left< m' \left| f_1 \left( I_{Ge} \right) \right| m'' \right>
\]
There seem to us two ways to explain our findings:

1. The actual instantaneous symmetry of the GeH₄ molecule departs slightly from tetraedral symmetry due to nuclear motion. Depending on the resulting symmetry, different line width pattern may result. As examples Fig. 4, a deformation to C₃ᵥ and D₂h has been assumed - that is Δm = ± 2 transition become allowed - or Fig. 3 greater symmetry distortion is assumed - where also Δm = ± 1 are allowed.

2. The next higher electric moment of a nucleus beyond the quadrupole-moment, i.e. the electric hexadecapole-moment, though it is smaller by many orders of magnitude than the octopole-moment, gives even for strict tetraedal symmetry a relaxation due to an interaction of this moment with the molecular electric field. This makes Δm = ± 4 transition allowed and an example is given in Fig. 5.

In Fig. 4 and 5 a reasonable amount of proton relaxation was included to give similarity with experiment.

We do not feel like making a final statement on these effects. However, we are studying these things further and would very much like if anyone who comes across related effects would let us know.

Sincerely yours

4. Fern and
E. Sachmann
Dr. R. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

Some time ago we assigned [Tetrahedron Letters 1517 (1963)] structures Ia and IIa, respectively, to the solvolysis products obtained from the 3a-

![Structure I](image1)  
![Structure II](image2)  

and 3β- mesylates IIIa. Based on NMR evidence, we have now concluded that structure I is incorrect.

These solvolysis reactions have been repeated using epimeric 3-mesylates(IIIb) in which deuterium is present at C-3 instead of hydrogen. The resulting 3,5-cyclosteroids "Ib" and IIb produce strikingly different patterns for the (now isolated) cyclopropane methylene protons. The α-mesylate product "Ib" shows these protons as an AB quartet: $\delta_A = 0.16$ ppm, $\delta_B = 0.27$ ppm, $J_{AB} = 5$ c/s. The β-mesylate product IIb exhibits the C-4 methylene protons as an AX pattern: $\delta_A = 0.125$ ppm, $\delta_X = 0.675$ ppm, $J_{AX} = 5$ c/s. The latter result is easily explained since models show a close proximity of the angular hydroxyl group and 4β-H of II, leading to deshielding. The absence of this effect in the α-mesylate solvolysis product is best explained by formulating it not as I but as IV in which the hydroxyl and methylene are trans to the 5-ring. This
new structure also avoids the boat form of ring B which is required by I.

The low field half of the AB pattern in IV is further split by long range coupling \( (J \sim 1 \text{ c/s}) \) which is removed by irradiation at 2.32 ppm. This effect may involve the 2\( \beta \) and 4\( \beta \) protons which, along with the connecting bonds, form the \( \equiv \) arrangement known to produce small couplings such as this. The rather low field position of the 2\( \beta \)-proton may result not only from its being "allylic" to the cyclopropane ring but possibly also from deshielding by the angular hydroxyl.

Charlie Moreland performed (or directed) all of the NMR work described here and I hope you will credit this letter to his "account."

Best personal regards.

Sincerely yours,

Sam

Samuel G. Levine
Associate Professor

SGL:mg
Professor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
CHICAGO, I11., 60616
--USA--

Dear Professor Shapiro,

At the Liquid Crystal Conference at Kent/Ohio (August 1965), Dr. Saupe and I reported on the

PMR Spectra of Some Acetylenic Compounds and of Acetonitrile

oriented in the nematic phase of 4,4-di-n-hexyloxy-azoxybenzene (I). Since our preliminary results will be published in "Molecular Crystals" not before April 1966, I should like to give here a short abstract.

The following compounds have been studied:

\[ H-C=CH_2X \quad X=Cl (1) \text{ and } Br (2) \]
\[ (3) H-C=CH_3 \quad (4) H-C=CH-C=CH_3 \]
\[ (5) H_2C-C=CH-C=CH_3 \quad (6a) NE=C-CH_3 \quad (6b) NEC-^{13}CH_3 \]

Chemical shift anisotropies:

From the chemical shift difference of the acetylenic proton in the isotropic and nematic phase and from the known molecular geometry (Microwave data) we obtained for compounds 1) to 4)

\[ \Delta \delta = \delta_{II} - \delta_{\perp} \approx (10.8 - 13.0) \times 10^{-6} \]

\[ \delta_{II}, \delta_{\perp} = \text{screening for parallel and perpendicular orientation of the carbon triple bond with respect to the magnetic field direction. It can be concluded that the C-C-axis are preferably parallel to } H_0 \text{ and the optical axis of the nematic liquid.} \]
The absolute sign of the indirect spin-spin coupling \( J (\text{^13C-H}) \) in compound \( 6b \) has been found to be \textit{positive}.

From the ratio of the direct spin-spin couplings \( D (\text{H-H}) \) and \( D (\text{^13C-H}) \) of compound \( 6b \) the H-C-H bond angle of the methyl group has been found to be \( 108^\circ \pm 6' \) in two different nematic solvents (I and 4-n-octyloxybenzoic acid). Similar measurements with Methanol-\text{^13C}, other \text{^13C}-species of acetonitrile and with \text{^13CH}_3J have also been successful in the meantime.

These experiments show that not only aromatic compounds can be oriented in nematic liquids but all other molecules - even gases - provided their molecular structure deviates sufficiently from a "spherical" shape (tetramethylsilane TMS cannot be oriented!).

As an example we present the 100 Mcps spectrum of oriented (2) plus TMS at 70°C in I. The theoretical spectrum has been calculated with the parameters:

\[
\begin{align*}
A & = 79.5 \text{ cps} \quad \text{(direct coupling \text{H, CH}_2)} \\
B & = -1169 \text{ cps} \quad \text{(direct coupling \text{CH}_2)} \\
\Delta \nu & = 193 \text{ cps} \quad \text{(chemical shift difference)}
\end{align*}
\]

All parameters are defined in ref. 1). First order explanation of the spectrum: the strongly coupled \text{CH}_2-protons give rise to a doublet, splitted by a smaller coupling with the acetylenic proton. The latter gives rise to a triplet (coupling with the \text{CH}_2-protons) in the central part of the spectrum shifted by \( \Delta \nu \), the chemical shift difference, with respect to the \text{CH}_2-lines.

ref. 1): G. Englert and A. Saupe; 
January 12, 1966

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

Dear Dr. Shapiro:

In response to inquiries, I would like to make a progress report on the analysis of NMR spectra using computer techniques which was mentioned in IITNMR 71 31 and reported at the 6th Experimental NMR Conference last February. The program for decomposition of overlapping spectral peaks (DECOMP) provides very accurate frequency values and moderately good intensities for peaks which are completely unresolved in a spectrum. These values are sufficiently good such that we have written a program (ASSIGN) which will find all possible sets of energy levels using the peaks resolved from the experimental spectrum by DECOMP. ASSIGN utilizes both frequency and intensity sum rules as constraints for the assignments, but is general for all systems of spins in that an input algorithm, which can be varied according to the system involved, is used to guide the computation.

A description of the method applied to the analysis 3-chlorothietane, is scheduled for publication in the Jan. 15,1966 issue of J. Chem. Phys. FORTRAN IV listings of the programs for use with an IBM 7094 and descriptions of their use are contained in appendices of reference 1; these appendices will be available as a separate report in the near future. Requests for these listings, when available, and questions regarding their use should be addressed to T. R. Lusebrink.

The present version of ASSIGN contains an option to take advantage of information from double resonance experiments, but only utilizes the information that certain lines have energy levels in common. This modification significantly
reduces the computer time required to solve a five spin system. The program is currently being rewritten so that it can take full advantage of the information identifying regressive and progressive lines from the Nuclear Overhauser Effect obtained by observing one line and frequency sweeping the rest of the spectrum. This modification is expected to further reduce the computer time by a significant amount, but it is not anticipated that the program will be completed and tested for several weeks.

It is hoped that this will be considered as a subscription to the IITNMR; please send the IITNMR to T. R. Lusebrink.

Very truly yours,

[T. R. Lusebrink]

C. H. Sederholm
IBM Systems Res. & Devel.
2670 Hanover Street
Palo Alto, Calif.

TRL/pl


The William Albert Noyes Laboratory

January 13, 1966

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

Dear Dr. Shapiro:

We have observed a difference in the F\textsuperscript{19} n.m.r. spectra of enantiomers when a suitable optically active solvent is used. The racemic fluorochloroalcohol I shows a doublet, |\textit{J}|_{HF} 6.7 c.p.s. in carbon tetrachloride but exhibits two sets of doublets |\textit{J}|_{HF} 7.2 c.p.s. when in 1-\textalpha-phenethylamine, II. The shift of one set relative to the other is 2.0 c.p.s. Only one set of doublets is observed in racemic amine.

By using this technique and measuring the intensities of the two sets of doublets, we have determined the optical purity of a sample of I (\textalpha)L + 1.6\textdegree neat) produced by an asymmetric induction to be 52%. The specific rotation of the dextro enantiomer is calculated to be 40 \pm 10\textdegree. To our knowledge, this is the first example of nonequivalence of n.m.r. spectra of enantiomers in an optically active solvent.

Respectfully,

W. H. Pirkle
Assistant Professor
of Organic Chemistry

WHP: sgm
January 10, 1966.

Dear Barry:

Benzene Shifts for Methyl Substituted Cyclohexanones.

By looking at cyclohexanones and tetrahydropyranones, methyl-substituted in the $\beta$ and $\gamma$ positions, we could enlarge the scope of the previous observations (S. Barry, M. Fétizon, P. Laszlo, and J. H. Williams, Bull. Soc. Chim. France, 2541 (1965)). The data presented here are less liable to precise interpretation in terms of conformational changes, since the experimental shifts for the $\beta$ position are now of the order of 22 cps (equatorial CH$_3$) and 12 cps (axial CH$_3$), differing much less than the corresponding values at the $\alpha$ position: 16 cps (axial CH$_3$) and -5 cps (equatorial CH$_3$). Nevertheless, the present results are consistent with strong deformations (into a flattened or twist chair conformation) for both tetramethyl-cyclohexanone and tetrahydropyranone, as well as for the trimethyltetrahydropyranone. Precise control of the concentrations, for such studies to be significant, is to be obeyed. This work was performed in collaboration with M. Fétizon, J. Goré, and B. Waegell, and is presently submitted for publication.

Sincerely,

Pierre Laszlo
<table>
<thead>
<tr>
<th>88-54 (cps, at 60 Mc)</th>
<th>chem. shift (CCl₄)</th>
<th>ΔCCl₄</th>
<th>ΔCDCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃ (t):e</td>
<td>60.7</td>
<td>21.7</td>
<td>-0.5</td>
</tr>
<tr>
<td>CH₃ (s)</td>
<td>58.5</td>
<td>16.7</td>
<td>-0.8</td>
</tr>
<tr>
<td>CH₃ (t):e</td>
<td>62.7</td>
<td>18.4</td>
<td>0.1</td>
</tr>
<tr>
<td>CH₃ (s):e</td>
<td>60.0</td>
<td>19.3</td>
<td>0.1</td>
</tr>
<tr>
<td>CH₃ (s):a</td>
<td>52.3</td>
<td>11.6</td>
<td>0.2</td>
</tr>
<tr>
<td>CH₃ (s)</td>
<td>62.3</td>
<td>13.6</td>
<td>-0.3</td>
</tr>
<tr>
<td>CH₃ (d):e</td>
<td>60.8</td>
<td>21.4</td>
<td>0.0</td>
</tr>
<tr>
<td>CH₃ (s)</td>
<td>65.5</td>
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<td>0.1</td>
</tr>
<tr>
<td>CH₃ (d)</td>
<td>75.5</td>
<td>21.1</td>
<td>4.0</td>
</tr>
<tr>
<td>CH₃ (s)</td>
<td>73.0</td>
<td>15.8</td>
<td>3.2</td>
</tr>
</tbody>
</table>
s = singlet; d = doublet; t = triplet.

e = equatorial; a = axial.
Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago, Illinois 63616

Dear Barry,

The time has come ... (I think), and so here is a brief report on some work done in collaboration with Peter Diehl of the University of Basel.

In the table below are shown all n.m.r. parameters involving H and F, of 1,2,3,5-tetrafluorobenzene, ("m-C₆H₂F₄"), and AA'XX' system with A = A' = H and all others F's.

In the subspectral treatment of this system all chemical shifts were ignored.

This cannot be done in a similar system, that of pentafluorobenzene, where M = H and all others are F's. At we = 56.4 MHz, $\delta_{RX}$ is about 475 Hz. In this case second order perturbation theory accounts for the observed splittings of the order of $J_{RX}^2/\delta_{RX}$ and predicts small shifts of lines in the R band, as seen in the figure (the diagram is not drawn to scale).

We should like to acknowledge the help of Bill Moniz (NRL), of Tom Farrar and Rolf Johanssen (NSB), and of Harlan Foster (Dupont), who supplied us with carefully recorded spectra.

Best regards and wishes.

Ernest Lustig  
Additives & Instrumentation Branch  
Division of Food Chemistry

$\delta$'s and $J$'s for m-C₆H₂F₄

<table>
<thead>
<tr>
<th>$\delta$</th>
<th>A</th>
<th>X</th>
<th>M</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.26</td>
<td>131.2 $\varphi$</td>
<td>112.8 $\varphi$</td>
<td>165.8 $\varphi$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$J_{ij}$</th>
<th>AX</th>
<th>AM</th>
<th>AR</th>
<th>AX'</th>
<th>AA'</th>
<th>RX</th>
<th>XX'</th>
<th>MX</th>
<th>MR</th>
</tr>
</thead>
<tbody>
<tr>
<td>±10.43</td>
<td>8.61</td>
<td>5.60</td>
<td>5.17</td>
<td>3.11</td>
<td>19.77</td>
<td>5.74</td>
<td>1.73</td>
<td>11.02 Hz</td>
<td></td>
</tr>
</tbody>
</table>

Refinement of $J_{ij}$'s was done by the application of LAOCOON II to the entire 116-line spectrum. R.m.s. error in fitting: 0.055 Hz. Values for neat, degassed liquid.
\[ 10 \text{Hz} \]

\[ \begin{array}{c}
\text{FIRST ORDER} \\
\text{SECOND ORDER}
\end{array} \]

\[
\begin{array}{cccccccccccccccccccc}
\text{INTENSITY} & 1 & 2 & 2 & 2 & 2 & 1 & 1 & 1 & 4 & 2 & 2 & 4 & 1 & 1 & 1 & 2 & 2 & 2 & 2 & 1 \\
\end{array}
\]
Dear Prof. Shapiro,

The Conformation of the Pterocarpan Ring System

Pterocarpin (I: 3-0Me; 8,9-OCH₂O⁻), a constituent of the heartwood of Swartzia madagascariensis, contains a coumarochromane ring system common to a variety of naturally occurring compounds. The name pterocarpan has recently been proposed for this system.¹ (Fig. 1).

A cis-fusion of the two heterocyclic rings has been suggested for homopterocarpin (I: 3-0Me, 8-0Me) on the basis of models (ring-strain) and n.m.r. evidence,² but there are still two conformers possible. We have determined the conformation by analysing the complex four-spin system of the 6, 6a, and 11a protons for a few compounds related to pterocarpin and homopterocarpin using an iterative computer programme.³ The average coupling constants for four closely related compounds are given below:

<table>
<thead>
<tr>
<th>Coupling Constants (c.p.s.)</th>
<th>J₆a,11a</th>
<th>J₆a,6</th>
<th>J₆a,6'</th>
<th>J₆,6'</th>
<th>J₆,11a</th>
<th>J₆',11a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.2</td>
<td>10.6</td>
<td>5.2</td>
<td>-11.0</td>
<td>-0.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

These values support the conformation given in Fig. 2 with protons 6 and 6a in an axial/axial relationship to each other. A high degree of conformational purity seems probable from the data above.¹

Figure 1

Figure 2 / ...
It is also interesting to note that the two four-bonded couplings are of opposite sign. Their relative magnitudes are in qualitative agreement with the calculations of Barfield.4

Yours sincerely,

K. Pachler
SENIOR RESEARCH OFFICER
CHEMICAL PHYSICS GROUP
NATIONAL CHEMICAL RESEARCH LABORATORY

References
2 H. Sugino, T. Iwadare, Experientia, XVIII, 164 [1962].
3 J.D. Swalen, C.A. Reilly, J. Chem. Phys., 27, 27 [1962]. We are grateful to the authors for a listing of their programme.
DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

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

January 14, 1966

Re: Carbon-13 Chemical Shifts in Some Methylcyclohexanes

Dear Barry,

We have recently recorded the carbon-13 chemical shift values for the ring carbons in 15 selected methylcyclohexanes of known structure. A numerical factor analysis of these 60 different chemical shift values has indicated that a limited set of structural parameters can be used to predict the experimental values with a considerable degree of accuracy. These parameters are given in Fig. 1 for the several conformational features which they represent, and they predict the chemical shift relative to the 101.44 ppm chemical shift of cyclohexane. Five of the significant parameters are methyl substituent terms, while an additional four parameters are required to account for important methyl-methyl pair interactions. All of these parameters reflect important conformational features in this molecular system and form a basis for conformational studies on such compounds. The success of the correlation by these seven significant parameters is exhibited in Fig. 2.

The factor analysis was originally carried out for the data taken on only 12 of the 15 available compounds. These compounds were those (4 compounds) in which the two possible chair conformations were equally populated because of their equivalence in energy and those (8 compounds) for which only one conformation makes a significant contribution to the ground state description of the molecule. Using the parameters obtained in this manner, the spectral data for methylcyclohexane, 1,trans-2,cis-4-trimethylcyclohexane and 1,1,2-trimethylcyclohexane were analyzed. The spectrum of methylcyclohexane was fit best if a conformational energy of +2.1 Kcal/mole (range in exp. error 1.4-3.0) for the axial and equatorial forms was used to predict the relative populations. Likewise, a ΔE value of 1.2 Kcal/mole (range in exp. error 0.9-1.6) gave a good fit of the spectral features in the 1,trans-2, cis-4 compound. All attempts to interpret the spectrum of 1,1,2-trimethylcyclohexane in terms of a mixture of the two chair conformations failed, as the spectral peaks fell outside of the range predicted for the two extreme chair conformers. When considered with the information from the FMR data on this compound that the axial and equatorial protons are averaged through interconverting structures, one may conclude that the skewed boat form may well contribute to a description of this rather sterically hindered molecule.

We hope to have a preprint on this work available for distribution by early spring, and we will be happy at that time to provide further details upon request.

Sincerely yours,

David M. Grant

Don K. Dalling

Don K. Dalling

DMG:fjc
SUBSTITUENT PARAMETERS OBTAINED FROM FACTOR ANALYSIS
(GIVEN IN PPM)

-5.71 ± 0.22
-1.09 ± 0.44
-8.89 ± 0.12
-5.24 ± 0.33

neg.
+5.37 ± 0.25
neg.

+3.51 ± 0.59
+1.22 ± 0.42
+3.22 ± 0.59
+2.33 ± 0.27

STANDARD ERROR OF FIT  0.51 PPM
MULTIPLE CORRELATION COEFF.  0.9990
CARBON-13 CHEMICAL SHIFT IN THE METHYLCYCLOHEXANES
Dear Professor Shapiro,

sometimes strange natural molecules allow the discovery of strange long-range couplings. In the course of the structure determination of a rare natural product "pederin" (1), we met an unusual long-range coupling, which may be of interest to readers of IITNMB.

The hydroxyl proton at C-6 (Fig. 1) is coupled to H-sax across oxygen with J = 2.0 cps, but not with the geminal H-3eq.

Although examples of long-range interactions across oxygen are known (2), this is, I suppose, the first case of such a coupling involving an hydroxyl proton in a saturated fragment. Freeman, Bhaooa and Reilly (3) have reported the unique example of splitting of a phenolic proton by a J = 0.4 cps.

The preferred chair conformation of the ring is deduced from the values of allylic coupling constants: J(CH₂H₃ax) = 2.0 cps, 1J(C₃H₃ax) = 0 cps, 2J(C₃H₃eq) = 15.18°; 3J(CH₂H₃ax)

if the orientation of the chain at C-6 is equatorial (this seems probable, but it is not yet proved), the partial chelation of OH-6 with the carbonyl could induce the molecular fragment H-C₅-C₆-O-H to adopt a "zig-zag" configuration, with the coupled protons in the C-C-O plane (φ₅ = φ₉ = 180°) (4). This may be an explanation of the relatively high magnitude (absolute value) of the J. The influence of substituents and the contribution of the oxygen, of course, has to be considered, the orbitals of which seem directly involved. These factors may be more important than stereochemistry, especially because the shift of 6.07 δ of OH-6 does not suggest a strong H-bonding.

It should be very interesting to get the sign of this J (Gagnaire, Payo–Subiza and Rousseau have reported a positive J across oxygen) (5), because without knowing it, no discussion is possible.

The long-range coupling is visible from the doublet of OH-6 at 6.07 δ, and the doublet (J = 13.5 cps) of quartets (J = 2.9) of H-sax at 2.93 δ partially overlapped by H-6.

These assignments are justified by decoupling experiments (Fig.1 and 2) and by the spectrum with a trace of D₂O (Fig.1a) : the OH signal disappears and the doublet of quartets is reduced to a doublet of triplets.
The signal at 6.07 \( \delta \) cannot be due to OH-12 because the same H-5ax interacting with OH-6, is coupled to CH = protons (triplets at 4.82 and 4.66 \( \delta \); \( J_{\text{gem-allyl}} = 2.0 \text{ cps} \)). Furthermore in the similar natural product with OCH\textsubscript{3} at C-6, the signal at 6.07 \( \delta \) and the long-range coupling lack.

In the structure determination of this biologically interesting substance, we have been successful using nmr, especially because of the small amount of material available.

We thank you very much for sending us the IITNMR News Letters and for all the trouble you have in doing it.

yours sincerely

R. Mondelli

-An unusual long-range coupling across oxygen-

Fig. 1- Spectrum at 100 Mc in acetone-\( d_6 \); a) with D\textsubscript{2}O; b) decoup. of H-5ax \( \Delta \omega = +306 \text{ cps} \); c) decoup. of H-5ax \( \Delta \omega = +189 \text{ and } +176 \text{ cps} \); d) decoup. of OH-6 \( \Delta \omega = -300 \text{ cps} \); e) signal of H-5ax at higher amplitude.

Fig. 2- Signal of H-5ax at 2.93 \( \delta \); without decoup. a) in acetone, b) in acetone + D\textsubscript{2}O; with decoup. of H-5eq at 2.05 \( \delta \); a') in acetone, b') in acetone + D\textsubscript{2}O; \( \Delta \omega = +88 \text{ cps} \).

b") decoup. of CH\textsubscript{2} at 4.82 and 4.66 \( \delta \) in acetone + D\textsubscript{2}O; \( \Delta \omega = -184 \text{ and } -177 \text{ cps} \).

I thank very much Dr. Wolfgang von Philippsborn for the kindly permission to use his nice Hz-100 instrument.

January 1966

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

Dear Barry:

"The Rich Get Richer and the Poor Get Poorer"

Reinhold Kaiser's recent description of a 'Feedback Spectrometer' (I.I.T. Newsletter 87, 38) brings up some interesting new concepts. Clearly a lot depends on the outcome of the promised theoretical analysis, but there are also some questions that might be answered experimentally. We would like to inject a note of caution on two points:

Although in the conventional linear systems one usually thinks of certain quantities as almost synonymous

\[
\text{Signal-to-noise} \equiv \text{Sensitivity} \\
\text{Line-width} \equiv \text{Resolution}
\]

this is not necessarily carried over into non-linear systems such as a feedback spectrometer, which favors strong signals over weak signals. Sensitivity should be examined in terms of the weakest detectable line, and resolution in terms of the smallest resolvable splitting.

The $^{13}$C spectrum of neat benzene (or dioxane) is not a very good test of the new spectrometer's sensitivity, since the signal is stronger than the noise on a single scan without feedback. Operating at 14 Kgauss but with a sample in a 9mm inner diameter tube (we feel that 23 Kgauss and 4mm i.d. tubes should give about comparable sensitivity) we obtained quite respectable signal-to-noise in a single scan (at 5 cps/sec) through the absorption mode in a conventional $^{13}$C spectrometer (Fig. 1). We were then able to 'improve' signal-to-noise by introducing a non-linear element into the circuit (the square-law portion of a diode characteristic). See Fig. 2. Enhancement through non-linearity does not of course improve sensitivity.

One would also like to establish to what extent the attainable resolution is degraded by the tendency to 'pull in' to the center of an nmr signal, particularly in the case of a weak line close to a very strong one (compare for example the AFC circuit in a radio).

It remains unclear whether the properly defined sensitivity and resolution of the feedback spectrometer are significantly better than in adiabatic fast passage.

Yours sincerely,

R. R. Ernst
R. Freeman
Analytical Instrument Research

Fig. 1
Fig. 2
January 17, 1966

Professor B. L. Shapire
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616
U. S. A.

Dear Barry:

"C₆ - Fluorinated Sugars"

We took delivery of our HA-100 just before Christmas and so we hope to get down to some new projects in the near future.

As a somewhat step-gap contribution I mention the chemical shift data which we have for hexose sugars having a single fluorine at the terminal position, (C₆). The compounds we have made so far, give a resonance somewhere in the range +230 to +232 p.p.m. (CHCl₃ solutions with CCl₄ as internal reference). We are now preparing a further selection of these derivatives for other reasons and hope that they will enable us to decide whether there is any regular steric dependence for these resonances - I suspect not. Anyway, these shifts are of use to identify such compounds.

With very best regards for 1966.

Yours,

L. D. HALL
Assistant Professor of Chemistry

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