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Deadline Dates: No. 177: 4 June 1973
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We are, in fact, very anxious to obtain a marked increase of advertising in the Newsletter, and your helpful suggestions along this line will be greatly appreciated. In particular, if any of you at commercial enterprises can induce support from your company, etc., for the Newsletter – either in the form of advertising or via becoming a Contributor or Sponsor – please try to do so. There are two purposes to be served by an increased level of advertising:

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As always, we will be very happy to receive any suggestions or criticisms aimed toward improving the Newsletter.

B. L. Shapiro
Dr. B. L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843  

Dear Barry,  

We have been determining distance ratios of the diazines from their PMR spectra in the lyotropic mesophase first reported by Lawson and Flautt (1). In Table I we show a comparison of our results with values obtained from thermotropic media and, where available, with x-ray and microwave results.

It is interesting to note that the lyotropic and thermotropic results for pyrazine and pyridazine are in considerably closer agreement than is the case with pyrimidine. This may in turn reflect corresponding differences in the effect of the ordered media involved on the diazine structures, a point which will require further investigation.

Sincerely,

Robert C. Long, Jr.
J. H. Goldstein  
Professor

---

(4) Schneider, R. F., Dissertations Abstr. 20, 3536 (1960).
Table I. Distance Ratios for Pyrazine, Pyrimidine and Pyridazine

<table>
<thead>
<tr>
<th></th>
<th>NMR Lyotropic</th>
<th>NMR Thermotropic(a)</th>
<th>X-ray(b)</th>
<th>Microwave(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrazine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_{14}/r_{12})</td>
<td>1.651 ± 0.004</td>
<td>1.66 ± 0.02</td>
<td>1.703</td>
<td>--</td>
</tr>
<tr>
<td>Pyrimidine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_{12}/r_{23})</td>
<td>1.680 ± 0.013</td>
<td>1.62 ± 0.01</td>
<td>1.670</td>
<td>1.695</td>
</tr>
<tr>
<td>(r_{13}/r_{23})</td>
<td>1.972 ± 0.011</td>
<td>1.90 ± 0.02</td>
<td>1.957</td>
<td>1.979</td>
</tr>
<tr>
<td>(r_{24}/r_{23})</td>
<td>1.704 ± 0.004</td>
<td>1.706 ± 0.004</td>
<td>1.720</td>
<td>1.712</td>
</tr>
<tr>
<td>Pyridazine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(r_{12}/r_{23})</td>
<td>0.983 ± 0.015</td>
<td>0.988 ± 0.010</td>
<td>--</td>
<td>1.030</td>
</tr>
<tr>
<td>(r_{13}/r_{23})</td>
<td>1.692 ± 0.008</td>
<td>1.693 ± 0.007</td>
<td>--</td>
<td>1.759</td>
</tr>
<tr>
<td>(r_{14}/r_{23})</td>
<td>1.897 ± 0.004</td>
<td>1.890 ± 0.004</td>
<td>--</td>
<td>2.033</td>
</tr>
</tbody>
</table>

(a) Thermotropic values for pyrazine, pyrimidine, and pyridazine taken from Refs. (2), (3), (4) and (5), respectively.

(b) X-ray data is from Refs. (6), (9).

(c) Microwave distance ratios for pyrimidine were reported in Ref. (4). The values for pyridazine were calculated from the model proposed in Ref. (8).

![Pyrazine](image1.png)  
![Pyrimidine](image2.png)  
![Pyridazine](image3.png)
Subject: F-F coupling of fluorocyclopentenes

Dear Prof. Shapiro,

Thanks for your blue reminder and my apologies for the delay in replying you. My contribution, concerns with the F-F coupling results Dr. Harris (E.A.U) and I have obtained on some fluorocyclopentenes. Four cyclopentenes containing the $-$CF$_2$CF$_2$- group have been, infact, fully analysed to yield values for the $^{19}$F chemical shifts and all the FF coupling constants (except that only relative values of $2J_{FF}$ are obtained). The Table hereby attached collects the F-F coupling values of the four cyclopentenes analysed. The vicinal coupling constants are found to be in the range $-8.5\pm4.4$ Hz for the trans orientation and in the range $-1.9\pm0.7$ Hz for the cis orientation. Details of the methods of analysis and discussion of the results obtained will appear in a forthcoming paper on J.Magn. Res.

Yours sincerely,

L. Cavalli
### Coupling Constants of the Fluorinated Cyclopentenes I to IV

<table>
<thead>
<tr>
<th>Compound</th>
<th>(2J_A)</th>
<th>(2J_M)</th>
<th>(3J_{AX})</th>
<th>(3J_{MX})</th>
<th>(h_{J_A})</th>
<th>(h_{J_M})</th>
<th>(h_{J_X})</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans</td>
<td>cis</td>
<td>trans</td>
<td>cis</td>
<td>trans</td>
<td>cis</td>
<td>trans</td>
<td>cis</td>
</tr>
<tr>
<td>I</td>
<td>255.30</td>
<td>255.30</td>
<td>-0.44</td>
<td>-1.37</td>
<td>-1.37</td>
<td>+1.24</td>
<td>+1.22</td>
</tr>
<tr>
<td>II</td>
<td>254.39</td>
<td>254.39</td>
<td>-5.73</td>
<td>-1.04</td>
<td>-1.04</td>
<td>+1.22</td>
<td>+3.06</td>
</tr>
<tr>
<td>III</td>
<td>255.70</td>
<td>254.70</td>
<td>-6.89</td>
<td>-0.70</td>
<td>-1.45</td>
<td>+1.28</td>
<td>+3.56</td>
</tr>
<tr>
<td>IV</td>
<td>260.46</td>
<td>250.80</td>
<td>-5.55</td>
<td>+0.66</td>
<td>-1.85</td>
<td>+1.68</td>
<td>+3.07</td>
</tr>
</tbody>
</table>

\(a\) The value of \(2J_X\) was kept constant at +240.0 Hz in the iterations.

\(b\) MIA for I and II.

![Diagram](https://via.placeholder.com/150)
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JOURNALS DEPARTMENT

Heyden & Son Ltd., Spectrum House, Alderton Crescent, London NW4 3XX
April 3, 1973

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

SUBJECT: ASSIGNMENT OF THE $^{13}$C RESONANCES OF THE C-8 SIDE CHAIN IN PROSTAGLANDINS

Dear Barry:

During the past 14 months we have examined the $^{13}$C nmr spectra of a number of natural and synthetic prostaglandin (PG) derivatives. Using 5 mm O.D. tubes, quite good spectra can be obtained on samples as small as 8 mg. Since a separate resonance is frequently observed for each carbon of the PG skeleton, far more structural information is available than is found in the $^1$H spectrum. This technique is proving to be of considerable value for the characterization of this class of biologically important compounds.

However, a completely unambiguous assignment of the observed resonances must be made. Such assignment for carbons 15-20 are possible by comparison with the spectra of 3-octanol[1], l-octyn-3-ol and the PG intermediate 3-(3-hydroxy-1-trans-octen-1-yl)-cyclopentanone(I). The olefinic carbons of I can be assigned tenuously, by considering substituent effects[3] and the ring carbons are assigned by comparison with the spectrum of 3-methyl-cyclopentanone.[4] As can be seen from the data in Table I, the chemical shifts of carbons 18-20 are essentially unaffected by changes on the 5 membered ring or C-7 side chain. The chemical shifts of C-13 and 14 do change considerable and are not reported here. The chemical shift of C-15 varies between 71.6 and 73.6 ppm and this is influenced somewhat by structural changes in the molecule. The standard deviations in the chemical
shifts of C-16 and C-17 are 3 and 2 times larger than expected and probably reflect some dependence on the structure of the remainder of the molecule.

Sincerely,

Michael L. Maddox

MLM:lo


## Table I

### $^{13}$C Chemical Shifts (a)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>C-1</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>C-5</th>
<th>C-6</th>
<th>C-7</th>
<th>C-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-octyn-3-ol</td>
<td>62.06</td>
<td>84.91</td>
<td>72.48</td>
<td>37.53</td>
<td>24.65</td>
<td>31.38</td>
<td>22.52</td>
<td>13.91</td>
</tr>
<tr>
<td>1-octyn-3-ol, hydroxy</td>
<td>132.43</td>
<td>132.96</td>
<td>72.32</td>
<td>37.24</td>
<td>24.94</td>
<td>31.59</td>
<td>22.45</td>
<td>13.06</td>
</tr>
<tr>
<td>C-15 C-16 C-17</td>
<td>72.54</td>
<td>37.27</td>
<td>25.07</td>
<td>31.70</td>
<td>22.57</td>
<td>13.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25-15 hydroxy PG derivatives (b)</td>
<td>±0.47</td>
<td>±0.15</td>
<td>±0.10</td>
<td>±0.05</td>
<td>±0.06</td>
<td>±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cyclopentane carbons</td>
<td>44.51-C2, 39.13-C3, 29.56-C4, 37.91-C5</td>
</tr>
</tbody>
</table>

### Notes

a. Chemical shifts are reported with respect to internal TMS

b. Standard deviations
Dear Barry,

Rumens (1), in an otherwise useful reiteration of warnings about solvent effects on reference compounds, has somewhat misunderstood, or at least misrepresented the results of our study with Ed Engler of the camphor ASIS (2). It should be clear that our work is entirely based on reference-independent ASIS, obtained by the procedure subsequently labelled "\( \Delta \)-difference method" by Rumens and Krystynak (1). Such differential information was altogether sufficient for our work, which addressed itself solely to the origin of the ASIS phenomenon, and is thus completely free of internal reference problems.

Your blue and pink reminders came at the same time as the Green letter (3), which I also find a bit hard to take. I must therefore restate the obvious: in principle, site factors should be calculated for each and every polar site in a solute molecule. Camphor is a particularly simple case, because to a very good approximation one may consider the \( \text{C} = \text{O} \) group as the only such polar site. Green (3) looks at the \( \text{C} = \text{O} \) group in crotonaldehyde, a molecule in which it is conjugated to a carbon-carbon double bond. Clearly, in that case, the polar "site" extends from the negatively charged oxygen to the positively charged \( \beta \) carbon; there is considerable ambiguity in locating the radius vector for each proton in the molecule. If we accept that "the solute, bornanone, is rather curious in that the negatively-charged end of the molecular dipole is quite small and readily accessible, whereas the positive charge is more dispersed" (3), what should one say about the unfortunate choice of crotonaldehyde, in which the positive charge is fudged all over?
We have now completed our study of the $T_1$ relaxation times for the various carbon-13 nuclei of camphor in benzene solution. We find molecular reorientation to be isotropic and to proceed by small angular steps at 297 °K. At that temperature, the orientational correlation time is $2.1 \pm 0.7$ ps. At higher temperatures, there is a substantial spin-rotation component. The mean angle of rotation between collisions, as estimated from the angular momentum correlation time, increases to ca. 25 ° at 329 °K (4).

It was very nice seeing you in Aachen, and hearing about your affair with Lisa. Best regards,

Yours sincerely,

[Signature]

Pierre Laszlo

(3) R.D.Green, TAMU-NMR, 172-1.
Professor Bernard L. Shapiro  
TEXAS A & M UNIVERSITY  
College of Science-Department of Chemistry  
College Station, TEXAS, 77843 (U.S.A.)

Title: 1H-NMR study on a conformationally rigid thiolanonium cation.

Dear Professor Shapiro,

Thank You for the "blue"reminder. I am sending also my own "reminder": we receive, normally, the TAMUNN issues with two or three months of delay.

We have studied the compound I, where the trans ring fusion constrains the thiolane rigidly in the half-chair conformation. This conformational rigidity ensures for each of the α-ring protons a fixed torsional angle with respect to the "direction" of the lone pair on the sulfur, making this system a very useful model for testing the Wolfe-Czimandia theory.

Under conditions of base catalysis sulfonium cations are known to undergo ready H-D exchange at a position. The \( \text{CH}_3 \) group exchanges much faster than \( \text{S}-\text{CH}_2- \), however, of the four \( \alpha \) ring protons, one of them, \( H_2 \), exchanges relatively rapidly with specific rates \( 9 \times 10^{-5} \) and \( 5 \times 10^{-4} \) \( \text{l.m}^{-1} \text{sec}^{-1} \) at 59° and 75° respectively (\( \text{D}_2\text{O}/\text{NaOD} 1.7 \) or 1.2 \( \text{N} \)). Of the remaining protons, two, \( H_3 \) and \( H_4 \), appear to have approximately the same reactivity; the second of
der specific rates are, approximately, $7 \times 10^{-6}$ and $2 \times 10^{-5}$ at 75° and 85° respectively. Thus, the rate ratio between $H_2$ and $H_3$ (or $H_4$) is about 75.

The fourth proton, $H_4$, is less reactive still; its apparent exchange rate is about 2-3 times slower than that of $H_3$ of $H_4$, hence some 200 times slower than $H_2$. It appears, however, that the observed ratio is an upper limit, as pyramidal inversion (which interchanges $H_1$ with $H_2$) becomes competitive.

It is remarkable that exchange of $H_2$ and, respectively, $H_4$ is accompanied by a gradual change of the signals for $H_3$ and $H_4$, which eventually become doublets, indicating that $H_1, H_4$ and $H_2, H_3$ are geminal pairs.

The irradiation of $\Theta S-CH_3$ in a derivative of (I) with deuterium replacing $H_1, H_3$ and $H_4$ gave a n.o.e. of $15\pm1\%$ for $H_2$.

In the parent ring cation (II), the n.o.e. were $12\pm1\%$ for the cis protons and $2\pm1\%$ for the trans protons (I). As the conformation of the 5-membered ring appears to be the same in (I) and (II), the $15\%$ n.o.e. indicates that, in (I) also, $H_2$ and $\Theta S-CH_3$ are cis with respect to each other.

1) A.Garbesi, G.Barbarella, A.Fava - Chem.Comm. in press.

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Dear Professor Shapiro,

NMR of viscoelastic micellar solutions

In this letter we would like to describe some results we have obtained on the NMR of mixed surfactant solutions. It is well known that surfactant molecules aggregate to form micelles above a certain concentration in water. In these low viscosity micellar solutions the molecular motion is rapid and a high resolution spectrum is observed for the surfactant. We have been investigating the properties of micellar solutions containing mixtures of surfactants which differ from normal micellar solutions in that they exhibit viscoelastic properties.

In addition to making rheological measurements we have studied the high resolution and pulsed NMR of mixtures of the surfactants sodium dodecyl sulphate (n.C\textsubscript{12}H\textsubscript{25}SO\textsubscript{4}Na, SDS) and octyl trimethyl ammonium bromide (n.C\textsubscript{8}H\textsubscript{17}NMe\textsubscript{3}Br, C\textsubscript{8}TAB) in D\textsubscript{2}O. At the 5% surfactant level the phase behaviour is complex since two phase regions can occur; but in aqueous solutions which are viscoelastic we observe differential broadening of surfactant resonances, with line widths of up to 40 Hz. This broadening is independent of measurement frequency over the frequency range 60 - 220 MHz indicating that it is due to proton dipolar relaxation. Spin-lattice and spin-spin relaxation measurements by pulsed NMR show that the system is
not characterized by a single $T_1$ or $T_2$ value (non-exponential recovery/decay curves) and that the $T_1/T_2$ ratio is ca 50 with $T_1$ in the range $0.5 - 1.0$ s. We interpret these results as suggesting the presence of a wide distribution of correlation times ($\tau_c$) for surfactant molecular motions with $\tau_c$ taking values in the range $10^{-8} - 10^{-11}$ s. It appears to be impossible to account for this behaviour by the presence of only normal spherical micelles in the aqueous solution. We propose that in addition to the normal micelles, restricted cylindrical micelles also occur, in which the surfactant molecules have the long correlation time molecular motions.

Because only a single NMR spectrum is observed rapid exchange ($>10^{-8}$ s$^{-1}$) of each surfactant molecule between the two environments must occur.

A more unusual situation occurs with aqueous mixtures of the surfactants SDS and hexadecylammoniopropene sulphonate $(n$-$C_{16}$-$H_{33}$-$N\left(Me\right)_2\left(CH_2\right)_3SO_3^{-}$, HDPS).

Some solutions of these surfactants above 2% total concentration are viscoelastic and show similar rheological and NMR properties to the SDS/C$_8$TAB solutions. In addition the properties of 1% solutions depend on their method of preparation. Samples prepared from 1% stock solutions of pure surfactants are similar to normal micellar solutions. Samples prepared by dilution of viscoelastic solutions with water initially exhibit viscoelastic properties and broadened NMR spectra, but these 'relax' over a period of hours or days to low viscosity normal micellar samples (see fig 1). We interpret this result as being due to the slow breakdown of the restricted micelles and the kinetics of this process (measured from NMR broadening) is first order in agreement with this. We are in the process of writing up these results for publication.

Yours sincerely,

P A WHEELER  
B A WHEELER  
G J T TIDDY
60 MHz HIGH RESOLUTION NMR SPECTRA OF A DILUTED VISCO-ELASTIC 5% HDPS/SDS SOLUTION
Spinning Liquid Crystal Solutions

The effect of sample rotation on the dipolar coupling constants is well known (1), but there are some misconceptions current about the effect on linewidths, and on ordering parameters. In a recent note (2) we discuss these latter effects under the somewhat obscure title of "Magnetohydrodynamic effects in nematic mesophases", and perhaps a more qualitative description will help those involved in studies of NMR spectra of partially aligned solutes.

Figure 1 shows the $^1$H spectrum from CH$_3$CN dissolved in Phase V at various spinning rates $w$. As $w$ increases the outer lines move towards the centre line, and they also tend to increase in width. This broadening increases very markedly as the critical speed $w_c$ is approached. Figure 2 shows the result of accurate measurements of the linewidth with rotation speed, and this trend to broader lines is clearly seen. There is in fact a slight decrease on going from $w=0$ to $w=w_c$, but this is overtaken by a broadening effect as $w$ increases. The increase with linewidth on rotating is in accord with theory (3), and a qualitative explanation is as follows. In a stationary sample the liquid crystal molecules are on average aligned at an angle $\theta$ to the magnetic field. On rotating, the angle $\theta$ increases and also acquires an uncertainty $\sigma_\theta$, giving rise to the line broadening. When $w$ is the liquid crystal molecules rotate about the spinning axis with a frequency $\omega_0^c = w$ and the outer components of the triplet broaden beyond detection. The centre line is unchanged, except for the effects of any chemical shift anisotropy, and remains sharp. Note that the sample is still anisotropic and the order is unchanged.
For solutes with lower symmetry the effects will be more complex since the lines depend on the ordering of the liquid crystal in different ways. For all solutes, however, we can state that in the absence of other effects (temperature or concentration gradients) rotating the sample will lead to broadening of some lines, and rapid rotation does not destroy the ordering.

Best wishes,

Jim

J. W. Emsley

References


Fig 1. Spectrum of CH$_3$CN in a nematic phase recorded at different spinning speeds.
Fig 2. 

$W = \text{linewidth at spinning speed } \Omega$ 

$A_0 = \text{Dipolar splitting at zero } \Omega$ 

$\Omega_c = \text{Critical spinning speed}$ 

$+$ and $\square$ refer to two separate samples.
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Dr. B. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77845

Title: More on Imidazole–N-H, $^{13}$C, $^{19}$F

Dear Barry:

Imidazole is the only amino acid residue which usually has a pK around neutrality, it is known to be involved in the mechanisms of several enzymes and its unusual chemical properties result in its NMR resonances being well resolved from others within a protein as well as giving rise to NMR titration curves. For these reasons we have been studying imidazole and its derivatives in some detail.

An unusual downfield titrating resonance of ribonuclease A in H$_2$O was described by Patel, Woodward and Bovey (1) which they attributed to an imidazole NH resonance. We have studied this resonance under several experimental conditions and have correlated it with one of the four imidazole C2-H resonances. For example, the figure shows the titrations of the NH resonance and three of the C2-H resonances carried out on the same sample in H$_2$O. As one can see the N-H resonance correlates only with resonance H-3. Further details will be described elsewhere (2).

We have recently reported the carbon-13 NMR titration curves of histidine (3) and are extending this to the (1-15) peptide of ribonuclease, as we have done previously using $^{13}$C enriched phenylalanine (4). We have also studied the $^{19}$F and $^1$H NMR of 2- and 4- fluoro-imidazole and histidine as a function of pH with some very interesting results (5).

Our Varian 220 FT system has been up and running since installation. With the expected S/N improvement over CW mode – more, as well as better, data for proteins are achieved.

With best regards,

Jack S. Cohen  
Physical Sciences Laboratory
References:


Figure Legend: PMR titration of RNase A in 0.1 M NaCl, H₂O at 22°. Chemical shift changes of the NH resonance are normalized with the chemical shift changes of the C2-H resonances to facilitate comparison.
Chemical shift (ppm) vs. pH

- C2-H (O, Δ, □)
- N-H (●)

pH range: 3.0 to 9.0

Chemical shift range: 7.5 to 8.7
April 10, 1973

OHOR/1590/Schr

Prof. B. L. Shapiro,
Department of Chemistry,
Texas A. & M. University,
COLLEGE STATION,
Texas 77843,
U.S.A.

Is there any nuclear Overhauser effect of OH proton in ortho-methoxyphenol?

Dear Professor Shapiro:

Recently we had to choose between the structures A and B for a compound.

\[
\begin{align*}
\text{A} & : \quad \text{(a)MeO} \\
\text{B} & : \quad \text{(a)MeO} \\
\end{align*}
\]

The \( ^1H \)-NMR spectrum of the compound consists of five lines at: 11.02, 7.45, 6.52, 3.95, and 3.38 ppm assigned to OH, H(1), H(2), Me(1), and Me(2) protons, resp.

The NOE results (% of enhancement) are:

<table>
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<th>H(1)</th>
<th>H(2)</th>
<th>OH</th>
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<td>Irradiated</td>
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<tr>
<td>Me(1)</td>
<td>0</td>
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<td>Me(2)</td>
<td>20%</td>
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<tr>
<td>OH</td>
<td>0</td>
<td>0</td>
<td>X</td>
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The twenty percent NOE enhancement allows to assign Me lines (employing the assignment of ring protons based on substituent increments; shifts calculated for H(a) 7.56 and H(b) 6.42\(\delta\): Me(1) and Me(2) lines belong to Me(b) and Me(a), resp. The nil effect observed on OH line would point to the structure A but caution called for additional experiments with model compounds.

NOE on guaiacol (o-methoxyphenol) gave also nil enhancement for the OH line! (Though NOE on ring protons was observed.) Apparently the scalar relaxation or unfavourable geometry reduced the effect.

So, after all, we had to resort to old familiar OH proton chemical shifts which are in o-nitrophenol in the region of 11\(\delta\) and in o-methoxyphenol around 5\(\delta\). Therefore the compound has the structure A (in agreement with the nil NOE!).

Sincerely yours,

J. Schraml  J. Dédina  W.S. El-hamouly
April 12, 1973

Professor Barry Shapiro  
Chemistry Department  
Texas A and M University  
College Station, Texas

TITLE: Post-doctoral and Industrial NMR Openings Plus an Address Change

Dear Barry:

This September I will be leaving General Electric and joining the chemistry department faculty at Florida State University. This move will generate two openings: my present position at GE and also a Post-doctoral appointment at Florida State University.

INDUSTRY - At the General Electric Research and Development Center we will have a staff opening for a Ph.D. chemist with experience in multi-nuclei nmr who is primarily interested in applying spectroscopic techniques to deal with organic and organometallic structure-mechanism problems. The position requires independent support for the research of, as well as consultation with, 30-40 organic chemists. NMR instrumentation includes a Varian XL-100-15 and two T-60 spectrometers.

ACADEMIC - The new nmr facility at FSU consists of two FT spectrometer systems: a Bruker HFX-90 and a Bruker HX-270, each interfaced to Nicolet 1080 series computers. The spectrometers are run by a technical supervisor and technician. This post-doctoral position will thus not require routine running of service samples.

The appointment will involve research in the area of carbon-13 spin-lattice relaxation studies and their applications to physical chemical problems. A physical chemist or physical-organic
Professor Barry Shapiro

April 12, 1973

chemist interested in molecular dynamics should find this experience very rewarding.

HOW TO APPLY: Whether you are interested in the Industrial or Academic position (or both!) send your resume to me at General Electric. Starting dates for the two positions are after July 1 (GE) and after September 15 (FSU).

Yours sincerely,

Dr. G. C. Levy
Corporate Research & Development
General Electric Company
Post Office Box 8
Schenectady, New York 12301

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CANADA Merck Sharp & Dohme Canada Limited, Isotope Division P.O. Box 899, Pointe Claire, Dorval 700, Quebec.
April 19, 1973

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

Dear Barry:

**PDIGM: A computer program for the simulation of LIS spectra.**

After several months of cleaning up the program we developed for the interpretation of LIS data we are ready to distribute it. It is written in Fortran IV. Requests should be addressed to Ray Davis as noted at the bottom of the letter.

The program is essentially the one described in *J. Amer. Chem. Soc.*, 94, 1742 (1972). It accepts as input the coordinates of the atoms in the molecule under investigation, the LIS shifts, and a variety of control characters. The output can be varied from stark (a few lines) to voluminous (reams) by the judicious use of the control parameters. In general we display all fits of reasonable agreement for all acceptable lanthanide positions, and find that the work-up of a single set of data requires a few seconds of computer time, and a thousand or so lines of output.

The approach uses a paradigm, hence the program name PDIGM. Its advantages and disadvantages become evident after one or two trial calculations. To those of you who are interested we say: "Try it. You'll like it."

Sincerely yours,

M. R. Willcott

R. E. Davis
Department of Chemistry
University of Texas at Austin
Austin, Texas 78712
Dear Professor Shapiro:

The phosphoranes, 1-3, were prepared by reaction of the appropriate phosphite with 3,4-bis(trifluoromethyl)1,2-dithietene. The relevant spectral data are tabulated below:

\[
\begin{align*}
\text{1} & : \quad ^{31}P \quad -16.5 \\
& \quad ^{19}F \quad 30^\circ \quad +54.2 \text{ doublet} \\
& \quad \quad -60^\circ \quad +52.7 \text{ doublet} \\
& \quad \quad \text{J}_{\text{PCCSP}} = 5.2 \text{ Hz} \\
\text{2} & : \quad ^{31}P \quad -12.5 \\
& \quad ^{19}F \quad 30^\circ \quad +54.1 \text{ doublet} \\
& \quad \quad 25^\circ \quad \text{coalescence temperature} \\
& \quad \quad -100^\circ \quad +52.38 \text{ double quartets} \\
& \quad \quad \text{J}_{\text{PCCSP}} = 3.6 \text{ Hz} \\
& \quad \quad \text{J}_{\text{FCCCCP}} = 11.0 \text{ Hz}
\end{align*}
\]
The results of the variable temperature $^{19}$F nmr experiments show that there is an intramolecular exchange process, which can be slowed sufficiently, on the nmr time scale, so that the trifluoromethyl groups in 2 and 3 become magnetically nonequivalent. This could not be demonstrated for 1; which showed no spectral changes on cooling.

These results can be explained in terms of intramolecular permutations, Berry pseudorotations, which allow the 5-membered di-oxygen containing rings to assume di-equatorial positions in the trigonal bipyramid. Alternatively a TR$^3$ process which bypasses these intermediates can be invoked. It has been reported that AS$^p$ for processes in which 5-membered di-oxygen containing rings go di-equatorial would fall in the range from 15.6 to 18.4 Kcal/mole. Using the method of coalescence temperatures and chemical shift differences at low temperatures one calculates energies of activation for such processes in 2 and 3 to be 14 and 12 Kcal/mole. However, these numbers are surely subject to large errors since the spectra display fine structure due to spin-spin coupling.

We are planning to do the line shape analyses to derive accurate thermodynamic parameters. These data will be of interest because they will illustrate further the effect of strain on pseudorotational processes.

Sincerely,

Dorothy Z. Denney

Norman J. De'ath

Subject: Structural Effects on Pseudorotation Rates.

(2) $^{31}$P shifts relative to $^{35}$% H PO$_4$. $^{19}$F shifts relative to CClF.

Professor B. L. Shapiro,
Texas A and M University,
College of Science,
College Station,
Texas,
U. S. A. 77843

Dear Professor Shapiro:

Since this is my first contribution to the TAMU NMR Newsletter I decided to confine myself to a brief description of the research activities and equipment in my laboratory.

We are using a Bruker variable frequency (4-60 MHz) pulsed spectrometer with an 18" Bruker magnet. The equipment was purchased in 1969, including the 18" magnet and a 1062 Fabricek signal averager. I knew we would eventually want to have Fourier Transform capability and felt this was the most versatile route. We have, over the last few years, managed to scrape together the high resolution accessories and are about to take off with variable frequency Fourier transform, having interfaced our signal averager (now a 1072) with a Sigma 5 computer in the Building. Our high resolution work is done at the Canadian 220 MHz NMR Centre which is located at Sheridan Park, just outside Toronto.

There are four problems of major interest to me at the moment.

1. Study of the 220 MHz high resolution proton spectrum of an enzyme from bacteriophage & (endolysin) and a series of temperature sensitive mutant forms of this enzyme. This is a basic study of primary structure influences on secondary and tertiary structure stability.

2. Proton relaxation enhancement (PRE) studies of a Mn²⁺ requiring allosteric enzyme from Salmonella - phosphoenolpyruvate carboxylase.

3. Structure function relationships of Con canavalin A, a metal requiring plant protein which binds to animal cell surfaces and shows differential effects with normal and malignant cells. We have examined the 220 MHz proton spectrum of the protein and the PRE of the solvent and sugars which bind to Con A.
4. Cell water proton relaxation time measurements of normal tissue, malignant tissues, and cultured cells with a view to understanding the possible role of water structure changes in malignancy and a variety of other abnormal and normal growth and differentiation conditions.

In solvent exchange studies with macromolecules, the ability to measure both $T_1$ and $T_2$ as a function of frequency has proved mandatory to adequate analysis. The variable frequency F. T. system will permit us, to some extent, to apply this type of analysis to single lines in the more complex spectra of the low molecular weight compounds which interact with the proteins we are studying.

Yours sincerely,

J. P. Carver, Ph.D.,
Assistant Professor.

Suggested Title: "NMR at the Faculty of Medicine, University of Toronto".
Your FT nmr system can provide results like these!

Spectra obtained on a Varian XL-100 Spectrometer with a TTI-1010 Fourier Transform Accessory.

DODECYL ALCOHOL
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32 Points per Spectrum
Inversion—Recovery Pulse Sequence ... \(T-180°-T-90°\)-Sample...

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After all spectra are obtained, they are processed all at once and displayed or plotted as shown. The spin-lattice relaxation times of each line can be estimated from the plots or calculated using a least squares treatment, from the equation 

\[ A = A_0 \left[1 - 2 \exp \left(-T/T_1\right)\right], \]

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Why not investigate the features of the 1080 Data System and find out how it can make your nmr spectrometer perform more efficiently.


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Nicolet Instrument Corporation
8329 Varona Road, Madison, Wisconsin 53711
Phone 608/273-3332 TWX: 910-336-5718
NON-EXPONENTIAL METHYL NUCLEAR RELAXATION FOR MACROMOLECULES

Dear Barry,

We have been interested in the NMR relaxation times of a methyl group on a macromolecule as a probe of flexibility at the site of the methyl group; specifically, we have now collected data on a number of arginine and lysine analogs as inhibitors of the enzyme, trypsin. We knew that non-exponential relaxation had been predicted\(^1\) and observed\(^2\) for solids, but was much less important for small molecules in liquids. Macromolecules might be expected to lie somewhere in between, so to settle the matter, we have extended Hubbard's\(^3\) treatment of intra-molecular dipole-dipole relaxation for a methyl group to the non-extreme-narrowed limit, \(4\omega_0 T_c > 1\). The details will appear in J. Mag. Res. (preprints are available on request), and the net outcome is shown in Figure 1.

A number of features deserve comment. First, both longitudinal and transverse relaxation become exponential for a spherical macromolecule (curve "P" in each plot). Second, in the "fast-motion" or "extreme-narrowing" limit, \(4\omega_0 T_c \ll 1\), the longitudinal ("\(T_1\)") and transverse ("\(T_2\)") relaxation become identical, even though the resultant can still be markedly non-exponential; this result is a generalization of the usual statement that \(T_1 = T_2\) under extreme narrowing conditions. (see plot a). Third, relaxation immediately following a 90\(^\circ\) or 180\(^\circ\) pulse approaches a single exponential—one would have to wait a couple of time constants in order to discover the non-exponentiality of the magnetization time-dependence.

In conclusion, it appears (as expected) that non-exponential methyl relaxation is most pronounced when internal rotation is rapid compared to isotropic tumbling of the molecular frame itself, and that the non-exponentiality for a macromolecule is intermediate between that of a small molecule and a solid. Practically speaking, any non-exponential effect would be difficult to observe experimentally, because both spin-rotation and inter-molecular effects would contribute exponential relaxation which might well mask any non-exponential effect. Finally, CF\(_3\) relaxation may also be non-exponential, but because of cross-correlation between different relaxation mechanisms—this problem is under attention and should be solved shortly.

Sincerely,

Alan G. Marshall and Lawrence G. Werbelow

FIGURE 1. Plots of log(magnetization) versus time, following a \( \Theta \)-pulse along the \( y \)-axis of a rotating frame, for a methyl group attached along the symmetry axis of a symmetric top molecule.

For plots 1b and 1d,
\[
\tilde{\xi}(t) = \frac{\langle I_z \rangle - \langle I_z \rangle_0}{(\cos \theta - 1) \langle I_z \rangle_0} ;
\]

for plots 1c and 1e,
\[
\tilde{\xi}(t) = \frac{\langle I_x \rangle}{\sin \theta \langle I_z \rangle_0} ;
\]

for plot 1a, longitudinal = transverse magnetization = \( \xi(t) \).

All rotational motion is taken as diffusional, with diffusion constants \( D_{\|}, D_{\perp} \), and \( D_{\text{int}} \) for rotational diffusion of the molecule about its symmetry axis, perpendicular to its symmetry axis, and for internal rotation of the methyl group, respectively. [Note that \( D_{\|} \) and \( D_{\text{int}} \) contribute in the same way to the net motion of the methyl group, and thus appear together as \( (D_{\|} + D_{\text{int}}) \) in the treatment.] Plot a corresponds to a small molecule, plots b and c to a macromolecule of molecular weight about 15,000, and plots d and e to a macromolecule of molecular weight about 150,000. Curves P, Q, \( \cdots \) V, correspond to either increasing ellipticity or increasing rate of internal rotation: respective values of \( [(D_{\|} + D_{\text{int}})/D_{\perp}] = 1, 7/4, 4, 6, 10, 20, \) and 100.

All calculations were based on a 100MHz resonance (\( \omega_0 = 2\pi \times 10^8 \text{ sec}^{-1} \)), and a proton-proton distance of 1.8 \( \text{Å} \) in the methyl group.
Additivity of Substituent Effects on the Proton-proton Coupling Constants of Disubstituted Pyridines

Dear Professor Shapiro,

We have recently completed a study of the proton-proton coupling constants of several mono- and disubstituted pyridines. From the J constants of pyridine and monosubstituted pyridines we have calculated the effects of several substituents. Assuming an additivity relationship when two of these substituents are present in the same molecule, we have also calculated the spin-spin coupling constants for all disubstituted pyridines. The experimental values of these constants are in very good agreement with those calculated using the additivity relationships. These results are shown in Table I.

Sincerely yours,

K.R. Contreras

D. G. de Kowalewski
<table>
<thead>
<tr>
<th>Substituents</th>
<th>$J_{34}^{\text{exp.}}$</th>
<th>$J_{34}^{\text{calc.}}$</th>
<th>$J_{35}^{\text{exp.}}$</th>
<th>$J_{35}^{\text{calc.}}$</th>
<th>$J_{45}^{\text{exp.}}$</th>
<th>$J_{45}^{\text{calc.}}$</th>
<th>RMS $J_{34}^{\text{exp.}}$</th>
<th>RMS $J_{34}^{\text{calc.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-CH$_3$-6-CH$_3$</td>
<td>7.75</td>
<td>7.77</td>
<td>1.09</td>
<td>1.11</td>
<td>7.72</td>
<td>7.68</td>
<td>0.007</td>
<td>0.043</td>
</tr>
<tr>
<td>2-NH$_2$-6-CH$_3$</td>
<td>8.19</td>
<td>8.19</td>
<td>0.85</td>
<td>0.81</td>
<td>7.29</td>
<td>7.30</td>
<td>0.006</td>
<td>0.036</td>
</tr>
<tr>
<td>2,6-diNH$_2$</td>
<td>7.83</td>
<td>7.81</td>
<td>---</td>
<td>---</td>
<td>7.83</td>
<td>7.81</td>
<td>0.006</td>
<td>0.041</td>
</tr>
<tr>
<td>2,6-diCl</td>
<td>7.86</td>
<td>7.83</td>
<td>---</td>
<td>---</td>
<td>7.86</td>
<td>7.83</td>
<td>0.005</td>
<td>0.019</td>
</tr>
<tr>
<td>2-CN-6-CH$_3$</td>
<td>7.65</td>
<td>7.68</td>
<td>1.04</td>
<td>1.01</td>
<td>8.01</td>
<td>8.01</td>
<td>0.005</td>
<td>0.033</td>
</tr>
<tr>
<td>3,5-diBr</td>
<td>2.00</td>
<td>1.89</td>
<td>---</td>
<td>---</td>
<td>2.00</td>
<td>1.89</td>
<td>0.014</td>
<td>0.043</td>
</tr>
<tr>
<td>3,5-diCl</td>
<td>2.12</td>
<td>2.11</td>
<td>---</td>
<td>---</td>
<td>2.12</td>
<td>2.11</td>
<td>0.020</td>
<td>0.025</td>
</tr>
<tr>
<td>23-diCl</td>
<td>7.96</td>
<td>8.00</td>
<td>1.69</td>
<td>1.62</td>
<td>4.69</td>
<td>4.76</td>
<td>0.005</td>
<td>0.022</td>
</tr>
<tr>
<td>2-NH$_2$-3-CH$_3$</td>
<td>7.20</td>
<td>7.33</td>
<td>1.80</td>
<td>1.71</td>
<td>5.21</td>
<td>5.32</td>
<td>0.011</td>
<td>0.049</td>
</tr>
</tbody>
</table>
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For details, write the Instrument Division, Perkin-Elmer Corp., XXX Main Avenue, Norwalk, Conn. 06856.
Professor B. L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843  

CARBON-FLUORINE COUPLING CONSTANTS

Dear Barry:

Recently we have been looking at $^{13}$C chemical shifts and $^{13}$C-$^{19}$F coupling constants in some fluorocarbons and their derivatives. The values obtained for coupling constants include a number of features of particular interest. Our spectra were obtained on an XL-100 instrument in CW mode using time averaging with the Varian C-1024, mostly in 5 mm sample tubes with external lock.

For several typical trifluorovinyl compounds, the one-bond and two-bond couplings to the terminal carbon atom in the vinyl group are as follows, with the shifts for this carbon given in ppm from TMS:

<table>
<thead>
<tr>
<th></th>
<th>$^1J$, Hz</th>
<th>$^2J$, Hz</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CF$_2$=CF-CF$_2$Cl</td>
<td>294, 292</td>
<td>41</td>
</tr>
<tr>
<td>II</td>
<td>CF$_2$=CF-SCF$_3$</td>
<td>304, 285</td>
<td>50</td>
</tr>
</tbody>
</table>

In line with these compounds are data for a third one, from a paper by Hinton and Jacques to appear in the Journal of Magnetic Resonance:

|   | CF$_2$=CF-CH$_2$-CH$_2$Br | 286, 272 | 46 | 155 |

When the trifluorovinyl group is conjugated with a carbonyl, the values of $^1J$ become slightly larger and, surprisingly, become equal, whereas the two-bond couplings remain about the same:

|   | CF$_2$=CF-C(O)F | 304, 304 | 40 | 163 |
| V | CF$_2$=CF-C(O)OCH$_3$ | 299, 299 | 42 | 158 |
| VI | CF$_2$=CF-C(O)CF$_3$ | 301, 301 | 39 | 153 |

Comparison of the shifts indicates an effect of unshielding when an electronegative atom is attached to the carbonyl carbon.

The most striking aspect of the results is the large value of $^2J$ observed for certain carbons adjacent to the carbonyl group to a fluorine attached to the carbonyl in the acid fluoride function. Thus in compound IV,
the coupling of the middle carbon to the fluorine in the acid fluoride is 90 Hz. We also have indications (from satellites; the $^{13}$C spectrum has not yet been obtained) of a value of 93 Hz for the coupling between the starred atoms in C(O)F-CF$_2$-O-CF$_2$-C(O)F. On the other hand, we see no indication of an extraordinarily large coupling in C(O)F-(CF$_2$)$_4$-C(O)F.

Very large values of two-bond C-F couplings have a few precedents in the literature. Reuben and Demiel reported a value of -102.5 for trans-BrFC=CBrF although the corresponding cis compound was found to have a normal value of -35.8 Hz. Bacon and Gillespie reported values of 103.2 and 97.0 for C(O)F-C(O)F and C(O)Cl-C(O)F, respectively. One is tempted to speculate about some unusual type of overlap of the back end of the -C-F bonding orbital with an orbital of the alpha carbon, the effect of which is emphasized by steric constraints. That the large value in compound IV is not a mere result of modification of the C-C bond by conjugation is indicated by the very reasonable value of 31 Hz for the coupling of the carbonyl carbon to the fluorine alpha to it, a coupling which presumably is transmitted through the same C-C bond. At the same time, the one-bond coupling in the acid fluoride group of IV is unusual in that it is only 33 Hz in magnitude, a value some 30 Hz smaller than that typical of a fluorocarbon acid fluoride such as C(O)F-(CF$_2$)$_n$C(O)F.

The behavior of the long range coupling constants also includes some unusual features. In compound VI, the olefinic CF$_2$ carbon is coupled by about 1 Hz to the trifluoromethyl fluorines, over four bonds. In the same molecule, the trifluoromethyl carbon, in addition to the doubling of 288 Hz from one-bond coupling, shows a tripling of 3.5 Hz, from coupling to two of the three fluorines in the trifluorovinyl group—which two, we do not yet know. In this molecule, as well as in IV, the carbonyl carbon is coupled equally to the two fluorines in the CF$_2$ unit, whereas the two-bond coupling from the olefinic =CF—carbon to these fluorines is quite stereospecific, values in each molecule (as well as in III) being of the order of 20 and 40 Hz.

Our results thus raise many questions about the mechanism of C-F coupling, and at the same time they indicate that the magnitudes of the coupling constants are often more specific indicators of structural features of fluorocarbon derivatives than are the chemical shifts.

Sincerely yours,

Wallace S. Brey
Professor of Chemistry

WSB/ewh
Dear Barry:

Here is another so-so contribution:

Position open

We are looking for a recent Ph.D. with good background in practical and theoretical NMR spectroscopy. NMR activities of the Abt. Physikalische Messtechnik (Division of Spectroscopy) involve analytical studies as well as research in NMR spectroscopy and instrumentation, generated in the NMR Branch of this Division.

Some knowledge of German and an interest in biologically oriented problems are desirable, but by no means a must.

Instruments available are: XL-100/FT, HA-100, A-60 and EM-360.

Best wishes and regards.

Sincerely,

Ernest Lustig
Dr. B.L. Shapiro,
Dept. of Chemistry,
Texas A & M University,
College Station, Texas,
77843.

Dear Dr. Shapiro:

COMMENTS ON PINK SURPRISES AND J_{14}^{13} N-C

We were very much dismayed to receive a shocking pink letter within days of seeing our latest contribution in circulation. However, the primordial guilt complex being what it is - we offer a further communication.

During the recent $^{13}$C workshop we ran a series of organic compounds of nitrogen. Normally coupling to $^{14}$N is not observed because of quadrupole effects. Some notable exceptions are tetraalkyl ammonium salts and isonitriles, both having a considerable degree of symmetry about the nitrogen. It has been previously illustrated that nitrogen-carbon coupling is affected considerably by the presence of a lone pair of electrons on the N atom (using $^{15}$N derivatives). This causes problems in attempts to derive correlations of the Fermi-Contact type which have proved useful in C-C and CH couplings. The one in use$^1$ does not fit the C-N coupling data for the above mentioned derivatives, the isonitriles being usually dismissed as unusual because of the cylindrical N-cloud. Yet logically, following the carbon-carbon case and the work of Frei & Bernstein for example$^2$, these two derivatives should be prime candidates for an s-character relationship, because in neither does the nitrogen carry a lone pair to play havoc with such things as $\Delta E$.

We have found a linear J to s-character correlation between pairs such as tetramethylammonium halide and methylisonitrile which passes almost exactly through zero. Thus N-C(H$_3$) in these derivatives uses an sp$^3$ and an sp nitrogen respectively so the correlation has three points, through zero to 25% to 50%, and one can derive (correcting for $\gamma$)

$$S_{N-C} = (-)120J_{15}^{13}N$$

Using this equation one finds that J$_{CN}$ in acetonitrile is smaller than predicted - which seems to be the general effect of introducing a lone pair. The cyanide ion and the N=C coupling of the isonitriles are both believed to be of opposite sign to the couplings discussed above - and both contain lone pairs which are essentially delocalized over the entire group.
Substitution of methyl by ethyl & higher homologues makes $^{1}J_{CN}$ smaller in the two series of compounds by the same ratio, so that for each homologue a modified linear correlation is obtained. This type of substituent effect has been predicted for C-C and C-H coupling $^{3}$, but is almost never noticed.

N-bond contributions to the coupling also seem to stand out from the linear correlation (which is derived only from single C-N bonds).

Although we do not wish to profess any lasting faith in s-character pronouncements for nitrogen at this stage, we nonetheless find it intriguing that these two types of nitrogen compound – hitherto outsiders in any s-character correlations – should fit together so well with each other. All the more so because in each case the nitrogen is in a "carbon-like" situation and should therefore be expected to come nearest to exhibiting relationships similar to carbon. Again we thank Varian Associates for use of an NV-14 spectrometer.

Yours sincerely,


Comments on Comments on Pink Surprises!

We goofed. Sorry! It is, however, terribly nice to be able to help out with your primordial guilt complexes. When I grew up in Ontario, we couldn't afford such luxuries!
CONFORMATIONAL PREFERENCES IN ARYL SUBSTITUTED HETEROCYCLIC COMPOUNDS

In the course of n.m.r. studies of hindered rotation about aryl C-N bonds in aryl substituted heterocyclic compounds, we have been interested in factors influencing the equilibrium constants between diastereomeric rotational isomers. In particular, we have been looking at some 3-aryl substituted hydantoins and 2-thiohydantoins, such as 3-([o-bromophenyl])-5-methyl-2-thiohydantoin, I.

\[
\text{\textbf{(I)}}
\]

Compound I has an equilibrium constant of \(1.9 \pm 0.1\) in pyridine solution. In addition to having non-unity equilibrium constants, the compounds unsymmetrically substituted on C-5 show "abnormal" activation parameters.

Slow crystallization from methanol of the mixture of diastereomers of I produced on synthesis yielded only the thermodynamically less stable isomer (> 99%). Equilibration of this isomer over a range of temperatures was followed by the method previously described, except that the composition of the mixture was determined from the n.m.r. spectrum using a DuPont curve resolver. The following activation parameters were obtained (25°C): \(\Delta G^\ast = 25.2 \pm 0.1\) kcal/mol, \(\Delta H^\ast = 17.6 \pm 1.7\) kcal/mol, \(\Delta S^\ast = -25.5 \pm 5.2\) e.u.\(^1\)

Since it was not clear how the stereochemical information was being transmitted from the asymmetric centre at C-5 to the unsymmetrically substituted aryl group, and also since the steric relationships between the bromine atom and the C-5 methyl group in the two rotational isomers were unknown, an X-ray crystallographic study of the less stable isomer was carried out.
The crystal structure shows that, in the thermodynamically less stable rotamer, the bromine atom is transoid to the C-5 methyl group (see figure) and the heterocyclic ring is planar. This eliminates one of the possibilities suggested earlier, namely a puckered hetero ring.3

We may infer that, in the thermodynamically more stable rotamer, the bromine atom is cisoid to the methyl group. In order to explain this behaviour, we conclude that the more stable rotamer must be strongly solvated on the less hindered side of the molecule in pyridine solution. Examination of models indicates that the transoid (less stable) isomer is appreciably more hindered to close approach of solvent molecules on both sides of the solute molecule than is the cisoid (more stable) on the favoured side. Hence it appears that the thermodynamic preference results from differences in the energies of the solute-solvent interactions of the two rotamers in their ground states, and that the stereochemical information is, in effect, transmitted between the methyl and the aryl group by means of an unsymmetric solvent shell. We have observed that, in general, the thermodynamically less stable isomer is the less soluble isomer.

It would appear that the unexpectedly large negative entropies of activation that we have measured for this and related compounds result from differences in the extent of solvation in the ground and transition states for rotation about the aryl C-N bond. Steric hindrance to approach of solvent molecules should be much reduced in the nearly planar transition state for rotation of the solute molecule.

Yours sincerely,

L.D. Colebrook  H.G. Giles  P.H. Bird  A.R. Fraser

1. 90% confidence limits
2. TAMU NMR Newsletters, 143, 16 (1970).
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Dear Professor Shapiro,

\( ^{13} \text{C} \) NMR of hydrogenated polybutadienes

As part of an investigation into the microstructure of polybutadienes we measured the \( ^{13} \text{C} \) spectra of the corresponding hydrogenated products.

An empirical chemical shift formula derived for saturated hydrocarbons\(^1\) was applied to predict the resonance positions of the various carbon atoms in the polymer chain.

Fig. 2 depicts the \( ^{13} \text{C} \) spectra of three hydrogenated polybutadienes, III, IV and V, having 43\%, 64\% and 75\% of 1,2 structure (hanging ethyl groups), respectively. The \( \text{CH}_3 \) groups at 11 ppm relative to TMS are not indicated. The spectra were recorded on a Varian XL-100-15 (500 scans each spectrum).

The stick spectra show calculated chemical shifts\(^1\) and line intensities. In calculating the intensities we assumed a random distribution of 1,4 and 1,2 elements in the polymer chain.

The numbering of the \( ^{13} \text{C} \) lines refers to the following polyad sequences:

The broadness of lines 9 to 15 is due to tacticity effects within the 1,2 blocks.

Please credit this contribution to Dr. R. Prins.

Yours sincerely,

J.A.M. van Broekhoven  A.D.H. Clague

Amsterdam, 11 April 1973
\( ^{13}\text{C} \) NMR SPECTRA OF THREE HYDROGENATED POLYBUTADIENES IN CCl\(_4\)

Shifts are in ppm relative to TMS
THOMPSON-PACKARD
wrote the book on
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TITLE

COMPANY

ADDRESS

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Dear Barry:

Varian HA-100 owners have recently been circularised with a Tech Note on maintenance of the water cooling system. This is intended to supplement the maintenance procedures contained in the system instruction manual, and suggests the installation of a deionizer resin bed in the recirculating water where some of the water will flow through it continuously. The suggested installation is in series with the existing loop but we have set up an alternative parallel system which has the following advantages:

1. Installation of system and renewing resin can be carried out without interruption of secondary water flow which would necessitate turning off magnet power.

2. The improvement is resistivity and pH which is given by the resin can readily be monitored by before and after measurements. Reduction in resin activity will be easily observed.

3. It follows from (2) that the use of a less expensive resin instead of the variety which changes colour is possible. Our local "Culligan Man" provided the first batch free of charge. The strong base anion and cation resin costs $120 per cu. ft. for the first loading but is renewed at the rate of $7 per cu. ft.

4. For those without a transparent filter bowl it is less expensive to install.

The system depends on the use of an aquarium power filter Cat. #3 SF-520 made by the Biozonics Corporation, 15 Tech Circle, Natick, Massachusetts 01760 obtained by us for about $15 in a local pet store. The diagram shows the installation which depends on siphoning water out of the V-3520 reservoir and pumping it back in. Minor flooding
may take place during the setting up but once installed it is self regulating and should be "fail safe" for most foreseeable possibilities. The junction at the entrance to the reservoir may be spliced together with silicon rubber and tape, although others may consider glass or metal more suitable. Our arbitrary resistance measurement showed the following:

- tap water (town mains) = 20 K ohm
- distilled water = 80 K
- water in magnet before installation of "polisher" = 40 K
- after several days "polishing":
  - before resin = 600K
  - after resin = 700K

pH measurement by pH indicator paper was unreliable. With a poor instrument and/or poor technique it was not much better. However, with an experienced operator on a good pH meter the value was 7.3.

It is appreciated that the topic of this letter verges on a forbidden zone - the suggested title is

Polishing Water for Spectrometer Cooling Systems.

Yours sincerely,

R.A. Bell,
Associate Professor of Chemistry.

P.S. Please consider this a contribution from McMaster in the name of R.J. Gillespie.

Professors Bell and Gillespie:

While I am happy to include this contribution in the TAMU NMR Newsletter, I am afraid it must be on a "No Credit" basis. As you will note in our most recent Statement of Policies and Practical Considerations, the time has come when I feel that water cooling system considerations are no longer appropriate for credit as a technical part of ones subscription - as you so kindly suspected. I hope you can see this matter from our point of view.

All best regards,

B. L. Shapiro
Dear Professor Shapiro,

I would like to report here another result of our investigation on four-membered rings. All C-H and H-H coupling constants of thiete-sulphone have been measured from $^{13}C$, $^1H$ and $^{13}C$ satellites spectra, and sign determinations performed by tickling and triple resonance experiments. The results are listed below:

\[
\begin{align*}
\text{J}_{AX} &= +1.60 \\
\text{J}_{AM} &= -0.52 \\
\text{J}_{MX} &= +4.10 \\
\text{J}_{C4,H_A} &= +150.5 \\
\text{J}_{C3,H_X} &= +186.5 \\
\text{J}_{C2,H_M} &= +198.5 \\
\text{J}_{C4,H_X} &= +9.0 \\
\text{J}_{C2,H_X} &= +6.5 \\
\text{J}_{C3,H_A} &= -6.5 \\
\text{J}_{C3,H_M} &= +1.8 \\
\text{J}_{C2,H_A} &= +6.5 \\
\text{J}_{C4,H_M} &= +14.5 \\
\end{align*}
\]

In the triple resonance experiments, the decoupling frequency ($\nu_2$) was provided by the Gyrocode of the XL-100-15 Spectrometer, and the ti-
ckling frequency ($\nu_3$) by a Hewlett-Packard 4204 oscillator, which was connected to the Spectrometer through a directional coupler module placed between the output of the 94-100 MHz Power Amplifier and the Low Power Attenuator (figure 1). Thus the audiooscillator provided two modulation sidebands by $2(\nu_3 - \nu_2)$ Hz; one of them (the low field one) was used for tickling, whereas the central band of the Gyrocode, still remaining, was used for the decoupling.

The sign determination of $^2J_{C_3,H_M}$ relative to $^1J_{C_3,H_X}$ is given in figure 2, as an example. All the spectra were obtained in a single scan. Through the decoupling of the methylene A protons (a), the five-spin system, $A_2MX_{13}C$, is simplified to a three-spin $MX_{13}C$. Only the low field satellite of $H_X$ can be observed. $H_M$ inner satellites are then tickled, while $H_X$ outer satellites are observed, by exploring with the $\nu_3$ frequency a range of 10 Hz around $\nu_M$ by 0.1 Hz (b).

$X_1$ and $X_2$ lines are split, when $\nu_3 - \nu_2 = 235.8$ (irrad. $M_1$) and $232.0$ Hz (irrad. $M_3$). Considering that $^2J_{C_3,H_M} = 1.8$ Hz, the expected tickling frequencies are 235.8 and 231.7 Hz. The pairs $M_1, X_1$ $M_3, X_2$ result regressive, while the pairs $M_1, X_2$ and $M_3, X_1$ progressive. According to the energy level diagram, the one-bond and the two-bond couplings have the same signs.

1 We thank L. Hlavka, Varian (Palo Alto), who drew and made for us this module.

sincerely yours

(R. Mondelli)
SPIN DECOUPLER
POWER AMPLIFIER

6 POSITION RELAY

3db ATTEN

ATTEN

INSERT HERE

IN5139

82
01
820
10μh

TRIPLE RESONANCE NETWORK
$H_X$ low field outer satellites

$H_M$ inner satellites

$\delta_{SO_2}$

(b) 235.8 234.0 232.0 229.9 $\delta_3 - \delta_2$ (Hz)

(a) $X_1$ $X_2$ 8.269 4.568 ppm (x)

figure 2
May 2, 1973

Professor Barry L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843  
U.S.A.

A Convenient $T_1$ Sequence

Dear Barry:

We have recently examined the various sequences available for measuring spin-lattice relaxation times, $(T_1's)$. Although the $(180^\circ, \tau, 90^\circ, T)_n$ sequence appears to be the one most commonly employed, the novel "intensity ratio" method for the $(90^\circ, \tau, 90^\circ, T)_n$ sequence recently reported by Freeman, Hill and Kaptein\(^1\) appears to have certain advantages over the $(180^\circ, \tau, 90^\circ, T)_n$. This is especially true for nuclei with inherently low sensitivity (i.e., $^{13}C$) where $(S/N)$ per unit time is of the utmost concern.

Along similar lines we have been employing a $(90^\circ-X^\circ, \tau, 90^\circ-X^\circ, \tau)_n$ sequence ($X^\circ < 90^\circ$), with a fixed $\tau$ value and where $X^\circ$ is varied from one spectrum to the next to characterize the $T_1$ dependence. Using the same notations as Freeman, et.al.\(^1\), the expression for the ratio of signal intensities of a given line for two different spectra "a and b" obtained with two different "flip angles" is given below:

$$\frac{S_a}{S_b} = \frac{(1-k_bE_1) \beta_a}{(1-k_aE_1) \beta_b} \quad E_1 = e^{-\tau/T_1}$$

where the $\beta$'s and $k$'s are as previously defined by Freeman. The expression above when rearranged allows computer calculation of all pairwise data with different flip angles.

The $^{13}C$ spectra for the aromatic region of toluene shown in Fig. 1 were obtained with a $\tau$ value of 0.5 sec. and a mean random delay of 50 msec. with 1500 transients collected for each spectrum. The total experimental time for the ten spectra was two hours. The $T_1$ measurements were repeated using the $(180^\circ, \tau, 90^\circ, T)_n$ sequence with $T = 220$ sec. and 16 transients collected requiring a total time of 11.5 hours for the ten spectra!
Spectra a and b of Fig. 2 give a comparison of the (S/N) for the C1 carbon atom, (T1 ∼ 50 sec.) obtained for the equilibrium magnetization (M0), (τ = 220 sec.) for the (180°, τ, 90°, T)n experiment and the (90°-X°, τ, 90°-X°, τ)n experiment with X°=80°, respectively. The derived T1's were in generally good agreement for the two sequences.

An apparent advantage of the (90°-X°, τ, 90°-X°)n sequence in comparison with the (90°, τ, 90°, τ)n sequence is the ability to correct for the problem of the finite rf field (H1) in comparison with the spectral width, (ΔH). This correction enters into the above expression in terms of the β's and k's and is also implemented in the computer program. Another slight advantage could be one of (S/N) per unit time depending upon the τ values necessary to characterize the T1's in the (90°, τ, 90°, τ)n experiment. A more detailed report of this sequence is being submitted for publication.

Sincerely,

Harry C. Dorn
NMR Application Chemist

Figure 1

Sample: 95% Toluene (Aromatic Region)
5% C₆F₆
Sequence: (90°, r, 90°, r')n, r = 0.55 sec.
1500 Pulsed Per Sequence
Sampling Frequency: 4000 Hz
Transform Size: 4K
Total Time: ≈ 2 hr.
Figure 2

Toluene Carbon Atom C1

a, b

\[
\left(180^\circ - \gamma, \eta \right)_{\text{Experiment}}
\]

\[
\gamma = 220^\circ \sec, \quad \eta \text{ Mo}
\]

\[
\left(90^\circ - \theta, \varphi \right)_{\text{Experiment}}
\]

\[
\eta = 65^\circ \sec, \quad \varphi = 10^\circ
\]
I will have a position available for a postdoctoral fellow in my research group effective approximately 1 September 1973, and interested persons are invited to contact me. The position available should be filled by either: (a) someone with extensive NMR experience, preferably with FT hardware, or (b) someone who might have less (but still significant) NMR experience but with a very strong background in organic synthesis, or preferably (c) someone with both types of qualifications. We are an equal opportunity employer, and applications from women and members of minority groups are particularly welcomed. Only in an exceptional case will it be possible to consider someone who is not a U.S. citizen.

All inquiries will be promptly acknowledged and held in complete confidence. Initial inquiries should include a complete vita and at least two names of people who will provide letters of reference, if such become appropriate.

Address all inquiries to:

Professor B. L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843
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