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August 24, 1982

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

Dear Barry,

Assignment of Some $^{13}$C NMR Chemical Shifts

A compound with beta-lysine was submitted for $^{13}$C NMR analysis. In an attempt to assign all carbons a sample of beta-lysine 1 was also titrated in D$_2$O. Table I shows the titration values of 1. The titration curve does not clearly assign C-4 and C-5 of 1 since they both have beta shifts. A literature search notes conflicting assignments. In 1 C-4 is assigned to the 23 ppm resonance and C-5 to the 29 ppm resonance. In 2 these assignments are reversed. Recently an acylated derivative of the original compound was submitted for analysis. Since $^{13}$C NMR chemical shifts are now available for the compound without beta-lysine, a titration curve of the sample showed that the acetyl group was attached to the amino group at C-3 of beta-lysine. The titration values for the 3-N-acetyl-beta-lysine group are shown in Table II. Since C-2 and C-4 showed no beta shifts, it is now clear that in beta-lysine C-5 is the resonance at 23 ppm and C-4 is the resonance at 29 pm at an acid pD. Therefore the assignments in 2 are the correct ones.

Sincerely yours,

Ruth Stanaszek

1 JOC 43, 1282 (1977).
August 24, 1982

\[
\begin{align*}
\text{NH}_2-\text{CH-CH}_2-\text{COOH} \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\end{align*}
\]

Table I

<table>
<thead>
<tr>
<th>Assignment</th>
<th>pD</th>
<th>9.8</th>
<th>9.6</th>
<th>8.9</th>
<th>4.4</th>
<th>3.8</th>
<th>Beta Shift</th>
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<tr>
<td>C-2</td>
<td>43.2</td>
<td>42.1</td>
<td>40.4</td>
<td>38.9</td>
<td>38.8</td>
<td>-4.9</td>
<td></td>
</tr>
<tr>
<td>C-3</td>
<td>49.3</td>
<td>49.4</td>
<td>49.5</td>
<td>49.6</td>
<td>49.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-4</td>
<td>32.3</td>
<td>31.6</td>
<td>30.7</td>
<td>29.9</td>
<td>29.9</td>
<td>-2.3</td>
<td></td>
</tr>
<tr>
<td>C-5</td>
<td>25.0</td>
<td>24.6</td>
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<td>23.7</td>
<td>23.7</td>
<td>-1.3</td>
<td></td>
</tr>
<tr>
<td>C-6</td>
<td>40.3</td>
<td>40.2</td>
<td>39.9</td>
<td>39.8</td>
<td>39.8</td>
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</table>

Table II

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<th>pD</th>
<th>12.3</th>
<th>9.6</th>
<th>8.0</th>
<th>6.3</th>
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<td>C-2</td>
<td>42.3</td>
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<tr>
<td>C-3</td>
<td>48.1</td>
<td>47.7</td>
<td>47.7</td>
<td>47.8</td>
<td>47.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-4</td>
<td>32.1</td>
<td>31.8</td>
<td>31.8</td>
<td>32.0</td>
<td>32.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-5</td>
<td>28.3</td>
<td>24.7</td>
<td>24.2</td>
<td>25.4</td>
<td>25.6</td>
<td>-2.7</td>
<td></td>
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<tr>
<td>C-6</td>
<td>40.9</td>
<td>40.0</td>
<td>39.9</td>
<td>40.0</td>
<td>40.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
14 September 1982

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

Dear Professor Shapiro

A RABBIT for breeding NOE's

It is my privilege to announce a new advance in animal husbandry which will be of interest to all those who do NOE experiments on small molecules.

We have been using kinetic NOE's to measure interatomic distances and to probe conformational equilibria, but the long $T_1$ values and slow NOE growth rates demanded painfully long relaxation delays. It took all night to do a simple kinetic NOE experiment. The reason is clear from eqn. 1 which shows that $\rho$ is proportional to the rotational correlation time $\tau_C$:

$$\rho_{dd} \propto \tau_C \cdot \tau^{-6}$$

Small molecules have short $\tau_C$ and so breed NOE's slowly.

Much impressed by the fecundity of rabbits we have attempted to emulate their example in the nmr tube. The necessary genetic engineering is indicated below.

\[ \text{short } \tau_C \rightarrow \text{long } \tau_C \]

\[ \text{slow } \rho \rightarrow \text{fast } \rho \]
In practice, this transformation is most easily achieved by binding the molecule of interest to a diamagnetic reagent such as La(FOD)₃, metallopehryrin, cyclodextrin, etc. τ₀ in the adduct is longer, τ₂ is bigger and T₁ is shorter. As a result, the NOE's grow faster and sometimes end up larger because τ₂ competes better against O₂ and rust particles. The figure below shows one example: the time saving for a given S/N for the NOE after 1 second irradiation is sixfold.

We hope to publish more examples soon. RABBIT is Relaxation Aided By Binding Tightly.

As usual,¹⁻³ the work was done by John Mersh.

Yours sincerely

J K M Sanders

2. SUDSY : TAMUNMR, January 82 & J. Magn. Reson., Nov. 82
13 September, 1982

Dr. Barry L. Shapiro
Department of Chemistry
Texas A and M
College Station, TX 77843

PARAMAGNETIC EFFECTS ON DEUTERIUM RELAXATION

Dear Barry,

Sorry about the delay, and the dreaded pink sheet.

We have been applying deuterium NMR to protein dynamics in solution, by studying motional narrowing of 2H resonances. Since we are primarily interested in paramagnetic proteins, nonquadrupolar 2H relaxation must be accounted for and excluded. Quadrupolar relaxation should be least effective for a deuterated methyl group, due to fast internal motion, and the quadrupolar spin-lattice relaxation should be much slower than the spin-spin relaxation as \( \omega_0 T_{1m} > 1 \) (\( \Theta 55 \text{ MHz} \)).

We measured the 2H \( T_1 \) of the deuterated methyls in 1,3-\( d_6 \) sperm whale metmyoglobin to be 49 ms; the corresponding proton \( T_1 \) is 3.8 ms. Upon addition of CN\(^-\) to yield the low spin form of the protein, the 2H \( T_1 \) was 73 ms; the proton \( T_1 \) is 100 ms. Simply scaling the \( T_1 \) rates by 1/42.4 and subtracting yields quadrupolar \( T_1 \)'s that are with 4% of each other. Thus scaling proton relaxation rates by the ratio of the \( y \)'s, to get the deuterium nonquadrupolar rates, seems to work well in this system.

We are interested in protein side chain dynamics in heme proteins; the deuterated hemins are synthesized by Professor Kevin Smith and his group.

Sincerely,

Robert D. Johnson
Gerd N. La Mar
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GX Report #2

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Professor B.L. Shapiro,
Department of Chemistry,
TEXAS A and M UNIVERSITY,
College Station,
Texas,
UNITED STATES OF AMERICA.

Dear Barry,

N.A.T.O. ADVANCED STUDY INSTITUTE ON N.M.R. OF LIQUID CRYSTALS

The above Advanced Study Institute will be held from 26th July to 7th August at San Miniato, a Tuscan village about 40 kms from Florence and Pisa. We aim to cover the whole range of the application of N.M.R. to studying oriented liquids including the determination of geometries of small molecules dissolved in liquid crystals, the characterization of order and structure in pure mesophases (thermotropics, lyotropics, discotics, membranes), and the study of dynamical behaviour.

The lectures will be given by N. Boden, J. Charvolin, P. Diehl, J.W. Doane, G.R. Luckhurst, Z. Luz, A. Pines, I.C.P. Smith, R.L. Vold, R.R. Vold, C. Zannoni and the two directors (myself and Carlo Veracini). Attendance at the Institute will be limited to about seventy students, who should preferably be engaged in the study of oriented systems. The cost of food and accommodation for the school will be of the order of $450.

Intending participants from N.A.T.O. countries may apply for a grant to cover a part of the accommodation costs. Those interested in receiving further details of the Advanced Study Institute should write to me.

Best wishes,

Jim.

J.W. EMSLEY.
Dear Barry,

the well known spin echo experiment can be applied with various types of broadband decoupling. We used the following sequence:

C-13: \[ \text{Delay} - \frac{\pi}{2} - \tau - \pi - \tau - \text{AQUISITION} \]

H-1: \[ \text{BB}(-15\text{dB}) | \quad \text{BB}(-5\text{dB}) \]

The J-modulated spin echo (JMSE) transforms signal multiplicities due to heteronuclear coupling to intensity modulations of the entire BB-decoupled resonance signal. Many applications with \( ^1J_{\text{CH}} = 125 \text{ Hz} \) have been reported. In special systems e.g. chloroalkanes, with \( ^1J_{\text{CH}} = 125 \text{ Hz} \) and \( ^1J_{\text{CHCl}} = 150 \text{ Hz} \), intensity modulations of resonance signals can be calculated as shown in fig. 1 for -CH- and -CHCl-. JMSE enables selective assignments of structural moieties by resonance signals of zero intensity. This procedure is time saving in comparison to a full 2D-experiment. However, it is limited to systems with definite coupling constants different by at least 5 Hz. Application is demonstrated in fig. 2 by JMSE spectra of 2,4-dichloro pentane taken at suitable \( \tau \).

Best regards
Your sincerely

[Signature]

(Prof. Dr. R. Kosfeld)

[Signature]

(Dr. K.-F. Elgert)
Fig. 2
C-13 nmr spectrum of 2,4-dichloro pentane

\[
\begin{align*}
\text{C}_1 & - \; \text{C}_2 - \; \text{C}_3 - \; \text{C} - \; \text{C} \\
& \text{Cl} \; \text{Cl} \\
\end{align*}
\]

(mixture of diastereomers)

a) broad band decoupled
b) - e) JMSE spectra with \( \tau = 8, 10, 12, 20 \) msec, resp.
X = solvent, CDCl₃
BRUKER WM 300, pulse repetition: 60 sec, pulse width: 17.3 μsec, pulse sequence generated by multipulser unit
Dear Professor Shapiro,

The great sensitivity gain of the INEPT sequence (1) is now well established and looks very attractive for the relaxation measurements of insensitive nuclei such as $^{15}$N. We have developed a method derived from INEPT (2) leading to the "antisymmetric" $^{15}$N $T_1$ a new parameter useful for peptides conformational analysis. The models chosen are $^{15}$N enriched (90%) enkephalin derivatives: Tyr-$^*$Gly-$^*$Gly-$^*$Phe, I, Boc-Tyr-$^*$Gly-$^*$Gly-$^*$Phe-OCH$_3$, II, and Tyr-$^*$Gly-$^*$Gly-$^*$Phe-$^*$Leu, III. If one considers in the peptide backbone each $^{15}$N and its $^1$H linked nucleus independently AX spin-systems ($A = ^{15}$N, $X = ^1$H), three observable parameters can be measured for each one: the total magnetization related to the symmetric $T_1^S$ for both nitrogen, $M_N$, and proton, $M_H$, and the intensity difference within each doublet $M_{NH}$, related to the antisymmetric $T_1^A$ (3).

Figure 1.

Pulse sequence used for relaxation measurements. 
A: Symmetric $T_1$ (Freeman-Hill method).
B: Antisymmetric $T_1$ (slightly modified INEPT sequence).
- $^{15}$N 180° pulse = 42 µs;
- $^1$H 180° pulse = 400 µs.
A sequence excitation (B) is proposed to measure \( T_1^a \) and compared with the sequence for measurement of the conventional \( T_1^s \) (A). The sequence A is characterized by \(^1H\) broad-band irradiation during the evolution period \( T_b \) whereas such irradiation does not occur in the sequence B. By contrast the \( T_1^a \) are obtained by using an excitation sequence based on the spin-echo polarization transfer method (INEPT) firstly described by Morris and Freeman. The original INEPT sequence which creates a \(^{15}N\) magnetization in the x-y plane by a \(^{15}N\) modulated proton spin-echo is just altered by suppressing the second \(^{15}N\) 90° pulse (Figure 1.).

After the INEPT excitation the two components of the \(^{15}N\) doublet are enhanced but in the opposite direction. Therefore the modified pulse excitation allows to observe the recovery (along the x-axis) of the magnetization-difference between the two components of the doublet for \( T_b \) (Figure 2.). As expected, in each peptide models \( T_1^s \) and \( T_1^a \) values differ one from each other as shown in Table 1. Moreover a large variation range in the \( T_1^a \) appears in free peptides what is not the case of the protected one according to large differences in conformational flexibility occurring in these compounds (4).
Table 1. $^{15}$N symmetric $T_1^S$ and antisymmetric $T_1^A$ spin-lattice relaxation times (in sec) at 310 K for compounds: Tyr-*Gly-*Gly-*Phe, I, Boc-Tyr-*Gly-*Gly-*Phe-OCH$_3$, II, and Tyr-*Gly-*Gly-*Phe-*Leu, III.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Residue</th>
<th>$T_1^S$</th>
<th>$T_1^A$</th>
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<tr>
<td>I</td>
<td>Gly$^2$</td>
<td>0.95</td>
<td>0.028</td>
</tr>
<tr>
<td>I</td>
<td>Gly$^3$</td>
<td>0.95</td>
<td>0.34</td>
</tr>
<tr>
<td>I</td>
<td>Phe$^4$</td>
<td>0.85</td>
<td>0.22</td>
</tr>
<tr>
<td>II</td>
<td>Gly$^2$</td>
<td>1.35</td>
<td>0.54</td>
</tr>
<tr>
<td>II</td>
<td>Gly$^3$</td>
<td>1.40</td>
<td>0.61</td>
</tr>
<tr>
<td>II</td>
<td>Phe$^4$</td>
<td>1.60</td>
<td>0.78</td>
</tr>
<tr>
<td>II</td>
<td>Gly$^2$</td>
<td>1.15</td>
<td>0.028</td>
</tr>
<tr>
<td>III</td>
<td>Gly$^3$</td>
<td>1.15</td>
<td>0.52</td>
</tr>
<tr>
<td>III</td>
<td>Phe$^4$</td>
<td>0.90</td>
<td>0.47</td>
</tr>
<tr>
<td>III</td>
<td>Leu$^5$</td>
<td>0.90</td>
<td>0.41</td>
</tr>
</tbody>
</table>

$^a$) $T_1$ have internal estimated error less than 10% (90% confidence interval), except for the Gly$^2$ $T_1$'s in the free peptides (~20%).

Sincerely yours.

D. Marion

Dominique MARION Christiane GARBAJ-JAUREGUIBERY Bernard P. ROQUES

When complex molecules are submitted to analysis—e.g., the oligopeptide Bradykinin sample in this experiment—two-dimensional spectra such as proton correlated spectroscopy (COSY) can often produce dramatic simplification of seemingly intractable spectra, even at high magnetic field. Here is evidence:

The pulse sequence for COSY is given by:

\[
90^\circ_x - t_1 - 90^\circ_x - t_2 - x - \text{Acc}(t_x)
\]

The chemical shifts of mutually coupled protons can be extracted from overlapping multiplets by means of a contour plot obtained from the COSY Experiment Data. The normal Proton Spectrum is represented along the diagonal axis, and the symmetrical off-diagonal cross peaks provide the clue to any coupled protons. The COSY Contour Plot of Bradykinins triacetate (Arg-Pro-Pro-Gly-Phe-Ser-Pro-Phe-Arg), illustrates the technique on the aliphatic moiety. With the known position of the H-Pro 2 (\(\text{Pro} \cdot \text{Pro}^*\)), the chemical shifts of all the six remaining protons (2\(\text{H}_2\); 2\(\text{H}_3\); 2\(\text{H}_4\)) can easily be located as shown by the connecting lines.

(1) Ad Bax and Ray Freeman, JMR 44, p. 542-661 (1984)

Q.E.D. Both spectrum and contour plot of this COSY experiment were produced on a WM 400 at the Bruker Applications Laboratory. The WM Series of high-field NMR spectrometer systems comes with an extensive software system, including programs for 2-D processing, display and plotting. A full-color graphic display processor further facilitates speed and clarity of stack and contour plots.

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New Literature Available from BRUKER

NMR-Tomography

A simple introduction into a fascinating NMR technique

The "NMR-imaging" technique is without any doubt a revolutionary new method for obtaining pictorial information about internal structures e.g. of the human body. The evolution of this method has now reached the state were non-specialists have recognized the extraordinary power of this technique and consequently BRUKER has now available an introductory six-page brochure for those not familiar with this new method. In order to facilitate the understanding of the physical background to this method the basic principles are given in a simplified manner and are illustrated by a large number of figures.

In a short survey it is shown that for the last twenty years the instrumental development in the pulsed NMR field has been synonymous with the name of BRUKER and it is pointed out that the first commercially available Fourier Transformation (FT) spectrometers were developed by BRUKER in 1969. Since NMR tomography is based on both "pulsed" and "FT"-NMR, the unique experience of BRUKER in these fields represents the ideal basis for the recently developed imaging systems.

After a short introduction, the principles of NMR are described in the brochure followed by a short representation of the "Projection-Reconstruction-Technique". Due to the expected extraordinary importance of NMR tomography in the field of diagnostic medicine a comparison of the average X-ray tissue contrast with NMR data is given as well as some remarks about theoretically possible risks for patients. At the end of this brochure an "outlook" is given into new applications and of the expected development of NMR tomography.

With the general title "BRUKER Info", periodically illustrations of BRUKER's latest results are added to the NMR Tomography brochure.

If you wish to obtain the new brochure containing two "BRUKER Info" illustrations please return the reply card.

Two-Dimensional NMR aspect 2000

A practical introduction into this new technique by an experienced spectroscopist.

The common 2-D experiments are described, measuring conditions and microprograms are given. Application examples on various spectrometers demonstrate the capabilities of the method and naturally the outstanding performance of BRUKER spectrometers in 2-D spectroscopy.

For Your Copy, Please Write to Your Nearest BRUKER Sales Office
Dear Professor Shapiro,

We have been studying ionophores which can be "switched on" and "switched off" by closure and cleavage of disulfide bonds. We have found $^{13}$C spectra of great utility in making structural assignments and following reactions. In the course of our work we have made a number of spectral assignments on final ionophores and intermediates, some of which are given in the table. Spectra were measured on an FX-60 spectrometer at 15 MHz. Of special interest are the shifts which follow closure of the disulfide: +15 ppm and -3.5 ppm for the $\alpha + 8$ carbons, respectively, due to the $\delta + \gamma$ effects of the second sulfur atom.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_4$</th>
<th>$C_5$</th>
<th>$C_7$</th>
<th>$C_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO(CH$_2$CH$_2$O)$_3$CH$_2$CH$_2$OH</td>
<td>61.4</td>
<td>72.7</td>
<td>70.0*</td>
<td>70.5*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO(CH$_2$CH$_2$O)$_4$CH$_2$CH$_2$OH</td>
<td>61.4</td>
<td>72.5</td>
<td>70.1</td>
<td>70.4</td>
<td>70.4</td>
<td></td>
</tr>
<tr>
<td>HO(CH$_2$CH$_2$O)$_5$CH$_2$CH$_2$OH</td>
<td>61.6</td>
<td>72.5</td>
<td>70.5</td>
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<tr>
<td>Br(CH$_2$CH$_2$O)$_3$CH$_2$Br</td>
<td>30.3</td>
<td>71.1</td>
<td>70.5</td>
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<td>Br(CH$_2$CH$_2$O)$_4$CH$_2$Br</td>
<td>30.3</td>
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<td>70.6</td>
<td>70.6</td>
<td>70.6</td>
</tr>
<tr>
<td>Br(CH$_2$CH$_2$O)$_5$CH$_2$Br</td>
<td>30.3</td>
<td>71.2</td>
<td>70.6</td>
<td>70.6</td>
<td>70.6</td>
<td>70.6</td>
</tr>
<tr>
<td>HS(CH$_2$CH$_2$O)$_3$CH$_2$SH</td>
<td>24.2</td>
<td>72.8</td>
<td>70.2*</td>
<td>70.6*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HS(CH$_2$CH$_2$O)$_4$CH$_2$SH</td>
<td>24.3</td>
<td>72.9</td>
<td>70.2</td>
<td>70.6</td>
<td>70.6</td>
<td>70.6</td>
</tr>
<tr>
<td>HS(CH$_2$CH$_2$O)$_5$CH$_2$SH</td>
<td>24.2</td>
<td>72.8</td>
<td>70.2</td>
<td>70.6</td>
<td>70.6</td>
<td>70.6</td>
</tr>
<tr>
<td>S(CH$_2$CH$_2$O)$_3$CH$_2$S</td>
<td>39.1</td>
<td>69.3</td>
<td>70.9*</td>
<td>71.0*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(CH$_2$CH$_2$O)$_4$CH$_2$S</td>
<td>39.1</td>
<td>69.5</td>
<td>70.3</td>
<td>70.6</td>
<td>70.6</td>
<td>70.6</td>
</tr>
<tr>
<td>S(CH$_2$CH$_2$O)$_5$CH$_2$S</td>
<td>39.2</td>
<td>69.2</td>
<td>70.2</td>
<td>70.8</td>
<td>70.8</td>
<td>70.8</td>
</tr>
</tbody>
</table>

*Assignments may be reversed

Sincerely,

Morton Raban
Professor of Chemistry

Farouk Kandil
Visiting Professor of Chemistry
(on sabbatical leave from the University of Aleppo, Syria)
Professor B. L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, TX 77843

Dear Barry:

RE: Hydrocarbon Type Analysis of Fossil Fuels Using Spectral Editing Techniques.

We have been examining the feasibility of utilizing $^{13}$C NMR spectral editing techniques to quantitate hydrocarbon types found in fossil fuel. Several methods for spectral editing are given in the literature (1-4), but only the Gated Spin-Echo Technique (GASPE) and the Distortionless Enhancement by Polarization Transfer (DEPT) are applicable to quantitative hydrocarbon type analysis.

In order to compare the GASPE and DEPT methods, a test mixture was prepared. The composition of this mixture and its method of preparation are given in Table I (attachment).

The GASPE, Conventional Spin/Echo (CSE) and DEPT sequences were written with modifications of the literature for the JEOL FX-270 NMR spectrometer. By appropriate combination of addition and subtraction of GASPE and CSE spectra at $T$ values of $1/J$, $1/2J$, $1/4J$, and $3/4J$, spectra containing only $C$, $CH$, $CH_2$, and $CH_3$ were obtained. From the integration of this spectra, the percent carbon types were calculated for the mixture. Table II lists the percent of aliphatic carbon types using the GASPE method. An examination of the data in Table II indicates that quantitation of carbon types present in minor amounts is not accurate.

We are now completing the work using the DEPT sequence. Hopefully a full paper discussing the pros and cons of the two methods will be published in the near future.

Sincerely,

Daniel A. Netzel and Ed Clennan  
LET C  
Chemistry Dept.  
Univ. Wyoming

Attach.
### TABLE I: TEST MIXTURE<sup>a</sup>

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>Moles used</th>
<th>#C</th>
<th>#CH</th>
<th>#CH&lt;sub&gt;2&lt;/sub&gt;</th>
<th>#CH&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>.01</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2,2,4-trimethylpentane</td>
<td>.01</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>o-ethyltoluene</td>
<td>.01</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>acenapthene</td>
<td>.01</td>
<td>4</td>
<td>6</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2,3-dimethylnaphthalene</td>
<td>.01</td>
<td>4</td>
<td>6</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>.01</td>
<td>3</td>
<td>7</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1,2,3,4-tetrahydro-</td>
<td>.01</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>naphthalene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hexane</td>
<td>.01</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>heptane</td>
<td>.01</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>tetradecane</td>
<td>.01</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>17</strong></td>
<td><strong>33</strong></td>
<td><strong>31</strong></td>
<td><strong>15</strong></td>
<td></td>
</tr>
<tr>
<td><strong>% TOTAL</strong></td>
<td><strong>17.71</strong></td>
<td><strong>34.38</strong></td>
<td><strong>32.29</strong></td>
<td><strong>15.63</strong></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>The samples were prepared by taking this mixture and diluting it to 25 ml with COCl<sub>2</sub>. The samples were sealed in 5 and 10 mm NMR tubes. Some of the samples were also .04 M in Cr(ACAC)<sub>3</sub>.

### TABLE II: QUANTITATION OF ALIPHATIC CARBONS WITH THE GASPE METHOD

<table>
<thead>
<tr>
<th>EXPERIMENTAL CARBONS</th>
<th>% CARBON</th>
<th>CALCULATED CARBONS</th>
<th>% CARBON</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>14.06&lt;sup&gt;a&lt;/sup&gt; (15.52)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>29.31 (32.34)</td>
<td>15</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>31.96 (31.93)</td>
<td>66.58 (66.53)</td>
<td>31</td>
</tr>
<tr>
<td>CH</td>
<td>10.48 (3.98)</td>
<td>21.84 (8.30)</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>1.24 (5.01)</td>
<td>2.6 (10.44)</td>
<td>1</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>57.74</strong> (56.44)</td>
<td><strong>120.33</strong> (117.61)</td>
<td>48</td>
</tr>
</tbody>
</table>

<sup>a</sup>First Attempt  
<sup>b</sup>Second Attempt

### REFERENCES

Dear Professor Shapiro

DOES THE BORN-OPPENHEIMER APPROXIMATION BREAK DOWN IN THE CASE OF LONG-RANGE ISOTOPE EFFECTS?

In response to your colorfull reminders a short description of some results from my latest visit to Harald Günther at Siegen.

From our results in a previous paper it is clear that substituents at one of the phenyl rings in the β-thioxoketonesystem may change the enol-enethiol equilibrium, but also that deuterium substitution at the S or O may perturb the equilibrium (I) giving rise to long-range equilibrium isotope effects on $^{13}$C as shown in Table 1.

\[
\text{D} \quad \text{H} \quad \text{O} \quad \text{S} \quad \text{D} \quad \text{H} \quad \text{O} \\
\text{I}
\]

What we did this time was to look at the pentadeuteroderivative as shown in II. As seen from table 1, did this derivative also show small, but significant isotope effects (large for
long-range isotope effects). As the effects furthermore are proportional to those observed when the equilibrium is perturbed by other means (D on S or O) we do not hesitate to claim that the penta-deuteration leads to a change in the equilibrium.

\[ \text{Diagram:} \]

\[ (\text{II}) \]

Table 1. Deuterium isotope effects on $^{13}$C nuclear shielding in ppm

<table>
<thead>
<tr>
<th></th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C-L</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-4.69</td>
<td>+1.69</td>
<td>+0.32</td>
<td>-0.59</td>
</tr>
<tr>
<td>II</td>
<td>-0.11</td>
<td>+0.04</td>
<td>+0.01</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

The change in the equilibrium shows that the $\beta$-thioxoketo-system is a very sensitive gauge of substituent effects. However, the remaining question is why does the equilibrium change.

The magnitude of the isotope effects in case II does not depend upon the ratio of H and D compound in the mixture and it is not changed upon a tenfold dilution.

We consider two possibilities. The first is that the COH-C$_6$H$_5$ part is not planar and as the five H are exchanged with five D the steric interaction between the COH group and the phenyl ring is reduced. The other possibility is that the C$_6$D$_5$ radical is slightly more electronegative than the C$_6$H$_5$ radical. This however means that the Born-Oppenheimer approximation is not valid in this case. A heretic thought among theoreticians. Nevertheless, many other data in the literature point towards a breakdown at least for the very small effects observed in long range isotope effects.
I hope some theoretician would like to comment on why they believe so strongly in the B-O app. and what experimental evidence on the same level as long range isotope effects support the B-O approximation.


Yours sincerely

Poul Erik Hansen

PE! The isotope effect is defined as $\Delta^H = \delta C(H) - \delta C(D)$
Some manufacturers claim these experiments are difficult

The above spectra were obtained during a 3-hour run on an XL-300 Superconducting FT NMR Spectrometer System.

**Varian owners perform them all before lunch**

Here's what one XL Series owner says:

Dr. Peter Rinaldi is a chemist at the Major Analytical Instruments Facility, Greenwood, Ohio. MAIF is a research and testing facility serving Case Western Reserve University and scientists throughout the Ohio Valley region. All quotes are from the MAIF NEWSLETTER, Vol. 1, Issue 3, March 1982, reprinted courtesy of MAIF.

Software written for chemists: “Special experiments are a standard part of the XL-200 NMR software package,” says Dr. Rinaldi. “We have been routinely running experiments such as INEPT, APT, solid state cross polarization, and most of the commonly used 2D-FTNMR experiments. Having run many of these myself, I can personally vouch for the tremendous advantage they offer.”

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Palo Alto, CA 94303
Shielding Constants of Copper and Gallium

Dear Barry,

As addition to the fruitful discussions on "shielding" and "screening" during the summer school at Stirling, I would like to direct the attention on further available shielding constants in the free atomic shielding scale (κ):

1) For copper κ is given in the following paper:
   O. Lutz, H. Oehler, and P. Kroneck, Z. Physik A 288, 17 (1978); in the meanwhile further shielding data are available on copper compounds:

2) For Gallium κ(71Ga3+ in H2O) = -880(45)·10^-6 was found:

From the figure given there, the influence of the different halides ligands is very obvious.

Sincerely yours,

(Otto Lutz)
Dr. B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, Texas 77843,
U.S.A.

Dear Barry,

APPLICATION OF NOED MEASUREMENTS TO STRYCHNINE

In the course of some work with Jack Edward, of McGill University, on the application of $^1$H spin-lattice relaxation measurements to the structure and stereochemistry of some strychnine sulfonic acids, we turned up some apparently anomalous relaxation rates. These anomalies seemed to disappear if some of the previously reported (1) $^1$H chemical shifts for strychnine (1) were re-assigned. We therefore undertook a re-examination of the assignments, using nuclear Overhauser effect difference (nOed) measurements at 400 MHz.

Those who attended the 1982 ENC meeting in Madison will recall that Dr. Suzanne Wehrli displayed in the Bruker suite two examples of applications of 2D techniques to strychnine - $^1$H-$^1$C and $^1$H-$^1$H shift correlation (COSY). We are indebted to Dr. Wehrli for copies of her plots. Her work provides an elegant verification of the assignment of the $^1$H signals to specific sites through scalar coupling connectivities. Our nOed work has determined the dipolar relaxation connectivities which establish the stereochemical relationships among the protons.

Strychnine is a good molecule on which to apply nOed measurements, since the spectra at 400 MHz (0.1 M in CDC$_3$ or DMSO-d$_6$) are well dispersed. We used a slight modification of
the NMRD procedure reported by Hall and Sanders (2). Degassing was unnecessary, since intramolecular relaxation is efficient in a molecule of the size and rigidity of strychnine. The data were interpreted with the aid of molecular models and calculated enhancements.

From irradiation of the H-8, 13, 15a, 15b, 18a, 18b, 20a, 20b, and 22 transitions we established that the assignments for the geminal pairs of protons at C-15, C-18, and C-20 should be reversed. The use of both CDCl₃ and DMSO-d₆ solutions to modify chemical shifts, and computer simulations using LAOCOON III led to a revised set of coupling constants for the four spin system H-17a, 17b, 18a, and 18b. The revised chemical shifts and coupling constants are listed in the Table.

Best regards,

Yours sincerely,

[Signatures]

Table. Revised ¹H chemical shifts and coupling constants for strychnine

<table>
<thead>
<tr>
<th>Proton</th>
<th>δb</th>
<th>Coupling constants, J (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15a</td>
<td>2.36</td>
<td>15a,15b = -14.5 15a,16 = 4.9 15a,14 = 4.0</td>
</tr>
<tr>
<td>15b</td>
<td>1.46</td>
<td>15b,16 = 2.0 15b,14 = 1.0</td>
</tr>
<tr>
<td>17a</td>
<td>1.88</td>
<td>17a,17b = -15.5 17a,18a = 8.4 17a,18b = 11.7</td>
</tr>
<tr>
<td>17b</td>
<td>1.89</td>
<td>17b,18a = -0.1 17b,18b = 6.9</td>
</tr>
<tr>
<td>18a</td>
<td>3.19</td>
<td>18a,18b = -10.2</td>
</tr>
<tr>
<td>18b</td>
<td>2.87</td>
<td></td>
</tr>
<tr>
<td>20a</td>
<td>3.70</td>
<td>20a,20b = -14.7 20a,22 = 0.9</td>
</tr>
<tr>
<td>20b</td>
<td>2.72</td>
<td></td>
</tr>
</tbody>
</table>

The remaining assignments were in agreement with those in Ref. 1. δb ppm from TMS, CDCl₃ solutions. Negative signs were assumed for geminal coupling constants.
Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A and M University  
College Station, Texas 77843

Dear Professor Shapiro,

Organoselenium compounds have received much attention as reagents in organic synthesis.\(^1\) Despite this interest, relatively little has been reported on the use of selenium-77 NMR as a tool for structural elucidation of organoselenium compounds\(^2\) and only one article appeared in the area of fluoroorganoselenides where the fluorines are on the hydrocarbon portion.\(^3\) The selenium-77 isotope has a natural abundance of 7.58% and has approximately 3 times the receptivity of carbon-13. In this note we wish to report the \(^{77}\text{Se}\) chemical shifts and \(^{77}\text{Se}-^{19}\text{F}\) coupling constants for a few fluorinated alkylphenyl and alkenylphenylselenides.

The proton decoupled \(^{77}\text{Se}\) spectra were recorded on a Varian FT80A spectrometer at 15.167 MHz in CDCl\(_3\). The \(^{77}\text{Se}\) chemical shifts, measured relative to phenylvinylselenide (i.e. 395.5 ppm downfield from dimethylselenide) and the \(^{77}\text{Se}-^{19}\text{F}\) coupling constants for the alkenylphenyl and alkylphenyl selenides studied are listed in Tables I and II.

From Tables I and II we see the following:

1. Trans Se-F coupling constants are larger than cis in the fluorinated alkenylphenyl selenides.

2. A selenium trans to a fluorine, as in compound 2, is 20 ppm upfield relative to the cis fluorine compound. However, when a resonance electron donor is trans to a selenium, such as methoxy, then the selenium trans to the fluorine is downfield relative to the cis, due possibly to greater contribution of resonance structure A than resonance structure B.
3. An alkyl group geminal to a selenium (compd 7) deshields the selenium and also reduces the trans $^3$J_{Se-F}$ coupling constant while increasing the cis.

4. A chlorine atom γ to a selenium in the case of alkyl selenides causes a 24 ppm downfield shift relative to a fluorine and methoxy group. This may be due to some conformational or electronic effect.

References


4. Preparation of compounds 4, 5, 6, 8, 10, 11: A. E. Feiring, J. Org. Chem. 45, 1958 (1980); compounds 7, 12, 13: ibid 45, 1962 (1980). Compound 9 was prepared by addition of PhSeCl to vinyl fluoride; treatment of 9 with methanolic KOH gave compounds 2 and 3 which were separated by careful spinning band distillation (A. E. Feiring, unpublished results).

We hope this limited amount of data can generate further study of selenium-77 NMR by your readers.

Sincerely yours,

F. Davidson

A. E. Feiring

FD:AEF/dew

Please credit this contribution to the account of D. D. Bly.
### Table I

Selenium-77 Chemical Shifts and $^{77}$Se-19F Coupling Constants for Fluorinated Alkenylphenyl Selenides

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\delta$ $^a$</th>
<th>$3J_{\text{Se-F}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. PhSeCH=CH$_2$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2. PhSe(\text{H-F}))</td>
<td>-125.4</td>
<td>51.1</td>
</tr>
<tr>
<td>3. PhSe(\text{F-H}))</td>
<td>-105.4</td>
<td>7.1</td>
</tr>
<tr>
<td>4. PhSe(\text{H-CH$_3$}))</td>
<td>-143.7</td>
<td>40.0</td>
</tr>
<tr>
<td>5. PhSe(\text{H-CH$_3$}))</td>
<td>-154.0</td>
<td>&lt;1</td>
</tr>
<tr>
<td>6. PhSe(\text{F-H}))</td>
<td>-141.7</td>
<td>3.3 (cis)</td>
</tr>
<tr>
<td>7. PhSe(\text{F-H}))</td>
<td>-95.5</td>
<td>5.9 (cis)</td>
</tr>
</tbody>
</table>

$^a$ - negative sign is upfield from phenylvinyl selenide.

$^b$ - absolute value of coupling constants are given.

### Table II

$^{77}$Se Chemical Shifts and $^{77}$Se-19F Coupling Constants for Fluorinated Alkylphenyl Selenides

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\delta$ $^a$</th>
<th>$3J_{\text{Se-F}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8. PhSeCH$_2$CF$_2$Cl</td>
<td>-101.5</td>
<td>3.9</td>
</tr>
<tr>
<td>9. PhSeCH$_2$CF$_2$Cl</td>
<td>-102.0</td>
<td>7.6</td>
</tr>
<tr>
<td>10. PhSeCH$_2$CF$_2$CH$_3$</td>
<td>-126.1</td>
<td>3.2</td>
</tr>
<tr>
<td>11. PhSeCH$_2$CF$_3$</td>
<td>-126.0</td>
<td>3.9</td>
</tr>
<tr>
<td>12. PhSeCH(CF$_3$)CH$_2$Cl</td>
<td>-26</td>
<td>3.5</td>
</tr>
<tr>
<td>13. PhSeCH(CF$_3$)CH$_2$CH$_3$</td>
<td>-9.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>

$^a$ - negative sign is upfield from phenylvinyl selenide.

$^b$ - absolute value of coupling constants are given.
Dear Barry:

We currently have a position available within the Departments of Chemistry and Medicine at Washington University for a postdoctoral research associate in the field of NMR of intact biological systems. I am soliciting applications and ask that you make this letter available to any qualified individuals whom you feel might be interested.

The primary focus of this position will be the hormonal regulation of liver metabolism as studied by H-1, C-13 and P-31 NMR experiments with rat liver in vivo and in vitro. The studies in vivo will make use of surface coil and chemical shift spin-imaging techniques while studies in vitro will utilize both perfused liver and isolated hepatocytes (liver cells). Time will also be available for independently motivated research within the context of our group interests.

The applicant should have a Ph.D. in chemistry, physics, biochemistry or other related field with extensive hands-on experience in magnetic resonance and a keen interest in biomedical applications. The initial appointment will be for a period of one year with additional extensions if mutually agreeable.

The NMR instrumentation available within our group for this project includes two state of the art Bruker NMR spectrometers, the WH-360 and CXP-200. Both spectrometers are fully multinuclear and employ widebore superconducting magnets of 72 mm and 85 mm inner diameter bores (inside room temperature shims) for the WH-360 and CXP-200 respectively. Extensive radio frequency design and test equipment is also available for NMR probe development and construction.

This position offers an exciting opportunity to gain extensive experience in the rapidly expanding field of intact tissue NMR while also becoming acquainted with the biomedical techniques needed to support such experiments. All interested applicants are invited to submit a letter detailing their background and interests along with a curriculum vitae; two letters of professional recommendation should also be submitted. Washington University is an Equal Opportunity, Affirmative Action Employer.

Sincerely,

Joseph J. H. Ackerman, Ph.D.
Assistant Professor of Chemistry
Research Assistant Professor of Medicine
September 27, 1982

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

University-Industry Collaboration; Positions Open

Dear Dr. Shapiro,

Since 1975 the Department of Radiology has had an NMR imaging program that has resulted in two imagers operating at 3.5 KGauss, one using a Varian 12-in pole tip magnet having a useful aperture of 6.5cm and a second incorporating an Oxford superconducting magnet and a useful aperture of 55cm. The small unit has been used to image rats, mice, gerbils, guinea pigs and phantoms that model disease conditions in humans (1,2) and the large unit has been used to evaluate the technology in volunteers and patients (3,4). Two examples of such images are shown below. An upgrading of this unit, as well as construction of additional ones, is now in progress. The University R & D program is supported by Diasonics, a medical imaging company based in South San Francisco. The UCSF effort is a continuing program designed to improve hardware, develop imaging techniques, study their clinical effectiveness, and understand the reasons behind the tissue characteristics observed in images. The Diasonics program involves the commercialization of this technology. We are interested in hearing from people interested in R & D or production responsibilities, either at the University or in Diasonics. Positions are open for NMR spectroscopists, digital, RF or software engineers, or technologists. Resumes should be sent to our attention.

Larry Crooks, Ph.D.
Associate Professor of Electrical Engineering
Assistant Director, UCSF Radiologic Imaging Laboratory

Leon Kaufman, Ph.D.
Professor of Physics and Director, UCSF Radiologic Imaging Laboratory


NMR images of patients with a large liver tumor (bright central region in the top image), and an arteriovenous malformation (bottom image). Vasculature is seen dark because of flow. In the head image the dark regions of the brain demonstrate the abnormal vasculature.
September 27, 1982

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

Dear Barry,

Two positions at the Research Associate or Postdoctoral Fellow level will become available at SMRL in early 1983 as the laboratory inaugurates a new program with the installation of a 600 MHz spectrometer, which is currently on order. We are looking for highly competent, highly motivated individuals with an active interest in biological applications of NMR, willing to learn and to function as members of an interdisciplinary team in this rapidly growing field. Proficiency in NMR electronics, hardware and software and familiarity with probe design and construction are essential. Readiness to accept challenges and spearhead new developments highly desirable. Experience with in vivo NMR and imaging technology helpful, but not mandatory. Rank and salary dependent on qualifications. All inquiries should be addressed to me at the above address.

With best regards,

Yours sincerely,

Oleg Jarecky

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