Texas A&M University N-M-R Newsletter

No. 167

AUGUST, 1972

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- No. 168: 4 September 1972
- No. 169: 2 October 1972

All Newsletter correspondence, etc. should be addressed to:

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

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B. L. Shapiro
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3J\textsubscript{31p-13C} AND DIHEDRAL ANGLES IN CYCLIC NUCLEOTIDES

Dear Barry:

In last year's report (1) we described Henry Mantsch's work on the $3\text{J}_{31\text{p}-13\text{C}}$ for a series of mono- and polynucleotides - they appeared to vary from 2-9 Hz depending on the relative populations of rotamers about the OC bond in the group $31\text{POC}_1\text{C}$. More detailed accounts of our progress in this type of system have now been prepared (2,3). During the last while, we have attempted to calibrate the dihedral angle dependence by a study of 3',5'-cyclic nucleotides. Molecular models suggest that these compounds have a rigid, well-defined conformation, and X-ray crystallographic analyses have been done on three of them (4-6). In the solid state the $3\text{T}_4$ (3'-endo, 4'-exo) conformation is observed (4-6). Their general formula is shown below,

\[
\begin{align*}
\text{where } R = \text{uracil (U), cytidine (C), adenine (A), guanosine (G)} & \text{ or thymine (T).}
\end{align*}
\]
In the conformation found in the solid state the phosphate is trans to C₂₁ and gauche to C₄. The experimental P-C coupling constants are shown below.

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>C</th>
<th>A</th>
<th>G</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl'-P</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>C2'-P</td>
<td>8.0</td>
<td>7.8</td>
<td>7.8</td>
<td>7.8(8.3)*</td>
<td>8.3</td>
</tr>
<tr>
<td>C3'-P</td>
<td>4.5</td>
<td>4.3</td>
<td>4.3</td>
<td>3.8(3.3)*</td>
<td>4.8*</td>
</tr>
<tr>
<td>C4'-P</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.8</td>
<td>4.5*</td>
</tr>
<tr>
<td>C5'-P</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.3</td>
<td>7.0</td>
</tr>
</tbody>
</table>

*Ambiguity due to overlap of resonances.

It is apparent that, although the R group varies widely, the conformation of the ribophosphate moiety is fixed throughout the series. The value for the trans coupling is 8.0 ± 0.3 Hz, and one can estimate the gauche coupling to be about 2.2 Hz. The latter is less certain since there are two paths for it.

To confirm that these compounds actually have the expected rigid structures, we have been analyzing their ¹H NMR spectra. Both the ¹J₃₁P-¹H and ¹J₁H-¹H couplings were helpful in proving this point. For example, in thymidine-3',5'-cyclic phosphate (R = T, no OH at position 2') the ¹J₃₁P-¹H to the two hydrogens at position 5' are 20.4 and 2.2 Hz. The molecular model suggests that one H is gauche to the P, and the other trans, in good agreement with the experimental couplings. The ¹J₁H-¹H are also in agreement with the rigid twist conformation.
Thus, having established the rigidity of the molecules and demonstrated that they have the expected conformation, we can rely on the value found for $^3J_{POCC}$ in the trans arrangement. We expect that this value will vary somewhat with pH, and are in the process of determining the extent of the variation.

These couplings have proved to be very useful for us in studying the conformations of compounds of biological interest such as polynucleotides, polysaccharides, phospholipids, dinucleoside monophosphates, and coenzymes. One can only regret that the range of the couplings is so small, making interpretation tricky unless careful control measurements are made.

Finally, we would like to second the motion made by Ernest Lustig on PMR and heteronuclei (7). Now is the time to reach an agreement before the literature gets any messier.

Yours sincerely,

Ian C.P. Smith/ Roy D. Lapper/ Barry J. Blackburn

July 19, 1972

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

Dear Barry,

I would like to submit a "post-doctoral position available" advertisement to the Newsletter.

**Post-doctoral Position Available**

We have an opening for a post-doctoral fellow in our NMR group. We have a Bruker HX-90 spectrometer with Fourier transform capabilities for $^1$H, $^{13}$C, and $^{15}$N. Our research concentrates on two main objectives: 1) identification by $^1$H and $^{13}$C NMR of unknown compounds in human urine and cerebrospinal fluid, 2) $^1$H, $^{13}$C, and $^{15}$N investigation of known aromatic acids and amines of biological interest. Some of our publications give examples of these endeavors. (J. Magn. Resonance 2, 361 (1970); 6, 55 (1972); Biochem. Med. 2, 164 (1969).

We are interested in a post-doctoral fellow with a strong high resolution proton NMR background. Familiarity with computer simulation of complex spectra, $^{13}$C NMR, and Fourier transform techniques would be helpful, but not essential. What we mainly want is a bright, dedicated, independent researcher.

The salary is open and depends on qualifications. The position is open as of this date and we want to fill it as soon as possible. Resumes should be sent directly to me.

With best wishes.

Sincerely,

Katherine N. Scott, Ph. D.,  
Assistant Research Professor

KNS:cas
Dear Professor Shapiro,

Nine Months of F.T. at 25 MHz.

Please accept my apologies for the delay in sending this contribution, which I hope will serve to renew our subscription.

Since receiving our PFT-100 system last Autumn, we have been very busy with demonstrations (up to six in one week) and doing applications work. The system has proved very reliable and apart from power cuts earlier this year and a recent shut-down for building alterations, has had only two days down-time, one of which was caused by failure in a particularly vulnerable gear in the teletype.

Until recently we had a prototype system which was limited to 13C observation at normal field strength. We have found more than enough to do with this nucleus, however, and have looked at practically everything from synthetic rubbers to organometallics to ground rats' livers. Some applications work we have done together with other groups has included T1 measurements on poly (benzyl glutamate), the study of spectra of rifamycins (a group of antibiotics containing 35-40 or more carbon atoms) and studies of intact membrane structures. In a rather different field, the abundance of 195Pt in Pt(CN)4 was calculated from peak heights given by data reduction as 32.1% (quoted figure is 33.8%). The 13C - 195P coupling constant here was ~1035 Hz. and not surprisingly, no isotope effect was observed.

Some of our early experiments demanded 19F decoupling, which is readily achieved by exchanging the 100 MHz. oscillator in the decoupler with the 94 MHz. one in the basic PS-100 and tuning for the 19F frequency. With this arrangement we have decoupled without difficulty over a range of more than 50 ppm.

By variation of the magnetic field we have looked at the following nuclei in F.T. mode:--
$^{55}$Mn as $\text{MnO}_4^-$: this signal is somewhat broadened on addition of acid or alkali and disappears on reduction to manganate or the manganous state (hence providing a method of following reaction rates for those who have spent all their money on an F.T. system and cannot afford a simple optical instrument).

$^{79}$Br and $^{81}$Br as Br$^-$

$^{27}$Al as chloride and aluminate: a small second peak, probably due to hydrolysis, was seen about $40$ ppm "upfield" of the main peak in the former sample.*

$^{23}$Na as various salts. $T_1$ measurements made on the hydroxide at various concentrations showed an increase on dilution which paralleled that of the $T_2$ as estimated by linewidth. The $T_1$ at high concentration was of the order of a millisecond. *

$^{71}$Ga as nitrate

$^{11}$B as boric acid

$^{7}$Li as chloride

Although, as the lines were mostly very broad (with the exception of the last two nuclei), there would seem to be no advantage in using F.T. rather than C.W. mode, it was found to be very easy to adjust the field to the correct value by using rapid pulsing (0.1 sec. repetition time) and observing the received signal on an oscilloscope, with the Butterworth filter switched out of circuit. Thus a signal may be seen even when the required nucleus is at least several tens of KHz. away from resonance, and it is easy to tune in on this signal using the intermediate field control. Accumulation may be performed at the same pulsing rate, only a small number of data points (say 1K) being required.

As our staff here is now being expanded and we are also increasing the number of instruments, I hope to be able to send my next contribution in good time.

Yours sincerely,

DR. P. J. BEYNON


2 To be presented at Piza Conference in September. For chemistry and biological properties see e.g. P. Sensi, N. Wagg, S. Furesz, G. Maffi Antimicrobial Agents and Chemotherapy 1966, 699.

3 To be published shortly.

* See enclosed spectra
SPECTRUM NO. 167-9

DATE

FREQ. 2.5 5.0 10.0 25.0 50.0

NUCLEUS 23Na

SAMPLE NaOH

SOLVENT

CONC.

REFERENCE

LOCK

TEMP.

R.F. LEVEL

A.F. LEVEL

ANALYTICAL

LOCK

SD

AMPLITUDE

ANALYTICAL

LOCK

INTEGRATOR

FILTER

OFFSET

FREQ.-FIELD/FREQ.-FIELD

OPERATOR

REMARKS 23Na n-polar

SWEEP TIME (SEC.) 25 50 100 250 500 1000 2500 5000 10000

SWEEP WIDTH [Hz](X0.00PPM) 27 54 108 270 540 1080 2700 5400 10800

WIDE SWEEP (GAUSS) 10.8 27 54 108 540

YO JAPAN

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

Dear Barry:  

A Shift Reagent Induced AX Methylene Group  

Using Lanthanide Shift Reagents, we have observed a dramatic enhancement of the chemical shift nonequivalence of the methylene group of the ethyl side chain of 2-ethylcyclohexanone. The 100 MHz nmr spectrum of this compound in the presence of Eu(FOD)$_3$-d$_{27}$ is shown in the Figure. The two septets centered at 8.05 and 6.01 ppm are assigned to the two nonequivalent methylene protons. Spin decoupling at the methyl resonance frequency resulted in the collapse of each of the septets to a doublet of doublets ($J_{\text{gem}} = 14.0$ Hz, $J_{\text{vic}} = 7.0$ Hz). The vicinal couplings were found to be identical for each of the methylene protons.

The lanthanide induced shifts for each of the methylene protons will be used in an attempt to determine the most favorable conformation for the 2-ethyl side chain. It appears that the conformational preference is not enforced by interactions between the Eu(FOD)$_3$ and the ethyl side chain in the complex since in the absence of shift reagents the methylene protons remain nonequivalent ($\Delta \delta = 0.4$ ppm) and maintain identical vicinal coupling constants to the ring proton of 7.0 Hz.

Very truly yours,

Kenneth L. Servis,  
Associate Professor of Chemistry

Donald Bowler
Figure 1. 100 MHz nmr spectrum of 2-ethylcyclohexanone, (0.55 M) in the presence of Eu(FOD)$_3$-$d_{27}$ (0.29 M) in CDCl$_3$. 
Dr. Bernard L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station, Texas 77843,
U. S. A.

Dear Dr. Shapiro:

We have been interested recently in the cycloaddition reactions of aryldiazoalkylphosphonates ArC(N2)P(O)(OCH3)2 with norbornadiene. In each case (except Ar=o-OCH3-C6H4 - where only the anti pyrazoline is obtained), a 9:1 mixture of the epimeric anti and syn pyrazolines is formed.

The 1H n.m.r. spectra of the compounds are readily interpretable in a first-order analysis. The assignment of configuration, anti or syn, is made as follows:

- the 9,10 exo junction is shown by the existence of 4J9,10 and 4J9,8s,9 (≈ 2.0 Hz and 1.2 Hz respectively) and the absence of 3J9,10,4 or 3J9,7 couplings.
- the assignment of configuration at C-3 stems from the existence of a large P,10 coupling (19.0 to 20.0 Hz) in the anti isomer, while the corresponding coupling is only 6.0 Hz in the syn, the first corresponding to a 0° P, H10 dihedral angle, the second to a -120° angle (Dreiding models).
The most interesting feature of the spectra is perhaps the stereospecificity of the $^3P_{9}$ homoallylic coupling which is equal to 4.0 to 4.5 Hz in the anti isomer and 5.5 to 6.0 Hz in the syn isomer. To my knowledge this is the first example of the geometrical dependence of homoallylic $^3P_{9},^1H$ coupling. In a similar system, the hydrocarbon corresponding to our compounds, similar stereospecificity was shown recently$^2$. 

\[ J_{H_2,H_9} = 3.1 \text{ Hz} \]
\[ J_{H_2,H_d} = 2.2 \text{ Hz} \]

Sincerely yours,

Claude Benezra
Assistant Prof. of Chemistry

WANTED: A THEORETICAL BASIS FOR THE EVALUATION OF LIS DATA

Dear Professor Shapiro:

Quantitative treatment of the lanthanide induced chemical shift is becoming more and more prevalent. Virtually every numerical approach relies on a computation of some hypothetical shift values using the McConnell-Robertson relationship and comparing these values to the experimental ones. The preliminary assessment of this method is that it works very well indeed. For instance, there were at least a half dozen people at the 13th ENC who had devised algorithms which gave reasonable correspondence between experimental and calculated values of induced chemical shifts. We are approaching a time when we can summarize the results of the first year's computations and make a more realistic assessment of the technique. To that end, Ray Davis and I have been thinking about the problem from a to a. It appears that we develop anxiety symptoms at the a stage, so this letter constitutes a plea for help.

In order to match experimental and calculated values one has, of course, to obtain a set of experimental values. These sets of data can take a variety of forms. Since the readers of the Newsletter are reasonably sophisticated I will omit appropriate literature references for the indices, but I might mention that one can use the slopes of the lines obtained when frequency is plotted vs. mol ratio of lanthanide to substrate, a limiting chemical shift at 1:1 mol ratio (\(\Delta E_g\) of Demarco), and plots advocated by Kelsey, Shapiro and Johnson (as presented at the ENC), ApSimon and Armitage. There are clearly other methodologies which I have overlooked, but these at least serve to indicate the dimensions of the problem. Now, everyone seems to have a favorite method for deriving the perturbation in chemical shift. Ray Davis and I and our students have kept out of this sweepstakes because we have been more impressed with the problem solving potential than with the nitty-gritty detail of how one obtains indices for chemical shift perturbations. What we have found is that, within broad limits, any carefully determined
set of indices is good enough that we can obtain R factors and interpret spectra to our satisfaction. However, we are beginning to feel that we could do a better job if we had better numbers on which to base our calculation.

Our question then is this: Do any of the readers of the Newsletter have a method of obtaining perturbations in chemical shift which also has a solid basis in theory? It would be a service to us, and indeed to anyone involved in shift measurements, to have replies to this question directed to the Newsletter. It would be especially appropriate to have whatever theoretical justification might be at hand spelled out so we could all use it.

This suggestion is made neither facetiously or light-heartedly. Neither Ray nor I have any concept of which of the various data workups are better than any others. In general we have noticed that when we work up a set of data we have obtained ourselves, any of the techniques give sets of indices which compare rather well with indices derived by other techniques. This can be determined by simply matching the two sets of indices via a least square procedure and calculating the agreement factor which is one of our fondest functions. Typically we see that any of the various sets of indices, when we have obtained all of them ourselves, give agreement factors on the order of 2 or 3%.

Replies anyone? Criticisms? Comments?

Sincerely yours,

M. Robert Willcott
We are aware of the very elegant work of W. McFarlane and more recently that of B. E. Mann on the $^{13}$C nmr spectra of phosphorus containing materials. We would like to add to their data. The triethylphosphine and tetraethylphosphonium iodide nmr parameters were previously reported (W. McFarlane, Proc. Roy. Soc. A., 266, 185 (1968)) and our results check quite closely. However, we do observe a 14 Hz coupling of the $\alpha$ carbon to phosphorus in the phosphine.

Attached is a table of chemical shifts and coupling constants of related compounds. It is interesting to note that the phosphine - phosphonium salt pair appear to be anomalous. In all of the other cases the $\alpha$ carbon is deshielded and the $\beta$ carbon shielded when a positive charge or an electronegative group is substituted on the central atom.

As previously pointed out (P. C. Lauterbur, Ann. N.Y. Acad. Sci. 70, 841 (1958).) highly polarizable groups attached to carbon atoms can lead to anomalous chemical shifts and large differences in chemical shifts between two carbons of an ethyl group. This is particularly pronounced in (Et0)4PBF4 where the difference is some seventy ppm.

The shielding of the carbons in the phosphine-phosphonium salt system is most likely due to neighboring anisotropy as stated by McFarlane but its interesting to note that this is not apparently the case for sulfur nitrogen nor oxygen.

Sincerely yours,

Dorothy Z. Denney

P.S. If anyone has encountered spinning problems during very low temperature operation on an HA-100, I might suggest using a 4mm tube and spinner from the T-60. It works!
### $^{13}$C Chemical Shifts

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_C$ (ppm)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
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<tr>
<td>(EtO)$_3$P</td>
<td>57.0(10.5)</td>
<td>16.4(4)</td>
<td></td>
</tr>
<tr>
<td>(EtO)$_3$PO</td>
<td>62.7(6.1)</td>
<td>15.5(6.2)</td>
<td></td>
</tr>
<tr>
<td>(EtO)$_4$PHF$_4$</td>
<td>64.0(11.5)</td>
<td>11.7(9.0)</td>
<td>$3.5$Hz</td>
</tr>
<tr>
<td>(EtO)$_2$P</td>
<td>61.5(11.5)</td>
<td>15.8(8.5)</td>
<td></td>
</tr>
<tr>
<td>Et$_2$S</td>
<td>25.2</td>
<td>14.6</td>
<td></td>
</tr>
<tr>
<td>Et$_2$S$^-$</td>
<td>44.8</td>
<td>6.7</td>
<td></td>
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<tr>
<td>Et$_3$OBF$_4$</td>
<td>32.6</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Et$_2$S$^+$ (s)</td>
<td>41.0</td>
<td>(s) 6.2</td>
<td></td>
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<tr>
<td>Et$_2$S$^+$ (o)</td>
<td>75.0</td>
<td>(o) 15.1</td>
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<tr>
<td>Et$_3$O</td>
<td>64.5</td>
<td>14.0</td>
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<td>Et$_3$OBF$_4$</td>
<td>83.5</td>
<td>11.8</td>
<td></td>
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<tr>
<td>Et$_3$N</td>
<td>46.3</td>
<td>11.9</td>
<td></td>
</tr>
<tr>
<td>Et$_3$K$^+$</td>
<td>58.9</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Et$_4$N$^-$Br$^-$</td>
<td>53.8</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Et$_3$P</td>
<td>18.9(14)</td>
<td>9.6(14)</td>
<td></td>
</tr>
<tr>
<td>Et$_4$P$^+$I$^-$</td>
<td>12.5(40)</td>
<td>6.7(4.5)</td>
<td></td>
</tr>
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<td>(nPr)$_3$N</td>
<td>56.0</td>
<td>20.6</td>
<td>11.5</td>
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<tr>
<td>(nPr)$_3$N$^+$Br$^-$</td>
<td>61.0</td>
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<td>11.0</td>
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<tr>
<td>(nPr)$_3$S$^-$</td>
<td>33.7</td>
<td>22.8</td>
<td>12.8</td>
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<tr>
<td>(nPr)$_3$S$^+$I$^-$</td>
<td>41.6</td>
<td>19.0</td>
<td>13.2</td>
</tr>
</tbody>
</table>

1. Chemical shifts are relative to TMS.
2. $\text{CH}_3 - \text{CH}_2 - \text{M}$
3. Coupling constant to phosphorus in Hz.

$\beta = \alpha$
Dear Barry,

Enzymatic hydrolysis by a carbohydrate which is followed by mutarotation, can be represented in the case of \([\text{Substrate}]_{t=0} \rightarrow [\text{Enzyme}]_{t=0}\) (the most convenient condition for PMR) by simplified scheme

\[
S \xrightarrow{k_0} P_1 \xrightleftharpoons{k_+^3 \quad k_-^3} P_2, \tag{E}
\]

where \(P_1\) and \(P_2\) are products of hydrolysis and mutarotation. The configuration of the sugars \(P_1\) and \(P_2\) liberated in the hydrolysis, can be found by PMR spectra. The question arises which of anomers is the product of hydrolysis \(P_1\) and which - of mutarotation \(P_2\).

By analysis of the equations corresponding to the above scheme it has been found that the accumulation of the \(P_1\) product with time has a maximum under the condition

\[k_0 > k_+^3 + k_-^3\]

which can be fulfilled by appropriate enzyme concentration.

This approach has been applied to the kinetics of hydrolysis of 1) amylopectin by barley \(\beta\)-amylase 2) \(\alpha\)-benzyl-1-acetamido-2-deoxy-\(\beta\)-D-glucopyranoside by boar epididymis \(\beta\)-N-acetylglucosaminidase and 3) hyaluronic acid by testicular hyaluronidase.
For example on Fig. 1 the PMR spectra observed during the hydrolysis of amyllopectin are shown. The doublet at 5.05 ppm has been attributed to H-1 of the product β-anomer (β-maltose) on the basis of 7.8 cps splitting. The peak intensity of this signal rapidly increases, reaches the maximum and then gradually decreases (Fig. 2, curve 1). On the contrary, the intensity of the H-1 doublet (5.63 ppm, 3.8 cps splitting) due to product α-anomer (α-maltose) is gradually increasing (Fig. 2, curve 2) until the equilibrium is established. Thus from the existence of the maximum on β-maltose

Fig. 1. PMR spectra, recorded during the enzymatic hydrolysis of amyllopectin by barley β-amylase. "G" is the signal due to H-1 of α-glucosyl units of substrate; α and β are signals due to α- and β-maltose respectively. Solvent D₂O, 100 Mcps, internally referenced to tert-butanol.
Fig. 2. Time dependence of the H-1 signals peak intensity (in per cent relative to one proton unit) in enzymatic hydrolisis of amylpectin by barley β-amylase. 1 - signal due to β-anomer; 2 - signal due to α-anomer; 3 - signals due to both anomers.

Accumulation curve we may conclude that this anomer is the product $P_1$ of the hydrolisis, and α-maltose is the product of mutarotation. The curve 3 on Fig. 2, which is a sum of curves 1 and 2, describes the total peak intensity increase of the H-1 signals and illustrates the kinetics of hydrolisis ($P_1 + P_2$).

The described approach can serve as a general method for determining the stereochemistry of enzymolysis by carbohydrates.

This work has been performed in collaboration with Dr. V.G. Sakharovsky from the Institute of Biochemistry and Physiology of Microorganisms and Dr. I.V. Vikha and Prof. A.Ya. Khorlin.

Sincerely yours,

Vladimir Bystrov
Dear Professor Shapiro,

Sensitivity of $^{13}$C-FT spectrometers

There are still many chemists who have not realised that current Fourier-Transform nmr spectrometers give good noise decoupled $^{13}$C-nmr spectra after an accumulation time of only about one hour with samples of 20-50 mg of even relatively complex organic compounds (molecular weight <500). As we are working with 5 mm sample tubes (there are only historical reasons for larger ones) we routinely run the $^1$H- and FT-$^{13}$C-nmr spectra in the same solution. By reducing sample volumes to about 0.12-0.15 ml and using a vortex plug, we get a further improvement of sensitivity by a factor of 2-3 (thus reducing accumulation time by a factor of 4-9).

In connection with our work on ion selectivity of antibiotics$^1$ and model compounds$^2$ we also investigated ion-ligand interactions by $^{13}$C nmr.$^3$ In cooperation with Professor Prelog's group we are now measuring the spectra of different salts of the des-D-valyl-boromycin$^4$ (Fig. 1, X=H). To demonstrate the available sensitivity we have run the spectrum of only 7 mg of boromycin itself (Fig. 1, X=D-valyl, molecular weight 873.4). The spectrum shown in Fig. 2 was obtained during a week-end (272,200 pulses, total averaging time 61 hours). Fig. 3 shows another example: the spectrum of 2.5 mg of cholesterol dissolved in 0.12 ml CDCl$_3$. This spectrum was also run during a week-end (204,541 pulses, 66 hours). In both cases we
Fig. 1  Structure of boromycin

Fig. 2  $^{13}$C-NMR-spectrum of 7 mg boromycin

Fig. 3  $^{13}$C-NMR-spectrum of 2.5 mg cholesterol
used a strong filtering by exponential multiplication.

Reduction of sample volume is also possible by the use of cylindrical micro-cells. For long-time averaging microcells are perhaps more convenient, because here one avoids problems with homogeneity-distrubing air bubbles.

These spectra were run on our four year old Bruker-Spectrospin HFX-10 spectrometer, which has been equipped for the last 10 months with an FT unit B-SC-FFT-12.

Sincerely yours,

E. Pretsch          H. P. Meier

E. Pretsch

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

Dear Barry,

Magnetic anisotropy effects of - NO₂ and - CHO in aromatic compounds

Some recent calculations we have made suggest that the - NO₂ and - CHO groups do not shield protons because of a magnetic anisotropy effect to any appreciable extent. Considering the two molecules

\[ \text{I} \quad \begin{array}{c}
\text{NO}_2 \\
\end{array} \]

\[ \text{II} \quad \begin{array}{c}
\text{NO}_2 \\
\text{CH}_3 \\
\end{array} \]

there is a difference in the shielding of proton 8 of 0.77 ppm, which has been attributed to a change in the effect of the magnetic anisotropy of the NO₂ group, because in I the NO₂ group is probably coplanar with the ring while in II it is probably perpendicular [1]. We have tried to calculate the magnetic anisotropy of the NO₂ group using CNDO-2 wavefunctions, and find that the calculated shifts are negligible. However, the calculation of the magnetic susceptibility could well be considerably in error, hence this alone does not shed much light on the origin of this shift difference. We have also explored the possibility that the shift is produced by a change in the electron
density on hydrogen $P_{1s\sigma}$ via the diamagnetic shielding term

$$\sigma_{H}^{\text{dia}} = \frac{e^2}{2mc} P_{1s\sigma} \langle r \rangle_{1s}. $$

For CNDO-2 wavefunctions the magnitude of $\Delta \sigma_{H}^{\text{dia}}$ on going from structure I to II is 1.04 ppm compared with the observed value of 0.77 ppm. This suggests to us that one need not look further for the origin of this shift difference.

A similar example is shown by the molecules

1-naphthaldehyde has been ascribed structure III (b) on the basis of NMR evidence [2], whereas IV is probably as shown. Again proton 8 is the sensitive indication of structure, and in 1-naphthaldehyde is shifted 1.525 ppm to low field of the a proton in naphthalene whereas it is $-0.495$ in 2-hydroxy-1-naphthaldehyde. Calculated shifts produced by the magnetic anisotropy of the - CHO group again are negligible whereas $\sigma_{H}^{\text{dia}}$ predicts shifts from naphthalene of $-0.128$ for III (a) $-1.048$ for III (b) and $-0.036$ ppm for IV. On this basis we assign structure III (b) to 1-naphthaldehyde and IV to the hydroxy derivative.

In conclusion we suggest that perhaps too much reliance has been put on the magnetic anisotropy effect, and that changes in $\sigma_{H}^{\text{dia}}$ are more reliably calculated and in some cases at least account satisfactorily for the observed shifts. We plan to test this hypothesis on some other molecules where magnetic anisotropy has been used to explain shift differences.

References
1. P. R. Wells Aust. J. Chem. 17, 967 (1964)

Best wishes,

Jim Emsley

J. W. Emsley, J. C. Lindon and S. R. Salman
THE KETO-ENOL EQUILIBRIUM CONSTANT FOR ACETYLACETONE: DETERMINATION IN THE GAS PHASE

Dear Barry:

The keto-enol tautomerism of \( \alpha \)-dicarbonyl compounds has been the subject of numerous studies (1). High accuracy gas phase values for the equilibrium constant, the importance of which has recently been emphasized (1), are, however, lacking. We have therefore begun gas phase studies and here wish to report our preliminary results for acetylacetone (\( I \)).

The gas phase \( ^1H \)nmr spectrum of \( I \) was obtained at 115°C; the chemical shifts are seen to differ little from those observed in the liquid phase (2) and assignments are made accordingly (see the Figure). From electronic integration of the signals appearing at \( \delta \) ca. 3.3 (keto methylene) and ca. 5.3 (enol methine), the enol:keto ratio has been determined to be 75:25. This corresponds to a value for \( \Delta G^\circ \) of 0.85 kcal/mol.

Previous gas phase determinations of the enol:keto ratio for \( I \) (at ca. 100°C) by infra red (3) and electron diffraction (4) spectroscopy led to values of 90:10 and 66:34, respectively.

Studies to determine the temperature dependence of the equilibrium constant for \( I \) and related systems are now in progress.

We would now like to take the opportunity to be among those to second E. Lustig's nomenclatural suggestions for nmr spectroscopy (TAMUNMR, 165, 47 (1972)); we shall henceforth watch our language.

Yours sincerely,

Bill Egan, Sture Forsén


100 MHz spectrum of I (gas phase; ca. 100°). Chemical shifts are in ppm (δ) and relative to TMS (δ, 0). The inset signal is from the enolic proton and is centered at ca. 15 ppm.
Dear Barry,

Would you please enter the following announcement into the TAMU NMR Newsletter:

POSTDOCTORAL POSITION AVAILABLE

We have an opening for a postdoctoral fellow for the academic year 1972/73 in our NMR research group in the laboratory for physical chemistry at the ETH. The fellowship may be started at any time after 1 October 1972 and pays a salary of approximately Swiss Francs 30'000.-- per year.

Our current research interests concern the development and application of pulse techniques for the investigation of liquids and solids, including high-resolution studies in solids.

The position is not burdened with any teaching or with routine NMR applications. The applicant should have practical NMR experience combined with a sound theoretical background. Some electronic skill would be very desirable.

Applications with resume and references should be sent directly to me at the earliest convenience.

Sincerely yours,

Prof. Richard R. Ernst
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July 24, 1972

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

Title: NMR Temperature Measurement

Dear Professor Shapiro:

We have developed a rather simple system for determining temperature within an NMR tube which we feel might interest readers. The system does not require access to the sample tube and, after proper calibration, is precise and accurate to ± 1°C from -150°C to -100°C and ± 0.5°C from -100°C to 0°C. While we were primarily interested in measuring temperatures from 0°C to -160°C and did not exhaustively check out the system above 0°C; those checks which we did make indicate that the system should perform satisfactorily up to 180°C. This system should prove to be of use when measuring below -100°C or in variable temperature studies of nuclei having no temperature dependent shift.

A. Temperature Readout Section

In order to place a thermocouple into the exchange gas stream, we built our own heater-sensor unit; a modification of the basic Varian design.

A six bore Mullite tube, threaded to serve as a bobbin for winding the heater wire, served as a guide for the heater return wire, the platinum resistance sensor and the copper-constantan thermocouple wires. The thermocouple wires were passed through the platinum resistance sensor and cemented in place at the intersections of the Mica spacers; adjusting the length above the sensor so that on final placement into the probe insert, the junction bead would be approximately 5mm from the bottom of the sample tube. The thermocouple wires lead through the mullite tube and out of the probe by way of an insulating clamp set in a machined out portion of the probe body. The heater and sensor wires pass out from the probe in the normal fashion.
Professor B. L. Shapiro  
July 24, 1972

This thermocouple, used in conjunction with a high input impedance digital millovolt meter and 0°C compensation device, enable us to measure the temperature at that point in the probe insert. A slight modification of a commercially available ice point device permits us to use the unit to compensate for the temperature gradient between the thermocouple junction and the interior of the NMR tube and for any fixed thermal errors in the system.

The readout unit was calibrated against a copper constantan thermocouple designed to be placed inside spinning EMR tube. 2-Methyl butane was used as the solvent below -100°C; above -100°C checks were made against the methanol shift.

B. Calibration Thermocouple Unit

The copper constantan thermocouple wire was encased in a 12" length of 0.0625" OD 2 alumina thermocouple sheath leaving the headed junction exposed. A standard Varian variable temperature pressure cap as used as the support for the sheath which passed through a 0.0635 O.D. hole bored in the pressure adjusted screw. The head of the adjustment screw was counter-bored and threaded to receive a gland nut and an "o" ring which held the sheath in place and provided a pressure seal. The rigidity of the thermocouple sheath coupled with careful boring of the adjustment screw will enable one to spin the sample with no difficulty. EMF measurements at this junction were made with a bridge potentiometer against an ice point both of the usual design. (1)

Beaded junction thermocouples 0.0005" in diameter were used in both devices to provide rapid response time and minimize any effect of heat transfer to the ambient via the leads.

While flow rate was somewhat critical the accuracy obtained with the rotameter settings was sufficient to maintain calibration.

We hope this will be of use to other readers.

Please accept this as a credit to Professor Kurt Mislow's account.

Sincerely yours,

E. Miller

EM: nc

Dear Professor Shapiro,

1,2,3,4-Tetrachloro-1,4-dibenzyl-butadiene \(1^g\) (1g) in decalin shows an AB spectrum \(d_A = 3.97, d_B = 3.76, J_{AB} = 15\) Hz) for the methylene protons at 39°C which coalesces at \(T_c = +75°C\). This means that \(1^g\) must be non-planar, i.e. chiral, in its ground-state and that the free enthalpy of activation for the interconversion of diastereotopic protons, i.e. of enantiomers \(R-1\) and \(S-1\), is \(\Delta G^\ddagger_c = 17.6\) kcal/mole. One of these enantiomers is shown in formula 1. The molecule has a choice between two planar transition states of interconversion: s-trans (formula 2) and s-cis. The non-bonded interaction between the chlorine atoms in the 1- and 4-positions should make the s-cis transition state less favorable (see diagram of free enthalpy \(G\) versus torsional angle \(\alpha\)). This means that essentially a partial rotation about the central \(C^2-C^3\) bond occurs.

---

<table>
<thead>
<tr>
<th>R¹</th>
<th>R⁴</th>
<th>Solvent</th>
<th>(T_c) (°C)</th>
<th>(\Delta G^\ddagger_c) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₆H₂-C₆H₅</td>
<td>CH₆H₂-C₆H₅</td>
<td>decalin</td>
<td>+75</td>
<td>17.6±0.3</td>
</tr>
<tr>
<td>CH₆H₂-C₆H₅</td>
<td>H</td>
<td>acetone-d₆</td>
<td>-7</td>
<td>13.1±0.3</td>
</tr>
<tr>
<td>SiMe³Me²C₂H₄</td>
<td>SiMe³Me²C₂H₄</td>
<td>acetone-d₆</td>
<td>+12</td>
<td>15.6±0.3</td>
</tr>
</tbody>
</table>
The barrier to rotation is lower in butadiene $\text{J}_2$ compared to $\text{J}_3$, because the chlorine atom in the 3-position of transition state $\text{J}_2$ is not buttressed by a benzyl group in 4-position. (Buttressing effects $^2$ in $\text{J}_2$ are symbolized by arrows.) There are several possible reasons for the low $\Delta G^\circ_c$-value in $\text{J}_2$; comments are welcome. As expected, replacement of chlorine by bromine or iodine atoms at the 2- and 3-positions raises the barrier.

These results were obtained in collaboration with G. Köbrich, R.A. Misra, G. Rissmann, M. Röpner, and W. Zündorff $^3$.

At our new location we are now starting $^{13}$C-FT work on enamines $^4$, hydrazones $^4$, and toluenes $^5$.

Sincerely yours,

Bernd Kolb

Albrecht Mannschreck

---

Dear Professor Shapiro,

The problem of relating the signs of spin-spin coupling constants $J_{CX}$, where $X$ stands for a spin $\frac{1}{2}$ nucleus other than the proton or $^{13}\text{C}$, to their proton analogs $J_{XH}$, has been tackled so far mostly by tickling of the $^{13}\text{C}$ transitions while observing $^{13}\text{C}$ satellites in the proton spectrum. This technique is often hampered by the impossibility of observing the satellite lines due to overlap with the two orders of magnitude stronger signals of the $^{12}\text{C}$ isotopomers. A much more convenient method has become possible with the advent of $^{13}\text{C}$ Fourier transform techniques combined with coherent proton decoupling. Proton irradiation off-resonance has the effect of reducing the splittings due to direct C-H coupling. The relationship is given by the following equation $1$:

$$J_{\text{CH}}^r = \frac{J_{\text{CH}} \cdot \Delta f}{\delta H_2/2\pi}$$

(1)

The expressions in (1) are defined as follows:

- $J_{\text{CH}}^r$: direct $^{13}\text{CH}$ coupling constant
- $J_{\text{CH}}$: reduced splitting
- $\Delta f$: decoupler offset from exact resonance in Hz
- $\delta H_2/2\pi$: decoupler power level in Hz
If the carbon under consideration is further coupled to a nucleus such as $^{19}$F, $^{31}$P etc., two reduced multiplets, of which one shows a wider spacing, will be observed. The latter depends on

(i) the decoupler frequency with respect to the particular proton resonance

(ii) the sign of the coupling constant $J_{CX}$ relative to $J_{XH}$.

In order to demonstrate the method we have selected a simple compound, methyldimethylphosphonate where two types of carbons are coupled to phosphorus ($J_{PC} = 142.0 \pm 0.5$ Hz, $J_{PC} = 6.2 \pm 0.2$ Hz). Fig. 1 shows the undecoupled $^{13}$C Fourier transform spectrum obtained from an 80% solution in DMSO on our XL-100-15, equipped with 620f/16k Fourier transform accessory. The 2500 Hz spectrum is the result of an overnight run (50k-transients). In the spectrum of Fig. 2, which required only 150 transients, the decoupler frequency was centered at -4 ppm from TMS. In the expansion of the multiplet centered at 18 ppm downfield TMS it can clearly be seen that the reduced quartet at high field is more widely spaced, indicating that $J_{PC}$ and $J_{PH}$ have opposite signs as originally obtained by spin tickling of the $^{13}$C satellites in the proton spectrum.

Because of the larger offset of the decoupler frequency from exact resonance and the smaller coupling constant $J_{PC}$, the two reduced quartets of the methoxyl carbons partly overlap, however, it is still possible to derive the relative signs of $J_{PC}$ and $J_{PH}$, which are again opposite.

Thus with one single experiment (total time: 4 minutes) the relative signs of two pairs of coupling constants could be determined.

References:


Sincerely,

F. W. Wehrli

Dr. F. W. Wehrli
Fig. 1 Undecoupled $^{13}$C FT spectrum of methyldimethylphosphonate (50,000 transients)
Fig. 2 Off-resonance CW decoupled $^{13}$C FT spectrum of methyldimethylphosphonate with proton irradiation at -4 ppm from TMS (150 transients). The upper trace is an expanded readout of the high field portion.
Dear Professor Shapiro,

Thank you for your blue letter. Previously, we have examined 14N chemical shifts (1) of the three trimethylsilylnitrobenzene-15N isomers in collaboration with Professor WITANOWSKY (Polish Academy of Sciences, Warszawa).

The results were consistent with the trend previously reported in the 14N shifts of nitroalkanes (2), where the electron-withdrawing effect resulted in an upfield shift of the nitro-resonance.

Recently, we have extended our study to 15N chemical shifts of the three isomeric nitrophenyltrimethylsilanes 15N. A Varian DFS-60 spectrometer was used (the spectra were recorded by J.W.) and the measurements were made upon deuteriochloroform solutions with respect to external 12 M aqueous tetramethylammonium chloride solution, which gives a peak 330.6 ppm upfield from aqueous nitric acid solution. The shifts in ppm from tetramethylammonium chloride, with downfield shifts taken to be positive, are shown in Table 1:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>δ15N</th>
<th>δ14N</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-NO2C6H4-SiMe3</td>
<td>+331.8 ±0.16</td>
<td>+330 ±1</td>
</tr>
<tr>
<td>m-NO2C6H4-SiMe3</td>
<td>+327.3 ±0.16</td>
<td>+328 ±1</td>
</tr>
<tr>
<td>p-NO2C6H4-SiMe3</td>
<td>+327.0 ±0.16</td>
<td>+325 ±1</td>
</tr>
</tbody>
</table>

a Originally measured relative to dimethylformamide, but reported with respect to nitromethane (276 ppm to lower field); we find that the chemical shift of neat nitromethane is +335.7 ppm relative to external 12 M aqueous tetramethylammonium chloride solution.
It is apparent from the data in Table 1 that the trends observed for $^{15}N$ and $^{14}N$ shifts are comparable within the experimental error of the $^{15}N$ shifts. With each, the NO$_2$-resonance for the ortho position occurred to lowest field, and for the para position to highest field. The difference in $^{15}N$ shifts between the meta and para isomers is smaller than the difference in $^{14}N$ shifts, but the trend is the same.

In conclusion, we are inclined to think that the SiMe$_3$ group may act as a feeble $\pi$-electron-withdrawing group by using its 3d-orbitals for conjugation with the phenyl ring.

Please credit this contribution to the accounts of J.C. MAIRE and J.D. ROBERTS.

Yours sincerely.

Y. LIMOUZIN J.C. MAIRE J.D. ROBERTS J. WARREN

this laboratory California Institute of Technology

Professor B. L. Shapiro  
Department of Chemistry  
Texas A & M University  
COLLEGE STATION, Texas 77843  
USA

Dear Professor Shapiro,

I want to describe briefly some of the ideas used in a computer programme designed to simulate NMR spectra of spin systems with D2, C2v, and C2h symmetry, containing up to 10 spins. The programme can also be used on systems with C2 symmetry and it can be extended to cope with systems of D2h symmetry.

The symmetrized spin functions are generated from the usual basic product spin functions using the formula:

\[ \psi_a = \eta_{\text{pc}}^{\text{py}} \rho_{1a} \]

giving

\[ \psi_a = \eta(\phi_1\phi_{1a} + \phi_2\phi_{2a} + \phi_3\phi_{3a} + \phi_4\phi_{4a}) \]

in the D2 case, where \( \psi \) are the symmetrized spin functions, \( \phi_{1a} \) the basic product functions, \( \text{C}_{\text{py}} \) the group character, \( \rho \) the permutation operator, and \( \eta \) a normalizing factor.

To sort out all different symmetrized spin functions with same total magnetic quantum number and same symmetry, all the generated functions are compared and all duplicates discarded. This comparison is facilitated by three facts:

1) \( \phi_{1a} = \phi_{2a} \) if \( N-1 \) spins are identical, \( N \) being the total number of spins.

2) The symmetrized functions generated from two different product functions are identical only if the sum of the spin quantum numbers within corresponding equivalent set of spins are equal for the two product functions.

3) If \( \phi_{1a} = \phi_{kb} \), then the two symmetrized wave functions \( \psi_{1a} \) and \( \psi_{kb} \) are identical.
This follows from the projection operator giving all the product functions within one equivalent set.

The symmetrized functions need only to be generated from the product functions in the total symmetrical case as the $\phi_a$'s, but different $C_p$'s.

The diagonal matrix elements in the Hamiltonian matrix are calculated according to Wilson

$$
(\psi_1^Y | H | \psi_1^Y) = \frac{1}{C_{11}} \sum_{l,j} C_{1j} \left( \phi_1 | H | \phi_j \right)
$$

A time analysis showed that the most time-consuming operation in the programme is the diagonalization of the Hamiltonian matrix. Two diagonalization methods have therefore been tested, the Jacobi method (taken from Laocoön III) and the Householder method (version written by Bob Davidson, Princeton University). The test showed that the Householder method was about twice as fast as the Jacobi method and that almost identical results were obtained. The data output is stored on a file and subsequently plotted using a Lorentzian line shape.

The programme is written in Fortran extended (CDC 6400). Maximum matrix size to be used 66 x 66. Computing time 950 sec.

Anybody interested in a copy should just send me a note.

Please credit this contribution to the subscription of this institute.

Sincerely yours,

Poul Erik Hansen

(1) E. Bright Wilson, Jr., J. Chem. Phys. 27 (1957) p. 60.
August 3, 1972

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

Change of Address: Carbon-13 Structure Coding System

Dear Barry,

To make it official for the TAU NMR Newsletter files, please let me report my recent move from Varian to Transform Technology, Inc.

As my first contribution from TTI, I would like to present a structure coding system which was adapted from the proton NMR coding system, and devised for use in $^{13}$C NMR spectra coding. Bill Jankowski of Varian, and I have used this system in assigning a collection of 500 $^{13}$C NMR spectra. Coding conventions follow those used in the proton system. Special methods are used for compounds containing a carbon-sulfur double bond which are coded as 9-thio-groups, and for isocyanate groups which are coded as 9-N groups.

Best wishes,

LeRoy F. Johnson

Carbon-13 Structural Coding System

MAIN GROUPS

1. \(\text{CH}_3 - R_1\)
2. \(\text{CH}_2 - R_{1,2}\)
3. \(\text{CH} - R_{1,2,3}\)
4. \(\text{C} - R_{1,2,3,4}\)
5. 
6. \(\text{C} = \text{NR}_3\)
7. \(R_1^+ \equiv \text{CR}_2\)
8. \(R \equiv \text{CN}\)
9. \(\equiv \text{C}_R_1\)
10. \(\equiv \text{R}_3\)
11. \(\equiv \text{R}_2\)
12. \(\equiv \text{R}_4\)
13. \(\equiv \text{A}_2\)
14. \(\equiv \text{B}_2\)
15. Misc. aromatic

SUB GROUPS

A. \(\equiv \text{CH}_3\)
B. \(\equiv \text{CH}_2 - R_1\)
C. \(\equiv \text{CH} - R_{1,2}\)
D. \(\equiv \text{C} - R_{1,2,3}\)
E. \(\equiv \text{Cl}\)
F. \(\equiv \text{F}\)
G. \(\equiv \text{Br}\)
H. \(\equiv \text{H}\)
I. \(\equiv \text{I}\)
J. \(\equiv \text{O}\)
K. \(\equiv \text{O} - \equiv \text{O}\)
L. \(\equiv \text{C} = \equiv \text{C}\)
M. \(\equiv \text{N} = \equiv \text{N}\)
N. \(\equiv \text{N}^+ \equiv \text{N}^+\)
O. \(\equiv \text{O} - \equiv \text{O}^+\)
P. \(\equiv \text{OH}\)
Q. \(\equiv \text{O} - \equiv \text{C}^+\)
R. \(\equiv \text{NO}_2\)
S. \(\equiv \text{S}^+\)
T. \(\equiv \text{C} = \equiv \text{C}\)
U. \(\equiv \text{CN}\)
V. Phenyl
W. Misc. aromatic
X. P
Y. Si
Z. Misc. atom
Dear Professor BERNARD L. SHAPIRO

Department of Chemistry
Texas A & M University
College Station
Texas 77843
U.S.A.

Re: Determination of the molecular geometry of Eu(fod)$_3$
complexes with Amides and Diamides, by G. Montaudo and P. Finocchiaro

Paramagnetic shifts, induced in the nmr spectra of some amides and
diamides by Eu(fod)$_3$, have been used to assign configurational isomers
in these compounds. The observed Eu induced shifts agree well with
values calculated on the basis that their origin is of pseudocontact
nature, and have been used to determine the molecular geometries of
the corresponding Eu(fod)$_3$-amide complexes.

Remarkably, all the structures could be fitted by the same
pseudocontact constant (equation 1, $K=1,200 \pm 100$), Eu-O distance
(3.0 Å), and average Eu-O-C angle (120°).

$$\Delta \nu_{obs} = K (3 \cos^2 \chi - 1) r^2$$  (1)

The spatial location of the Eu ion in the complexes seems always
to correspond with an orientation of amide molecule which has minimal
intramolecular steric interaction with the other ligands. Consequently,
the Eu-O-C-N dihedral angle varies appreciably in the amides studied
(50°-90°).

We are going to submit these results in a paper to J. Org. Chem.
Preprints will be available pretty soon on request.

Sincerely,

Giorgio Montaudo
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tris (1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) Europium (III) and Praseodymium (III)

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