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Have you looked after your 1971-1972 subscription yet? Your promptness will be greatly appreciated.

Deadline dates: No. 157: 4 October 1971
No. 158: 1 November 1971

All Newsletter correspondence, etc., should be addressed to:

Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843
Title: NMR of Membrane Surfaces.

Dear Barry,

In the course of investigation /Doklady Akad.Nauk SSSR (Proc.Acad.Sci. USSR) 194, 222 (1970)/ of the effect of paramagnetic ions on the NMR spectrum of a sonicated lecithin dispersion in water (Fig.1A) we have found that addition of Eu(NO$_3$)$_3$ splits the $N^+(CH_3)_3$ signal in two components (Fig.1B): a low field one, whose position is the same as for the salt free solution, and one shifting to higher field, the higher the salt concentration. The integral intensity of the high field $N^+(CH_3)_3$ component is 1.5 fold that of the low field component. The addition of MnSO$_4$ to this sample broadens the higher field component (Fig.1C).

We explain these results as being due to the interaction of the paramagnetic Eu$^{3+}$ and Mn$^{2+}$ ions with the polar lecithin termini (probably phosphate groups) situated only on the external surface of the bilayer vesicles (Fig.2). On resonication the sample gives spectrum indicating that the paramagnetic ions are now both "outside" and inside" the vesicle cavity. This could have been the result of breakdown of the vesicles on additional sonication followed by their reforming during which they incorporated paramagnetic ions in the internal aqueous phase.

The spectrum of the sample with "external" ions on standing did not undergo change for at least 24 hours. Obviously, paramagnetic ions of themselves do not penetrate into the internal
Fig. 1. NMR spectra of a sonicated 5% w/v dispersion of egg yolk lecithin in D$_2$O (A); after addition of 2·10$^{-3}$ M/L Eu(NO$_3$)$_3$ (B) and 3·10$^{-3}$ M/L MnSO$_4$ (C).

Fig. 2. Schematic representation of lecithin vesicles.
cavity. On the other hand, the water molecules can easily penetrate through the semipermeable membrane. This has been shown by a special experiment with a sonicated lecithin-water (H₂O) dispersion in the presence of "external" MnSO₄. The NMR spectrum revealed only a broad and no narrow H₂O signal, which in the absence of the exchange must be due to 0.5% of over all water content incorporated in the internal cavity of the vesicles.

We also have found that the Pr³⁺ and Nd³⁺ ions shift the N⁺(CH₃)₃ signal from the external surface of the lecithin vesicle in opposite direction than the Eu³⁺ ions, that is in lower field. The effect for the 0.02 M/l salt concentration is: for Eu(NO₃)₃ + 0.25 ppm, Pr(NO₃)₃ -0.66 ppm and NdCl₃ -0.15 ppm.

The use of paramagnetic ions considerably widen the possibilities of NMR spectroscopy in the study of membrane structure, permitting differentiation of the internal and external surfaces of membrane without their impairment. The method thus may find application in studies of structural asymmetry and exchange phenomena in membrane systems.

Sincerely yours,

Vladimir Bystrov

L.I. Barsukov

N.I. Dubrovina

L.D. Bergelson
July 31, 1971

Dear Professor Shapiro:

In collaboration with Jeolco's group (Mr. K. Goto et al.), we have recently completed a $^{13}$C contact shift study on the charge transfer interaction between free radical and various halogenated molecules. This study is one of our continuous studies on the molecular interaction between closed and open shell molecules (the previous works on this problem, J.A.C.S., 93, 2048 (1971), Chem. Phys. Letters, 9, 143, 203, (1971)).

$^{13}$C contact shifts induced by the addition of di-tert-butyl nitroxide (DTBN) radical were observed for halomethanes. The downfield $^{13}$C contact shifts were more pronounced for bromide and iodide than for chloride. These results were interpreted in terms of the charge transfer interaction in the manner of C-X.....DTBN interaction. The CT nature of this interaction was further substantiated by open shell INDO SCF MO calculations of the electron spin density on the halomethane carbon atom: the positive spin density on DTBN is transferred directly onto the C-X antibonding orbital of halomethane by spin delocalization mechanism.

Sincerely yours,

Teijiro Yonezawa

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

Dear Barry:

Please credit this letter to Jim Engle's dying subscription.

Studies of the Enzyme Citrate Synthase using a Paramagnetic Analog of the Substrate, Acetyl CoA.

As a continuation of our interest in paramagnetic substrate analogs (1), we have made use of a paramagnetic analog of acetyl coenzyme A (\(-R\)-CoA) synthesized by S. Weidman and G. Drysdale of Washington University, St. Louis:

\[
\text{O} \quad \text{O}
\]
\[
\text{C} \quad \text{S} \quad \text{CoA}
\]

In collaboration with these workers (2) we have found by EPR that the enzyme citrate synthase binds \(\approx 2\) molecules of \(-R\)-CoA at its 2 acetyl CoA binding sites. Binding to the enzyme enhances the effect of the unpaired electron on \(1/T_1\) of water protons (\(\epsilon_p = 3\)). Ternary enzyme-(\(-R\)-CoA)-substrate complexes are detected with oxalacetate and citrate by changes in \(1/T_1\) of water protons, and by changes in the EPR spectrum of bound \(-R\)-CoA.

In a preliminary experiment, a significant paramagnetic effect of bound \(-R\)-CoA on \(1/T_1\) and \(1/T_2\) of the protons of oxalacetate was detected suggesting that the analog of acetyl CoA is bound within \(\approx 7\)\AA{} of the other substrate, oxalacetate, in the ternary complex.


Sincerely yours,

Albert S. Mildvan

ASM:tab
Computer program VICO

Dear Barry,

We have developed a short computer program VICO which calculates vibrational corrections for direct couplings of oriented molecules. The geometry and orientation of the molecule together with its mean and mean-square amplitudes of vibration are used as input data. VICO has been tested in the case of benzene-13C


A copy with description is offered to anyone who is interested.

Sincerely yours,

P. Diehl
P. M. Henrichs
W. Niederberger
Dear Barry:

We have recently had occasion to measure deuterium isotope shifts on $^{13}$C and $^{13}$C-$^2$H coupling constants in some common deuteriated NMR solvents. Although it seems likely that others have observed such isotope shifts on $^{13}$C, a quick scan of the literature was negative. The results of our measurements are given below.

### $^2$H Isotope Shifts and $^{13}$C-$^2$H Couplings

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Delta \delta$ (ppm)</th>
<th>$J_{C-D}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDCl$_3$</td>
<td>-0.15</td>
<td>32</td>
</tr>
<tr>
<td>C$_6$D$_6$</td>
<td>-0.55</td>
<td>24</td>
</tr>
<tr>
<td>CD$_3$CN</td>
<td>CD$_3$ -0.45</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>CN =0</td>
<td>Note (1)</td>
</tr>
<tr>
<td>(CD$_3$)$_2$CO</td>
<td>CD$_3$ -0.72</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>CO +0.27</td>
<td>Note (2)</td>
</tr>
<tr>
<td>(CD$_3$)$_2$SO</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note (1): No splitting resolvable. Total line width of approx. 8 Hz probably results from a combination of D and N couplings and a small isotope shift.

Note (2): No splitting resolvable, but the line width of approx. 5 Hz was about 5 times that of the carbonyl group of the acetone in the mixture.
The difference in shift between the deuteriated and the non-deuteriated molecule, a negative shift being upfield, i.e., greater shielding. When $^{13}$C is directly bonded to D rather than to H, it is shielded more. These shifts due to the heavier isotope are in the same direction as, but considerably greater than, for $^1$H and $^{18}$F bonded to heavier isotopes [Gutowsky: J. Chem. Phys. 12, 1683 (1949); Gillespie and Quail, Ibid. 39, 2555 (1963)]. However, when the $^{13}$C is one bond removed from the heavier isotope, the isotope effect appears to be in the opposite direction.

These results are presented in order to alert those who may wish to use deuteriated solvents as secondary internal references for $^{13}$C that the isotope effect cannot be ignored. They should also stimulate the theoreticians to look more carefully into the origin of such shifts. We do not plan to pursue the matter further except possibly to make some relaxation time measurements.

The observed spectra for a CD$_3$CN + CH$_3$CN + HMDX (hexamethyl disiloxane, $b_0 = +2.0$ ppm) mixture are shown in the Figure.

Sincerely yours,

C. A. REILLY
SAMPLE:  
\[
\begin{align*}
\text{CD}_3\text{CN} & \quad 7 \\
+ \text{CH}_3\text{CN} & \quad 3
\end{align*}
\]

SOURCE: MERCK
REFERENCE: 
SOLVENT: 
CONCENTRATION: 
TEMPERATURE, °C: 37
INTERNAL STANDARD: HMDSX

\[f_1 \approx 4264 \text{ Hz}, f_2 \approx 8500 \text{ Hz}\]
STABILIZATION: \(\text{C}_6\text{F}_6, \text{ Ext Cap}\)

BRUKER HFX-90 SPECTROMETER
SCAN WIDTH SETTING: 100 Hz/cm
SCAN TIME SETTING: 1000 sec
SCAN RATE: 56 Hz/sec
SCAN TIME: 50 sec
SCAN RANGE (A): 4100 TO 4394 Hz
(B): 6700 TO 6994 Hz
SCALE: 1 PPM/cm
NUMBER OF SCANS: 32

OSC: \[f_2 \approx 13.8 \text{ W}, -21 \text{ db}\]
FREQUENCY OF \(f_2\) (A): \(-8348 \text{ Hz}\)
(B): \(-8348 \text{ Hz}\)
DECOUPLING MODE: \(\square\) SELECTIVE
\(\square\) BB MOD: 3
OPERATOR: CAR
DATE: 6/6/71
Dr. B. L. Shapiro  
Department of Chemistry  
Texas A and M University  
College Station, TX 77843

Dear Dr. Shapiro:

We have found that Eu(DPM) added to mixtures of syn and anti isomers of oximes causes sufficient separation of signals to make accurate analysis of the amounts of the isomers. The method is very good on an A-60 instrument and gives results superior to any published.

Table I. α-Methyl Resonances\(^a\) for oximes 1-6 in DCCl\(_3\)\(^b\) (\(\delta\)) and in DCCl\(_3\)-Eu(DPM)\(_3\)\(^c\) (\(\delta'\))

<table>
<thead>
<tr>
<th>R(_1)R(_2)C=NOH</th>
<th>(\delta) (Syn)</th>
<th>(\delta') (Syn)</th>
<th>(\Delta\delta) (Syn)</th>
<th>(\delta) (Anti)</th>
<th>(\delta') (Anti)</th>
<th>(\Delta\delta) (Anti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>1.86</td>
<td>2.12</td>
<td>0.26</td>
<td>1.83</td>
<td>2.72</td>
<td>0.89</td>
</tr>
<tr>
<td>CH(_3) (CH(_2))(_2)CH(_3)</td>
<td>1.85</td>
<td>2.17</td>
<td>0.32</td>
<td>1.81</td>
<td>3.01</td>
<td>1.20</td>
</tr>
<tr>
<td>CH(_3) (CH(_3))(_4)CH(_3)</td>
<td>1.83</td>
<td>2.13</td>
<td>0.30</td>
<td>1.81</td>
<td>2.85</td>
<td>1.04</td>
</tr>
<tr>
<td>CH(_3) (CH(_2))(_2)CH(_3)</td>
<td>1.83</td>
<td>2.13</td>
<td>0.32</td>
<td>1.81</td>
<td>2.91</td>
<td>1.10</td>
</tr>
<tr>
<td>CH(_3) CH(CH(_3))(_2)</td>
<td>1.82</td>
<td>2.05</td>
<td>0.23</td>
<td>1.76</td>
<td>3.11</td>
<td>1.35</td>
</tr>
<tr>
<td>CH(_3) CH(_2)CH(CH(_3))(_2)</td>
<td>1.83</td>
<td>2.03</td>
<td>0.20</td>
<td>1.83</td>
<td>2.97</td>
<td>1.14</td>
</tr>
</tbody>
</table>

\(^a\)Chemical shifts in \(\delta\), TMS internal reference. \(^b\)0.001 Mole of the oxime in 0.5 ml DCCl\(_3\). \(^c\)0.001 Mole of the oxime in 0.5 ml DCCl\(_3\) containing 20 mg of Eu(DPM)\(_3\).

Table II. α-Methylene or α-Methine Resonances\(^a\) of Oximes 1-6 in DCCl\(_3\)\(^b\) (\(\delta\)), and in DCCl\(_3\)- Eu(DPM)\(_3\)\(^c\) (\(\delta'\))

<table>
<thead>
<tr>
<th>R(_1)R(_2)C=NOH</th>
<th>(\delta) (Syn)</th>
<th>(\delta') (Syn)</th>
<th>(\Delta\delta) (Syn)</th>
<th>(\delta) (Anti)</th>
<th>(\delta') (Anti)</th>
<th>(\Delta\delta) (Anti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>2.21(q)</td>
<td>2.58(q)</td>
<td>0.37(q)</td>
<td>2.38(q)</td>
<td>3.05(q)</td>
<td>0.67(q)</td>
</tr>
<tr>
<td>CH(_3) (CH(_2))(_2)CH(_3)</td>
<td>2.17(t)</td>
<td>2.60(t)</td>
<td>0.43(t)</td>
<td>-2.13(t)</td>
<td>3.25(t)</td>
<td>0.92(t)</td>
</tr>
<tr>
<td>CH(_3) (CH(_2))(_4)CH(_3)</td>
<td>-2.15(t)</td>
<td>2.55(t)</td>
<td>0.40(t)</td>
<td>-2.21(t)</td>
<td>3.13(t)</td>
<td>0.92(t)</td>
</tr>
<tr>
<td>CH(_3) (CH(_2))(_2)CH(_3)</td>
<td>-2.17(t)</td>
<td>2.57(t)</td>
<td>0.40(t)</td>
<td>-2.22(t)</td>
<td>3.13(t)</td>
<td>0.98(t)</td>
</tr>
<tr>
<td>CH(_3) CH(CH(_3))(_2)</td>
<td>-2.37(m)</td>
<td>2.77(m)</td>
<td>0.40(m)</td>
<td>-2.37(m)</td>
<td>4.70(m)</td>
<td>2.40(m)</td>
</tr>
<tr>
<td>CH(_3) CH(_2)CH(CH(_3))(_2)</td>
<td>-2.07(d)</td>
<td>2.31(d)</td>
<td>0.24(d)</td>
<td>-2.07(d)</td>
<td>3.15(d)</td>
<td>1.08(d)</td>
</tr>
</tbody>
</table>

\(^a\)Chemical shifts in \(\delta\), TMS internal reference. \(^b\)0.001 Mole of the oxime in DCCl\(_3\). \(^c\)0.001 Mole of the oxime in DCCl\(_3\)-Eu(DPM)\(_3\).
0.5 ml DC13. 0.001 Mole of the oxime in 0.5 ml DC13 containing 20 mg of Au(DPM)3.

δ values for δ-δ resonances. δ-Methine resonances. d = doublet; t = triplet; q = quartet; m = multiplet.

Table III. Syn, anti percentages

<table>
<thead>
<tr>
<th>R1R2C=NOH</th>
<th>% Syn</th>
<th>% Anti</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3 CH2CH3</td>
<td>72.2</td>
<td>27.8</td>
</tr>
<tr>
<td>CH3 (CH2)2CH3</td>
<td>72.6</td>
<td>27.4</td>
</tr>
<tr>
<td>CH3 (CH2)4CH3</td>
<td>75±1</td>
<td>25±1</td>
</tr>
<tr>
<td>CH3 (CH2)5CH3</td>
<td>74±1</td>
<td>26±1</td>
</tr>
<tr>
<td>CH3 CH(CH3)2</td>
<td>85.7</td>
<td>14.3</td>
</tr>
<tr>
<td>CH3 CH2CH(CH3)2</td>
<td>71.0</td>
<td>29.0</td>
</tr>
</tbody>
</table>

aFrom the nmr spectra of 0.001 mole of the oxime in 0.5 ml DC13 containing 20 mg of Au(DPM)3.

Sincerely yours,

K. D. Berlin
Professor

Short titles: NMR of ketooximes
Determination of ratios of syn,anti isomers of ketooximes
Use of Au(DPM)3 to effect large chemical shifts
Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A and M University  
College Station, Texas 77943  

Dear Barry,  

Recent interest in shift reagents prompts us to report our negative results with a variety of these compounds. We are specifically interested in the possibilities of using shift reagents to simplify the spectra of biologically interesting materials such as sugars, lipids, phospholipids, nucleic acids, etc. The difficulty is that these materials are polyfunctional having several hydroxyl, amino, carboxyl, phosphate or what have you groups present. Further, the groups are either sufficiently close together or the molecules are sufficiently flexible that more than one functional group can interact with the shift reagent at the same time. The net result is the immediate decomposition of the shift reagent, extensive broadening of lines from the solute under consideration and no useful results.

The search for a suitable shift reagent for use with such polyfunctional compounds (or suitable conditions for the use of existing common shift reagents) involved the following experiments: (1) hexanol or hexylamine were used as monofunctional solutes in all experiments to test various shift reagents or experimental systems. 3-amino-1-propanol or glycerine were used as typical polyfunctional solutes. Occasionally other compounds were used at random. (2) A variety of appropriate transition metal ions and lanthanides were used usually as the dmp complexes. In a few cases the free metal ions (salts) were used in polar solvents such as water. In one or two cases some of the less commonly used metals were tried as complexes with ligands other than dmp. (3) Europium complexes with a variety of ligands (trifluoroacetylacetone, hexafluoroacetylacetone, phenyl, benzoyl, furanoyl, etc. groups) having pK values varying by up to 4 or 5 units were studied looking for more stable complexes. (4) Experiments were conducted, for the most part with Eu(dpm)₃, in different solvents and at different temperatures.

As indicated above, none of these approaches produced significant useful results for ethylene glycol, 3-amino-1-propanol, glycerine or biologically interesting materials. We would be greatly interested in any information anyone has on this subject.
In a different vein we have a position available for a technician to operate our NMR and ESR service program. We would prefer someone with a BS or MS degree and some experience with HA-60-HA-100 instruments. The position is permanent and is not suitable for people interested in postdoctoral type positions. U. K. is an equal opportunity employer. Applicants should write directly to me.

Best wishes,

S. Smith
Associate Professor of Chemistry

Terrance A. Scahill

SLS:rrk

Titles: Negative Results with Shift Reagents and Polyfunctional Compounds; Position Available.
August 24, 1971

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

Stereospecific $^{1}J_{\text{CP}}$ and $^{3}J_{\text{CP}}$ in Phosphetanes

Dear Barry,

It looks like phosphetanes are getting popular (TAMU NMR 140-2, 148-17). I would like to report some unusually stereospecific $^{13}C-3^{1}P$ couplings in a number of four-membered phosphorus heterocycles, or phosphetanes.

As can be seen there are definite stereospecificities in these couplings. The one-bond exocyclic coupling is dependent on pseudoaxial or pseudoequatorial character of the coupled carbon. The most surprising aspect of the results is the high stereospecificity of the $^{3}J_{\text{CP}}$ and $^{5}J_{\text{CP}}$. Here the coupled atoms remain fixed in their relative orientation while the exocyclic phosphorus substituents are merely switched (of course there is no stereospecificity for identical X and Y). Normally, stereospecific couplings result from dependence of the coupling on dihedral angle. I am not aware of any comparable three-bond coupling which exhibits such a high degree of stereospecificity. These results allow facile determination of cis-trans ratios in mixtures, for the above ring structures, where the $^{1}H$ nmr results are ambiguous.

The stereospecificities are not necessarily extendable to different ring methyl substitution patterns since for the 2,2,3,3,4 pentamethyl ring system the $^{3}J_{\text{CP}}$ cis/trans ratio is reversed for 0,0CH$_{3}$ and 0,0Cl as exocyclic phosphorus substituents. It remains to be seen how the $^{1}J_{\text{CP}}$ fares in those cases where there are directly bound exocyclic carbons.

These and a large number of other phosphetane oxides and salts are considered in an article Sheldon Cremer (Marquette) and I have submitted for publication.

Sincerely,

George A. Gray
Assistant Professor of Chemistry

GAG: mw
enc
Ph = phenyl, Bz = benzyl, $^3J_{CP}$ for lone ring methyl carbon, $^2J_{CP}$ for ring carbon opposite P, trans coupling is for situation where * carbon is trans to lone ring methyl.
August 24, 1971

Dear Barry:

When the effect of exchange processes on nmr line shapes was first described coalescence measurements were frequently employed to obtain an estimate of the magnitude of some rate constant. At first the novelty of the technique was sufficiently fascinating that even crude estimates of rate constants were of general interest.

One point kinetics is inherently inaccurate, with any technique. Only in simple symmetrical systems such as the uncoupled AB exchange case it is possible to define a coalescence point.

Chemically it is of interest to compare the rates of some process taking place in a series of related compounds at a common temperature. Unfortunately coalescence measurements apply to a series of different temperatures. To compare the results it is necessary to assume that the $\Delta G^\ddagger$ values are all the same. There is no a priori reason to assume this, even in cases of hindered rotation, and inspection of the literature confirms this suspicion. Converting the results from sec$^{-1}$ to kcal does not improve the validity of the method. The $\Delta G^\ddagger$'s invariably fall within the region 15±5 kcal. No respectable kineticist accepts such treatment of data.

Now, however, there is no reason to live with the vicissitudes of coalescence measurements. With properly used, improved instrumentation and canned programs which extract the rate data the nmr line shape technique has become an acceptable method for the study of rate processes.

Although coalescence measurements may sometimes give useful clues when research is in progress, I believe it is now time to ban such data from the literature.

With best regards,

Sincerely yours,

Gideon Fraenkel
Guest professor
Professor B. L. Shapiro,
College of Science,
Texas A & M University,
College Station,
Texas 77843, U. S. A.

Your ref Our ref Tel ext Date
MCM/FT 304 26.8.71

Dear Professor Shapiro,

Field Plot Device for Supercon Spectrometers

In this contribution I would like to describe an accessory for our high field spectrometers which we have found of immense value in the establishment of magnetic fields in the superconducting magnets of our HR-220s.

A profile of the distribution of flux across the business portion of the solenoid is useful for the determination of a satisfactory probe position and for the optimization of the superconducting shim controls.

Field plotting devices suitable for use in this type of exercise are quite simple to build but various reasons, for this particular application, it is advantageous to include as many of the spectrometer components as possible. The spectrometer field sweep coil, which has the same geometrical centre as the R.F. receiver coil, can be passed through the field by raising and lowering the probe whence it receives an induced e.m.f. By modifying the spectrometry circuitry, according to fig. 1, this induced voltage can be fed into the V-3523 Integration unit, amplified and integrated and used to drive the Y axis of an X-Y recorder. The X axis of the recorder is controlled from a 20cm displacement transducer attached to the vertical support of the magnet at one end and the mobile probe platform at the other. The integrator reset control is used for reproducing the start position for the Y axis but extra "back-off" is required to balance excessive drift of the pen. The X axis can be calibrated in terms of probe position (fig. 2).

A typical field plot experiment is illustrated in fig. 2. Plot (i) was the profile obtained soon after establishment field in the solenoid. Plots (ii) and (iii) were obtained after current adjustments had been made to the end coils. Plot (iv) shows something like the desired profile with slight dishing about the centre (52.5 cms) thus providing the best field and best location for the probe.

Yours sincerely,

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

Dear Professor Shapiro,

NMR Spectra of Adamantyl-substituted Phenols

The synthesis of adamantyl-substituted phenols has been reported.\(^1\) In order to study the shielding properties of the adamantyl "cage", we have synthesized the series of 2,6-di-adamantyl-4-R-phenols and obtained the n.m.r. spectra in CDCl\(_3\). The chemical shifts of the phenolic H and the 2,5-H are tabulated in Table 1 and compared with those of the corresponding 2,6-di-tert-butyl-4-R-phenols.

Table 1. Chemical shift data of 2,6-di-tert-butyl-4-R-phenols and 2,6-di-adamantyl-4-R-phenols in dilute CDCl\(_3\) solutions.

![Diagram of phenol structures](attachment:image.png)
<table>
<thead>
<tr>
<th>R</th>
<th>3,5-H</th>
<th>Phenolic-H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>Me</td>
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<td>6.92</td>
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<tr>
<td>Et</td>
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<td>6.93</td>
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<tr>
<td>i-Pr</td>
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<tr>
<td>t-Bu</td>
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<td>7.15</td>
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<tr>
<td>Ad</td>
<td>7.12</td>
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2,4,6-tri-Me-phenol: 6.77  4.40

The adamantyl-protons appear as two broad peaks at $\delta = 2.14$ (9 protons) and $\delta = 1.78$ (6 protons). In the adamantyl-substituted phenols, the 3,5-protons appear at slightly higher field than those of the t-butyl-substituted phenols, but the phenolic proton appears at lower field. The latter might indicate more restricted rotation of the OH group in the 2,6-di-adamantyl-substituted phenols.

We are obtaining the spectra of these compounds in other solvents.

Yours sincerely,

(SOON NG)

Dear Dr. Shapiro:

Conformational Interconversions in 9,10-Dihydrophenanthrene

In the course of our studies of long-range F-F coupling, we have prepared cis-1,8-dimethyl-4,5-difluoro-9,10-dihydro-9,10-phenanthradiol, I. The 94.1 MHz 19F nmr spectrum of I obtained with complete proton decoupling, is strongly temperature dependent. The single 19F resonance absorption progressively broadens as the sample temperature is decreased. At the low temperature extreme, a characteristic AB pattern results ($J_{AB} = 92.9$ Hz, $\Delta v_{AB} = 1.56$ ppm). Analysis of the temperature dependence of the nmr line shapes using the Binsch and Klein DNMR2 program allowed assignment of rate constants for the exchange process over the temperature range -36 to -10°C. From these rate constants, activation parameters were calculated: $\Delta G^\ddagger = 9.7$ kcal; $\Delta H^\ddagger = 10.1$ kcal; $\Delta S^\ddagger = -5.4$ eu.

The process which permits fluorine exchange results in greater proximity of the 4- and 5-position substituent groups. The activation energy for this process in the 4,5-difluoro compound is considerably less than that observed in 4,5-dimethyl-9,10-dihydrophenanthrene ($\Delta H^\ddagger = 22.4$ kcal$^1$). Studies of a related 4-methyl-5-fluoro-9,10-dihydrophenanthrene are in progress and will be reported on at a later date.

Very truly yours,

Frederick R. Jerome
Kenneth L. Servis

Fig. 1. $^{19}$F nmr spectrum of 1,8-dimethyl-4,5-difluoro-9,10-dihydro-
9,10-phenanthrenediol (I) at 94.1 MHz (at low temperature)
31 August 1971

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

Dear Barry:

I would like to pass along a very useful tip that was given me by Rolf Tschudin, our excellent Varian service engineer. This concerns excessive sensitivity of magnet field homogeneity to fluctuations in cooling water temperature and applies particularly to Varian 12" high impedance magnets (but not the very very old ones). In our case, small fluctuations in the cooling water temperature caused the Y-gradient to be so unsteady that lock could not be maintained longer than a few minutes at a time. Acting on a suggestion by Mr. Tschudin, we removed the homogeneity coils and pole caps from the magnet and tried to pass a brass shim (1" x 10" x 0.010") around the pole piece, between it and the coil. The coil had settled, or drooped, so that it rested on top of the pole piece and transmitted thermal changes from the water to the pole piece rather promptly.

The wedges supporting the coil were loosened at the top and driven in at the bottom - using a heavy hammer and a wooden block - until the shim showed at least 0.010" clearance all the way around. All of the wedges were then tightened with the through-bolts and the clearance re-checked. We have had no more instances of extreme sensitivity to temperature since this re-setting of the wedges was done about 8 months ago.

Yours truly,

Rolf B. Johannesen
Inorganic Chemistry Section
Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843  
U.S.A.

Title: Conformational Study of Cyclohexapeptides

Dear Barry,

In the course of systematic conformational studies of cyclic peptides and depsipeptides (valinomycin, enniatin B, antamanide and their complexes with monovalent cations, gramicidin S) we have carried out an NMR investigation of two series of cyclohexapeptides synthesized in our Institute, namely, those with all possible combination of L-alanine and glycine residues and all possible diastereomeric cyclohexaalanlys (excepting the antipodes).

In (CD$_3$)$_2$SO at 25° the spectra revealed as a rule two groups of NH signals - at higher field given by two protons and at lower field due to the remaining four protons. Temperature studies showed the $\Delta^{\delta}/\Delta^{\tau}$ values to be lower for the high field signals. This indicated that two higher field resonating NH protons form intramolecular H-bonds (IHB), whereas the four remaining NH protons interact effectively with the solvent. According the dominant spatial structure of the molecules is Schwyzer's "pleated sheet" form, in which the two NH groups are engaged in transannular IHB of the type $4 \rightarrow 1$, each H-bond closing a 10-membered ring (Fig. 1).

![Fig. 1.](attachment:image_url)
Most of the cyclopeptides show no differentiation in the 
NH deuterio exchange rates with added D₂O, which is explained 
by fast conformational A, B, C equilibrium as shown on Fig. 2.

Indeed, cooling to -40° the solution of cyclo-(Ala-Gly)₃ 
in CF₃COOH + + D₂O(7:1 v/v) mixture causes significa-
cant broadening of the CH₂ signal, an 
indication of ra-
pidly interconverting conformers.

On the basis of the NH chemical shifts, temperature gra-
dients and NH-CαH(Ala) spin-spin coupling constants the pre-
dominant structural types of the cyclic (Ala₆, Gly₆₋₆) peptides 
should be such as shown on Fig. 3 (with the coupling constant 
values).

Fig. 2

-2-

Fig. 3
From the stereochemical dependence of the $^{3}J_{(NH-C^\alpha H)}$ coupling constant it follows that the alanine methyls situated:

1) at the "C-corner" (positions 2 and 5 on Fig.1) of the "pleated sheet" are chiefly pseudoequatorial with respect to the C$_2$ axis of the molecule with low $^{3}J$ values $\sim$ 5-7 cps; 2) at the "N-corner" (position 3 and 6) are preferably in pseudo-axial orientation with higher $^{3}J$ values $\sim$ 8-9 cps; 3) at the "fold" (positions 1 and 4) of the "sheet" are also pseudoaxial with intermediate $^{3}J$ values $\sim$ 5-8 cps.

This investigation has been performed in collaboration with Drs. S.L.Portnova, V.V. Schilin, T.A.Balashova, J.Biernat, V.T.Ivanov and Prof. Yu.A.Ovchinnikov.

Sincerely yours,

Vladimir Bystrov

Vladimir Bystrov
Professor Barry Shapiro  
Chemistry Department  
Texas A & M University  
College Station, Texas 77843  

Dear Barry,  

We have recently developed an NMR chemical shift search program. The program allows one to specify chemical shift(s) (with a built in deviation of ± .02 ppm) and find those spectra in the 742 spectra from the Varian catalogs that contain the shift(s). About 2800 individual shifts have been put into computer readable form. When more than one shift value is entered, in addition to the references to each value, the program performs an AND logic search which narrows down the number of possible spectra containing two or more peaks. For example, a chemical shift of 1.12 (+ .02 ppm) appears in 19 spectra and a chemical shift of 2.29 (+ .02 ppm) appears in 35 spectra, but only two spectra, #178 and #574 contain both shifts.  

The programs to generate the file and search it are written in FORTRAN IV with a small section in assembly language. The programs are designed to run on a time-sharing DCE PDP-10 computer and are highly interactive.  

Requests concerning the availability of the file, file generation and file search programs should be addressed to Dr. A.W. Pratt, Director, Division of Computer Research and Technology, National Institutes of Health, Bethesda, Maryland 20014.  

Best wishes.  

Sincerely yours,  

Stephen Heller  
Heuristics Laboratory  

Richard Feldmann  
Computer Center Branch  

P.S. Please credit this to Jim Ferretti's account.
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