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Deadline Dates: No. 132: 3 September 1969
No. 133: 6 October 1969

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

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

During the operation of our Varian HA-100 NMR spectrometer, we have been bothered by the frequent breakdown of ballast tubes type 304 TL. These tubes last about one year and must then be replaced; occasionally, we have had to replace them at shorter intervals. One then has to wait at least one day after replacement until the magnetic field stability is attained. We decided, therefore, to replace the ballast tubes by service-free semiconductors.

We hereby describe a modified V-2100 B regulated magnet power supply system. This modification has the desirable effects of reducing both the breakdown rate and diminishing the heat production; in addition, the voltage requirement is substantially reduced due to the lower collector voltage of the transistors compared with the ballast tubes. The V 3505 Chopper-amplifier is used as before for the control and regulating functions.

Sixteen groups of power transistors, each group containing three transistors, are placed in series in order to obtain the necessary voltage stability; the detailed circuit is reproduced in an accompanying circuit diagram. The individual
amplifier plates are mounted on a 4 mm aluminium sheet measuring 295 x 290 mm. The sixteen plates are accommodated on two rods of insulating material mounted at the same place in the power supply which the ballast tubes formerly occupied. Furthermore, the built-in fan can now be used for cooling the transistors. The temperature of the emergent cooling air is ca. 40°C.

The interlock circuit has to be modified as follows: a self holding contact relay is placed in series with the S 201 (high voltage) switch. In this manner the automatic switching on of the magnetic voltage following a mains breakdown is avoided. The microswitch in parallel with the relays is conveniently operated by setting the variable transformer to zero.

Those interested in our modified power supply are invited to write for photographs showing the detailed arrangement of the individual parts.

Sincerely yours,

(W. H. Stegemann)
Schaltung der transistorisierten Stromstabilisierung
Dear Barry,

PHASE-LOCKED FIELD-FREQUENCY STABILIZATION OF 100 MHZ FOURIER TRANSFORM SPECTROSCOPY

In order to do Fourier transform nmr, we have recently constructed our own 100 MHz pulse modification for use on a Varian HA-100.

We have found it necessary to devise a low-frequency phase-locked oscillator. This was done to insure that the lock signal which we derive from a component of the free-induction decay will not vary from pulse to pulse. This, of course, is required for coherent accumulation of signal in a CAT experiment.

Figure 1 shows the connection of the pulse generator units.

In Figure 2 are the details of the low frequency locked oscillator. The FREQ. ADJ. control varies the RC time constant which determines the firing rate of the 2D21 Thyatron. A 4.3 v p-p sync voltage obtained from J1307 (SWEEP OSC. OUTPUT) permits the thyatron to fire only at the positive peak of each cycle. This locks the phase of the free-induction decay lock signal from one pulse to the next.

During operation, the R.F. reference phase control on the V-4311 is adjusted for the best lock. This is indicated by minimum jitter of the Slow Sweep galvonometer.

Some economy and savings in time resulted from the discovery that our Wavetek (model 114) VCG could be used as a versatile pulse generator. For use as a pulse generator, the Wavetek 114 (if you happen to have one around) controls are as follows:

a. Freq. Hz: x10K
b. Sweep width: max counterclockwise
c. Start/Stop point: -90°
d. Trigger mode
e. Slope: +
f. Level: +
g. Sweep rate Hz: off
h. Attenuator:  

The pulse width may be conveniently varied by the frequency dial and is given (in μ sec) by $\frac{1}{500/\text{dial reading (kHz)}}$. Pulse height can be varied from 0 to ~30 volts.
We have obtained and transformed a number of spectra successfully. Some subtle pitfalls in the Fourier technique have appeared, especially when multiple pulse experiments (i.e., signal averaging) are desired. These electronic bugs are in the process of being exterminated and we hope to have some results to report in a few weeks.

Very truly yours,

Stanley Gross
S. Gross
Richard E. Graves
B. Graves
P. Rose
Research Laboratories

**Figure 1**

**Figure 2**
Dear Dr. Shapiro,

We wish to report here what we believe to be the first example of an internal nuclear Overhauser effect between aromatic protons.

The molecule chosen for this investigation was dibenz[a,j]anthracene (I) whose N.M.R. spectrum is shown in fig I. In this system, H_{14} is very close to (and thus strongly relaxed by) H_1 and H_13. We could thus hope to observe a N.O.E. between these nuclei.

Double irradiation experiments (Bruker HX 90 Mc) were performed on a saturated CDCl_3 solution of freshly recrystallized dibenz[a,j]anthracene, which had been thoroughly degazed under high vacuum and sealed in an atmosphere of nitrogen. The integrated area of proton H_7 was used as an internal reference for measurements.

Saturation of the singlet of H_{14} produces an enhancement of 23.8 % of the integrated area of the multiplet of (H_1+H_{13}). The reverse experiment, i.e. saturation at the center of the multiplet of (H_1+H_{13}) results in an enhancement of 40.2 % of the integrated area of proton H_{14}.

No N.O.E. was detectable between peri or ortho protons (internal reference : H_{14}).

These results can be interpreted qualitatively by assuming that proton H_{14} is "protected" by H_1 and H_{13} against intermolecular relaxation effects whereas protons H_1 and H_{13} are more accessible and thus more readily relaxable by an intermolecular mecanism.
A more detailed account of this work will be published later.

With best regards.

Yours sincerely,

M.J. MARCHANT  
N. DEFAY  
R.H. MARTIN.
MAGNETIC RESONANCE COMPUTER SYSTEM

The Union Carbide Research Institute at Tarrytown, New York, is developing a computer system for multi-purpose NMR spectroscopy in a time-averaging mode. Since a C-1024 computer was already available, they were interested in incorporating it into their expanded system which consists of a PDP-8/I Computer, Varian C-1024 Analyzer, Frequency Synthesizer, Nuclear Magnetic Resonance (NMR) Interface Unit and an NMR Spectrometer. The central element in the system is the PDP-8/I Computer which is used to control the frequency spectrum of the Synthesizer and process digital data developed by the C-1024 Analyzer.

The computer, under program control, is capable of selecting up to 1,024 successive frequency settings of the Synthesizer in a predefined sequence. The output of the Synthesizer in turn is utilized to drive the Spectrometer. The analogue output of the Spectrometer is sampled and converted to binary data by the Varian C-1024 Analyzer. It is therefore possible to generate repetitive programmed frequency scans and achieve enhanced signal-to-noise characteristics by the utilization of time averaging correlation techniques. The C-1024 may also be easily detached and used normally in a remote time averaging experiment, freeing the central computer for other applications.
Magnetic Resonance Computer System

The NMR Interface Unit, designed by Custom Computer Systems, Inc., Plainview, New York, contains the specialized electronics and control logic required to interface the PDP-8/I computer to the Varian C-1024 Time-averaging computer and the Digitized Frequency Synthesizer. The Interface Unit is designed to accept 17 bit data words from the Varian C-1024 Analyzer, and reformat the data for transfer into the 12 bit word PDP-8/I computer. The interface Unit also will accept address information from the PDP-8/I computer, which in turn is processed and provided as an input to the Varian C-1024 Analyzer. Special devices in the Interface Unit are utilized to interface the PDP-8/I computer to the Frequency Synthesizer. Noise suppression networks have been included in the Interface Unit to minimize susceptibility to noise transients.

The flexibility that can be achieved by the proposed system will enable researchers to develop varied systems. Both broadline and high resolution resonance patterns can be developed. Furthermore, the data processing capability of the PDP-8/I computer can be utilized to filter, edit and otherwise enhance the quality of the resultant experimental data.

Anyone interested in further details about the system is invited to contact Robert Trocchio, Custom Computer Systems, Inc., 40 South Mall, Plainview, New York 11803.

Robert Trocchio
Re.: Impurities in Tetramethylsilane

Dear Professor Shapiro,

In the course of studying highly diluted solutions with internal standardisation by TMS we came across an impurity in the Tetramethylsilane-standard-substance which proved to be Tetrahydrofurane. This impurity for instance is present in Merck-Uvasol-Tetramethylsilane and in Fluka-Tetramethylsilane.

Fig. 1 is the CAT-1000 output after 40 scans showing the two multiplets of Tetrahydrofurane being centered at 161,0 c/s and 325,9 c/s downfield from TMS at a standard frequency of 90 Mc. The CAT-1000 was attached to a Bruker KIS HFX 90/60 NMR Spectrometer operating at 90 Mc.

Studying dilute solutions with the aid of "time-averaging" this impurity could give rise to erroneous signals which have nothing to do with the substance under study. Being a cyclic ether tetrahydrofurane could interfere when studying association equilibria.

We succeeded to eliminate the Tetrahydrofurane by simple column chromatography with Al₂O₃ basic, Merck.

Sincerely yours,

(E. Lippert) (U. Jentschura)
Fig. 1

* Shifts are in $\text{c/s}$ downfield from TMS
SPECTRUM ANALYSIS USING A DUPONT 310 CURVE RESOLVER

In many applications band overlap problems greatly inhibit the extraction of analytical data from NMR spectra. In recent years attempts have been made to overcome these overlap problems using a variety of techniques (1). Where the spectrum of interest consists of a number of overlapping symmetrical bands with the same basic line shape the system can be resolved or at least partially resolved eg by deconvolution methods, (1). However, in many industrial applications spectra given by commercial products, eg petroleum fractions, are usually composed of overlapping bands of very different widths and shapes which makes the application of mathematical methods difficult. To overcome these difficulties we have recently been conducting some experiments with a Dupont 310 Curve Resolver, where the composite (experimental) spectrum is synthesized by summing a number of component peaks which are generated by the instrument. The original spectrum, the matching synthesized spectrum and the component peaks can be readily displayed, superimposed or otherwise on the instrument viewing screen. Further details of the instrument and its operation have appeared elsewhere, (2), (3).

In practice we have found the instrument very simple to use and the changes that can be observed in the synthesized spectrum on the addition of various peaks can be most illuminating. Figure 1 shows a typical analysed spectrum given by a petroleum fraction of which it was desired to know the various concentrations of CH₃, CH₂ and CH groups. Analyses of this kind are not possible at this time by any other method.

While the use of the 310 Curve Resolver is obvious equally obvious is its abuse. Clearly, realistic band shapes must be generated using knowledge gained by the examination of the spectra of suitable reference materials. Also the positioning of bands must be done carefully using reference chemical shift data. If these dangers are realised and accommodated the 310 Curve Resolver can be a most useful aid in spectrum analysis.

We should like to acknowledge the kind co-operation of Mr I.G. Wylie of Dupont Instruments, Hitchin, Herts, England in this work.

S.A. Knight
REFERENCES

(1) R.R. Ernst, Advances in Magnetic Resonance, Vol 2, 50.

(2) 310 Curve Resolver, Instrument Products Division, E.I. Du Pont de Nemours and Co. (Inc), Wilmington, Delaware 19898.


ALKYL REGION OF HYDROGEN-NMR SPECTRUM OF AN AROMATIC PETROLEUM FRACTION

CURVE ASSIGNMENT

1. CH $\alpha^*$
2. CH$_2$ $\alpha$
3. CH$_3$ $\alpha$
4. CH$_3$ $\alpha$
5. (CH$_2$ + CH)$_\beta$
6. CH$_2$ + CH (8--)
7. CH$_3$ $\beta$
8. CH$_3$ (8--)

$^*$ $\alpha$, $\beta$, 8 WITH RESPECT TO THE AROMATIC RING
DEAR Barry,

One of the main handicaps for using computers in connection with spectrometers is to get the necessary interfaces. We were faced with the situation having a good computer (Varian 620i) and several spectrometers (A60D, DA60, HR220 and a self-made one) but no interface to connect them. We decided to use our C1024 time averaging device to accumulate the data from the spectrometers and, later, to transfer them to the computer for data handling. Actually, for many people, this may be one of the easiest ways to feed NMR spectra into a computer. Even if a direct interface is available (we got ours in the mean time from Varian), it can well be justified to use a C1024 for tedious time averaging instead of blocking a computer for the entire time (we want to use, for example, the computer at the same time for IR interferometry). At present, we are using this system for stochastic resonance experiments, employing noise to excite the resonances.

The attached scheme should be self-explanatory. The interface connects the binary output of the C1024 to the I/O bus of the 620i. Except for the levelconverters, integrated circuits from Texas Instruments are used. It is important to interconnect pins 32 and 48 at the C1024 connector P1, otherwise, the address advance does not work. The address of the interface arbitrarily was selected to be 158.

The following little routine will load 1024 words from the C1024 into the computer memory starting at address FADDR. The C1024 controls are switched to BINARY READ OUT mode.
,.LDB ,FADDR load address of first memory location
,.LDX1 ,1024 load number of words to be transferred
START ,CIA ,015 transfer one word into A register
,.CPA , complement content of A register
,.STA ,0,2 store content of A register
,.IBR , form next address
,.DXR , count transferred words
,.JXZ ,STOP stop if 1024 words transferred
,.JMP ,START go to next transfer
STOP ,HLT , halt

This shows that it is not too difficult to build simple interfaces yourself.

With best regards

Richard R. Ernst
INTERFACE
C1024 - 620i
7-7-69 R.E.
July 11, 1969

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

Some Observations of Proton-Fluorine Coupling Constants

Dear Barry:

In 1965 we reported observation of spin-spin coupling between $H_5$ and $H_6$ and between $H_5$ and $H_7$ of the purine cation.* We have since observed spin-spin coupling of $H_5$ of 9-benzyl-2,6-difluoropurine, 1, with at least one of the fluorines, presumably $F_6$.

![Diagram of purine molecule]

It was not possible to resolve the $H_5$ peak sufficiently well to determine whether $H_5$ is coupled to both fluorines, but the broadness of the "doublet" suggests that this may well be so. This coupling was observed on the neutral molecule in CDCl$_3$, whereas that reported for purine was not observable on the neutral molecule, but only on the cation. $J(F_6, H_5)$ of I is approximately 1.6 Hz, whereas $J(H_5, H_6)$ of the purine cation was found to be about 0.3 Hz.

Over a period of several years, we have had occasion to determine the pmr spectra of 23 nitrosoureas of the form

![Diagram of nitrosourea molecule]

* The asterisk is used to denote an earlier reference.
where R varied among aliphatic and aromatic groups. In all cases the proton spectrum of the 2-fluoroethyl group was of the general form (eliminating some fine structure on the "triplets"):

\[ \delta_a - \frac{1}{2} J(H_a, F) \approx \delta_b - \frac{1}{2} J(H_b, F), \]

thus giving rise to the upfield singlet which represents half of the total absorption from the (a) and (b) protons. As measured from the center peaks of the "triplets" to the singlet: \( J(H_a, F) \approx 22 \text{ Hz}, J(H_b, F) \approx 49 \text{ Hz}, \) with variations of 1-2 Hz over the range of 23 compounds.

Ureas without the nitroso group, of the form

\[
\begin{align*}
\text{R-N-C-N-CH}_2-\text{CH}_2-\text{F} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{(a')} & \text{(b')}
\end{align*}
\]

III
Southern Research Institute

Professor Bernard L. Shapiro
July 11, 1969

-give more complex and predictable spectra, since \( \delta_{a'} \) is smaller, and \( J(Ha',F) \) greater (~27 Hz), than in compounds of type II.

Sincerely yours,

Martha Thorpe, Research Chemist
Molecular Spectroscopy Section

MT fh

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

ADDUCTS OF MIXED BORON TRIHALIDES

Dear Dr. Shapiro:

With this contribution I would like to begin a subscription to the TAMU NMR Newsletter. Brock University's small n.m.r. group, consisting primarily of Dr. Jack Miller and myself and our students, is mainly concerned at present with the study of Lewis acid-base complexes. We have an A-60 with CAT and spin decoupler at Brock, and have had access to more extensive n.m.r. facilities through the courtesy of McMaster University's Chemistry Department.

We have recently observed low-temperature proton, fluorine and boron-11 n.m.r. spectra of the mixed boron trihalide adducts Me₂O.BF₂Cl and Me₂O.BFCI₂. These form readily through halogen scrambling when a methylene chloride solution of the adducts Me₂O.BF₂ and Me₂O.BCl₂ is warmed briefly to room temperature. Adducts of the mixed boron trihalides do not appear to have been reported previously although the mixed trihalides themselves, which are unstable to disproportionation, are well known.

As expected, the proton complexation shifts of the mixed adducts are intermediate between those of the BF₃ and BCl₃ adducts; however they do not vary linearly with the number of chlorines. (Me₂O complexation shifts in p.p.m: BF₃, 0.59; BF₂Cl, 0.65; BFCl₂, 0.78; BCl₃, 0.96). Trends in the fluorine spectra of the adducts resemble trends in the free mixed trihalides:

<table>
<thead>
<tr>
<th>Trihalide</th>
<th>¹⁹F Chemical shifts (ppm from CFCl₃)</th>
<th>J₁¹B - ¹⁹F (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>free trihalide (1)</td>
<td>free trihalide (1)</td>
</tr>
<tr>
<td>BF₃</td>
<td>124.2</td>
<td>15</td>
</tr>
<tr>
<td>BF₂Cl</td>
<td>73.5</td>
<td>34</td>
</tr>
<tr>
<td>BFCl₂</td>
<td>36.0</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Me₂O.BF₂Cl</td>
<td>Me₂O.BFCl₂</td>
</tr>
<tr>
<td></td>
<td>158.2</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>132.6</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>116.2</td>
<td></td>
</tr>
</tbody>
</table>

July 11, 1969.
If the $^{19}$F chemical shift pattern of the free trihalides is attributed to $\pi$ bonding, survival of much of the $\pi$ bonding in the adducts is indicated, in line with recent calculations (2).

We attempted boron - $^{11}$ resonance at 11.46 MHz to verify the coupling patterns seen in the fluorine - $^{19}$F spectra. We did not get sufficient resolution for this. However, in related work with solutions containing $\text{Me}_2\text{O.BCl}_3$ and $\text{Me}_2\text{O.BBr}_3$, boron - $^{11}$ resonance provided evidence for the existence of the mixed complexes $\text{Me}_2\text{O.BCl}_2\text{Br}$ and $\text{Me}_2\text{O.BClBr}_2$.

Preliminary studies show that the mixed boron halide adducts of a number of other Lewis bases form readily by halogen scrambling. We are investigating the scope and limitations of this reaction.

Yours sincerely,

\[\text{Steve Hartman}\]

JHS:nd

J. S. Hartman.

References:


Dear Dr. Shapiro,

I have been recently interested in measuring the 60 MHz. spectra of a series of mercury-furan derivatives in concentrated DMSO solutions, and thus I also measured the furan itself in the same solvent. I observed that in a 50% solution in DMSO the central peaks of the two triplets of its spectrum are actually resolved in three bands, each other separated by 0.11 Hz. Furthermore also the bands of much smaller intensity have been detected, so that the whole spectrum displayed 18 out of the 24 theoretical bands of an AA'BB'C.

The spectrum of the furan is normally formed by only two triplets and for such a reason was at first believed to be an A2X2 system. Abraham and Bernstein [Can. J. of Chem. 39, 216, 905, (1961)] pointed out however that it had to be considered a case of deceptive simplicity and later Reddy and Golinstin [J. Am. Chem. Soc., 84, 583, (1962)] by resolving in a doublet each of the central peaks of the triplets, observed an 8 band spectrum. Grant, Hirst and Putowsky, enhancing the bands of very small intensity, obtained a 14 bands spectrum [J. Chem. Phys., 38, 470, (1963)].

In the present case a still more resolved spectrum is displayed and therefore measurements of the greatest precision hitherto attained for the furan could be carried out by means of the LAOCN III computing program.

Tables with the chemical shifts (referred to the DMSO which is 151.87 Hz. downfield in respect to TMS) and J coupling constants as well as the experimental and calculated frequencies are reported.

Only very few lines are still degenerate in the present spectrum, as it can be seen in the figure in which the upfield symmetrical half spectrum is reported (upper) together with the calculated one (below), drawn for greater convenience in a twice enlarged scale.

It can be thus concluded that in such conditions of solvent and resolution (band width = 0.15 Hz.) the deceptive simplicity of the 60 MHz. spectrum of the furan is completely removed.

Yours sincerely,

Vedovico Lunazzi
TABLE 1 - Chemical shifts (in Hz. in respect to DMSO) and $J_{HH}$ coupling constants for the 60 MHz. spectrum of the furan.

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Ref. 2</th>
<th>Ref. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1 = v_4$</td>
<td>306.892 ± .009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_2 = v_3$</td>
<td>236.028 ± .009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_{12} = J_{34}$</td>
<td>1.752 ± .030</td>
<td>1.75</td>
<td>1.8</td>
</tr>
<tr>
<td>$J_{13} = J_{24}$</td>
<td>0.814 ± .030</td>
<td>.85</td>
<td>0.8</td>
</tr>
<tr>
<td>$J_{14}$</td>
<td>1.486 ± .012</td>
<td>1.4</td>
<td>1.55</td>
</tr>
<tr>
<td>$J_{23}$</td>
<td>3.271 ± .014</td>
<td>3.3</td>
<td>3.53</td>
</tr>
</tbody>
</table>

![Diagram of Furanc molecule]
### TABLE 2 - Experimental and calculated 60 MHz. spectrum of the furan.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Calculated frequencies</th>
<th>Intensity</th>
<th>Experimental frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>231.203</td>
<td>0.017</td>
<td>231.15</td>
</tr>
<tr>
<td>48</td>
<td>234.125</td>
<td>0.109</td>
<td>234.14</td>
</tr>
<tr>
<td>54</td>
<td>234.722</td>
<td>1.928</td>
<td>234.76</td>
</tr>
<tr>
<td>42</td>
<td>234.742</td>
<td>1.929</td>
<td>235.90</td>
</tr>
<tr>
<td>28</td>
<td>235.909</td>
<td>1.879</td>
<td>235.90</td>
</tr>
<tr>
<td>5</td>
<td>235.960</td>
<td>1.977</td>
<td>236.01</td>
</tr>
<tr>
<td>29</td>
<td>236.050</td>
<td>1.982</td>
<td>236.13</td>
</tr>
<tr>
<td>52</td>
<td>236.141</td>
<td>1.891</td>
<td>237.34</td>
</tr>
<tr>
<td>2</td>
<td>237.288</td>
<td>2.072</td>
<td>237.99</td>
</tr>
<tr>
<td>13</td>
<td>237.308</td>
<td>2.074</td>
<td>237.99</td>
</tr>
<tr>
<td>27</td>
<td>237.925</td>
<td>0.121</td>
<td>240.76</td>
</tr>
<tr>
<td>6</td>
<td>240.807</td>
<td>0.022</td>
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<tr>
<td>34</td>
<td>302.113</td>
<td>0.022</td>
<td>302.07</td>
</tr>
<tr>
<td>22</td>
<td>304.995</td>
<td>0.121</td>
<td>305.00</td>
</tr>
<tr>
<td>37</td>
<td>305.612</td>
<td>2.074</td>
<td>305.62</td>
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<td>53</td>
<td>305.632</td>
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<td>306.779</td>
<td>1.891</td>
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<tr>
<td>11</td>
<td>306.870</td>
<td>1.982</td>
<td>306.92</td>
</tr>
<tr>
<td>30</td>
<td>306.960</td>
<td>1.977</td>
<td>307.03</td>
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Professor B. L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station,
Texas 77843,
U. S. A.

Dear Barry,

Diastereoisomeric N,N'-diacylhydrazines

Hindered rotation about the N–N' bond of the N,N'-diacyl-
hydrazines (I) results in the possible existence of three racemates
(Ia, Ib, and Ic) associated with enantiomers having the indicated
absolute configurations. The Cahn–Ingold–Prelog designations used
in the formulae (Ia, Ib, and Ic) refer in the following order to the
chirality of (i) the acyl residue on the left, (ii) the N–N bond, and
(iii) the acyl residue on the right.

\[
\begin{align*}
\text{PhCHX} & \quad \text{CO} \quad \text{N} \quad \text{N} \quad \text{CO} \quad \text{CHXPh} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

(I)

(a) RRR : SSS
(b) RRS : RSS
(c) RSR : SRS

This possibility of associating the formula (I) with three racemates
has been examined by treating N,N'-dimethylhydrazine with 2-phenyl-
propionyl chloride. This yielded two compounds, A, m.p. 87-90°, and B, m.p. 116-119°. The compound A in pentadeuterionitrobenzene solution at 140° showed a doubling of all the signals assignable to the N–CH₃, CH–Me, and CH–CH₃ groupings. This identifies compound A as giving the racemate ( Ib; X = Me) in solution and appropriate coalescences are observed in its nuclear magnetic resonance spectrum at 200° due to a more rapid equilibration between the enantiomers ( Ib, R R S) and ( Ib, R S S).

Compound B gives a nuclear magnetic resonance spectrum in C₆D₅NO₂ solution at 140° showing that it is an equilibrium mixture derived from the racemates ( Ia and Ic; X = Me) in a 4 : 1 ratio; it is not yet possible to determine which of the two racemates ( Ia or Ic; X = Me) predominates. At higher temperatures (200°) the changes in the nuclear magnetic resonance spectrum of compound B correspond to a more rapid interconversion of the racemates ( Ia and Ic; X = Me) resulting in an N–Me singlet and a C–Me doublet.

The temperature-dependence of the nuclear magnetic resonance spectra of compound A depends upon the rate of interconversion between the enantiomers ( Ib, R R S) and ( Ib, R S S), whereas for compound B, the temperature-dependence involves the equilibrium between the racemates ( Ia) ⇌ ( Ic). Both these phenomena involve N–N bond rotation and the rotational barrier determined for both cases is of the same order as that found for other N,N'-diacylhydrazines (G. J. Bishop, B. J. Price, and I. O. Sutherland, Chem. Comm., 1967, 672). Below 140°, spectra were as expected further complicated by the consequences of hindered rotation about the N–CO bond.

Similar results have been obtained by acylation of N,N'-dimethylhydrazine with (+)-2-phenylbutyryl chloride giving the compounds ( I; X = Et). In this case the configurational assignments have been checked using optically active S-(+)-2-phenylbutyryl chloride as the acylating agent.

We feel that these results are of general interest in that they indicate a new approach for the examination of certain processes involving bond rotation and ring inversion.

Yours sincerely,

R. P. Gellatly W. D. Ollis I. O. Sutherland
Dear Professor Shapiro:

Long range coupling in sulfones

In connection with synthetic work on epoxysulfones we have measured the NMR-Spectra of several unsymmetrical sulfones. It turns out that in most cases a long range coupling could be observed as seen in the data of the following samples:

\[
\begin{align*}
H_2C\text{-C} - & \text{SO}_2CH_3 & \text{Ph COC} - & \text{SO}_2CH_3 \\
\delta 8.13 & \text{Cl} & \delta 6.99 & \\
(1) = 7 & & (1) = 0.8
\end{align*}
\]

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Only in the spectra of 1 and the acetate 6 no coupling could be observed. There is one further point which might be of interest: The extremely downfield shift of the dq. 3.64 in compound 5 in DMSO. In (CD₃)₂CO this signal is located at 4.69, while all the other signals are nearly unchanged. Perhaps in DMSO the following solvate may be the reason:

\[
\begin{align*}
H_3C\text{[C≡C]_2 CH₂ SO₂ CH₃} & \text{[C≡C]_2 C} - \text{SO₂ CH₃} \\
\delta 9.66 & \text{[C≡C]_2} & \delta 6.89
\end{align*}
\]

Yours sincerely,

F. Bohlmann
Cher Professeur SHAPIRO,

"Mise en évidence, par R. M. N., de la structure d'aldoxy-aldéhydes α éthyléniques α deutériés".

Des alcoxy-aldéhydes α éthyléniques α deutériés avaient été préparés par la méthode suivante (1)(2):

\[
\begin{align*}
RO-CH-C\overset{\text{H}}{\equiv}C-CH_2OR & \xrightarrow{\text{base DMSO}} \text{ROCH-CH=C=CHOR} \\
\text{(I)} & \\
\end{align*}
\]

\[
\begin{align*}
\text{RO-CH-CH=CD-CH}_2OR & \xrightarrow{D_3O^+} \text{cis et trans} \\
\text{(II)} & \\
\end{align*}
\]

La chromatographie en phase vapeur n'avait pas permis de différencier les composés deutériés de leurs homologues hydrogénés. Par R. M. N., nous prouvons immédiatement que la deutérisation s'est bien effectuée et, de plus, nous définissons sans ambiguïté la position du deutérium dans la molécule.
En effet, alors que dans le composé hydrogéné (III) on observe un doublet pour le proton aldéhydique 1 par couplage avec le proton 2 ($J_{1-2}^\text{trans} = 7.6$ Hz trans ; $J_{1-2}^\text{cis} = 7.3$ Hz cis), dans l'homologue deutérié, il apparaît un triplet de constante de couplage très faible ($J_{\text{cis}}^\text{parf} = 0.3$ Hz), qui témoigne de la présence d'un deutérium en position 2.

D'autre part, la R. M. N. distingue les isomères cis et trans pour lesquels le déplacement chimique du proton aldéhydique est différent :

$$\delta_1^\text{cis} = 10.08 \text{ p.p.m.}$$
$$\delta_1^\text{trans} = 9.54 \text{ p.p.m.}$$

La figure ci-jointe représente les spectres obtenus pour $R = R' = \text{CH}_3$ sur un appareil Varian A 60, à température ambiante.

Récérences :


Bien cordialement,

R. FREYMANN

[Signature]

R. MANTIONE

G. MARTIN
"Conformation of Five-membered Ring Phosphites"

The interest in the synthesis of cyclic five-membered ring phosphate esters from analogous phosphite precursors has led Gary Newton and myself to examine the stereochimstry of trivalent phosphorus, and the conformational preferences in these systems. Previous nmr studies of cyclic phosphites have agreed that inversion at phosphorus is very slow.\(^1\)-\(^4\) Furthermore, it has been shown that ethylene phosphites\(^3\), ethylene chlorophosphite\(^2\),\(^3\) and propylene phosphites\(^4\) possess non-equivalent protons. However, two explanations have been offered for the different magnetic environments in these compounds: (1) a stable pyramidal stereochemistry at phosphorus with a planar five-membered ring\(^1\),\(^2\),\(^4\) and (2) a twist-envelope conformation of the five-membered ring with a O-C-C-O dihedral angle of 30°.\(^3\)

We have examined the nmr spectra of a series of isobutylene phosphites I a-e and propylene phosphites II. The data obtained from a detailed analysis of these spectra are given in Table I. The P-O-C-H couplings constants observed in I are considerably different from those observed in ethylene phosphites\(^3\). It has been suggested that the different P-O-C-H couplings in ethylene phosphites are due to the orientation of the protons with respect to the lone-pair on phosphorus in a planar ring\(^2\). At least two factors are not consistent with this interpretation for the compounds reported here. (1) If the ring were planar, expected P-O-C-H couplings in the iso-butylene phosphites, I, would be of similar magnitude as those observed for the ethylene phosphites\(^3\). The larger P-O-C-H couplings observed in I (13.0 vs 9.0 Hz) are incompatible with a planar ring. (2) Replacement of a proton cis to the phosphorus lone pair with a methyl group, as in II, should not alter the overlap of the remaining cis proton. However, significantly different
P-O-CH couplings are observed in II.

Thus, the nmr data for I and II are not consistent with a planar ring, but are in accord with a twist - envelope conformation for the five-membered ring similar to that proposed for methyl ethylene phosphite\(^3\) (a twist of \(\sim 30^\circ\)). The coupling constants in II are consistent with this value whereas the larger P-O-C-H couplings in I suggest a somewhat larger degree of twist.

\[
\begin{align*}
\text{Table} & \\
V_1 & V_2 & V_3 & V_4 & J_{24} & J_{35} & J_{45} \\
\text{Ia} & 1.447 & 1.248 & 3.796 & 3.802 & -8.45 & 13.43 & 0.29 \\
\text{Ib} & 1.437 & 1.228 & 3.738 & 3.826 & -8.32 & 12.99 & 0.27 \\
\text{Ic} & 1.440 & 1.206 & 3.714 & 3.874 & -8.25 & 13.20 & 0.32 \\
\text{Id} & 1.479 & 1.336 & 3.723 & 3.803 & -8.32 & 13.12 & 0.31 \\
\text{II} & 4.486 & 1.217 & 3.368 & 4.167 & -8.22 & 8.17 & 1.94 (J_{15} = 0.40) \\
\text{methyl ethylene phosphite}^c & 3.656 & 3.405 & 3.405 & 3.656 & -8.44 & 8.97 & 1.87 \\
\end{align*}
\]


Sincerely yours,

Dick

Richard H. Cox
Assistant Professor

RHC:jlw

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

Dear Dr. Shapiro:

"Decoupling" of $^{31}$P-$^1$H in a Phosphine by Complexation  
with Nickel Chloride

We wish to describe a particularly striking case where complexation of trivalent phosphorus with Ni$^{2+}$ results in complete disappearance of $^1$H-$^{31}$P coupling. Such "decoupling" in metal complexes of phosphines is not unknown, although not well understood [for a recent discussion, see Fackler, et al, J. Am. Chem. Soc., 91, 1941 (1969)]. Our case is of interest in demonstrating the valuable simplification of the spectrum that results, and we point it out thinking that others unaware of the effect may find it useful in studying nmr spectra of phosphines. The spectrum may also interest those studying the spectra of complexes.

The spectrum of 1-methyl-3-phospholene is reproduced in Fig. 1. $^{31}$P-Coupling causes the methyl group and the vinyl protons to appear as doublets, and the non-equivalent methylene protons to appear as an ABX signal. Fig. 2 is the spectrum of the NiCl$_2$ complex of this phosphine. The complex forms readily, although its analysis suggests a ratio of phosphine to NiCl$_2$ between 2 and 3. The spectrum shows the complete absence of any coupling to $^{31}$P. Singlets are now present for the P-CH$_3$ group and the vinyl protons. The ABX of the methylenes is reduced to an AB signal. The result is precisely what would be expected for the phosphine under hetero-nuclear decoupling.

The same effect has been noted for 3,4-dimethyl-3-phospholene, which forms an exact 2:1 complex with NiCl$_2$.

Please credit this submission to Dr. Peter W. Jeffs, Department of Chemistry, Duke University.

Louis D. Quin  
Jay G. Bryson
Fig. 1

Fig. 2

in CDCl₃

(neat)
Dear Professor Shapiro,

Geometry of the 1,3-oxathiane ring as found from NMR

In our laboratory, an extensive investigation into the geometry of cyclic organic compounds has been carried out\(^1\), mainly by means of X-ray analysis. One of our present interests is to correlate the physical properties (viz. dipole moments, vibration spectra and coupling constants) with the geometrical arrangement of the atoms in non-aromatic ring compounds\(^1-4\). Recently, the so-called "R-value method", introduced by Lambert\(^5\), was extended as follows\(^4\): For cyclic compounds having two equivalent conformers (i.e. conformer population ratio is 1:1, viz. 6-rings with two equivalent chair forms) and having a \(-\text{CH}_2\text{-CH}_2-\) or a \(-\text{CH}_2\text{-CHR-}\) moiety for which two vicinal proton coupling constants \((J_{\text{trans}} \text{ and } J_{\text{cis}})\) can be evaluated from the NMR spectrum, the ratio

\[
R = \frac{J_{\text{trans}}}{J_{\text{cis}}} \approx \frac{3 - 2\cos^2 \psi}{4\cos^2 \psi}
\]  

\(\psi\) is the ring dihedral angle in the \(-\text{CH}_2\text{-CHR-}\) fragment. The results for more than 20 compounds indicate\(^4\) that the \(\psi\) values calculated from the experimental vicinal coupling constants with the aid of eq. (1) agree with the results from diffraction analyses within about 2°.

We are currently interested in investigating saturated \(1,3\)-dihetero six-membered rings and in this paper the results of the NMR analysis of 6,6-dimethyl-1,3-oxathiane (see Figure) are reported.

The AA'BB' spectrum of the \(C_4-C_5\) moiety (taken at 100 Mc/s with a Varian HA-100 and at 60 Mc/s with a Jeol JNM-MH-60) yields: \(\nu_A\) (protons at \(C_5\)) = 1.7 ppm, \(\nu_B\) (protons at \(C_4\)) = 2.7 ppm, \(L = 5.3\), \(M \approx 0\), \(N = 12.4\) c/s.
K cannot be extracted from the spectrum. The low value of M is not unexpected, as the geminal coupling constant in the -CH₂-S-(thiaine) and in the -CH₂-CH₂-moity (cyclohexane) has about the same value (-13 c/s). The vicinal couplings in the -CH₂-CH₂-moity follow from N and L and are, thus, 8.8 and 3.5 c/s, respectively. This yields for R 2.49 and for the ring dihedral angle \( \psi = 60^\circ \) (consistent with a normal chair geometry).

The corresponding 1,3-dioxane and 1,3-dithiane ring geometries are known from X-ray analyses on 2-substituted derivatives. The ring dihedral angles in the C₄-C₅-C₆ moiety are 62° in the sulfur compound and 59° in the oxygen compound, the latter value being in fair agreement with the R-value for 1,3-dioxane and its 4,4-dimethyl derivative. The geometry found from NMR for the 1,3-oxathiane ring is, thus, intermediate between those of the 1,3-dioxane and the 1,3-dithiane systems, a trend also observed in the case of the corresponding 1,4-dihetero rings.

Syntheses of other derivatives of 1,3-oxathiane are in progress in order to evaluate the ring dihedral angle about the C₅-C₆ bond, whereas an X-ray analysis on 2-p-chlorophenyl-1,3-oxathiane will be carried out for obtaining the entire ring geometry and for a further test of the validity of the "R-value method".

10. N. de Wolf and C. Romers, to be published.

Yours sincerely,

[Signatures]

H. R. Buys

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

Department of Chemistry

July 28, 1969

DNMR III Computer Program

Dear Barry:

Today just a brief progress report on our general NMR line-shape computer program DNMR (cf. TAMUNMRN 117-21).

Those of your readers who have obtained copies will have noticed that the original (loc. cit.) matrix diagonalization routines were replaced by ALLMAT (this version is now referred to as DNMR II). This change resulted in a tremendous boost in efficiency. Just to convince ourselves of what the program is now capable of doing we have performed a sample calculation on a ABCD ≠ EFGH exchange problem, a copy of which is attached. One such spectrum consumes 14 minutes of CPU time on our second-generation computer, and we are told that this will be reduced to about 1 minute once our new machine becomes operational (shall we believe it?).

In the meantime we have done more work on this program. We are reasonably convinced that the last bugs are now removed from an updated version (called DNMR III) that can handle magnetic equivalence and "twofold" symmetry, both in conjunction with mutual exchange if desired. Computation times can be reduced much further in cases where these options are applicable, and the extension to a greater number of spins becomes economically feasible. For example, treatment of an exchanging AA'BB' system now takes only 16 seconds. The theory is presently being written up for publication, and we plan to submit DNMR III to QCPE around Christmas time.

Sincerely yours,

Daniel A. Kleier  
Gerhard Binsch

DAK:GB:sk

Attachment
Einfluss eines Porphyrinderivates auf die chemischen Verschiebungen der Protonen von DSS

Sehr geehrter Herr Professor Shapiro,

In der Protonenresonanzspektroskopie wässriger Lösungen werden die chemischen Verschiebungen heute generell bezüglich des Methyssignals von Natrium-2,2-dimethyl-2-silapentan-5-sulfonat (DSS) gemessen. Bei der Verwendung von DSS besteht jedoch die Gefahr, dass spezifische Assoziationen zwischen Referenz und Probe die chemische Verschiebung des Referenzsignals beeinflussen. Dieser Effekt kann besonders bei der Untersuchung aromatischer Protonen gross sein. So ist z.B. das Signal der Methylgruppen von DSS in einer 0.8-molaren wässrigen Lösung von 1,3-Dihydroxy-naphtalin gegenüber dem in reinem Wasser gemessenen Wert um 48 Hz (vermutlich bei 60 MHz) nach höherem Feld verschoben. (E. S. Hand und Th. Chohen, JACS 87, 133 (1965)).

Bei der Untersuchung des folgenden Porphyrinderivates (I) hat sich gezeigt, dass eine derartige Verschiebung des Referenzsignals grösser als 1.5 ppm sein kann.

Bei der Untersuchung von 1,4-Dimethylpyridiniumjodid konnten keine derartigen Effekte beobachtet werden. Dementsprechend sind die Effekte auf die chemische Verschiebung von Protonen in DSS bei der Untersuchung des Porphyrinderivats I nicht nur auf das Vorhandensein von N-Methylpyridiniumgruppen in dieser Verbindung zurückzuführen.

Mit freundlichen Grüßen

R. Scholer  K. Klätschi  E. Pretsch
Konzentrationsabhängigkeit der chemischen Verschiebungen der Protonen von Natrium-2,2-dimethyl-2-silapentylsulfonat

\[
\text{CH}_3\text{-Si-CH}_2\text{CH}_2\text{CH}_2\text{SO}_3^-\text{Na}^+
\]

\[
\text{CH}_3 \quad \gamma \quad \beta \quad \alpha
\]

(\(\delta\) in ppm; siehe Text)

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I am only mildly surprised that someone as completely urbanized as you are (or would like to be) should be unaware of the fact that a Cheetah may be trained for hunting. For your information, therefore, I enclose a copy of the appropriate page from a book for the "general reader" (Desmond Morris, "The Mammals", Harper & Row, New York, N.Y. 1965; note picture of topless Cheetah). Those desiring a deeper introduction to the subject, should consult M. Chasseur and A. Emmod, "The Hunting Felidae, being a Disquisition on the Capture, Handling, Diseases, and Dietary Proclivities of Acinonyx Jubatus and Divers Small Cats of the Genus Felis, with Particular Attention to Their Training in Duties Useful to Man, as is Done in Eastern Countries, and with Especial Consideration of Their Possible Importation into These Islands for the Purposes of Augmenting the Sport of Hunting with a New Pursuit Similar to That of the Falcons, and Reducing the Population of Noxious Vermin", Venery and Sons, London, 1873.

The main point of this letter, however, is that I am more than a little shocked, and, indeed, deeply concerned, that you, to whose taste I have always deferred in all matters, particularly those concerning cheesecake of any variety, should have been so desperately in search of something to say to fill the bottom of the page as to have penned the last sentence of your comment. Say it isn't so, Barry! To show that you are not beyond redemption, your first step on the long way back to a State of Grace might be to publish the kind of picture that really turns you on (if it still does). Are you game?

Yours in sorrow,

[Signature]

Paul C. Lauterbur
Associate Professor of Chemistry

PCL: st

Enc.

*Title provided by BLS.*
Although dogs are the typical running hunters, the fastest four-legged animal, the Cheetah, is a member of the cat family. Most cats have to bound up to their quarry once they have stalked it. The Cheetah too uses stealth to approach the prey initially, but because it lives in open country it cannot get very close in this way, and is compelled to make its final onslaught from a greater distance. Because of this, it has become specialized as a lanky, powerful sprinter, and has often been described as the most dog-like of the cats. The adult Cheetah is the only cat with permanently extended claws.

Over a distance of up to 400 yards it can reach speeds of about 60 miles an hour, but it lacks stamina and if the prey is not caught inside this distance it soon slows down to await a more favourable opportunity. Cheetahs often hunt in pairs or family groups, usually during the cooler parts of the day. The prey consists of gazelles, Impala, Waterbuck or Ostriches.

Man has used tame Cheetahs as hunting animals for hundreds of years and it is therefore remarkable that this was the last of the large cats to be bred successfully in captivity. Even today it has only been bred in zoos in a few instances, the first occasion apparently being as late as 1960, at Krefeld. Young Cheetahs have a characteristic silver mane that runs down the whole length of the back. This mane, or crest, disappears after the tenth week, at the same time that the cubs lose the ability to retract their claws.
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