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Deadline Dates: No. 84: 20 September 1965
No. 85: 20 October 1965

A monthly collection of informal private letters from laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication."

Dr. B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Chicago,
Illinois 60616,
U.S.A.

Dear Dr. Shapiro,

May I take advantage of the widespread circulation of I.I.T. NMR newsletter and ask if anyone could suggest a source of supply of perdeuterochlorobenzene (C₆D₅Cl). I need only a few ml.

Yours sincerely,

R. Figgins

R. FIGGINS
Dear Barry:

What Causes Proton Chemical Shifts in Saturated Unstrained Hydrocarbons?

You will recognize in this question a variation on the title of the recent letter from Dr. R. F. Züchter. The origin of proton chemical shifts remains perhaps the one most intriguing puzzle in NMR, and I have long felt that unstrained, saturated hydrocarbons are materials of unusual significance in this regard, since here one expects only a few key parameters to be involved, and the tricky influences of strongly polar groups, or aromatic ring currents, or pi bonds, all are absent.

Bill Tosch and I called attention to some very puzzling features of hydrocarbon shifts in J. Chem. Phys., \textit{27}, 1167 (1962), but at the time we could not assign accurate numerical values to many of the shifts encountered because of the complexity of the spectra we had. Since then, Dick Hughes has looked at a number of additional compounds, and through the courtesy of the Varian people at Pittsburgh he has obtained several 100 Mcps spectra. In particular, the spectrum of cis-1,3,5-trimethylcyclohexane is beautifully simplified at 100 Mcps and yields numerical data which allow at least one major anomaly to be brought very sharply into focus.

The following table gives the shifts we found, with values for conformationally fixed cyclohexane, from J. Phys. Chem., \textit{68}, 2026 (1964) for comparison:

<table>
<thead>
<tr>
<th>Proton Type</th>
<th>cis-1,3,5-trimethylcyclohexane</th>
<th>cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>-0.86</td>
<td>-----</td>
</tr>
<tr>
<td>Axial methine</td>
<td>-1.40</td>
<td>-----</td>
</tr>
<tr>
<td>Axial methylene</td>
<td>-0.43</td>
<td>-1.19</td>
</tr>
<tr>
<td>Equatorial methylene</td>
<td>-1.66</td>
<td>-1.66</td>
</tr>
</tbody>
</table>

One fact jumps out at you: Introduction of the equatorial methyl groups has no effect on the shift of the adjacent equatorial methylene proton, but a large effect on the adjacent axial methylene proton. This is seen also when one looks at other cycloalkanes with cis-1,3-dimethyl substitution.
To try to account for this, we can play with the various "effects" that people have invented over the past decade or so. But there is an obvious joker: Each methylene group has a local symmetry plane, bisecting the H-C-H angle and perpendicular to the plane of the H-C-H group. When methyl groups are introduced on the adjacent carbon atoms, the newly formed C-C bonds lie in this local symmetry plane. In other words, the two methylene protons are symmetrically disposed with respect to the entering methyl substituents, and no matter which "effect" is tried out, they ought to suffer the same perturbation.

I do not know how to resolve this anomaly.

Every now and then you see something in print which implies that on the basis of one or more "effects" we are really in a rather good position to understand and predict chemical shifts. On the basis of data like those presented here, it seems hard to escape the conclusion that any simple theory of the origin of chemical shifts must be wrong. At any rate, my attitude on these publications is neatly expressed in the refrain of one of my number-one daughter's favorite folk songs:

And as I look around me I'm very apt to smile
To see so many people putting on the style.

With the best of wishes,

Sincerely,

Norbert Muller
Dr. Bernard L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology Research Institute,
10, West 35th Street,
Chicago,
Illinois,
U.S.A.

Dear Dr. Shapiro,

1. Cooling System for A-60

Some readers may be interested in the details given below of the home-made closed-circuit water system we use for cooling our A-60 spectrometer. The help of Mr. J. Whitley is gratefully acknowledged.

Heat Exchanger

24 in. x 14 in. diam. cylindrical copper tank with flanged top (material £12). Cooling tubes: three coils in parallel, each consisting of 25 ft. of 3/8 in. O.D. soft copper tubing wound on a 4½ in. diam. former.

Reservoir

25 in. x 3 in. diam.

Pump


Motor


Motor and pump are set within a frame 18 x 18 x 10½ in., which supports the heat exchange and reservoir.


Continued*****
Flow Gauge
Platon water Gapmeter A-10 14.5/HS (0.3-3.0 litres/min.) with brass end-blocks.

Closed-circuit System
All copper piping is \( \frac{1}{2} \text{in.} \) diam. The deionised water contains about 5 p.p.m. 'Panacide' (B.D.H., Poole, Dorset, England).

2. Sample Thermostat for Broad-line Spectrometer

In order to keep steady the temperature of a solid sample cooled by heat leaking down a brass rod from a refrigerant container, Mr. J. E. Pearson has fixed a small platinum resistance coil, labelled Pt, between the probe (linked to the spectrometer from below) and a 100 ohm heater. The platinum coil consists of about four feet of 46 SWG wire and forms one arm of an a.c. bridge, the output of which is caused by the transistor circuit shown to actuate the above-mentioned heater when the temperature drops. (Reversal of the relative phase of the two a.c. sources will cause the heater to operate when the temperature has risen slightly.) Several temperature ranges can be selected by choice of \( Q \).

Resistance \( R \) is a 1 kohm potentiometer and resistance \( \| \) is chosen to have about the mid-range value of the Pt resistance, which is about 27 ohms. If \( a \) and \( b \) are the minimum and maximum values of Pt for a given range setting of \( Q \), then the other bridge elements are given by:

\[
R = \frac{AP}{b-a} = 2.5 \text{ kohm for a } 100^\circ C \text{ range}
\]

\[
Q = \frac{AP}{b-a} \text{; in our case, the four values 0.536, 1.52, 2.50, 3.48 kohms}
\]

for \( Q \) give overlapping temperature ranges to cover +200 to -200°C.

Yours sincerely,

D. W. Jones

J. E. Pearson
A simple method of obtaining a 6DB improvement in S/N ratio in A-60's

Without becoming involved in quoting relative noise figures of various devices I would like to pass on what I consider to be a significant improvement in signal to noise ratio of our A-60 here at C.S.I.R.O. Canberra. It is easily ascertained that the first stage of the receiver is the main source of electrical noise. On looking around I found that as far back as July 1960 Electronics (P73) Radio Corporation of America claimed a 2-4DB improvement in S/N for their 6CW4 nuvistors. Without further ado two were mounted on a noval plug and the 6922 at V201 was directly replaced. Realignment of the receiver and probe was necessary. A check of characteristics showed that the operating conditions of V201 Cascode first stage would be quite satisfactory without any circuit value alterations.

Although Varian quote 5:1 signal to noise we had been able to obtain 7 or 8:1. With this simple replacement we were able to obtain 15 or 16:1 on the quartet of 1% ethyl benzene without any degradation of the .3 cps resolution with acetaldehyde over the last month.

I don't think this matter should rest here as there is still room for improvement possibly with Field effect transistors or tunnel diodes although this would require a lot more work to install. I am sure that this could have other possible applications in other instruments. Just at the moment I cannot see any advantage in incorporating this in the control receiver.

William P.A. Pascoe
27.VII.65
Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry,

An Unusual Chemical Shift in Propenyl-Benzene Derivates

In initiating our subscription to IIT NMR Newsletter, I would like to report an unusual chemical shift.

We have examined compounds of the type Ia and Ib by PMR.

\[
\begin{align*}
\text{Ia} & \quad \text{Ib} \\
\begin{tikzpicture}
  \node (a) at (0,0) {\text{C}};
  \node (b) at (0.5,0) {\text{CH}_3};
  \node (c) at (0.5,-0.5) {\text{H}};
  \node (d) at (1,0) {\text{C}};
  \node (e) at (1.5,0) {\text{H}};
  \node (f) at (1.5,-0.5) {\text{CH}_3};
  \node (g) at (2,0) {\text{Ar}};
  \node (h) at (2.5,0) {\text{Ar}};
  \draw (a) -- (b); \\
  \draw (c) -- (d); \\
  \draw (e) -- (f);
\end{tikzpicture}
\end{align*}
\]

The aryl groups were varied as shown in the table below.

We attempted to assign the geometrical isomer structure to the compounds on hand by assuming that the olefinic proton in Ia would be shifted downfield relative to the olefinic proton in Ib due to the nearby aromatic ring current. In every case, assigning structure in this way gave the same assignment as that arrived at by other chemical and physical methods, i.e., retention times and pyrolysis rates to known products.

The isomeric shift of the methyl group is a phenomenon that is surprising. If the assignments shown below are correct, then the methyl group in compound Ib is upfield from the methyl group in Ia by 0.4 ppm.
The methyl proton resonance in cis- and trans-propenyl benzene shows no large shift.

Furthermore, the methyl proton shift in Ia is normal for such systems while the shift in Ib is at higher fields than is normally found in the propenyl benzenes.

We feel that this shift is due to cyclopropyl-double bond conjugation, in Ib, which is absent in Ia. We are testing this idea by studying similar compounds. IR and uv data do not show differences, however, that give weight to this hypothesis.

We welcome any suggestion as to the cause of this chemical shift.

Sincerely yours,

A. J. Berlin

TABLE I

Chemical Shifts of Olefinic and Methyl Protons in Various Compounds of the Type Ia and Ib

<table>
<thead>
<tr>
<th>Compound</th>
<th>Olefinic Proton</th>
<th>Propenyl Methyl Protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia, Ar = p-methoxyphenyl</td>
<td>4.40</td>
<td>8.12</td>
</tr>
<tr>
<td>Ib, Ar = p-methoxyphenyl</td>
<td>4.58</td>
<td>8.53</td>
</tr>
<tr>
<td>Ia, Ar = phenyl</td>
<td>4.29</td>
<td>8.12</td>
</tr>
<tr>
<td>Ib, Ar = phenyl</td>
<td>4.52</td>
<td>8.52</td>
</tr>
<tr>
<td>Ia, Ar = p-fluorophenyl</td>
<td>4.33</td>
<td>8.12</td>
</tr>
<tr>
<td>Ib, Ar = p-fluorophenyl</td>
<td>4.52</td>
<td>8.52</td>
</tr>
</tbody>
</table>

Dear Professor Shapiro,

Proton Resonance Spectra of 11-Oxosteroids

We have recently recorded the p.m.r. spectra of a wide range of 11-oxosteroids and have examined the effect of various ring-C and ring-D substituents on the proton resonances of the 12-methylene, 10-methyl, and 13-methyl groups. Since the spectra of the simpler 5α-androstan-11-ones have been the subject of several recent papers, we are submitting for publication in the Journal of the Chemical Society a summary of our work, which might be of interest.

\[
\begin{align*}
\text{(I)} & \quad \text{(II)} \\
\text{(III)} & \quad \text{(IV)}
\end{align*}
\]
The 12-methylene protons of simple androstane-11-ones, pregnane-11,20-diones (e.g., I; \( R' = R'' = H \)), and 11-oxo-isosapogenins show a two-proton singlet in CDCl₃ solution, but an AB quartet in pyridine or benzene solution, whereas the 12-methylene protons of ergostane-11-ones and 21-acetoxy pregnane-11,20-diones (e.g., I; \( R' = H, R'' = OAc \)) form an AB quartet in CDCl₃, benzene and pyridine solution. Provided the steroid does not have a 17\(^\alpha\)-substituent, the doublet for the equatorial 12\(^\beta\)-proton appears at lower field than the axial 12\(^\alpha\)-proton. In 17\(^\alpha\)-hydroxypregnane-11,20-diones (e.g., I; \( R' = \text{OH}, R'' = OAc \)), the 17\(^\alpha\)-hydroxyl deshields the 12\(^\alpha\)-proton and causes the 12\(^\alpha\)-proton peaks to appear at lower field than those for the 12\(^\beta\)-proton. Introduction of a 9\(^\alpha\)-halogen (e.g., II) deshields the 12\(^\alpha\)-proton still further, the extent of the downfield shift depending on the size of the halogen atom.

The 12-methylene protons of 9\(^\alpha\)-halogeno-11\(^\beta\),17\(^\alpha\)-dihydroxy- (e.g., III) and 9\(^\alpha\),11\(^\beta\)-dihalogeno-17\(^\alpha\)-hydroxy- pregnane-20-ones (e.g., IV) also give an AB quartet, the doublet for the axial 12\(^\alpha\)-proton appearing at lower field than that for the equatorial 12\(^\beta\)-proton.

Yours sincerely,

J.E. Page

G.F.H. Green

J.E. Staniforth

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AIRMATT

Professor Bernard Shapiro
Chemistry Department
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Barry:

Audio-Frequency, Voltage-Swept Generator for a Field-Frequency Lock

We are now in the process of completing an internal field-frequency lock of the Anderson-Freeman type for our HR-100. The only unusual feature of the system is the frequency-sweep generator. Since one of the main reasons for our putting this system together was a need to use the 100 with a CAT, we decided that the sweep generator should not employ any mechanical elements such as a motor-driven potentiometer or capacitor. We therefore turned to a solid-state voltage-to-frequency converter which could be driven by the ramp output of an integrator of the type which we described in our last two letters.

We are using a specially modified Vidar (Mountain View, Calif.) Model 241 Converter. This unit provides a pulse-rate output proportional to the DC input voltage with a normal range of 0 to 10 Kc. for an input change of 0 to 10 V. Our unit was ordered with an extra "flip-flop" circuit board which divides the output frequency by two and provides a square wave rather than a pulse output. In addition we specified a special span and zero input frequency that has since been modified so as to give 1000 to 4000 cps (square wave) for an input variation of 0 to ±10 V with a full scale linearity of better than 0.025% and a short-term stability (1 record averaging time) of the order of 2 to 3 ppm.

Since a true square wave contains no second harmonic component, it is possible to use a low pass filter with a sharp cutoff characteristic to obtain a uniform sine wave output over somewhat less than a 2.5:1 frequency range. We increased the frequency of our integrator to 2.5 Kc so it would lie somewhat within a 2 Kc continuous sweep (from about 2 to 4 Kc) which should be more than ample for most 100 Mcps. work. We also have provided a second range which will let us
sweep down from 2.5 Kc to 1.0 Kc with only a little distortion at the lowest frequencies so that we can use the lock on our 56.4 Mcps system in either the field-or the frequency-sweep mode without having to compensate for the severe eddy-current losses in the thicker-walled probe that begin to set in above 2 Kc.

Our locking system utilizes two Varian integrators. One is tuned to 2.5 Kc and contains at the input a very narrow-band, 2.5 Kc notch filter employing a transistor amplifier and twin-tee network that can be switched into the system when we are decoupling in the frequency-sweep mode to prevent the decoupling frequency from disturbing the lock. The second integrator has been extensively modified so that it can be driven by the output of the variable frequency generator. It's amplitude response is flat to within about 5% over either sweep range, and there is little detectable change in the phase of the signal.

A means has also been provided for obtaining, for counting purposes, the frequency representing the difference between the fixed and variable frequencies. This unit is used to provide the locking signal in the field-swept mode and the spectrum in the frequency-swept case. We would be glad to supply details to anyone interested.

Sincerely yours,

R. E. Lundin, Principal Chemist

R. H. Elsken, Electronics Engineer
Molecular Structure Investigations
Wool and Mohair Laboratory
Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois

Dear Barry,

I had better pay my dues to your magazine or else my credit rating will be in jeopardy from some IIT collection agency.

We have very recently received our A-56/60 spectrometer and are learning how to use it and all its idiosyncrasies. Thus far this instrument has been considerably more stable than our old A-60 and to have about 3-4 times the signal to noise figure of the latter. However, to obtain good resolution is still a tricky problem so far and the 19F frequency offset oscillators seem to draft rather more than one would wish.

Enclosed are some 19F spectra of a sample of CF3CF2CF2H which I cooked up several years ago. These spectra reveal the magnitudes of two small coupling constants which were not observed by my colleague Dan Elleman back in the late 1950's when he first looked at the n.m.r. spectra of this molecule with the spectrometer he built in his thesis work. Below are listed the observed first order coupling constants derived from measurements of both the 1H and 19F spectra recorded with our A-56/60 spectrometer with calibrated sweep widths.

\[
\begin{align*}
J_{F1H1} &= +51.96 \pm 0.04 \text{ cps} \\
J_{F2H1} &= +4.57 \pm 0.04 \text{ cps} \\
J_{F3H1} &= 0.88 \pm 0.02 \text{ cps} \\
J_{F1F2} &= -4.50 \pm 0.04 \text{ cps} \\
J_{F1F3} &= 7.23 \pm 0.05 \text{ cps} \\
&\quad \text{(probably +)} \\
J_{F2F3} &= 0.35 \pm 0.02 \text{ cps}
\end{align*}
\]

Now that we know the small couplings are there we will try to determine some signs in frequency - sweep experiments with our HR instrument. The signs given above are from our previous work on this and other fluorocarbon molecules involving field-sweep 19F - [19F], 19F - [1H] and 1H - [19F] experiments.

With best regards,

Stanley L. Manatt

Telephone 354-4321  
Telex 213-649-2431
$^{19}$F Spectrum of $\text{-CF}_2\text{H}$ of $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$

250 500 SW
500 ST

5 CPS
A 56/60 $^{19}$F Spectrum of CF$_3$- of CF$_3$CF$_2$CF$_2$H
50 SW 500 ST
A 56/60 $^1$F Spectrum of $-\text{CF}_2-$ of $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$

50 SW 500 ST
July 27, 1965

Professor B.L. Shapiro, Editor
NMR
Illinois Institute of Technology
Chicago, Illinois
U.S.A.

Dear Barry:

From my summer travels, the abstract of a paper I have recently submitted to J. Chem. Phys., which might be of interest to your readers.

"On the Magnetic Susceptibility of Aromatic Hydrocarbons and Ring Currents".

It is shown that the anisotropic magnetic susceptibility (and chemical shift) of aromatic hydrocarbons generally attributed to π-electron "ring currents" can be correctly represented as the sum of contributions from localized electrons of both π- and σ-character. The "delocalization" of the electronic distribution plays no part whatever in the effect and is only an artifact of London's approximate calculation. Anisotropic Pascal's constants for aromatic carbon atoms are determined empirically and excellent agreement with the experimental anisotropic susceptibilities is obtained.

I will be pleased to send a Xerox copy of this to anyone who is desperately interested when I return to Rockefeller Institute in September.

The implications of this work for NMR are (1) π-electrons in aromatic rings are to be treated no differently than any other anisotropically distributed electrons, such as the σ-electrons in benzene or in cyclohexane; and (2) a definition of aromaticity based on "ring currents" does not really make sense. My feeling on aromaticity of large monocyclic rings is that all bonds should be of equal length so that a regular two-dimensional geometry is obtained for a molecule to be called aromatic. The bond alternation discussed by Longuet-Higgins and Salem, plus an angle alternation occurs in the annulenes: by any non-ring current argument these molecules cannot be considered aromatic.

With best regards.

Yours sincerely,

Jeremy I. Musher
Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago, Illinois 60616  

Dear Barry:  

In IITNMR #73, Page 4, we mentioned a cabinet which we built to improve the field stability of our HR60 and promised to send our plans. We have had the drawings completed for some time but have been derelict in our duty to send them in for general circulation.

The need for the various access doors shown in the attached plans is for the most part obvious except possibly those denoted "E" and "C". These doors were installed simply to enable us to uncable and recable the magnet completely without removing the cabinet. To do high-temperature work, we simply open doors "A" and "C". The leads connecting the super stabilizer and the sweep coils are passed through the small hole above door "C".

We particularly recommend that anyone who builds a cabinet based on the enclosed design recheck the gross dimensions for his particular system. Our magnet was removed from the wooden pallet during installation and was set on an "I" beam frame to distribute the floor load. For this reason, it is probably atypical.

We built this cabinet ourselves. However, Scientific Advances, Incorporated, (SAI) 1400 Holly Avenue, Columbus, Ohio, 43212, has indicated that they might be willing to quote on and build a "cabinet kit" for anyone who is interested. Bob Watkins of SAI can be contacted by writing to the above address or by calling him at (614) 294-5436.

Best personal regards,

Thomas F. Page, Jr.

Warren E. Bresler  
Molecular Spectroscopy  

TFP:WEB/gf  
Enclosures
Screw holes around edges of all panels approx. 5 1/2" between centers.
Doors overlap openings 1/2".
CROSS SECTION OF SLIDING DOOR TRACKS

CROSS SECTION OF CENTER PORTION OF BOTTOM TRACK. CUT OUT FOR TOP EDGE OF PANEL B.

BACK
FRONT PANELS AND ALL DOORS \( \frac{1}{2} " \) THICK,
OTHER PANELS \( \frac{3}{8} " \) THICK.
ALL HARDWARE IS SOLID BRASS.
SCREWS ARE \#10-24 x \( \frac{7}{8} " \) RH WITH \( \frac{1}{4} " \)
FLAT WASHERS.
HINGED DOORS HELD SHUT WITH THUMB SCREWS.
THIS SECTION SCREWED IN PLACE, ALL OTHER JOINTS WELDED.

ALUMINUM BLOCKS WITH TAPPED HOLES

1X1/2 ALUMINUM ANGLE
HOLES TO MATCH THOSE IN PANELS, TAPPED #10-24

CABINET FRAME
Dear Dr. Shapiro:

Perhaps the NMR-data of the following compound is of interest to you as an example of long range coupling ($H_{EG}$ and $H_{EH}$):

![Chemical structure]

<table>
<thead>
<tr>
<th>Chemical</th>
<th>multiplicity</th>
<th>Chemical Shift (ppm)</th>
<th>J Values (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_A$</td>
<td>m</td>
<td>2.84</td>
<td></td>
</tr>
<tr>
<td>$H_B$</td>
<td>dd</td>
<td>3.08 ($J = 4.7$ and 4.0)</td>
<td></td>
</tr>
<tr>
<td>$H_C$</td>
<td>m</td>
<td>2.84</td>
<td></td>
</tr>
<tr>
<td>$H_D$</td>
<td>d</td>
<td>4.36 ($J_{DE} = 12$)</td>
<td></td>
</tr>
<tr>
<td>$H_E$</td>
<td>ddd</td>
<td>3.42 ($J_{DE} = 12$; $J_{EG} = 0.6$; $J_{EH} = 0.6$)</td>
<td></td>
</tr>
<tr>
<td>$H_F$</td>
<td>d</td>
<td>2.99 ($J_{FG} = 3.4$)</td>
<td></td>
</tr>
<tr>
<td>$H_G$</td>
<td>ddd</td>
<td>3.63 ($J_{FG} = 3.4$; $J_{GH} = 1.8$; $J_{EG} = 0.6$)</td>
<td></td>
</tr>
<tr>
<td>$H_H$</td>
<td>ddd</td>
<td>2.69 ($J_{GH} = 1.8$; $J_{EH} = J_{FH} = 0.6$)</td>
<td></td>
</tr>
</tbody>
</table>

We have now finished the rearrangement of our NMR-combination. We have transformed the HR 100 to the HA 100 and combined it with a DP 60 using a second magnet but the same consol. Also the "Cat" is working well with the HA 100. Dr. Arndt perhaps will write down the special requirements when he is returning from holydays.

Yours sincerely,

[Signature]

F. Bohlmann
Dear Barry,

I hope I beat the deadline before leaving for Copenhagen.

When preparing a review article on NMR studies on phosphorus compounds \textsuperscript{1} except F\textsubscript{3} resonance - I have found that, generally speaking, any accurate interpretation of observed spin-spin couplings and, to a greater extent, chemical shifts is deceiving. Some rough correlations with hybridization, electronegativity, a.s.o., are obtained in restricted series, but they are complex, due to many significant overlapping factors. The only case where it seems possible to improve the description of published data on the same grounds is the following.

F\textsubscript{19}-F\textsubscript{3} couplings are observed in a number of pentacoordinated phosphorus compounds \textsuperscript{2}. With R\textsubscript{2}PF\textsubscript{3} compounds, it is possible to distinguish axial and equatorial fluorine atoms, R's occupying generally \textsuperscript{3} rally equatorial positions in a trigonal pyramidal conformation (sp\textsubscript{2}d with d=d\textsubscript{z2}).

\begin{center}
\includegraphics[width=0.5\textwidth]{diagram.png}
\end{center}

\textsuperscript{1} To appear in Adv. in NMR spectroscopy (L.H.Sutcliffe ed.), vol.2;
\textsuperscript{2} See R.Schmutzler, Angew.Chem.\textbf{77}, 530, 1965 for an extensive review of experimental data;
\textsuperscript{3} but exceptions are known : (Me\textsubscript{2}N)\textsubscript{2}PF\textsubscript{3} for example, Muettteries etal. Inorg.Chem. \textbf{3}, 1298, 1964.
One observes that \( J_{axial} < J_{equ} \), (the ratio ranging from 0.8 to 0.95), axial resonance being downfield relative to equatorial one; these facts being interpreted as a noticeable difference in a character of P-F bonds. Our interest is especially in \( J \) couplings, as they reflect directly phosphorus hybridization. To study more quantitatively this relation, we describe orbitals in such a pentacoordinated phosphorus by the two following kinds of hybrids (F.A. Cotton, "Chemical applications of group theory", Interscience 1964, p.116 sqq):

- **Equatorial**:
  \[
  \frac{1}{\sqrt{3}} (s \sin \alpha - d_{z^2} \cos \alpha) + \frac{2}{6} P_x
  \]

- **Axial**:
  \[
  \frac{1}{\sqrt{2}} (s \cos \alpha + d_{z^2} \sin \alpha) + \frac{1}{2} P_z
  \]

\( \alpha \) an adjustable parameter. If we assume that the Fermi contact is preeminent and that it varies mainly with a content of P orbitals, we have:

\[
\frac{J_a}{J_e} = \frac{3}{2} \cot^2 \alpha = \frac{\left( \frac{J_a}{J_e} \right)}{\frac{3}{2} + 2\left( \frac{J_a}{J_e} \right)}
\]

with:

\[
(s \text{ character})_a = \frac{1}{2} \cos^2 \alpha = \frac{\left( \frac{J_a}{J_e} \right)}{\frac{3}{2} + 2\left( \frac{J_a}{J_e} \right)}
\]

\[
(s \text{ character})_e = \frac{1}{3} \sin^2 \alpha = \frac{1}{\frac{3}{2} + 2\left( \frac{J_a}{J_e} \right)}
\]

The experimental ratios yield an estimate of these characters. To illustrate:

<table>
<thead>
<tr>
<th>R's</th>
<th>( J_a/J_e )</th>
<th>( s_a )</th>
<th>( s_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂</td>
<td>0.804</td>
<td>0.174</td>
<td>0.217</td>
</tr>
<tr>
<td>Me₂</td>
<td>0.840</td>
<td>0.179</td>
<td>0.213</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0.924</td>
<td>0.190</td>
<td>0.206</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0.945</td>
<td>0.193</td>
<td>0.204</td>
</tr>
</tbody>
</table>

As R's electronegativity increases (F electronegativity being always greater), axial and equatorial bonds tend to an equal s character. This is consistent with WALSH's rule (\( \star \)): phosphorus has orbitals of a content with the most electropositive substituents. The following figure illustrates this dependence (\( G_1 = Taft's \) inductive constant).

Despite its roughness (assuming all equatorial orbitals equivalent underestimate \( s_e \) and surestimates \( s_a \)), this model seems of some interest. Of course, similar data on PF₅, RPF₄ would be of

\( \star \): (See H.A. BENT, Chem. Revs. 60, 275, 1960 and other references)
considerable interest, but fluorine intramolecular scrambling occurs (at room temperature at least) in PF₅ and perhaps in RPF₄. For the latter compounds, another explanation for fluorine equivalence is the possibility of another sp²d hybridization (with d = \( d_{2} - 1/2 \)). (See E.L. Muettet et al., Inorg. Chem. 2, 673, 1963).

With my very best regards,

G. MAVEL.
$J_a/J_e$ in $RR'PF_3$
It's character in $RR'PF_3$.\[2.5\]

Equatorial $\Sigma \sigma_1$ of $R'$s: [Graph shows a curve for equatorial character]

Axial $\Sigma \sigma_1$ of $R'$s: [Graph shows a curve for axial character]
Dear Barry:

An accurate method of measuring $^{13}$C transition frequencies is to monitor the splitting that occurs on a $^{13}$C satellite line in the proton NMR spectrum when a weak rf field ($H_2$ at $\omega_2$) is swept through a connected $^{13}$C transition. Baker has called this the INDO experiment ([J. Chem. Phys. 37, 911 (1962)]). The resulting spectra consist of a series of negative-going peaks that correspond in general to certain $^{13}$C subspectra, which may be combined to form an (inverted) replica of the $^{13}$C spectrum, but with the benefit of the higher sensitivity of proton NMR. Although this is perhaps not self-evident, the statistical weights of the lines in an INDO multiplet are the same as those of the corresponding $^{13}$C multiplet (i.e., 1:3:3:1 for a quartet). The resemblance to ENDOR is rather superficial; the experiment is basically spin tickling observed in the frequency sweep ($\omega_2$) mode. Although theoretically it may be complicated by population redistributions, these are usually negligibly small because of the lower magneto-zygic ratio and much longer relaxation times of $^{13}$C.

Unfortunately $^{13}$C satellites are themselves rather difficult to find in proton spectra, particularly those that correspond to the weak long-range $^{13}$CH couplings, because they may be hidden in the wings of the strong lines from $^{12}$C molecules. It is even harder to monitor their peak heights effectively in the presence of a very strong sloping background signal and the residual instability of the field-frequency control.

We have managed to circumvent these two problems by imposing a slow pulse modulation on $H_2$ and synchronously detecting the modulation appearing in the proton spectrum. For a sufficiently slow modulation frequency (in practice 0.25 cps) one obtains simply the difference between the steady-state signals that are observed with $H_2$ off and with $H_2$ on. If $\omega_1$ is held at the exact resonance frequency of a $^{13}$C satellite all components of the strong $^{13}$C proton signals cancel and the output is at a null until $\omega_2$ sweeps through a connected $^{13}$C transition, when a "burst" of modulation is received. We have therefore chosen to represent the responses as positive-going peaks (in contrast with conventional INDO), for example the figure illustrates the pulsed INDO responses of 1,3,5 trichlorobenzene ($^{13}$C at position 2) corresponding to the two $^{13}$C subspectra generated by the directly bonded proton. This illustrates a general result for systems of three or more non-equivalent spins: the relationship between the particular $^{13}$C satellite that is monitored and the subspectrum obtained indicates the relative signs of the relevant spin coupling constants. In this case, $J$(HH, meta) and $J$(13CH) are found to have like signs.

Readers may wish to suggest a suitable name for this technique to prevent us from dubbing it GUSPIDOR (Carbon-13 Unravelling by Slowly Pulsed Internuclear Double Resonance). Preprints available.

Best wishes,

Ray

Analytical Instrument Research

Ray Freyman

2 August 1965
PULSE MODULATED DOUBLE RESONANCE OF SYM-TRICHLOROBENZENE

$^{13}$C IRRADIATION FREQUENCY $\frac{\omega_2}{2\pi}$
Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Ill.

M.O. Calculation of the Coupling Constant in HF

Dear Professor Shapiro:

Pople and Santry showed by elegant arguments that some of the coupling constants between directly bonded nuclei could be negative by explicitly considering excited states. In their treatment, two-center integrals were neglected, and only the lowest unoccupied molecular orbital was taken into account for excitation. Dr. Kato and I have attempted to extend their calculations by 1) including two-center integrals, 2) taking into account higher unoccupied M.O.'s, and 3) employing energywise better M.O. wave functions. As an example we have chosen hydrogen fluoride for which several functions are available and among them used wave functions by Ransil, Nesbet, and Karo and Allen. The configuration for the ground state of HF is

\((\sigma)^2 (2\sigma)^2 (3\sigma)^2 (1\pi)^2 (\pi')^2 \downarrow \Sigma^+\).

Most of the two-center integrals can be evaluated by the Barnett-Coulson method, but some need the help of Gegenbauer's function.

The results obtained so far have revealed the following features.

Excitations from \((1\sigma)\) to \((n\sigma)\) can be neglected. In general the main contribution comes from \((3\sigma)\rightarrow(4\sigma)\) and \((2\sigma)\rightarrow(4\sigma)\), giving rise to negative coupling in agreement with Pople's suggestion. For Nesbet's function, contributions from \((3\sigma)\rightarrow(n\sigma)\) and \((2\sigma)\rightarrow(n\sigma)\) almost cancel each other, when \(n = 4, 5, 6\) and 7, although they are, of course, very sensitive to their respective excitation energies. For \(n = 5\) and 9, however, contributions from \((3\sigma)\rightarrow(n\sigma)\) and \((2\sigma)\rightarrow(n\sigma)\) are large and do not cancel each other, finally giving rise to positive coupling. This situation may arise from the fact that these SCF M.O.'s are for the ground state of the molecule and higher unoccupied orbitals are particularly inappropriate for describing excited states, as may be noticed from unusually large coefficients for some basis functions of these higher orbitals. Thus the excitation may better be truncated at \((n\sigma)\) with Nesbet's function. Whether the sign of coupling is positive or negative experiment. The fact that Karo's function gives the seemingly best result and Nesbet's the poorest, while they are energetically equally good, is
very interesting. The two functions are representative of the two approaches to the construction of molecular functions, namely use of 'best atomic orbitals' and use of as 'many' basis orbitals as to describe deformation of atomic orbitals on formation of the molecule. The Fermi term is dependent on the electron density only at the nuclei, and that the former function gives a better result may suggest that the density at the nuclei is little affected on molecular formation. In any event, coupling appears to be very sensitive to several parameters to be used, but agreement with experiment could be obtained by arbitrary choice of them, irrespective of whether it may be the proper choice or not. We also plan to make variational calculation.

Yours sincerely,

A. Saika

A. Saika

Dear Dr. Shapiro,

We thought readers of the IITNMR newsletter might be interested in some modifications which we have made to our HA 100 spectrometer when used in conjunction with a C 1024 Time Averaging computer. As supplied, this system has certain undesirable features for those wishing to sweep small portions of a spectrum repetitively with the object of measuring splittings in the observed spectrum. An example of such a use is the determination of the temperature dependence of splitting in 1,2-disubstituted ethanes. (T. N. Connor and K. A. McLaughlan, J. Phys. Chem., 69, 1888, 1965). The main problems arising are the following:

1. It is not possible to sweep a width of less than 50 cps, which if the spectrum of interest is ~10 cps wide leads to considerable waste of time and channels when sweeping repetitively.

2. More seriously, the read-in time for the computer is not always the same as the read-out time for identical settings of the appropriate sweeps. We have found the read-in time to be stable, whereas the read-out time varies considerably depending on the temperature of the apparatus, i.e. on how long the computer has been switched on, how many windows or doors are open, etc. In order to preserve the chart calibration it is essential that the read-in and read-out times are the same, and whilst it is possible to adjust the latter using trimmers in the computer, the high temperature coefficient makes accurate calibration difficult for those not working in temperature controlled rooms.

The first of these points is easily coped with by connecting a second microswitch across the right-hand limit switch in the recorder. This is actuated by the bar joining the two halves of the pen carriage, and is mounted on a slotted bar on the underside of the recorder. This movable limit switch can be placed in any desired position along the bar so that possible in repetitive sweeps < 50 cps are possible. In fact the number of possible positions is limited by the available recorder and computer sweep speeds.

As a cure rather than prevention of the second difficulty we have made provision for putting calibration marks on the spectrum which appear on the recorder chart and are fed into the computer memory simultaneously. This is done by feeding a small voltage onto the lead connecting the integrator/decoupler to the computer (Pin P; J 009). This voltage is provided by the circuit shown, the microswitches being actuated by a suitable attachment to the above mentioned bar joining the halves of the pen carriage. These two microswitches are also mounted on the slotted bar, one being attached to the same mounting plate as the movable limit switch. The size of the mark is controlled by the

Dr. B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago,
Illinois,
U.S.A.
two potentiometers and also depends on the position of the coarse and fine output controls on the integrator/descaler. The switch and potentiometers are mounted below the gain and damping controls on the recorder control panel and when not required, the movable limit switch can be placed at the right hand end of the slotted bar so that the right hand limit switch again comes into play.

We have found that this device produces precise and coincident marks on repetitive sweeps, and does not interfere with the spectrometer when in normal use.

Yours sincerely,

Tom Connor

TOM CONNOR
August 3, 1965

Professor B.L. Shapiro
Associate Professor
Illinois Institute of Technology
Chicago, Illinois
U.S.A.

Dear Professor Shapiro,

Thank you for your letter of July 23, 1965 addressed to Professor Dharmatti. I regret to say that Professor Dharmatti passed away on May 2, 1965. He had been keeping indifferent health for two years after he had suffered an heart attack. Inspite of this he was taking keen interest in the research programme of the Nuclear and Electron Magnetism Group of the Tata Institute of Fundamental Research which he helped to build after his return from Stanford in 1953. The Group at present has about twentyfive research people working under five disciplines: Wideline NMR, High Resolution NMR, Magnetic Susceptibility, Electron Paramagnetic Resonance, Mössbauer Effect and Microwave Spectroscopy of Gases. I do not want to enumerate here the important contributions Professor Dharmatti made during his lifetime since they are well known to the readers of the Newsletter. I would appreciate the insertion of the news of his death, which, I am sure, will be mourned by the workers in NMR. I am sending, in a separate letter, the activities of our Group.

Yours sincerely,

R. Vijayaraghavan

R. Vijayaraghavan
August 3, 1965

Professor B.L. Shapiro  
Associate Professor  
Illinois Institute of Technology  
Chicago, Illinois  
U.S.A.

Dear Professor Shapiro:

The following problems are currently being studied:

1. Temperature effects on the n.m.r. lines in borates

2. Proton and deuteron resonances in glycine and its addition compounds at various temperatures

3. Fluorine resonance in uranium fluoride compounds

4. Study of $^{119}$Sn resonance in rare-earth tin alloys

5. Chemical and Knight shift studies in CdSe, SnSe and InBi semiconductors.

Yours sincerely,

R. Vijayaraghavan

R. Vijayaraghavan
Professor Bernard L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois

Dear Professor Shapiro:

During the past year we have been calculating coupling constants according to the theory developed by Pople and Santry [Mol. Phys., 8, 1 (1964)]. We are using the extended Hückel theory [R. Hoffmann, J. Chem. Phys., 39, 1397 (1963)] including all overlaps to generate one-electron wave functions and energies. In addition to the dominant terms involving one-center integrals (see Pople and Santry) we include a number of contributions involving the product of a one- with a two-center integral. The additional contributions can have a significant effect on the final result, especially for couplings through one and two bonds. The specific details of the calculations will not be given here, but it should be emphasized that none of the parameters, other than structural, were varied from molecule to molecule. We will gladly provide the details to anyone who is interested.

Selected results are given in the accompanying table. The corresponding experimental results have been omitted to save space.

Calculated values of the directly bonded $^{13}$CH couplings for a variety of hydrocarbons correlate well with observed couplings, but the magnitudes in all molecules are low by a factor of 1.5. For long range couplings agreement between theory and experiment ranges from excellent (methane, ethane, cyclohexane) to miserable (gem coupling in ethylene and the $^{13}$CH coupling in acetylene). For the ortho, meta and para couplings in benzene, we obtain 5.5, -0.5 and 1.2 c.p.s., respectively, as compared to 7.7, 2.5 and 1.8 calculated by Gil and Murrell (JITNMRL NL, No. 81, 6).

Sincerely,

Robert C. Fahy
Gary C. Graham
Robert L. Piccioni
# TABLE. Calculated values of coupling constants (in c.p.s.)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$^{13}C_H^a$</th>
<th>$^{13}C_H^b$</th>
<th>gem$^a$</th>
<th>gem$^b$</th>
<th>vicinal$^b$</th>
<th>$^{13}C_C^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>66</td>
<td>83</td>
<td>-17.8</td>
<td>-16.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>69</td>
<td>84</td>
<td>-20.5</td>
<td>-16.7</td>
<td>7.8</td>
<td>-4.0</td>
</tr>
<tr>
<td>$\psi = 0^\circ$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>$\psi = 30^\circ$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>$\psi = 60^\circ$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>$\psi = 90^\circ$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>$\psi = 120^\circ$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>$\psi = 150^\circ$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.9</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane$^c$</td>
<td>73</td>
<td>85</td>
<td>-22.5</td>
<td>-17.0</td>
<td>11.0 ax-ax</td>
<td>-4.1 ax</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.8 ax-eq</td>
<td>-4.2 eq</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>1.9 eq-eq</td>
<td></td>
</tr>
<tr>
<td>Cyclopentane$^d$</td>
<td>73</td>
<td>85</td>
<td>-23.1</td>
<td>-17.0</td>
<td>7.8 cis</td>
<td>-4.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.8 trans</td>
<td></td>
</tr>
<tr>
<td>Cyclobutane$^d$</td>
<td>93</td>
<td>85</td>
<td>-18.1</td>
<td>-17.0</td>
<td>5.4 cis</td>
<td>-3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.1 trans</td>
<td></td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>107</td>
<td>107</td>
<td>-19.3</td>
<td>-15.2</td>
<td>3.7 cis</td>
<td>-2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.6 trans</td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>89</td>
<td>107</td>
<td>-21.4</td>
<td>-15.2</td>
<td>5.9 cis</td>
<td>-8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.8 trans</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>88</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>-6.9</td>
</tr>
<tr>
<td>Acetylene</td>
<td>142</td>
<td>169</td>
<td></td>
<td></td>
<td></td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-5.9</td>
</tr>
</tbody>
</table>

$^a$Includes one-center integrals only

$^b$Includes terms containing a product of a one- with a two-center integral

$^c$Chair form

$^d$Planar
Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois  60616

Dear Barry:

Our Laboratory's contribution to IITNMRN consists of the attached description of "A Convenient Power Source for the Varian G-14 Event Marker," which was designed and built by Mr. B. W. Joseph.

Current research interests in our Lab are tending toward wide line NMR and we are making a beginning in NQR.

Some recent reprints which are available consist of the following:


Dr. B. L. Shapiro
page two
July 30, 1965


Yours very truly,

[Signature]

George W. Smith
Physics Department

GWS:ms

Encl.
A CONVENIENT POWER SOURCE FOR THE VARIAN G-14 EVENT MARKER

B. W. Joseph

Varian Associates sell an Event Marker Kit as an accessory for their G-14 recorder. The marker can be obtained with a variety of actuating voltages from 6V d.c. to 115V a.c. In all cases the marker requires an external power source for actuation.

In many cases the 115V a.c. model is the most convenient: no external batteries or transformers are required, only a line cord and switch. However, we have recently developed a modification which is even more convenient and has the added advantages of safety and neat installation.

The modification consists of a capacitor-discharge system to actuate a 6V d.c. marker. The capacitor charging current is obtained from the power transformer T-101 in the recorder. The simple circuit is shown below.

![Circuit Diagram]

The diode, resistor and electrolytic capacitor are mounted on a small piece of phenolic circuit board. The board in turn is mounted with a single screw to one of the tapped posts on the side plate of the recorder. Each side of the recorder has two spare posts, and there is more than enough room to mount two circuit boards when two markers are installed.

$J_1$ is an Amphenol 80-PC2F two-pin receptacle which is mounted in a 5/8 inch hole about 2 inches toward the rear from, and on the same side as the chart roll-out knob. $P_1$ is an Amphenol 80-MC2M two-pin plug with a convenient length of cable to the push-button switch SW1. We can use either hand or foot switches as expediency dictates. Again, there is more than enough room to mount a pair of receptacles on either or both sides of the recorder when two markers are installed.

One slight disadvantage is that marks cannot be placed on the chart at extremely short time intervals. Due to the 1/2 second time constant of the charging circuit, it is necessary to wait at least 3 seconds between marks. This should not cause any difficulty in most operations, but if it does, the 10K
resistor can be changed to 5K with an attendant halving of the time constant. We do not advise decreasing the capacitance since the energy stored in the 50µF capacitor is about the minimum for satisfactory operation of the marker.

We made a number of checks with various input signals and recorder sensitivities as high as 1 millivolt full scale and detected no interaction or interference between marker and signal. With SW1 closed, the constant current is only 2.5 milliamps. This added drain on T101 is insignificant.
Aug. 12, 1965

Professor B.L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois 60616

Dear Professor Shapiro:

**NMR Determination of Aggregation Number**

Since dinonyl naphthalene sulfonic acid (HD) is an excellent extractant of metal ions into CCl₄, it was considered of interest to devise an NMR method to determine its aggregation number, x. With this objective, we have measured the SO₃H proton signal of 0.1 F HD in anhydrous CCl₄, in the absence and presence of various concentrations of dimethylformamide (DMF), and the frequencies are given below:

<table>
<thead>
<tr>
<th>Table I</th>
<th>Concn. of DMF</th>
<th>1/2, ppm. downfield from TMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>d, M</td>
<td></td>
<td>-13.5°</td>
</tr>
<tr>
<td>0.00</td>
<td></td>
<td>12.47</td>
</tr>
<tr>
<td>3.00</td>
<td></td>
<td>9.90</td>
</tr>
<tr>
<td>6.45</td>
<td></td>
<td>9.47</td>
</tr>
<tr>
<td>10.07</td>
<td></td>
<td>8.96</td>
</tr>
</tbody>
</table>

Since the initial concentration of DMF, d, is much greater than that of HD (b = 0.1 F), we need to consider only the reaction

\[(\text{HD})_x + x \text{DMF} \rightarrow x \text{HD} \cdot \text{DMF}\]  \hspace{1cm} (1)

If \( f \) is the equilibrium concentration in formality of uncomplexed HD, then the equilibrium constant would be given by

\[ K = \frac{(b - f)^x}{(f/x)(d-b+f)^x} \]  \hspace{1cm} (2)

The observed SO₃H proton frequency may be taken to be
the weighted average of the characteristic frequencies of
the uncomplexed and complexed HD, $\nu_x$ and $\nu_c$, respectively, so that

$$\nu_{\text{es}} = \frac{f}{b} \nu_x + \frac{b - f}{b} \nu_c$$  \hspace{1cm} (3)

The value of $\nu_x$ is the frequency of $SO_3H$ in the absence
of DMF. The value of $\nu_c$, 8.33 ppm., is obtained by
plotting $\nu$ vs. d at the various temperatures and
extrapolating to $d = \infty$. The value of $f$ is obtained by
rearranging eq. (3) to give

$$f = \frac{\nu_{\text{es}} - \nu_c}{(\nu_x - \nu_c)/b}$$  \hspace{1cm} (4)

In order to determine the aggregation
number, $x$, trial values of $x$ from 1.0 through 4.0 in
increments of 0.1, were substituted into eq. (2) and
the corresponding values of K computed. A portion of
the computed results for 35° are shown in Table II.
It is seen that the value of $x$ which yields a constant
value of $K$ is $x = 2.0$. For $x < 2.0$, the computed values
of $K$ increase monotonically when $b$ increases from 3.00
to 10.07 M; whereas for $x > 2.0$, the computed values
of $K$ decrease when $b$ increases in the same range.

Table II

<p>| Computed Values of K at Various Assumed Values |</p>
<table>
<thead>
<tr>
<th>of $x$, 35° (eq. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b = 3.00M$</td>
</tr>
<tr>
<td>$x = 1.6$</td>
</tr>
<tr>
<td>1.9</td>
</tr>
<tr>
<td>2.0</td>
</tr>
<tr>
<td>2.1</td>
</tr>
<tr>
<td>2.5</td>
</tr>
</tbody>
</table>
At 35° therefore, HD in CCl₄ is a dimer. This result agrees with the value x = 2.0 obtained by Little and Singleterry (J. Phys. Chem. 68, 3453 (1964)) for HD in benzene at 35°, using a vapor pressure method.

The values of x in (HD)ₓ at -13.5°, 1.5°, 35° and 61°, obtained by the present NMR method, are 3.2, 2.8, 2.0 and 1.4, respectively. A plot of x vs. t° yields a straight line. A simple linear extrapolation of the plot gives x = 1 at 78°. The frequency data in Table I, extrapolated to 78°, yields \( \nu_M \sim 8.27 \text{ ppm} \), where \( \nu_M \) is the characteristic frequency of monomeric HD.

When no DMF is present, the frequency of the SO₃H signal at 35° remains constant at 11.67 ppm, in the range of HD = 0.05 to 0.45 F in CCl₄. This means that x is constant in this concentration range. Kaufman and Singleterry (J. Colloid Sci. 10, 139 (1955)) have estimated the critical range for micelle formation of dinonyl naphthalene sulfonates at 10⁻⁶ to 10⁻⁷ F, and that the aggregation number, from vapor pressure measurements, is independent of concentration. Our NMR result therefore is in agreement with these findings.

It will be noted from Table I that in the absence of DMF, \( \nu \) decreases by 2.15 ppm, in the temperature range -13.5 to 61°. In the same temperature range, as the concentration of DMF increases, the decrease in \( \nu \) becomes smaller. This is easily accounted for, because in the absence of DMF, as temperature increases, only the reaction (HD)ₓ \( \rightarrow \) x HD occurs; whereas in the presence of DMF, eq. (1) needs to be considered. The relative values of \( \nu_X \), \( \nu_C \) and \( \nu_M \)
account for the trend of frequencies listed in Table 1 nicely.

This research was carried out in the laboratory of Professor Norman C. Li at Duquesne University.

Sincerely yours,

William J. Busler

William J. Busler

1 Research Assistant to Brother Edward Doody on an ACS Petroleum Research Foundation grant with Christian Brothers College at Memphis, Tenn.
Dr. Bernard L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616

Dear Barry:

Short Title: Variable Temperature of Isobutyl Vinyl Ether and Computer Program

Recently, we began NMR and far infrared studies on a number of ethers and esters. Enclosed are some preliminary temperature studies of isobutyl vinyl ether, taken on our Varian A-60. Clearly, multiplet B arises from the geminal vinyl protons. As the temperature decreases, it can be seen that distinct changes occur in the structure of the B multiplet. Refined measurements on this and related vinyl ethers are now in progress and will be reported in the near future.

The NMR computer program of Stanley, Marquardt and Ferguson (1,2) has been converted from its original language of IBM 7040 Fortran IV to that of IBM 7094 Fortran IV for use at our computational facilities.


Sincerely yours,

T. Altpeter  
A. D. H. Clague  
A. Danti

jep
DATE: 7/16/65
SAMPLE: ISOBUTYL VINYL ETHER
OPERATOR: A.D.H.C., T.A.
SOLVENT: Neat
R.F. FIELD: 0.04 mG
SPEC. AMPL.: 1.0
FILTER B.W.: 4 cps
SWEEP WIDTH (S.W.): as shown
SWEEP TIME: 500 sec.

\[ \delta_a = 2.228 \text{ ppm}; \quad J_{ab} = 4.05 \text{ Hz}; \]
\[ \delta_b = 2.447 \text{ ppm}; \quad J_{ac} = 8.58 \text{ Hz}; \]
\[ \delta_c = 3.189 \text{ ppm}; \quad J_{bc} = 14.81 \text{ Hz}; \]
\[ |J_{a,N}| = 5.51 \text{ Hz}; \quad |J_{b,N}| = 2.52 \text{ Hz}; \quad |J_{c,N}| = 3.52 \text{ Hz}. \]
Die δ-Werte sind auf das nicht aufgespaltene Methylsignal bezogen und wachsen nach kleinerem Feld.


Seit ein paar Wochen verfügt das NMR-Labor der BASF auch über eine "CAT" (time averaging computer C 1024 von Varian). Damit haben wir nicht nur die Möglichkeit, Lösungen mit sehr geringer Konzentration der interessierenden Substanz zu messen, sondern auch so etwas wie "kompensierte NMR-Spektren" (Kompensation im Sinne der optischen Zweistrahlspiektrospiektroskopie) herzustellen, ein Verfahren das wir in Bereich der IR-Spektroskopie häufig anwenden und bisher für die NMR-Spektroskopie sehr vermißt haben. Dazu speichern wir zunächst das Spektrum einer Lösung auf Stellung "add" in der CAT und dann in demselben Probenröhrchen und unter peinlicher Einhaltung der Bedingungen das Spektrum des Lösungsmittels auf Stellung "sub". So gelingt es meist recht einfach, die Substanzlinien überlagenden Lösungsmittellinien aus dem Endspektrum zu entfernen. Dieses Verfahren scheint mir wichtig, einmal im Hinblick auf Einsparung der teueren deuterierten Lösungsmittel, zum anderen aber vor allem im Hinblick auf die Reinheitsforderungen, die an das Lösungsmittel zu stellen sind. Bis hier brauchte man sich darum nicht sehr zu kümmern. Jetzt aber, mit der Verfügbarkeit der CAT, kann bei der Untersuchung von Lösungen mit 0,1 % oder weniger der interessierenden Substanz die Reinheitsforderung entscheidend werden. Hier hilft die Kompensation der etwaigen Verunreinigungsbanden häufig schneller und einfacher weiter als eine zeitraubende und teuere Extremreinigung der Lösungsmittel - vorausgesetzt natürlich,
daß ein so teuerer Apparat wie C 1024 vorhanden ist. Ich glaube mit der Ansicht nicht fehlzugehen, daß dieses Kompen- sationsverfahren bei zunehmender Erfahrung mit der CAT in manchen Fällen Möglichkeiten eröffnet, die uns bisher verschlossen sind.

Mit freundlichen Grüßen

Ihr

( Dr. W. Brügel)
The spectrum (100 MHz) of the vinyl group of trimethyl vinyl ammonium bromide (ca. 20 °C in D₂O).

Top: = CH-group; bottom: = CH₂-group. The figures are c.p.s. downfield from the N(CH₃)₂-signal.
Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Chemistry  
Technology Center  
Chicago, Illinois  

Re: SPECTRA OF CYANINE DYES-EVIDENCE FOR A  
DYNAMIC EQUILIBRIUM

Dear Barry:

For some time we have been examining the spectra of cyanine dyes such as \([2\text{-bis}(3\text{-ethyl thiazolinyi})\text{trimethine cyanine iodide,}]

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{S} \\
\text{H}_2\text{C} + \text{C} - \text{C} & \quad \text{H} \\
\text{N} & \quad \text{H} = \text{C} - \text{C} = \text{C} \\
\text{C}_2\text{H}_5 & \quad \text{N} \\
\text{C}_2\text{H}_5 & \quad \text{CH}_2 \\
\end{align*}
\]

We have had difficulty in obtaining sufficiently concentrated solutions and finally used as solvent a fifty percent mixture of chloroform and tetrafluoro-dichloroacetone-deuterate \([ (\text{CF}_2\text{Cl})_2/\text{CO} \cdot 2.5 \text{D}_2\text{O} ] \). At dye concentrations, (200mg of dye per millimeter of solvent) in which we could obtain reasonable spectra, we were not able to observe and identify the bridge protons. Roy Johnson ran the trimethine for us in a mixed solvent at 2 and 20mg per liter, at 100Mc and with \(_4\text{C}_1\text{O}_2\text{r}4\) for 100 traces. We failed to observe the bridge protons. We finally decided to try a run in pure chloroform at 0.1mg of dye per ml., it was run with the C1024 for 820 scans. The expected bridge proton spectra appeared at 614 c.p.s. and 748 c.p.s., apparently in the mixed solvent at the higher concentrations (we couldn't use chloroform alone for the higher concentrations) a dynamic monomer-dimer equilibria exists or the dye and solvent form a complex in a dynamic equilibria which washes out the bridge proton spectra. In support of this idea we found that for 2-methyl thiazoline ethiodide in chloroform, the TMS-chloroform separation of 433 c.p.s. in pure solvent changed to 481.6 c.p.s. when the quaternary
Salt was dissolved in the chloroform; apparently the quaternary salt and chloroform interact quite strongly.

Within a vinylogous group of dyes the fine and hyperfine structure disappears as we go from the monomethine to the pentamethine. As the heterocyclic nucleus is varied, the observable hyperfine structure varies. Even the CH₃ and CH₂ groups of the N-ethyl group smear out. It has been known that the dyes either polymerize or form coordinated structures in water and when adsorbed on silver bromide. It now appears that the cyanines tend to polymerize in other solvents as well as water.

The data on the chemical shifts and coupling constants of the thiazolinyl dyes in Table I and Table II were obtained by Asa Leifer before he left. The quaternization of 2-methyl thiazoline caused the 2-methyl group to exhibit a greater chemical shift and changed the ring A₂B₂ group coupling constant to a lower value. However, for the dyes, surprisingly, the chemical shifts of the CH₂ and CH₃ group of the ethyl group attached to the nitrogen and for the ring A₂B₂ group do not vary significantly from dye to dye.

There is, as was expected, a difference between the chemical shift for the quaternary salt CH₂ and CH₃ group of the nitrogen ethyl group and the dyes; however, there was no observable difference in the coupling constants. On the other hand the coupling constant for the ring A₂B₂ group is quite different for the quaternary salt and the dyes. See Table II. The chemical shift of the A₂B₂ groups was much larger for the quaternary salt than for the dyes. However, there was no discernible trend within the vinylogous series of dyes.

Unfortunately the data for other series of dyes than the thiazolinyl were even more difficult to interpret. We will have to modify our DP60 for proton stabilization and obtain a C1024 to continue the dye investigations.
### TABLE I

**CHEMICAL SHIFTS AND COUPLING CONSTANTS OF THIAZOLINYL DYES**

<table>
<thead>
<tr>
<th>2-Methyl</th>
<th>CH₃ of ethyl group</th>
<th>2-Methyl</th>
<th>CH₃ of ethyl group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ</td>
<td>J</td>
<td>δ</td>
</tr>
<tr>
<td>8</td>
<td>Jₜₑ</td>
<td>c.p.s.</td>
<td>8</td>
</tr>
<tr>
<td>2-Methyl thiazoline</td>
<td>121.2</td>
<td>1.6</td>
<td>---</td>
</tr>
<tr>
<td>2-Methyl thiazoline ethiodide</td>
<td>168.4</td>
<td>---</td>
<td>88.1</td>
</tr>
<tr>
<td>2-bis(3-ethyl thiazolinyl) cyanine iodide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monomethine</td>
<td>77.4</td>
<td>7.4</td>
<td>214.2</td>
</tr>
<tr>
<td>Trimethine</td>
<td>76.4</td>
<td>7.4</td>
<td>214.3</td>
</tr>
<tr>
<td>7-Methyl trimethine</td>
<td>78.4</td>
<td>7.2</td>
<td>214.3</td>
</tr>
<tr>
<td>Octamethine</td>
<td>76.9</td>
<td>7.1</td>
<td>214.2</td>
</tr>
<tr>
<td>8-bromopentamethine</td>
<td>80.2</td>
<td>7</td>
<td>214.6</td>
</tr>
<tr>
<td>Heptamethine</td>
<td>76.3</td>
<td>7.3</td>
<td>214.2</td>
</tr>
</tbody>
</table>

### TABLE II

**CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR RING A₂B₂ GROUP**

<table>
<thead>
<tr>
<th>A Group</th>
<th>B Group</th>
<th>J₂ₐ</th>
<th>(J/δ)₂ₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>δ</td>
<td>δₐ₂</td>
<td>J₂ₐ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methyl thiazoline</td>
<td>245.8</td>
<td>194.6</td>
<td>51.2</td>
</tr>
<tr>
<td>2-Methyl thiazoline ethiodide</td>
<td>283.2</td>
<td>232.2</td>
<td>51.0</td>
</tr>
<tr>
<td>2-bis(3-ethyl thiazolinyl) cyanine iodide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monomethine</td>
<td>241.8</td>
<td>202.8</td>
<td>39.1</td>
</tr>
<tr>
<td>Trimethine</td>
<td>244.8</td>
<td>199.8</td>
<td>45.1</td>
</tr>
<tr>
<td>7-methyl-trimethine</td>
<td>239.3</td>
<td>201.6</td>
<td>37.7</td>
</tr>
<tr>
<td>Pentamethine</td>
<td>243.0</td>
<td>199.8</td>
<td>43.4</td>
</tr>
<tr>
<td>8-bromopentamethine</td>
<td>247.2</td>
<td>202.2</td>
<td>45</td>
</tr>
<tr>
<td>Heptamethine</td>
<td>241.8</td>
<td>199.2</td>
<td>43.0</td>
</tr>
</tbody>
</table>
August 13, 1965

Professor B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center, Chicago, Illinois 60616

Re: Position Wanted

Dear Professor Shapiro:

As the delivery of the new N.M.R. spectrometer to my Prague laboratory is delayed and as my postdoctoral year here at Harvard will finish in February 1966, I would like to join an N.M.R. group for some time.

I am wondering whether there exists such a group with a vacancy?

Sincerely yours,

Jan Schraml

P.S. I am interested mainly in high-resolution N.M.R. work and spent about three years doing applied N.M.R. on organosilicon compounds which meant especially trouble-shooting on a semi-home-made instrument.
August 19, 1965

Prof. Barry Shapiro
Department of Chemistry
Illinois Institute of Technology
Chicago, Illinois

Dear Barry:

Several years ago Narasimhan and Rogers (J. Chem. Phys., 34, 1049 (1961); J. Am. Chem. Soc., 82, 34, 5983 (1960)) reported internal chemical shifts and spin coupling constants for a series of compounds of type $M(C_2H_5)_n$, where $M = Hg, Ge, Sn, Pb, Zn,$ etc. The internal chemical shifts were shown to fit a modified Dailey-Shoolery relationship between $\delta$ and the electronegativity of $M$; however, they were determined using pure liquids and the question has always remained whether values obtained at infinite dilution in an inert solvent might differ in an important way.

We have now measured the NMR parameters for a series of these organometallic compounds at infinite dilution in carbon tetrachloride solution. The values do not differ from those reported previously by more than about 6%. Since electronegativity values for the metals are uncertain by more than this the new data do not alter the previous conclusions.

We should also point out an error in the values of $J_{CH_2 - Sn}$ reported previously [J. Chem. Phys. 34, 1049 (1961)]. These should have been $J_{CH_2 - Sn^{117}} = 50.8$ cps and $J_{CH_2 - Sn^{119}} = 52.2$ cps (rather than 30.8 and 32.2 cps). Klose [Ann. Phys. 8, 220 (1961); 9, 262 (1962)] has reported coupling constants in good agreement with the above values.

Yours sincerely,

Max T. Rogers

Roy L. Foley
"The Signes of the Side-chain Couplings in Methylthiophenes as Determined by Multiple Resonance Techniques"
S. Gertlm and R. Mathiasen
Acta Chem. Scand. 18, 1965 (1964)

"Preparation and Dehydration of 9-Demethyl-9-hydroxy-9, 10-dihydropyrene"
K. O. Flynn and G. Bergman
Acta Chem. Scand. 18, 2002 (1964)

"Tautomorphism in Isotopically Substituted Idoxene"
G. Bergman
Acta Chem. Scand. 18, 2003 (1964)

"Algal Carotenoids. IV. On the Structure of Papavartixin" Arne Jensen
Acta Chem. Scand. 18, 1965 (1964)

"Resource Letter BBR-1 on Nuclear Magnetic Resonance and Electron Paramagnetic Resonance" H. N. W. Berg
Am. J. Phys. 33, 71 (1965)

" Zur Chemie des Benzolpyrylen, XII. Synthese von Deoxy-x-ioninen"
M. Makujima, A. Hamagawa and F. W. Lichtenstaller

"Kynononitin (Deoxynorcanetin) and Deoxycanetin" Y. Tesho, O. A. Svetosivtov Jr. and I. Marion
Ann. Chem. 680, 85 (1964)

"Diploeinone and Magnetic Properties of Benzol-Mercurate" U. Goetz, P. Margel and K. Haase
Ann. der Chem. 692, 1 (1965)

"Zur Bildungswise von cis-trans-trans-3-Cyclohexatrien-(1,5,9)
Mittels Titanzintaliger Ziegler-Katalysatoren"
E. Weber, W. Ring, U. Hochmuth and R. Schrake
Ann. der Chem. 692, 10 (1965)

"Organic Fluorine-Bindings, VIII. Synthesen und Reaktionen
Natur Fluor-Vitamin-A-Bliureseter"
H. Maschietto and J. Bulaishi
Ann. der Chem. 692, 21 (1965)

"Ubers Neu Hydroxydichinoline" H. Bachman
Ann. der Chem. 691, 84 (1965)

"Die Absolute Konfiguration Des Tetratolyl-(-)-8-Isooctachlorolactida"
K. Weisger und D. Paulus
Ann. der Chem. 691, 154 (1965)

"Datechin-Resorcin-Kondensate"
K. Weisger and F. Toribio
Ann. der Chem. 691, 161 (1965)

"Ubers Reaktionen am Podophyllin-Lignan"
J. Zsch. R. Fann and A. Wurtberg
Ann. der Chem. 691, 207 (1965)

"Kleine Kohlenstoff-Ringe, VIII. Valenzisorerung von cis- und trans-2-Vinyl-Cyclopropylisocyanatan"
Ann. Chem. 692, 1 (1965)

"Ubers Alkaloid, V. Inhaltsstoffe von Lespedeza bicolor"
var. japonica. L. Ubers Lespedeza, ein neues Alkaloid"
I. Hontoto and H. Onici
Ann. Chem. 692, 212 (1965)

"8,9-H Spin-Spin Coupling in Vinyl and Ethynyl Mercurials"
P. R. Wells and W. Kilting
Aust. J. Chem. 17, 1269 (1964)

"Dinodene (5,9-Dihexyloctahexene-2,5-Dione) As a protecting Agent for Amino Groups in Peptide Synthesis"
B. Halperin and J. B. James
Aust. J. Chem. 17, 1759 (1964)

"Nuclear Magnetic Resonance Spectra of Angelicin and Related Compounds"
T. J. Bateman and J. A. Lambertson
Aust. J. Chem. 17, 1295 (1964)

"Spin-Spin Coupling in Vinyl and Ethynyl Mercurials"
P. R. Wells and W. Kilting
Aust. J. Chem. 17, 1269 (1964)

"The Identification of Trans-L-Isocitron-2-Ketone by its Proton Magnetic Resonance Spectrum"
A. B. Gilby and D. P. Warnerhouse
Aust. J. Chem. 17, 1313 (1964)

"Organosilicon Compounds. VIII. The Reactions of Organosilicon Hydrides with Phenylenesilane"
J. R. Surtees
Australian J. Chem. 18, 14 (1965)

"Partaking of an Alkali from Call Pepee (Passiflora Arundinacea"
S. O. Yates and E. L. Tooke
Australian J. Chem. 18, 22 (1965)

"The Synthesis of 5,8,Anuralic Triplatezide"
G. M. Badger, J. A. Elia and G. E. Lewis
Australian J. Chem. 18, 70 (1965)

"Flavon Derivatives, XII. Conversion of Flavan-3,4-diol into 1,3-Oxodiene-2,3-Dichloro"
J. W. Cram-Liebigs and L. A. Williams
Australian J. Chem. 18, 90 (1965)

"Studies in Aerial Oxidation: Salts of Methylbenzoic Acid"
J. W. Melin, J. S. Shannon, and S. Sternhell
Australian J. Chem. 18, 129 (1965)

"Organophosphorus Compounds, IV. The Reaction of Alkyl-ynes with Phosphate Pentahydrates, and a New Route to Alkyl-1,2-Dienes" A. Meisters and J. M. Swan
Australian J. Chem. 18, 155 (1965)

"Organophosphorus Compounds. VI. The "Abnormal" Michaelis-
Bach Reaction. Diethyl 1-Phenylcylohexyl-phosphosphate and Diethyl 1-Phenylvinyl Phosphates with Phosphonites and Phenyl Chlorides" A. Meisters and J. M. Swan
Australian J. Chem. 18, 269 (1965)

"Characterisation of N-Dicyclohexyl(cyclopentadienyl)ironium-
Cyclodek Computer Containing the 3-Ethyl-3-Cyclopentadienyl-
1,1-Diethyl-3-Hexyl-5,6-Dioxide"
A. J. Reid, J. S. Shannon, J. M. Swan, and P. C. Wallis
Australian J. Chem. 18, 173 (1965)

"Phenanthridines, IV. Four Reactions with Sulphonecarbides
Derived from 2-Aminoanibinoxalidines: Synthesis of 2-Aminophenanthridine and Formation of 6-(2-Phe-nyl)-2-aminophenanthridine" J. J. Huppers and K. N. P. Sasse
Australian J. Chem. 18, 206 (1965)

"Colouring Matters of Australian Plants, XII. Quinones from Mimosella Revoluta and Bymanstrea Grandis"
R. D. Cooke and L. O. Sparrow
Australian J. Chem. 18, 219 (1965)
"Nature of the Coactor for the Acid Lipase of Rhus communis"  
E. L. Croy, R. H. Walker, and G. J. Routhenaux  

"The Absolute Configuration of α-Hydroxy-β-carboxyisocaproic Acid (3-Isopropylmalalactic Acid), and Intermediate in Linseed Biosynthesis"  
J. M. Calvo, C. M. Stevens, N. G. Kalyansur, and H. R. Umbarger  
Bull. Soc. Chim. France 228 (1964)

"Some Principles in the Proton Magnetic Resonance Spectra of α,β-Unsaturated Compounds"  
A. R. H. Hopwood, M. L. Shih, and V. A. Mosevan,  
G. Ya. Zueva and G. A. Rauvav  

"Stérols halogénés et instaurés en 3, 7-Méthyls en 1°, Préparation et étude spectroscopique des iminoesters allantoptiques. II"  
P. Payraud and R. C. Moreau  

"Préparation et étude spectroscopique des iminoesters allantoptiques. III"  
P. Payraud and R. C. Moreau  

"Dérivés pentacycliques de stéroïdes (1). Préparation d'éthers et de dérivés"  
H. L. Bich and J. G. Parisean  

"Dérivés pentacycliques de stéroïdes (II). Réductions d'éthers à des alcools"  
H. L. Bich and J. G. Parisean  

"Étude de la réaction de Fried. Étude descriptive des systèmes formyl-butane-1, formyl-butane-2 et formyl-butané"  
M. R. Kellin, M. Davidson, D. Lumbruso, P. Guitian and P. Guionnean  

"Dérivés phosphorés d'hormones stéroïdes. I. - Phosphates de stéroïdes"  
J. M. Bich  

"Dérivés phosphorés d'hormones stéroïdes. II. - Acides bis-stéroïdes-phosphoriques et Py2Pb-bis-stéroïdes-phosphoriques"  
J. M. Bich  

"Composés Acétyléniques de l'Étain"  
M. Le Quan and P. Cadot  

"Composés propargyliques et alléniques de l'éthain"  
M. Le Quan and P. Cadot  

"Symbiose, structure, et propriétés des acétyloxy-6 aminio-β-pyrillos et ses transformées qui en dérivent"  
N. F. Bacone, M. L. Shih, and N. T. Xue  

"Dérivés du A-nor [5α] androstane. II. - Synthèse et caractérisation de l'alcool aétyloxy et chloroacétyloxy en position 2"  
J. Jacques, M. Wisniewski, and D. Varvich  
J.-M. Rasseler  

"Réactivité d'α-amino-alcools en série décanalique et stéréoïd"  
S. Lasadon, P. Potin, P. Monnier, and R. Wyse  

"Action des Magnésiens Vinylique sur les Esters O-Benzyl-ethéniques. Détermination de Génotypes O, γ-éthéniques"  
C. Lumbruso and P. Mattie  

"Orientation et normales" et "anormales" dans les réactions de substitution des benzènes 1,2,3-trisubstituées. I. l'acylation de l'homoléthylène"  
M. P. Bui-Hoi, P. Jacques, and C. Roussel  

"Spectres de Résonance Magnétique Nucleaire de Quelques Nitro-Acrylamides. (Note de Laboratoire)"  
J.-P. Moreau and P. Petit  

"Seulement Magnétique de Dérivés Cellulaires"  
D. Gagnaire and M. Vinson  

"Études Stéréochimiques en Série Dihydrofuranne. V. Configuration de Dérivés Synthétiques D'acides Dihydrofuranne. V. Dihydrofuranne"  
D. Gagnaire and P. Monzeglio  

"époxidation Sélective du Maxou"  
M. Mousseron-Cant et G.-C. Holm  

"époxidation Sélectives dans la Série du Molécule"  
M. Mousseron-Cant et G.-C. Holn  

"Spectres de Résonance Magnétique Nucleaire de Quelques Nitro-Acrylamides. (Note de Laboratoire)"  
J.-P. Moreau and P. Petit  

"Spectrométrie de Résonance Magnétique Nucleaire de Dérivés Cellulaires"  
D. Gagnaire and M. Vinson  

"Spectres de Résonance Magnétique Nucleaire de Quelques Nitro-Acrylamides. (Note de Laboratoire)"  
J.-P. Moreau and P. Petit  

"Spectrométrie de Résonance Magnétique Nucleaire de Quelques Nitro-Acrylamides. (Note de Laboratoire)"  
J.-P. Moreau and P. Petit  

"Transition Metal Complexes of a Constrained Phosphite Ester. III. Metal Carbonyl Complexes of 4-Methyl-6,7-triazolo-1-phosphoripinone" F. Beck, H. W. Whitlock, and M. E. Huddleston Inorg. Chem. 4, 987 (1965)

"Preparation of Tetraakis(trifluorophosphine) palladium(0)" G. F. Smuts and R. F. Flagg Inorg. Chem. 4, 987 (1965)

"Knight Shifts and Relaxation Times of Alkaloid-Metal and Nitrogen Nuclei in Metal-Amines Solutions" J. E. O'Byrne J. Chem. Phys. 41, 3739 (1964)


"Linear Correlation of the Phosphorus-Hydrogen Spin Coupling Constant with Proton Chemical Shifts in a Series of Polyphosphorus Compounds" J. G. Verkade, T. J. Hutterman, M. K. Fung, and N. W. King Inorg. Chem. 4, 483 (1965)

"Linear Correlation of the Phosphorus-Hydrogen Spin Coupling Constant with Proton Chemical Shifts in a Series of Polyphosphorus Compounds" J. G. Verkade, T. J. Hutterman, M. K. Fung, and N. W. King Inorg. Chem. 4, 483 (1965)


"Histidine Complexes of Molybdenum(V) and Molybdenum(VI)" M. G. F. Spring and J. B. Lew Inorg. Chem. 4, 395 (1965)

"Substitution Patterns in Phosorphosphonitritiles" G. S. Ford, F. E. Dickson, and J. I. Reiman Inorg. Chem. 4, 419 (1965)

"Preparation and Properties of Tetrakis(trifluorophosphine) palladium(0)" G. F. Smuts and R. F. Flagg Inorg. Chem. 4, 422 (1965)
The Preparation and Some Biological Properties of 1-[2-ethyl-1-piperidino-3-oxo-2-pyridyl]pentane-3-carboxylic Acid
R. Y. Kihara and P. B. Doffman
J. Med. Chem. 8, 268 (1965)

Interaction of Cumulene Systems with Organometallic Complexes: I. Diamal Complexes
A. Makabe, F. J. K. and K. Nagahara
J. Organometal. Chem. 2, 7 (1965)

Über Aromatkompounds von Metallen. XXXI. Über ein Bis-Cyclopentadienyl(di-sec-butyldimethyl)beryllum und Design Reaktionsprodukte mit Elektrodonatoren
E. O. Fischer and S. Wexer
J. Organometal. Chem. 2, 16 (1965)

Use of a Relationship between J(15N-14N) and g to Evaluate Anisotropie Contributions to X-Ray Polarization in the g-Values of the Group IV Tetramethyl Derivatives
R. S. Drago and K. A. Maitlyoff
J. Organometal. Chem. 2, 69 (1965)

Exchange of Substituents in Nitrogen in Molybdenum Sulfates and Amines
H. K. Hofmeister and J. R. Van Wazer
J. Phys. Chem. 69, 723 (1965)

Mechanisms of Homogeneous Gas-Phase Partial Oxidation of n-Butane
J. Lotus and C. H. Buttersfield
J. Phys. Chem. 69, 909 (1965)

143 Magnetic Resonance Study of the Protonation of Acetic and Amino Acids and their Methyl Ethers in Concentrated Sulfuric Acid
G. H. Matias and D. L. Traubietra
J. Phys. Chem. 69, 1030 (1965)

Réponse à une Linéaire D’un Système de Spins Nucléaires A une Excitation Extérieure
J. F. Ofer-Addad
J. Physique 26, 19 (1965)

Stereoregularity of Polymer Acrylate and Polyacrylonitrile
K. Watanabe, T. Uryu, A. Itozawa and T. Ohki
J. Polymer Sci. 62, 1139 (1964)

Intramolecular Hydride Shift Polymerisation by Cationic Mechanism. V. Polymerisation of 3-Phenyl-1-Butene
J. F. Kennedy, C. A. Cohen and W. Naegele
J. Polymer Sci. 62, 1139 (1964)

NMR Characteristics of p-Di- and p-Nitrobenzenes
B. H. Wiseley and T. W. Crabtree
J. Polymer Sci. 63, 289 (1965)

Coordination Polymerisation of the Bicyclo[2.2.1]heptene-2 Ring System (Borstone) in Polar Media
J. U. Hiscott and W. M. Keaveny
J. Polymer Sci. 63, 395 (1965)

Some Low Molecular Weight Polymers of p-Limazone and Related Terpenes Obtained by Ziegler-Type Catalysts
A. H. Whalen, R. P. Beggan and H. M. Culbertson
J. Polymer Sci. 63, 989 (1965)

Proton Magnetic Resonance Study of the Structures of Phenol-Formaldehyde Resins
T. C. Woodhury, R. P. Higginbottom and H. M. Culbertson
J. Polymer Sci. 63, 1079 (1965)

Dilute Solution Properties of Nylon 66 Dissolved in 2,2,3,3,4,4,5,5-Octafluoropropane
F. R. Maxime
J. Polymer Sci. 63, 1821 (1965)

A One-Parameter Model for Isotactic Polymerisation Based on Emulsion Cationic Catalyst Sites
R. A. Ballelden, T. Porto, T. Ohtani and J. Fumakura
J. Polymer Sci. 63, 23 (1965)

Tacticity of Poly(vinyl Alcohol) and Poly(vinyl Trifluoroacetae) by NMR
R. G. Ramsey and R. D. Field
J. Polymer Sci. 63, 63 (1965)

Tacticity of Poly(vinyl Acetate) by NMR
K. C. Ramsey and R. D. Field
J. Polymer Sci. 63, 69 (1965)

NMR Spectra of the Mono and Di-Isomers of Dimethylglycinate and S-Alkyl-Diphenylacetates
D. Fakourlova and B. Schneider
J. Polymer Sci. 63, 213 (1965)

Über die Reaktion von N-Halokyl-hydroxyamiden mit Bromcyan unter Bildung von di(alkyl-N)-cyan-hydroxyamiden
W. Schulte, O. Lach and H. Fritzschke
J. Prakt. Chem. 63, 268 (1964)

Spin Echo Study of Translational Molecular Diffusion in Alcohol-Water Mixtures
K. A. Volkov and M. I. Krabichov
J. Struct. Chem. 3, 5 (1964)

The Estabilishment of the Structure of Water by Nonelectrolyte Molecules, from NMR Data
J. T. M. T. and V. I. Nofechkover
J. Struct. Chem. 63, 10 (1964)

Experimental Study of the Rate of Nuclear Spin Relaxation in Electrolyte Solutions
S. K. Sombarzavan
J. Struct. Chem. 3, 13 (1964)

The second moment of a magnetic resonance absorption line
A. A. Kokkin and A. K. Chirkov
J. Struct. Chem. 3, 37 (1964)

Practical sensitivity of a high-resolution NMR spectrometer
P. V. Petrovetski and Z. I. Yedun
J. Struct. Chem. 63, 118 (1965)

Progress in the Chemistry of Vobsaline and Related 2-Acyliso-ole Alkaloids
J. A. Pertchand and D. Douglas
Lloydia 37, 374 (1964)

Alkaloids aus Schizosyaz Carinoides, III. Strukturelle Beschreibung einer Schizozyaz und deren Nebenalkaloiden
U. Werner
Lloydia 37, 56 (1964)

On Alkaloids, XIV. Spectral Studies of Lochnerina and Lochneronine
Lloydia 37, 316 (1964)
"On a Statistical Theory of Spin Relaxation"  
H. Rakuno and A. Yoshinari  

"Etude de Diacettes par Rezonance Magnétique Nucléaire"  
J. Deau  

"Sulfur: Role in Genesis of Petroleum"  
A. S. Douglas and R. S. Mair  
Science 157, 495 (1967)

"Phosphorus-31 Nuclear Magnetic Resonance Studies of Phosphorus-fluorine Compounds"  
J. F. Hixon and R. Schmitzer  
Spectrochim. Acta 20, 1835 (1964)

"Nuclear magnetic resonance studies of tetraalkyl compounds of group III and group V elements--III"  
A. D. Breyer, R. K. Poskel and B. Shaw  
Spectrochim. Acta 21, 263 (1965)

"A study of the reaction course of triphenylphosphine with bromoacetyltriphenylphosphonium bromide"  
D. W. Grisley, Jr., C. G. Alm and C. N. Matthews  
Tetrahedron 21, 5 (1965)

"Synthesis of Tricyclic Ketones by Copper-catalyzed Cyclization of Monocyclic Alkyl Diazoketones"  
W. N. Dearing, R. T. Possel and R. L. Kaye  
Tetrahedron 21, 65 (1965)

"Allylic Eiketones and Eikals--V. The Preparation and properties of Cyclohexane-1,3-Dione"  
I. Makland and J. A. Bresgen  
Tetrahedron 21, 1 (1965)

"A Proton Magnetic Resonance Study of Carbonyl 3,3-Epoxides and related Compounds"  
D. H. Buss and L. Hough, L. D. Hall and J. F. Mansfield  
Tetrahedron 21, 65 (1965)

"Citrus bitter Principles--II. Application of NMR to Structural and Stereochemical Problems"  
L. L. Drayer  
Tetrahedron 21, 75 (1965)

"Auranthrol, a common Compound in Bitter (Seville) Orange Oil"  
W. L. Stanley, A. C. Weiss, Jr., R. R. Landis and S. H. Vanier  
Tetrahedron 21, 89 (1965)

"Structure of Opuntia, A Constituent of Opuntia Elatior"  
Tetrahedron 21, 93 (1965)

"Terpenoids--XIII. Studies in the Conversion of Podocarp Acid to Atisine"  
K. R. Gokula and L. R. Kalos  
Tetrahedron 21, 303 (1965)

"Terpenoids--XXII. The Constitution of Agarospirol, A Sesquiterpenoid with a new Skeleton"  
R. R. Varma, M. S. Wastwater and S. C. Bhattacharyya  
Tetrahedron 21, 125 (1965)

"Terpenoids--XXVI. Ring Contraction in Cadinnes and Sesimene Compounds"  
C. C. Henrys and A. K. Chakravarti  
Tetrahedron 21, 129 (1965)

"The Stereochemistry of Phelimine"  
R. K. Hill, T. H. Gann and J. A. Joule  
Tetrahedron 21, 347 (1965)

"The Electrophilic Substitution of Benzocyclobutene -- II. Benzylation, Sulphonation, Bromination and Chlorination"  
J. B. P. Lloyd and P. A. Ogley  
Tetrahedron 21, 349 (1965)

"Strongly Basic Systems, V. N-Acidity Scale Based on the Ionization of Carbon Acids"  
K. Bowden and R. Stenegro  
Tetrahedron 21, 351 (1965)

"The Structural Characterization of Heterocyclic Carbocyclic: A New Streptomycin Antibiotic"  
L. A. Mitscher, W. B. McPhail and E. R. Nois  
Tetrahedron 21, 367 (1965)

"The Bromination of Isopinocamphor"  
M. F. Hartshorn and A. S. A. Wallis  
Tetrahedron 21, 373 (1965)

"On the Conformation of Cyclohexane-1,4-Dione and its Derivatives. I. Infrared and Raman Spectra of Cyclohexane-1,4-Dione and Infrared Spectrum of its Octahydrocycloheptane Analogue"  
W. T. Eshel, J. Sertel and F. M. Kalsstein  
Tetrahedron 21, 421 (1965)

"NMR Studies on Steroids -- VII. Substituent Effects due to Sulur-Containing Groups in Ring A of Steroids"  
K. Jori and T. Komoto  
Tetrahedron 21, 507 (1965)

"Eile Acids and Steroids -- XXVII. Thioesters (18) Steroidal 2,3- and 3,4-Diglycerides and Related Compounds"  
Tetrahedron 21, 509 (1965)

"NMR Spectra and w-Electron Densities of Some Eilial(1,2-4) Pyridines"  
W. L. Paulier and E. L. Blument  
Tetrahedron 21, 533 (1965)

"Thyroxine Analogues--XIII. NMR Evidence for Hindered Rotation in Diphenyl Ether"  
P. A. Lehman and E. C. Jorgenson  
Tetrahedron 21, 535 (1965)

"The Chemistry of the Oleo Resin From Pinarotica Pinaster : A Series of New Sterpenoids"  
E. Mia, R. C. Palley and R. Dev  
Tetrahedron Letters 2751 (1964)

"Allochotanolol, A New Type in Sesquiterpenoids"  
S. C. Himaya and S. Dev  
Tetrahedron Letters 2761 (1964)

"The Diterpenoids of Erythraxon Monogynum -- IV Allodavaroil, Dedararolic and Hydroxydavaroil"  
K. Nozou, R. Dev and R. Mia and R. C. Panley  
Tetrahedron Letters 3767 (1964)

"The oil of Sultoria Chamaemyrrhassae L: A new, non Isoprenoid C18 Hydrocarbon"  
A. F. Thomas and B. Willihan  
Tetrahedron Letters 3773 (1964)

"Solvolytic Cyclization of 2-a,-Cyclopentenyl) Butyl Eosylate"  
W. R. Cleasmon and G. T. Kudavok  
Tetrahedron Letters 4031 (1964)
The rearrangement of 6-hydroxycurcumin to curcullone
C. F. Murphy and W. C. Woldman
Tetrahedron Letters 3867 (1964)

"The rearrangement of 6-hydroxycurcumin to crivellone"
C. F. Murphy and W. C. Woldman
Tetrahedron Letters 3867 (1964)

"The 3-Methyl-6,10-Diazoniaphenanthrene Dication, An Aromatic Ring System with two Quaterary Nitrogen Bridged Aromes"
L. G. Calvert and W. E. D. Sasse
Tetrahedron Letters 371 (1964)

"Verticiliosa, A Novel Type of Conifer Interpane"
H. Sutcliff, T. O'Brien, N. Sumimoto, A. Morrison
Tetrahedron Letters 3707 (1964)

"Alkaloid Studies II. The Structure of Aspidinomassaii"n
K. Oishi, J. A. Joulle and C. Djerassi
Tetrahedron Letters 3899 (1964)

"The Constitution of Arotiopirin"
M. Sash, V. Boccut and P. Scm, P. de Mayo, A. N. Starrett and J. R. Stothers
Tetrahedron Letters 3907 (1964)

"Revised Structure of Parthenolide"
T. R. Givingswack, E. S. Join and V. K. Knott
Tetrahedron Letters 3907 (1964)

"Long-Range Shielding Effects of the Nitro Groups in 6α- and 6β-Nitrotestosterones"
K. Tori and K. Kuriyama
Tetrahedron Letters 3599 (1964)

"New Models for Conformational Analysis by N.M.R."n
K. Antweil and D. Taverman
Tetrahedron Letters 3599 (1964)

"Zur Stereoelektricität: Der Addition Der Alkynocarbonyl-Nitrile und Gießen"
K. Hafner, Wolfgang Kaiser and R. Puttnir
Tetrahedron Letters 3915 (1964)

"Salamin"n
R. Henderson, R. McRindle and K. H. Overton
Tetrahedron Letters 3919 (1964)

"Structural Investigstions on Studies of the Structure of 6-HydROYocumarins"
H. Bartsch and H. Faust
Tetrahedron Letters 3923 (1964)

"On the structure of Allantone"n
C. G. Castori and F. Coccobelli
Tetrahedron Letters 3925 (1964)

"Doppelresonanzexperimente Am 100 Mz Kernresonanzspektrum von Picraline, Einen Alkaloid aus Picralina Mitta Berg"n
L. J. Turn, R. Bracon, R. H. Adaklevics
Tetrahedron Letters 3 (1965)

"The Photoysis of N,N-Diethylacrylamylacrylamide"n
H. T. Lasdon and R. I. Assenijewich
Tetrahedron Letters 23 (1965)

"The Structure of Cinnamaldehyde"n
Tetrahedron Letters 29 (1965)

"Scytoalcaloid"n
N. S. Eide, A. V. Baez Rao and K. Yenkataraman
Tetrahedron Letters 35 (1965)

"Photo-Isomerization of 2,2,5,5-Tetramethyl-1,3-Cyclohexadiene"n
H. Nosk, Z. Wynapiti and N. Royo
Tetrahedron Letters 37 (1965)

"Formulation of N-termini"n
B. M. Pelletier, R. L. Chappell and P. G. Parhamethy

"Zur Konjugation in Makrocyclischen Bindungssystemen II. Synthese und Eigenschdes des 3,6'-1';6'-3, 3-Triglycosamidyns"n
H. A. Stahl and H. Baumling
Tetrahedron Letters 45 (1965)

"Steroid Alkaloids of Saracopsis Parviflora Linn"n
A. Chatterjee, B. Das, C. P. Dutta and R. N. Majherjer
Tetrahedron Letters 67 (1965)

"Hydrogen Bond Studied by Aliphatic Magnetic Resonance 1"n
E. Baité and K. Sůká
Tetrahedron Letters 111 (1965)

"The Structure of the C-Nor-D-Homo Endocyclic Cyclic Derived from Heconegen"n
J. N. Coxon, M. P. Hartshorn and D. H. Kirk
Tetrahedron Letters 115 (1965)

"Transformation of a Planar Pyrrole in an Atrilline-Pyrroline"n
R. Nicotelli e M. L. Forcella
Tetrahedron Letters 153 (1965)

"Structure of Venoxidine, an Alkaloid of Alstonia Vesicata R.M.B."n
A. Chatterjee, P. L. Mahender and A. B. Ray
Tetrahedron Letters 159 (1965)

"Über Eine Anomale Reaktion Mit Matrikunkarant"n
F. Rohmann and N. Mayer-Haber
Tetrahedron Letters 174 (1965)

"Über die NMR-Spektren von Chinoloid-Derivaten"n
F. Rohmann, D. Schumann and H. Schulz
Tetrahedron Letters 173 (1965)

"Aatamerin in 3-Bromotropolone"n
H. Sugiyama, S. Tadz and T. Noda
Tetrahedron Letters 173 (1965)

"Chir- und Trans-Dimercaptopol"n
K. Schrot
Tetrahedron Letters 195 (1965)


"Nucleophilic 1,2-Addition to the Carboxyl Group of p-Dicarboxylic Acids and a New Molecular Rearrangement of a Pentaerythrocyclophosphane" P. Ramirez, H. A. Kruger and G. F. Smith Tetrahedron Letters 251 (1965)

"Solvent Effects in Conformational Analysis of 1,4-Cyclohexadecanols" W. F. Trappo, J. B. Mist and A. C. Hattie Tetrahedron Letters 267 (1965)


"Isolation and Valency Isomerization of Cis-Cis-Cis-1,3,5-Cyclooctatetraene (1,3,5)" R. Cross, J. W. H. Mattyhey and B. K. Steiner Tetrahedron Letters 577 (1965)

"Thermal Valency Isomerization: Stereochemistry of the 2,6,7-0ctatriene to 2,5,6-Dimethyl-1,3-Cyclooctadione Ring Closure" E. R. Marvell, G. Cople and J. Schats Tetrahedron Letters 296 (1965)


"The Variation of Vicinal Proton-Proton Coupling Constants with Orientation of Electroactive Substituents" H. Booth Tetrahedron Letters 411 (1965)


"The Synthesis of a Methyleneoxycyclopropane (TTIbDulfene) by Proton Abstraction from a Cyclopropanacyl Cation" W. N. Jones and R. S. Byton Tetrahedron Letters 479 (1965)


"Lectone Intermediates in the Microbial Oxidation of (+)-Camphor"
H. E. Conrad, J. Heidegard and I. C. Gamusus, and E. J. Corey and B. Uda
Tetrahedron Letters 561 (1965)

"N.M.R. Spectra of N-Nitrosamines and Carbonium Ions"
J. G. Trayhan and W. T. Yang
Tetrahedron Letters 573 (1965)

"The Breyer-Billiger Oxidation of A-4-Ketosteroids: A Route to Some Novel A-Norsteroids"
J. T. Pinhey and K. Schaffner
Tetrahedron Letters 617 (1965)

"Oxepin-Benzolxyd-Valentautomere"
E. Vogel, W. A. Hill and E. Günther
Tetrahedron Letters 627 (1965)

"Ozonolysis. VI. Existence of the Cis Molozonide. Lack of Stereoselectivity in the Molozonide Rearrange-ment"
P. L. Greenwood and B. J. Haake
Tetrahedron Letters 659 (1965)

"Two New Flavones from Atractylosis heterophyllus"
P. V. Mahakrishana, A. V. Manohar Rao and R. Venkataraman
Tetrahedron Letters 663 (1965)

"The Structure and Stereochemistry of Erythromycin A"
D. W. Harris, B. G. Mcintosh and R. H. Mills
Tetrahedron Letters 679 (1965)

"Photochemical Reactions of a Bicyclic Ketone"
E. U. Matttler
Tetrahedron Letters 687 (1965)

"Kernmagnetische Relaxation und Korrelation in Zwei-Spin-Systemen"
P. Hauser und F. Haack
Z. Phys. 166, 93 (1964)

"Zur Verbindung der Kernquadrupolmomente der beiden Polyalkoholisotope 1999 und 2001"
J. Kaufmann
Z. Phys. 166, 97 (1964)

"Formula Index to NMR Literature Data. v. 1"
H. G. Broad, A. S. Kend and J. B. Webb