**Illinois Institute of Technology N-M-R Newsletter**

**No. 74**

**November, 1964**

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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 "Private Communication".
Dear Professor Shapiro,

A-60 Cooling System

Several contributors to the MELLONMR and IITNMR Newsletter have reported trouble with water-flow in the A-60 cooling system, but we do not recall any comments on the flow-rate recommended by Varian (36 g.p.h. at 30 p.s.i.). Since a good flow-rate is likely to minimise the possibility of coil-blockage, we believe that flow-rate is of some importance.

We cannot comment on the original flow-rate in our closed water-circulating system (see MELLONMR No. 49, p. 26 and No. 58, p. 28), since we did not measure the flow-rate when the system was installed in July, 1962. However, when in September, 1963, we fitted water-pressure and water-flow gauges after blowing out the cooling coils, we obtained a flow-rate of 23 g.p.h. at 45 p.s.i. with an outlet-water temperature of 41° (35° when new, the temperature regulator being set at 25°). The outlet-water temperature, nevertheless, tended to creep up so that in January of this year, we again blew out the magnet coils and stripped and cleaned the water-filter and inlet magnetic valve assembly. On reassembly, we omitted a small rubber valve between the water-filter and magnetic valve, which appeared to be intended to control water-pressure in the system. We now obtained a flow-rate of 40 g.p.h. at 24 p.s.i. with an outlet temperature of 33-34°; these values have remained constant for eight months with no further attention to the system other than topping up with distilled water and cleaning the filter. The water-pressure, which is set by adjusting a needle-valve in a by-pass pipe from the Mono pump to the heat-exchanger, rarely requires adjustment.

With reference to Dr. Chen's request (IITNMR No. 71, p. 58) for information on an anti-clogging additive for a closed-cooling-water system, we would point out that we have now used Panacide (cf. MELLONMR No. 58, p. 28) for over 18 months and have not experienced further trouble from the growth of micro-organisms.

We have recently submitted for publication in the Journal of the Chemical Society a paper on the p.m.r. spectra of cephalosporin and penicillin analogues. P.M.R. spectroscopy is an invaluable technique for elucidating the structure of and identifying water-soluble compounds of this type.

Yours sincerely,

J.E. Page

G.F.H. Green
Dr. B. L. Shapiro,
Dept. of Chemistry,
Illinois Institute of Technology,
Technology Centre,
CHICAGO, Ill. 60616,
U.S.A.

Measurement of $T_1$ on Varian DP-60.

Dear Dr. Shapiro,

The enquirers in I.I.T.N.M.R.N. number 70, page 1 may be interested to hear that we have been using a modified Varian DP-60 spectrometer for $T_1$ measurement for some time. The adiabatic fast passage method is used.

The necessary condition for A.F.P. is

$$\frac{H_1}{T_2} \ll \left| \frac{dH_0}{dt} \right| \ll 8H_1^2$$

For (say) 5dB below 0.5 watts in the transmitter coil, as used by Konijnenberg et al, $H_1$ will be about 45mG and for shorter $T_1$'s, at least,

$$\frac{H_1}{T_1} = 0.01 \text{ (For liquids } T_1 \ll T_2).$$

This could well be the order of magnitude of $\left| \frac{dH_0}{dt} \right|$ even at the maximum speed of the slow sweep, and so the inequality is violated, perhaps explaining their difficulty.

Our solution is to inject a faster sweep from an external waveform generator (Servomex type LF 51) into both the probe sweep coils and the horizontal plates of the spectrometer oscilloscope. An output of 150 volts from the Servomex produces a total sweep of 0.5 gauss and if we chose a sweep time of 2 seconds,

$$\left| \frac{dH_0}{dt} \right| = 0.25.$$ 

Hence an attenuation of about 18 dB is convenient when the three terms in the basic inequality are, 0.001, 0.25 and 2.7 respectively.

This attenuation is also convenient as it enables one to use a reasonable receiver gain without the danger of receiver saturation (i.e. the detector level should not rise much above 30µA).
The R.F. phase can now be adjusted without difficulty to give the best possible absorption signal which is that with maximum amplitude.

Our sweeps are timed and triggered as follows. A continuously variable oscillator (Harrhead D 695 A) feeds a decade counter unit so that every thousandth cycle trips a bistable amplifier. The resulting voltage step of about 30 volts, triggers the waveform generator.

Signals proportional to the equilibrium magnetization and the magnetization after known times are read directly from the oscilloscope. Using this method, relaxation times from 0.1 to 100 seconds have been measured. Our experimental arrangement is discussed in Powles, J.G. Berichte der Bunsgesellschaft für physikalische Chemie 67, 328, 1963.

I hope this short note entitles us to be placed on your mailing list.

Yours sincerely,

Roger Figgins

Roger Figgins.
Coupling Constants in Rotamers of Cis and Trans $\text{I}_3\text{C}_F\text{CH} = \text{CHF}$


Recently we have measured the temperature dependence of $\langle J_{\text{H}2\text{F}_3} \rangle$ in cis and trans $\text{I}_3\text{C}_F\text{CH} = \text{CHF}$ over a range of about 200°C. To obtain the accuracy demanded by the mathematical treatment employed to analyse the data, we recorded at least forty spectra at each of eighteen temperatures. The data for each geometric isomer (A and B) is consistent with the population of only two (I and II) of the six possible rotameric states. The analytical method devised by Gutowsky, Belford and McMahon (J. Chem. Phys., 36, 3353 (1962)) enabled us to extract the enthalpy differences between rotamers and the individual coupling constants. A least squares computer programme was written to achieve the necessary curve fitting. The derived enthalpy differences are 1700±100 cal/mole and 900±200 cal/mole for the cis and trans isomers respectively. On the figure are shown the calculated coupling constants of the individual rotamers. Less extensive temperature measurements were made on $\langle J_{\text{H}1\text{F}_3} \rangle$, $\langle J_{\text{F}_1\text{F}_3} \rangle$ and $\langle J_{\text{F}_1\text{C} \text{F}_3} \rangle$ and the data were found to be in accord with the above results.

The large long range coupling constants $J_{\text{F}_1\text{F}_3}$ in IA and $J_{\text{F}_1\text{C} \text{F}_3}$ in IIA are between spatially close fluorine nuclei; however, a large spin-spin interaction also exists between widely separated F1 and F3 nuclei in IB and IIB. Before data of this type can be used in attempting to establish a distance versus coupling constant relation for fluorine nuclei one would need to know the signs of all the coupling constants being compared. We intend to determine the relevant signs in these molecules in the near future.
Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Illinois 60616  

Dear Barry and other members of the IIT NMR Club:

For our contribution this time, I would like to describe briefly an adaptation of the proton nmr coding system presented in the Varian Spectra Catalog which we have found useful. Our adaptation is still in the stage of flux--any improvements which the other club members may have will be appreciated.

First it seemed best to be able to put the code on IBM cards so that up-to-date lists could be made periodically without a great deal of trouble and so that the cards could serve as a source for computer search routines which may be developed later. Secondly we have expanded the number of types of "functional groups" by using a two character code.

Each code is listed on a single card together with the spectrum number and chemical shift (in our case in τ units; however, if δ units become standard it will be simple to write a program to convert our system). The first column represents the numbered main group. The next three columns represent the functional groups. The secondary functional groups which are represented in the Varian Catalog by the small case letters are placed after the main functional groups separated by a slash. Thus 3-BeEOb becomes 3 B/E E 0/B. I have included several examples which may be compared with the Varian Catalog (the spectrum number is the same as used there). You will note from the second example (VO666) that we have allowed space to use parentheses for rings.

We have added several new functional groups to take care of more types of proton environments. These are listed below the examples. It seemed worthwhile in the use of the 19 functional group to make use of the same rule that Varian does for substitution on olefinic main groups, the first substitution listed being gem, the second cis and the third trans. An example of the use of this convention comes from the two types of methyl groups present in VO279.

We have found this helpful in coding our own spectra and spectra from the literature.

Sincerely,

THE PROCTER & GAMBLE COMPANY  
Research & Development Department  

T. J. Flautt  
Research Division

cc
Enc.
<table>
<thead>
<tr>
<th>MAIN FUNCTIONAL GROUPS</th>
<th>FUNCTIONAL GROUPS</th>
<th><em>T</em> VALUE</th>
<th>SPECT. NO.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 B/E</td>
<td>E</td>
<td>4.37</td>
<td>V0075</td>
</tr>
<tr>
<td>(3) C/A/B</td>
<td>D/A/C/J</td>
<td>7.40</td>
<td>V0666</td>
</tr>
<tr>
<td>1 L9/A/B/H</td>
<td></td>
<td>8.32</td>
<td>V0279</td>
</tr>
<tr>
<td>1 L9/B/H/B</td>
<td></td>
<td>8.38</td>
<td>V0279</td>
</tr>
<tr>
<td>21 SULFUR</td>
<td>B/L</td>
<td>8.10</td>
<td>V0101</td>
</tr>
<tr>
<td>1 S2/D</td>
<td></td>
<td>6.97</td>
<td>TIERES</td>
</tr>
</tbody>
</table>

**Additional Functional Group Codes**

- B1: \( B^- \)
- P6: \( -\text{PO}_3^- \)
- B2: \( -\text{PO}_3^- \)
- P9: \( -\text{PO}_3^- \)
- L4: \( -\text{C} = \text{C}^- \)
- S1: \( -\text{O}^- \)
- L9: \( -\text{C} = \text{C}^- \)
- S2: \( -\text{O}^- \)
- P1: \( -\text{P}^- \)
- S3: \( -\text{P}^- \)
- P2: \( -\text{P}^- \)
- S4: \( -\text{P}^- \)
- P3: \( -\text{P}^- \)
- S4: \( -\text{P}^- \)
- P4: \( -\text{P}^- \)
- S5: \( -\text{P}^- \)
- P5: \( -\text{P}(\text{O}^-)_2 \)
- S6: \( -\text{P}(\text{O}^-)_2 \)
- P6: \( -\text{P}(\text{O}^-)_2 \)
- Z1: \( -\text{Si}^- \)
- P7: \( -\text{S}^- \)
- Z2: \( -\text{Al}^- \)
Dr. B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Technology Center  
Chicago 16, Illinois 60616  

Dear Dr. Shapiro:

Recently we examined the $^1$H and $^{19}$F spectra of some "alkyl fluoroazoxy" compounds ($N$-alkyl-$N^1$-fluorodimide-$N$-oxides). The proton spectra (Fig. Ia, $R$ = benzyl; Fig. IIa, $R$ = $\beta$ phenylethyl) show two and four peaks, respectively, in the region of 4-4.56 due to transitions of the $N$-methylene hydrogen nuclei; the $^{19}$F spectra show only a rather broad single peak in the vicinity of -45 $\phi$. Although the apparent 1:1 and 1:3:3:1 intensity patterns of the proton spectra are strongly suggestive of H-F coupling, the spectra can result from fortuitous chemical shifts of the isomers A and B with $J_{HF} \equiv 0$.

The fluorine spectra are uninformative due to characteristic broadening by $^{14}$N.

However a decoupling experiment removed all ambiguity, since the normal proton doublet of I (Fig. Ia at 40 Mc) collapsed to a singlet (Fig. IIb) on simultaneous irradiation of $^{19}$F at 37.650 Mc. Similarly the quartet of IIa collapses to a slightly perturbed triplet in Fig. IIb.
Shift and coupling data are summarized in Table I.

**Table I**

<table>
<thead>
<tr>
<th>alkyl</th>
<th>methylene δ</th>
<th>fluorine φ</th>
<th>J_{HF} cps</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzyl</td>
<td>5.02, 5.14</td>
<td>-46.9 φ</td>
<td>7.1</td>
</tr>
<tr>
<td>phenyl ethyl</td>
<td>4.10, 4.22, 4.32, 4.44</td>
<td>-47.7 φ</td>
<td>~7.0</td>
</tr>
<tr>
<td>neopentyl</td>
<td>3.83, 3.95</td>
<td>-46.4 φ</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Our conclusions are in agreement with similar work by Frazier, Holder and Worden,¹ who find J_{CF3-F} = 7.1 cps for the O-related CF3–N=NF. Lack of significant N-H coupling makes the present hydrocarbon case somewhat simpler.

We would like the preceding to be applied to the subscription of Dr. Charles B. Colburn of this division.

Sincerely,

Frederic A. Johnson
Carolyn P. Haney
Travis E. Stevens

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NORMAL SPECTRUM  
**Fig. Ia.**
Proton n.m.r. spectrum of $\phi$CH$_2$NONF before (left) and after (right) radio frequency irradiation.

DECOUPLED SPECTRUM  
**Fig. Ib.**

NORMAL SPECTRUM  
**Fig. IIa.**
Proton n.m.r. spectrum of $\phi$CH$_2$CH$_2$NONF before (left) and after (right) radio frequency irradiation.

DECOUPLED SPECTRUM  
**Fig. IIb.**
November 22, 1964

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

Dear Professor Shapiro:

The following account of the first few months of my sabbatical year at Harvard is submitted for the IIT NMR Newsletter under the title

Negative Electronic Intermolecular Nuclear Overhauser Effect

Part I: Complete Mystery

The solution will follow next month in Part II.

An equimolar solution of cyclohexane, dioxane and tetramethyilsilane (TMS) yields a high resolution proton nmr spectrum consisting simply of three sharp resonances. If the TMS resonance, for example, is used to lock the field/frequency ratio of the spectrometer, the dioxane resonance can then be irradiated at a fixed frequency while the cyclohexane resonance can be observed by sweeping a second frequency using magnetic field modulation and lock-in detection at several audio frequencies with the equipment constructed here by Noggle. 1

Fig. 1 shows repeated scans through the cyclohexane resonance with alternately increasing and decreasing observation frequency. Irradiating the dioxane resonance
with $\gamma H_2/2\pi \approx 1$ cps caused an 85% decrease of the peak height of the cyclohexane resonance. The decrease was strongly dependent on the exact centering of the irradiation frequency on the dioxane peak; it did not occur when the irradiation was applied more than 5 cps off resonance. When the mixture was diluted with CS$_2$ to give a solution with the approximate mole ratios C$_4$H$_8$: C$_6$H$_{12}$: TMS: CS$_2$ = 1:1:1:6, only a 50% decrease of the cyclohexane resonance was observed when the dioxane peak was irradiated, and the decrease went to zero upon further dilution. Very similar effects were observed when the roles of cyclohexane, dioxane, and TMS were permuted, or when other 3-component solutions with simple 3-line spectra were examined (e.g. benzene+acetone+TMS). The effect was independent on whether or not the sample had been degassed by repeated freeze—pump—thaw cycles on a high vacuum line. However, no effect could be observed with a sample of CHCl$_3$+CHBr$_3$+TMS when the TMS signal was used for spectrometer stabilization.

One naturally suspects that the application of a moderately strong audio modulation signal to the sweep coils to produce the irradiation sideband may upset the stabilization loop or saturate one of the amplifiers. However, monitoring the stabilization loop with a Lissajous figure on the oscilloscope disclosed no phase shift, and monitoring the outputs of the control and signal channel amplifiers (positions No. 1 and 6 in our circuit) showed no distortion of the sine waves when the irradiation frequency was swept through or held on resonance. Furthermore, as mentioned above, the effect disappeared when the irradiation occurred more than 5 cps off resonance. The dependence on dilution with CS$_2$ and the absence of the effect in the CHCl$_3$ + CHBr$_3$ solution were interpreted as indicating a genuine nuclear Overhauser effect caused by intermolecular interactions, since such interactions would become weaker when the sample is diluted with a magnetically inert solvent, and the hydrogen bonds in CHCl$_3$ + CHBr$_3$ might tend to hold the interacting protons apart.

However, both the sign and the magnitude of this intermolecular Overhauser effect are surprising. The negative sign (decrease) requires that the intermolecular coupling
mechanism provide terms of the form \( I_+(1)I_-(2)+I_-(1)I_+(2) \) in the spin Hamiltonian\(^2,^3\) where (1) and (2) refer to nuclear spins in a pair of interacting molecules. Such terms could be caused by an intermolecular electron coupled spin-spin interaction of the form \( J(t)I(1)·I(2) \) where the coupling constant \( J(t) \) would be modulated at the rate of exchange of interacting pairs of molecules. Solomon and Bloembergen\(^4\) have successfully interpreted the nuclear Overhauser effect in HF on the basis of such a mechanism. The rate \( \omega_0 \) of \( \Delta m = 0 \) flip-flop transitions arising from this mechanism is given by

\[
\omega_0 = 2\pi^2 \frac{\tau_C}{1+\left(\omega(1)-\omega(2)\right)^2} \frac{\tau_C}{1+\left(\omega(1)-\omega(2)\right)^2}
\]

where \( \tau_C \) is the average lifetime of an interacting pair and \( \omega(1), \omega(2) \) are the resonance frequencies of nuclei (1) and (2). Since this rate must compete with the rate of \( \Delta m = 1,2 \) transitions which is measured by the spin-lattice relaxation time \( T_1 \approx 10 \text{ sec} \) of the components of the mixture, the observed magnitude of the effect requires \( \omega_0 \approx 1 \text{ sec}^{-1} \). Such a magnitude can only be reached with \( \sqrt{J^2} \approx 10 \text{ cps} \) for \( \tau_C = \left(\omega(1)-\omega(2)\right)^{-1} \approx 10^{-3} \text{ sec} \) for the cases investigated. Both values appear rather implausible.

One might then suppose that the required intermolecular coupling may be produced by a stochastic external magnetic field whose fluctuations at the sites of spins (1) and (2) are statistically correlated. Such a field may originate from dissolved paramagnetic impurities (oxygen) or from the anisotropy of the molecular screening tensor. But this mechanism does not yield the required \( I_+(1)I_-(2) \) interaction terms in the Hamiltonian.

Such terms do arise, however, from the intermolecular dipole-dipole interaction. This mechanism also produces \( \Delta m = 1,2 \) relaxation transitions in addition to the required \( \Delta m = 0 \) transition, and with the usual assumption of a "white" Fourier
spectrum for the random molecular motions, the rates $w_0, w_1, w_2$ of the $\Delta m = 0, 1,$ and 2 transitions respectively are in the ratio 2:3:12. The $\Delta m = 2$ transition would therefore dominate and a positive Overhauser effect should be observed. Since it is difficult to construct other coupling mechanisms of the required form and strength one may be tempted to postulate that the Fourier spectrum of the random motions of the vector connecting spins (1) and (2) is not of uniform intensity. This could explain the observed effect since $w_0, w_1, w_2$ are proportional to the spectral intensities at frequencies $\{\omega(1) - \omega(2]\}, \omega(1), \{\omega(1) + \omega(2]\}$ respectively. Thus if the spectral intensity at the audio frequency $\{\omega(1) - \omega(2]\}$ is considerably greater (factor 50) than at the radio frequencies $\omega(1)$ and $\{\omega(1) + \omega(2]\}$, $w_0$ arising from this mechanism would be greater than $w_1$ and $w_2$.

In addition to these difficulties in finding an intermolecular coupling mechanism that would give the required magnitude of $w_0$ to explain the large negative Overhauser effect, there is the problem that any such mechanism would make the transverse relaxation time $T_2$ shorter than the spin-lattice relaxation time $T_1$. While $T_2$ is not known for the solutions studied, it is known that $T_2 < T_1$ for the neat liquids. The variety of solutions for which the negative Overhauser effect has been observed (CHCl$_3$ + CHBr$_3$ is the only apparent exception) suggests that the effect is a fairly general phenomenon, and the intermolecular coupling mechanism should therefore be effective also in the neat liquids. To this extent the experimental observation of the equality of $T_1$ and $T_2$ directly contradicts the observation of a large negative intermolecular Overhauser effect.

\textbf{STATEMATE!}$^5$

Sincerely yours,

\[ R. \text{ Kaiser}\]

REFERENCES


5. Private comments in addition to those already received from J. D. Baldeschwieler and J. Waugh will be gratefully accepted and not disclosed.
Fig. 1: Repeated scans through cyclohexane resonance
(a) with irradiation $\gamma H_2/2n=1$ cps applied
50 cps off dioxane resonance
(b) with irradiation $\gamma H_2/2n=1$ cps centered
on dioxane resonance.
ON METAL-EXTRACTING ABILITY OF ORGANO PHOSPHORUS COMPOUNDS

Dear Barry,

It seems interesting to correlate the results presented in IIT NMR #70-65 by Jane L. Burdett and L.L. Burger on proton and phosphorus spectra of organo phosphorus-uranyl complexes with a wider discussion of the intermolecular properties of O.P. compounds, just out of print (J. Chim. Phys. 61 1190, (1964)). From a simple Hückel model, it is possible to estimate roughly the electron distribution in molecules such as $R_3PO$, $(RO)_2PO$, $(R_2N)_3PO$ and so on, and especially on the phosphoryle oxygen, mainly responsible for metal-extraction abilities. $R = CH_3$ and all inductive or mesomeric effects when turning to higher R'S are neglected; but they are significant, as shown by Burdett and Burger's results. Nevertheless, compare B and B. $P_{31}$ shifts (in C/S at 24.3 MC) with $(P=)0$ electronic charge (in electron units).

.../...
<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>$\delta P_{31}$</th>
<th>Electronic Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3\text{CH}_2\text{O})_3\text{PO}$</td>
<td>-22</td>
<td>$(\text{RO})_3\text{PO}$</td>
</tr>
<tr>
<td>$(\text{CH}_3\text{CH}_2\text{O})_2\text{P(O)(OCH}_3)$</td>
<td>+29</td>
<td>$(\text{RO})_3\text{PO}$</td>
</tr>
<tr>
<td>$(\text{CH}_3\text{O})_2\text{P(OH)}$</td>
<td>+172</td>
<td>$(\text{RO})_2\text{RPO}$</td>
</tr>
<tr>
<td>$(\text{CH}_3\text{CH}_2\text{O})_2\text{P(O)(CH}_2\text{CH}_3$</td>
<td>+177</td>
<td>$(\text{RO})_2\text{RPO}$</td>
</tr>
<tr>
<td>$(\text{CH}_3\text{O})_2\text{P(O)(CH}_2\text{CH}_3$</td>
<td>+340</td>
<td>$(\text{RO})_2\text{RPO}$</td>
</tr>
<tr>
<td>$[\text{CH}_3(\text{CH}_2\text{O})_7]_3\text{PO}$</td>
<td>+830</td>
<td>$R_3\text{PO}$</td>
</tr>
</tbody>
</table>

As the two sets of data seem quite sensitive to the molecular structure, it is worth-while to collect a larger number of NMR results and to improve the theoretical model.

With all best regards of

G. MAVEL
23 October 1964

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

Subject: Stabilization of Varian 4210A Variable Frequency Unit - Electronic Scan Unit for Wide Line Work with DP 60.

Dear Barry:

We are doing wide line work on several atoms including Cl³⁵, Cl³⁷, Br⁷⁹, Br⁸¹ and I¹²⁷. In this work it is convenient for us to work at different fields. The frequency stability of the Varian 4210A is not sufficient for our purposes. We have found that the Hewlett-Packard 5100A Frequency Synthesizer and 5110-A Synthesizer Driver is a superb source of immediately available stable synchronising frequencies. We set the frequency we wish to use on the 4210A with a frequency counter, punch in the same frequency on the Frequency Synthesizer and connect the two units. As the Frequency Synthesizer has only 1 volt output, it is necessary to boost the output below ten Mc with an Instruments for Industry Model 500 Wide Band Amplifier. With the amplifier we can synchronise the 4210A between 2Mc and 16Mc.

Since we have obtained a new magnet with Field Dial for ESR work, we have transferred our magnetic field scanning integrator unit into the DP 60 system. It utilizes a Philbrick R100B Power supply, a Philbrick UPA2 Operational Amplifier and a feedback network which permits a choice of some 90 fixed scan speeds. We have found that we only use about ten of the fixed scan speeds. The magnetic field may be set anywhere in the range of the power supply by use of a supplementary network circuit. The unit is sufficiently stable to give linear sweeps in the range of interest and to reset to the starting field by the flick of a switch. Reset is as reproducible as the Field Dial System. For anyone wishing to
discard the atrocious Varian Precession Drive, an integrator circuit built around the two Philbrick units and the best 1 mfd condenser available will give excellent results.

Sincerely yours,

James E. LuValle  
Director, Basic Research
October 27, 1964

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

Dear Barry:

We are at present investigating the spectra of a number of acetylenes, including some vinyl acetylenes. In the course of this work we have determined the relative signs of the coupling constants of cis-1-methoxy-1-buten-3-yn

\[ \text{HC} = \text{C}_2\text{CH}_3 \]

by the double resonance method described by Freeman and Whiffen.\(^1\) Our apparatus was described in an earlier newsletter.\(^2\) Chemical shifts and coupling constants with their relative signs are as follows:

<table>
<thead>
<tr>
<th>Chemical shift ((\tau))</th>
<th>Coupling constants (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>6.28</td>
</tr>
<tr>
<td>H-1</td>
<td>3.68</td>
</tr>
<tr>
<td>H-2</td>
<td>5.61</td>
</tr>
<tr>
<td>H-3</td>
<td>7.05</td>
</tr>
<tr>
<td>J(_{1-2})</td>
<td>(\pm 6.4)</td>
</tr>
<tr>
<td>J(_{1-4})</td>
<td>(\pm 0.9)</td>
</tr>
<tr>
<td>J(_{2-4})</td>
<td>(\pm 2.5)</td>
</tr>
</tbody>
</table>

An approximately 50% solution in carbon tetrachloride was used.

We note that J\(_{2-4}\) is opposite in sign to the other two coupling constants and is presumably negative. Snyder, Altman and Roberts\(^3\) and Hirst and Grant\(^4\) have found that the corresponding coupling constant in vinyl acetylene is also negative.

The chemical shift of the acetylene proton showed a significant concentration dependence, moving to higher field as the concentration in carbon tetrachloride was decreased. Evidently this proton is involved in weak intermolecular hydrogen bonding.
Preliminary dilution studies (CCl₄ solutions) indicated that the total dilution shift for this proton is greater than 0.3 p.p.m. The vinyl proton resonances are also concentration dependent but to a much smaller extent. In contrast, the methyl chemical shift proved to be almost independent of concentration.

We attribute the difference between the chemical shifts reported by Hirst and Grant for this compound and our own values to such a solvent effect.


Yours sincerely,

L. D. Colebrook

LDC/pn
Wir haben die $^{11}$B-Kernresonanz einer Anzahl von Borsäureestern
und Boraten im Hinblick auf die Koordinationszahl des Bors
untersucht (15,08 MHz, 1molo G, 10 mm Probenrohr) und dabei ge-
funden, daß die Quadrupol-Verbreiterung des Signals durch die
axiale Potentialkomponente in der ebenen BO$_3$-Koordination eben-
so charakteristisch ist wie die chemische Verschiebung. Wir
haben daher beide Größen für die von uns gemessenen Substanzen
zusammengestellt. Leider sind bisher von anderen Autoren (außer
bei festen Boraten) keine Halbwertsbreiten angegeben worden.

Beim Borsäuredipentandiolester ist vor allem $\Delta v_{1/2}$ stark vom
Lösungsmittel abhängig. Wir deuten die besonders große Breite
in H$_2$O und HCCl$_3$ durch einen
Protonen-Austausch unter un-
ter kurzzeitiger Benutzung der
BO$_4$-Konfiguration. Das $^1$H-NMR-
Signal der OH-Gruppe ist scharf,
as damit erklärt werden kann,
daß die chemische Verschiebung
zwischen I und II für die $^1$H-Resonanz anders, wahrscheinlich
kleiner als für die $^{11}$B-Resonanz ist. Die Austauschgeschwindig-
keit bei 250 kann daher gerade so groß sein, daß sie das
$^{11}$B-Signal bereits verbreitet, das $^1$H-Signal aber noch nicht.

Im K-Disalicyltriborat, dessen Struktur nicht genau bekannt ist,
sind BO$_3$ - und BO$_4$-Konfiguration nebeneinander nachweisbar. Eine
Ausnahme in unserer Reihe ist der Borsäuretrimethylster, der
zwar die für eine BO$_3$-Konfiguration charakteristische chemische
Verschiebung, nicht aber die erwartete Breite aufweist. Ein
Vergleich mit dem Bortrifluorid wäre interessant, wir konnten
BF$_3$ aber nur als Ätherat messen.

Es bleibt hinzuzufügen, daß die Kernresonanz bis auf einen Fall,
der noch untersucht wird, die gleiche Koordination ergab wie die
Infrarotspektroskopie, mit der dieses Problem auch untersucht
wurde.
Chemische Verschiebung (NaBO$_2$ = 0) und Halbwertsbreite
der $^{11}$B-Kernresonanz von Borverbindungen.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (ppm)</th>
<th>$\Delta v_{1/2}$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ebene BO$_3$-Koordination (sp$^2$):</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Borsäuredi-2,4-pentandiolester ($H_2O$)</td>
<td>- 17</td>
<td>218</td>
</tr>
<tr>
<td></td>
<td>($HCCl_3$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>($CH_2Cl_2$)</td>
<td></td>
</tr>
<tr>
<td>Borsäuretrimethylester (Äther)</td>
<td>- 16,4</td>
<td>26</td>
</tr>
<tr>
<td>Borsäure ($H_2O/HCl$)</td>
<td>- 15,1</td>
<td>64</td>
</tr>
<tr>
<td>K-Disalicyltriborat ($CH_3OH$)</td>
<td>- 15,1</td>
<td>54</td>
</tr>
<tr>
<td>Bortrichlorid</td>
<td>- 46,0</td>
<td>75</td>
</tr>
<tr>
<td><strong>Tetraedrische BO$_4$-Koordination (sp$^3$):</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-Metaborat ($H_2O$)</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>K-Dihydroxodifluoroborat ($CH_2Cl_2$)</td>
<td>2,5</td>
<td>23</td>
</tr>
<tr>
<td>Na-Di-2,4-pentandioxoborat ($H_2O$)</td>
<td>0</td>
<td>27</td>
</tr>
<tr>
<td>Na-Disalicylatoborat ($CH_3OH$)</td>
<td>0,1</td>
<td>31</td>
</tr>
<tr>
<td>K-Disalicyltriborat ($C_6H_5OH$)</td>
<td>0,55</td>
<td>32</td>
</tr>
<tr>
<td>Na-Dimethoxo-o-phenylenedioxoborat ($C_6H_5OH$)</td>
<td>- 5,7</td>
<td>31</td>
</tr>
<tr>
<td>Acetylacetonato-o-phenylenedioxoboran ($CHCl_3$)</td>
<td>- 6,8</td>
<td>25</td>
</tr>
<tr>
<td>Acetylacetonatodiacetoxoboran ($HCl$)</td>
<td>0</td>
<td>33</td>
</tr>
<tr>
<td>Acetylacetonatodifluoroboran ($CHCl_3$)</td>
<td>0,95</td>
<td>18</td>
</tr>
<tr>
<td>Bortrifluorid-Diäthylätherat</td>
<td>- 3,3</td>
<td>20</td>
</tr>
</tbody>
</table>

L. Imbery      E. Funck

Institut für physikalische Chemie
75 Freiburg i.Br., Deutschland
nebelstrasse 38
November 3, 1964

Dr. B. L. Shapiro
Department of Chemistry
I.I.T.
Chicago, Illinois

Dear Barry,

We would be appreciative if you could print this letter in your NMR NEWSLETTER. The Third Annual High Resolution Proton Magnetic Resonance Workshop will take place on this campus December 17-19, 1964 and will consist of a series of lecture-discussions and laboratory demonstrations.

The program is designed primarily for those scientists with a working knowledge of NMR spectroscopy and contains the following lectures and speakers:

Thursday, December 17 - Suggested for Beginners only.

"Elementary Theory of NMR Spectroscopy" Dr. Roy H. Bible, Jr.
G.D. Searle and Co.

"Application and Elementary Interpretation" Dr. Charles L. Bell
University of Illinois at the Medical Center

Friday, December 18

"Interpretation of More Complicated Spectra" Dr. LeRoy F. Johnson
Varian Associates

"Double Resonance Techniques" Dr. Ray Freeman
Varian Associates

"Geminal Coupling and Rotational Isomerism" Dr. Bernard L. Shapiro
Illinois Institute of Technology

Saturday, December 19

"Structure Elucidation of Natural Products by Use of NMR Dr. G. Slomp
The Upjohn Company

"Conformational Analysis and Equilibria Dr. Frank A.L. Anet
University of California at Los Angeles

(continued)
2.

"Conformation of Aliphatic Aldehydes and Carbonyl Compounds" Dr. G.J. Karabatsos Michigan State University

In the laboratory there will be demonstrations on the use of the A-60 instrument, the A-60 spin decoupler and the C-1024 computer of average transients.

Any further inquiries should be directed to me for additional information.

Sincerely yours,

Ludwig Bauer
Associate Professor of Chemistry

LE/sf
Dr. B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Centre,
CHICAGO, U.S.A.

Phosphorus-fluorine coupling constants.

Dear Dr. Shapiro,

Joe Lee has become more theoretically minded in the last year or so, and has decided to move out of the N.M.R. field. We have, therefore, taken over our Department's contribution to the N.M.R. Newsletter. We apologise for the delay in sending our contribution.

Recently a series of perfluoroarylporphosphorus compounds have been made in our Department. We have measured the $^{19}$F spectra of some of these and have observed that in a number of cases the $^{31}$P to ortho $^{19}$F coupling constant is rather large.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}$P</th>
<th>$^{19}$F c/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C$_6$F$_5$)$_2$P-NMe$_2$</td>
<td>51.0</td>
<td>1.7</td>
</tr>
<tr>
<td>C$_6$F$_5$PMe$_2$</td>
<td>30.1</td>
<td>1.7</td>
</tr>
<tr>
<td>C$_6$F$_5$PCl$_2$</td>
<td>63.2</td>
<td>0.8</td>
</tr>
<tr>
<td>(C$_6$F$_5$)$_3$P</td>
<td>29.0</td>
<td>0.8</td>
</tr>
<tr>
<td>C$_6$F$_5$PH$_2$</td>
<td>4.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>

We are looking into these rather unexpected observations further.

Coding $^{19}$F environments.

Since the arrival of our Perkin-Elmer R.10 (60 Mc/s) spectrometer our production rate of $^{19}$F spectra has increased rapidly, so that we have been forced to devise some means of indexing the spectra and coding the environments of the nuclei.
The Varian code offers a ready method of doing this for protons, and we are in full accord with Douglas and Heeschen (I.I.T. N.M.R., 42, on the method of indexing, but there seems to be no similar method published so far for fluorine. Modification to the Varian code as follows below seems to work fairly satisfactorily so far.

1. Main Groups. Replace each H in the main group as printed by F. This leaves the unlikely group $1_2(\text{RC-OF})$, but for the sake of the parallel with hydrogen the groups have not been renumbered.

2. Functional Groups. The functional groups used as sub-groups and sub-sub-groups remain as listed for hydrogen, except that:

(a) The functional groups $-\text{CF}_3 = \alpha, \alpha; -\text{CF}_2 = \beta, \beta; -\text{CF} = \gamma, \gamma$; (underlining the Greek letter for the sub-group for ease of typing, rather than using the capital) are added, and are conveniently listed, at least for fluorine work, before the English alphabet. The inclusion of these groups makes it possible to distinguish in the code between such sub-sub-groups as $-\text{CF}_3$ and $-\text{C(CH}_3)_3$ (e.g. in CH$_2$F·CH$_2$·CF$_3$ and CH$_2$F·CH$_2$·C(CH$_3$)$_3$) which would otherwise be shown in both cases simply as quaternary carbons (functional group d), and also makes it quicker to code polyfluorinated groups.

(b) We are happy to incorporate the addition of phosphorus $= \phi$, and suggest also silicon $= \sigma$.

(c) The definition of group $y = \text{thiophenyl}$ is extended to include all heterocyclics, which are named in parentheses after the code.

It may be that the ranges for a given environment will be comparatively a good deal greater for fluorine than for hydrogen, but we certainly need some method of coding and indexing here. If anyone can either point out snags that we have missed, or can suggest a better method, we shall be glad to hear from them -- preferably before we get too deeply involved with this system to change.

Yours sincerely,

K. Fields. (R. Fields)

M. Green.
Associate Professor B. L. Shapiro,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago 16, Illinois,
U.S.A.

Dear Barry,

In our last contribution to IITNMRN (No. 70 p. 30) the low and high field multiplets in the spectra of the pyrones and thiopyrones, were incorrectly assigned. The corrected version now is:

\[
\begin{align*}
\text{Chemical shifts (\(\delta\) values)} \\
H_A & 2.08 & 2.15 & 2.48 & 2.10 \\
H_B & 3.62 & 2.95 & 2.85 & 2.40
\end{align*}
\]

I must apologise for any inconvenience which has been caused by this error, which was pointed out to me by Dr. Sternhell of the University of Sydney.

Yours sincerely,

[Signature]

Dr. Peter Bladon.
LONG-RANGE SPIN-SPIN COUPLING BETWEEN AROMATIC PROTONS LOCATED IN DIFFERENT RINGS OF A MONOSUBSTITUTED POLYCYCLIC AROMATIC HYDROCARBON: 4-methoxybenzo[c]phenanthrene.

Associate Professor B.L. SHAPIRO,
Department of Chemistry,
Illinois Institute of Technology,
Technology Center,
Chicago 16, Illinois 60616

Dear Dr. Shapiro,

In the course of recent work on monosubstituted polycyclic aromatic hydrocarbons, we have examined the spectrum of 4-methoxybenzo[c]phenanthrene* (I) and have observed some interesting long-range spin-spin coupling between aromatic protons located in different rings.

As anticipated, the OCH$_3$, which comes out as a sharp singlet (240 c/s 60 Mc), has a shielding effect on H3 (ortho) and H1 (para),

* We are very grateful to Professor M.S. NEWMAN for a gift of 4-hydroxybenzo[c]phenanthrene, which was used to prepare the corresponding methoxy derivative.
and a deshielding effect on H5 (peri) (fig. 1).

H3 gives rise to a normal double doublet \( J_{2,3} = 7.8 \text{ c/s; } J_{1,3} = 0.8 \text{ c/s} \) but the signals of H1 (double quartet) and H5 (double doublet) are more complex than expected.

H1 must be coupled with H2 \( J_{1,2} = 8.4 \text{ c/s} \) and H3 \( J_{1,3} = 0.8 \text{ c/s} \) and with two other protons \( J \sim 0.8 \text{ c/s} \). It is very likely that one of these is H5 (see below) while the other one could be H7 (H6 seems unlikely from the study of other derivatives).

H5 is coupled with H6 \( J_{5,6} = 8.7 \text{ c/s} \) and with another proton \( J = 0.8 \text{ c/s} \) which, as already mentioned, it believed to be H1 (H1 H H5).

As far as we are aware, this is the first example of well resolved long-range spin-spin coupling between aromatic protons located in different rings of a (monosubstituted - non planar) polycyclic aromatic hydrocarbon (this type of long-range spin-spin coupling is, of course, quite common in polycondensed heteroaromatic compounds).

If any of yours readers should know of other cases, we would be most grateful to hear about them.

With best regards,

Yours sincerely,

N. DEFAY.  
R.H. MARTIN.

P.S.: The coupling constants \( J \) mentioned in this letter are the coupling constants measured on the spectrum.
Fig. 1

$H_{12}$ $H_1$ $H_5$ $H_{2,6,7,8,9,10,11}$ $H_3$ $OCH_3$

in CDCl$_3$

2 c/s
Dr. B.L. Shapiro  
Department of Chemistry  
Illinois University of Technology  
Technology Center  
Chicago  
Illinois, (U.S.A.)

Dear Dr. Shapiro,

Our first subscription to the I.I.T. N.M.R. Newsletter would be  
our introduction by way of a summary of the recent investigations being  
carried out by our high resolution group, which I am sure your readers  
would like to know.

The substitution and solvent effects on $^{13}$C-$^{19}$F coupling con-  
stants are being studied. The solvent effects on these coupling con-  
stants observed in our laboratory are of much larger magnitude than  
those previously found by other workers on the gem proton-proton coupling  
constants in ethylenic compounds. Further, we believe that the changes  
in the coupling constants are due to the variations in the ionic charac-  
ter of the C-F bond resulting either from substitution or from the  
bond polarisation by the solvent. Similar effects are expected on the  
H-F coupling constants. The dilution shifts of the aromatic compounds  
in isotropic non-polar solvents have also been measured. From these, a  
method has been developed to estimate the aromaticity in such compounds.  
The effect on aromaticity by substitution in the aromatic rings has also  
been studied. This has led to an interesting method for the study of
molecular association in aromatic compounds.

We have also recently started some work on the proton magnetic resonance spectra of both diamagnetic and paramagnetic iron complexes.

Correspondence with groups working on similar problems is most welcome.

A list of publications from the high resolution and wideline NMR groups working in the Institute is attached for your information so that those of our papers which may not have been listed in the I.I.T. Newsletter may be brought to the notice of interested readers.

Thanking you,

Yours sincerely,

(S.S. Dharmatti)
Following list of publications from our Group is given so that appropriate papers not listed in the Newsletter may be brought to the notice of your readers:

List of publications from Nuclear and Electron Magnetism Group, TIFR

1. High resolution nuclear magnetic resonance spectroscopy

2. Nuclear magnetic moment as a tool for detection, analysis and structure of chemical compounds

3. Construction and working of a wideline NMR spectrometer and the measurements of some chemical shifts

4. Chemical shifts in the nuclear magnetic resonance of Co$^{59}$ and the ligand field theory
   S.S. Dharmatti and C.R. Kanekar, J.C.P. 31, 1436, 1959

5. Physics of the solid state
   R. Vijayaraghavan, Curr. Sci., 28, 482, 1959

6. Applications of nuclear magnetic resonance and high resolution radiofrequency spectroscopy

7. Nuclear magnetic resonance in halogen complexes of mercury

8. Nuclear magnetic resonance study of co-ordination compounds of trivalent cobalt

9. Proton magnetic resonance study of hydrogen bonded systems

10. Electron spin resonance studies of the free radicals derived from tetraphenylhydrazine,

11. Varenna Summer School on radiofrequency spectroscopy

12. Nuclear magnetic resonance spectra for a system ABC of spin 1 nuclei and their linewidths

13. Proton magnetic resonance in sesamin and asarinins
14. Proton magnetic resonance spectrum of coumarin

15. Radiofrequency spectroscopy and crystal structure
S.S. Dharmatti, 'Symposium on Spectroscopy' edited by Dr R.K. Asundi and published by the Bihar University, 4, 89-104, 1959

16. Spin-lattice relaxation in tellurium,

17. Electron spin resonance studies of the free radicals derived from tetraphenylhydrazine

18. Synthesis of p-benzohydroquinone-1-C13

19. High resolution nuclear magnetic resonance spectra of some trisubstituted benzenes


21. Knight shifts in inter-metallic compound PtSn2

22. Knight shifts in inter-metallic compound PtSn2

23. Substitution effects on the NMR spectra of benzenes

24. Proton magnetic resonance in coumarins

25. NMR spectra of five spin systems I (NMR spectra of nitrobenzenes)

26. Para proton-fluorine splittings in fluorobenzenes

27. Nuclear magnetic resonance in the intermetallic compound Na14Pd4
28. C\textsuperscript{13} Hyperfine interactions in semiquinones
29. C\textsuperscript{13} hfs in the ESR spectra of p-benzosemiquinone ions
30. Nuclear magnetic resonance in hydrates of sodium tetraborates
31. Knight shifts in intermetallic compounds Pt-Sn, Pt-Pb and Pt-Hg systems
32. Nuclear magnetic resonance in cobaltic complexes
33. Quadrupole coupling constants of deuteron in some compounds
34. Nuclear magnetic resonance in metals and alloys
35. NMR of five spin systems - II. The spectrum of m-fluoronitrobenzene
   S.S. Dharmatti, G. Govil, C.L. Khetrapal and Y.P. Virmani
36. NMR of thiacromens and related compounds
   M.M. Dhingra, G. Govil, C.L. Khetrapal and V.M. Vaidya, Tetrahedron Letters, 6, 497, 1963
37. Hydrogen bonding studies in thiols
   S.S. Dharmatti, M.M. Dhingra, G. Govil and C.L. Khetrapal
   Proc. Symp. on Solid State Physics (1964)
38. Solvent effects on the proton chemical shift in heteroaromatic molecules
   S.S. Dharmatti, M.M. Dhingra, G. Govil and C.L. Khetrapal
   Proc. Symp. on Solid State Physics (1964)
39. Use of Mössbauer effect in inorganic chemistry
   C.B. Kar,war, Proc. Symp. on Solid State Physics (1964)
40. Synthesis of p-benzohydroquinone -1,3,5- C\textsuperscript{13}
41. ESR studies on developing seeds
42. Dynamic polarization of nuclei using magnetic resonance methods
43. Production & decay of radiation induced free radicals in seeds of different chemical composition,
   B.B. Singh, N.K. Notani, B.Venkataraman & K.C. Bora, I.A.E.A.Symposium on "Biological Effects of Ionizing Radiation at Molecular Level"
Dear Dr. Shapiro:

In the last month we have done a lot of work in connection with structure determination of natural products with the Varian HR 100. As we were able to get a signal to noise ratio of 1:80, it was possible to work often successful with only 2 - 5 mg. Perhaps the data of two unpublished examples may be of interest to the readers of the IIT NMR Newsletters.

\[
H_3C - \left(\begin{array}{c}
\text{C} \\
\text{C} \\
\text{C}
\end{array}\right)_3 - \text{C} = \text{C} 
\]

- \[H_A \text{ ddd } 3.57 \ (J_{AB}=J_{AC}=J_{AD}=2.5)\]
- \[H_B \text{ ddd } 4.98 \ (J_{AB}=J_{BC}=J_{BD}=2.5)\]
- \[H_C \text{ ddd } 7.66 \ (J_{CD}=16; J_{CE}=8; J_{AC}=J_{BC}=2.5)\]
- \[H_D \text{ ddd } 7.02 \ (J_{CD}=16; J_{DE}=11; J_{AD}=J_{BD}=2.5)\]
- \[H_E \text{ ddd } 4.42 \ (J_{CE}=8; J_{DE}=11; J_{EF}=8; J_{EG}=1.5)\]
- \[H_F \text{ dd } 3.50 \ (J_{FG}=11; J_{EF}=8)\]
- \[H_G \text{ dd } 4.26 \ (J_{FG}=11; J_{EG}=1.5)\]
- \[H_H \text{ s } 7.98\]
The only surprising point in the spectrum of II is the chemical shift of $H_O$. The only explanation we could find is the possible effect of the double bond and perhaps of a free electron pair on the ring-oxoxygen. In models with a special conformation this could be understandable. But perhaps one of your readers can give a better explanation.
Finally I wish to give a better explanation for the earlier (Mellon-Letters No. 57) discussed NMR-date of the cis-trans isomeric enolether polyynes of type III and IV becoming clear at 100 MHz.

\begin{align*}
H_A & \text{ dd } 3.94 \ (J_{AD} = 5.8; J_{AC} = 0.7) \\
H_B & \text{ dd } 3.81 \ (J_{AB} = 5.8) \\
H_C & \text{ m(dq) } 5.55
\end{align*}

\begin{align*}
H_A & \text{ dd } 3.87 \ (J_{AB} = 5.0; J_{AC} = 1.6) \\
H_B & \text{ dd } 3.39 \ (J_{AB} = 5.0; J_{BC} = 0.5) \\
H_C & \text{ m(dq) } 5.21
\end{align*}

In the cis-case the $H_B$-proton is shifted by the magnetic anisotropy of the acetylenic bonds, and there is a small coupling between $H_B$ and $H_C$ and a large between $H_A$ and $H_C$, while there is a small coupling in the trans-case only between $H_A$ and $H_C$.

Yours sincerely,

\[\text{[Signature]}\]
Dear Professor Shapiro,

In collaboration with Drs. Boden, Feeney, and Sutcliffe of Liverpool, I have been investigating the "ortho effect" observed for $^{19}$F chemical shifts, and your readers may be interested in the work so far. In a recent paper (1) we showed that in fluoro aromatic compounds the magnitude of $^{19}$F chemical shifts are proportional to $\pi$-electron charge densities, in accord with the theories of Karpplus and Das (2), and Prosser and Goodman (3), except when the fluorene nucleus has a neighbour other than fluorne. In the latter case the $^{19}$F shift can be at much lower applied fields than one would expect from the dependence on $\pi$-electron density, and in reference (1) we show that these ortho shifts arise from internal electric fields in the molecule. The theory works quite well for halogen substituents Cl, Br, I, when the most important contribution to the ortho shift is a term $-\Delta \langle \mathbf{E}^2 \rangle$, where $\Delta \langle \mathbf{E}^2 \rangle$ is the change in the mean square electric field arising from replacement of F by halogen. B is a constant and for aromatic fluoro-carbons has a value in the region of $(42-49) \times 10^{-18}$ esu. $\langle \mathbf{E}^2 \rangle$ is given approximately by

$$\langle \mathbf{E}^2 \rangle = 3a \alpha \mathbf{I} \rho \delta \quad (1),$$

where $\alpha$ is the polarisability, $I$ the ionisation potential, and $\rho$ is the distance between the mid-point of the C-X bond and the $^{19}$F nucleus.

The term $\langle \mathbf{E}^2 \rangle$ is particularly large for large, polarisable atoms such as iodine, and because of the dependence on $\rho^{-6}$ it will also be important for two fluorine nuclei which are exceptionally close to one another. This has been tested by examining the spectrum of perfluorobiphenyl, C$_{12}$F$_{10}$, in which the $^{19}$F nuclei in positions 2, 6, 2', 6' are likely to be nearer together than neighbouring $^{19}$F's in hexafluorobenzene, consequently the resonance peaks

should be at lower applied field than those at positions 4 and 4' where the $\pi$-electron density is similar in magnitude. The observed shifts from C$_6$F$_6$ are (2) 24.03, (3) 1.52, (4) 12.01 ppm, all to low field.

/The two....
Professor Shapiro.

The two rings will not be coplanar and \( \theta \), the angle of twist, has been calculated from the nmr data in two ways. Firstly by calculating the \( \pi \)-electron density at positions 4 and 4' as a function of \( \theta \) with Hückel MO theory, and then calculating the chemical shift from the equation of Prosser and Goodman; secondly, by assuming that the shift at the ortho positions is determined by the sum of the electronic contribution and the term \(-\Delta \phi^2\). The two methods give for \( \theta \) the values 45° and 50° respectively, which are in agreement with values determined by other methods, and suggests that equation (1) is basically correct in describing ortho \(^{19}\text{F}\) shifts. We are at the moment extending this work to other molecules containing sterically hindered fluorine nuclei.

Yours sincerely,

J.W. Emsley.

References.

Prof. B. L. Shapiro  
Illinois Institute of Technology  
Technological Center  
Chicago, Illinois 60616

Dear Barry:

First let me thank you for agreeing to preside at the 16th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (PCACAS) NMR symposium, which is to be held on March 1, 1965. Enclosed you will find a copy of the program schedule which may be of interest to IITNMRN readers.

We have recently completed an $^{19}\text{F}$ chemical shift compilation, and copies of this data are available for the asking to any parties who may be interested. We will send these out upon request until the supply is exhausted (thereby providing us with some badly needed shelf space).

Very truly yours,

John J. Burke

JJB: jai

Enclosure
**NMR SYMPOSIUM ON THE THEORETICAL AND EMPIRICAL ASPECTS OF CHEMICAL SHIFTS AND COUPLING CONSTANTS**

**Monday Morning**

9:00 ( )**  
A Molecular Orbital Theory of Nuclear Spin Coupling--John A. Pople, Carnegie Institute of Technology

9:30 ( )  
Coupled Hartree-Fock Calculations of Second Order Magnetic Properties--Richard M. Stevens, IBM Watson Laboratory, Columbia University

10:00  
Recess

10:20 ( )  
Nuclear Magnetic Shieldings in Ionic Crystals--Paul C. Lauterbur, State University of New York at Stony Brook

10:50 ( )  
Proton Magnetic Resonance Spectra of Organophosphorus Compounds--C. E. Griffin, University of Pittsburgh

**END OF SYMPOSIUM**

**NMR AND ESR SPECTROSCOPY**

**Monday Afternoon**

John J. Burke, Presiding  
Herbert L. Retcofsky, Presiding

1:00 ( )  
1:20 ( )  NMR Studies of the Hydroxy Complexes and Exchange Phenomena of Zinc (II)--EDTA--Richard J. Kula, University of Wisconsin


2:40  Recess

3:00 ( )  Identification and Estimation of the Nitration Products of Diphenylmethane by Nuclear Magnetic Resonance Spectroscopy--D. G. Gehring and G. S. Reddy, E. I. du Pont de Nemours Company

3:20 ( )  The Rapid Quantitative Analysis of Hydrazine Mixtures by Nuclear Magnetic Resonance--John C. MacDonald, Monsanto Research Corporation


4:00 ( )  Effect of Environmental Growth Parameters on ESR Spectra of Chlorella Pyrenoidosa--Richard W. Treharne and Howard E. Bales, Charles F. Kettering Research Laboratory
4:20 ( )

Relation between ESR Spectra and Metabolism of the Tumor Cell--Paul Y. Sakagishi and Tetsuo Akabe--presented by Paul A. Strauss, Perkin-Elmer Corporation

4:40 ( )

Analytical Instruments Designed Primarily for Education and Training--Leonard Eisner and Frederick Engel, Barnes Engineering Company
Professor B. L. Shapiro  
Department of Chemistry  
Illinois Institute of Technology  
Chicago, Ill.

Dear Professor Shapiro,

Unsuccessful identification of dimethyltetrabromonaphthalene

We brominated 1,5-dimethylnaphthalene for the purpose of obtaining 

\[
\begin{array}{c}
\text{Br} \\
\text{CH}_3 \\
\text{Br}
\end{array}
\quad (A)
\]

and obtained two products I (m. p. 204°C) and II (m. p. 190°C). According to chemical analysis I contains 4 Br while II contains 5 Br. The NMR spectrum of I shows one single methyl resonance and one single ring proton resonance. The spectrum is consistent with 3 possible symmetrically bromo-substituted naphthalenes, but (A) may be most probable among them. II shows one methyl, one \(\text{CH}_2\text{Br}\), and two ring proton resonances. The methyl resonance is a doublet which collapses to a single line by irradiating one of the ring protons, while the \(\text{CH}_2\text{Br}\) resonance is a single line. Consequently we inferred that II must be 

\[
\begin{array}{c}
\text{Br} \\
\text{CH}_3 \\
\text{Br}
\end{array}
\quad (\text{CH}_2\text{Br} \rightarrow \text{CH}_3)
\]

To confirm this inference we reduced II (\(\text{CH}_2\text{Br} \rightarrow \text{CH}_3\)) and obtained III. A mixture of I and III gives one methyl resonance and one proton resonance, which indicates that I and III are the same compound. Thus we are confronted with inconsistencies.

Sincerely yours,

A. Saika
"Phantom Resonance"

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

Dear Barry:

The double resonance spectrum of a single nucleus of spin-$\frac{1}{2}$ observed with a weak rf field $H_1$ of frequency $\omega_1$ in the presence of a strong rf field $H_2$ of frequency $\omega_2$ consists of two resonances - one above the line and one below the line. Bloch suggested in 1956 that two resonances should be observed in the double resonance spectrum of a single nucleus, and in fact the two signals 180° out of phase can be readily observed with reasonable values of $A$ and $v_2$, where

$$A = v_o + \frac{\omega_2}{2\pi}, \quad v_o = -\gamma H_o, \quad \text{and} \quad v_2 = -\gamma H_2.\quad (2, 3)$$

A double resonance spectrum of the proton of CHCl$_3$ obtained by sweeping $\omega_1$ is shown in Fig. 1, where $A = 2.98$ cps., and $v_2 = 9.8$ cps. The beat pattern in the center of this trace as usual indicates the point where the observing frequency $\omega_1$ equals the irradiating frequency $\omega_2$. The frequencies of the two resonances can be readily calculated neglecting relaxation complications, and the relative intensities of the two signals are consistent with a density matrix description of the double resonance experiment.\(^3\)

A careful analysis of the double resonance problem, however, indicates that this experiment should yield not two, but in fact
four signals. If the resonances in Fig. 1 occur at values of \( \omega_1 = \omega_1^* \) and \( \omega_2^* \), additional signals at \( 2\omega_2 - \omega_1 \) and \( 2\omega_2 - \omega_1 \) should be present in the output of the spectrometer. Since the usual NMR experiment involves stimulation of the spin system at frequency \( \omega_1 \) and detection of the response of the system only at \( \omega_1 \), the signals at \( 2\omega_2 - \omega_1 \) are usually rejected. "Observation" of an NMR signal usually means synchronous detection of the coherent response of the spin system to stimulation at \( \omega_1 \), so that the "Phantom Resonances" at \( 2\omega_2 - \omega_1 \) are never observed.

It is in fact possible to decide whether the phantom signals are really in the output of the spectrometer by stimulating the spin system at frequency \( \omega_1 \), but referencing the synchronous detector to a third frequency \( \omega_3 \). By sweeping \( \omega_3 \) for fixed values of \( \omega_1 \) and \( \omega_2 \) it is possible to scan the output of the spectrometer for all the signals present for any stimulating frequency \( \omega_1 \). Such an experiment is straightforward, for example, with the popular frequency-sweep double resonance system by simply scrambling some cables, and finding still another audio-frequency oscillator. It is only necessary to be careful that the lock-in-detector does not see any \( \omega_1 \), and that the molecule does not perceive \( \omega_3 \). Since \( \omega_3 \) is of course not coherent with either \( \omega_1 \) or \( \omega_2 \), all phase information is lost, and the phantom signal will appear only as a beat pattern.

A spectrum obtained by sweeping \( \omega \) with \( \omega_1 = \omega_1^* \) is shown in Fig. 2. Three beat patterns at \( \omega_3 = \omega_1^*, \omega_2^* \), and at the phantom resonance frequency \( \omega_3 = 2\omega_2 - \omega_1 \) are apparent. It was impossible for Les to refrain from turning a switch to let the proton see \( \omega_3 \), as well as \( \omega_1 \) and \( \omega_2 \). An incredible spectrum results, including four signals coherent with \( \omega_3 \) (two up and two down) beat patterns at \( \omega_1 \) and \( \omega_2 \), and at least two phantom resonances. Are we really obliged to understand everything it is possible to do to a single spin-\( \frac{1}{2} \)?

Best regards,

Leslie R. Anders
John D. Baldeschwieler

References:

November 11, 1964

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

Dear Dr. Shapiro:

A Quick Method of Making Frequency Assignments

During the course of our NMR-hydrogen-bonding studies, we have found a quick method for making frequency assignments of the thiophene ring protons in thenoyltrifluoroacetone, TTA

\[
\begin{align*}
\text{H(b)} & \quad \text{H(d)} & \quad \text{H(e)} \\
\text{H(c)} & \quad \text{O} & \quad \text{O} & \quad \text{C} = \text{CH} & \quad \text{C} - \text{CF}_3
\end{align*}
\]

A p.m.r. spectrum of 0.350 M solution of this compound in CCl$_4$ is shown in I, with the OH(e) signal omitted. All signals are downfield from TMS. It is reasonable to assign the lowest field multiplet to two of the thiophene ring protons and the problem is: which two? In order to answer this question, we have added tri-n-octyl-phosphine oxide, TOPO, to the above solution. The resulting spectra, in the presence of 0.622 and 1.306 M TOPO, are shown in II and III, respectively. It is seen that the lowest field multiplet in I is now resolved into two doublets, and that the lower-field doublet is shifted further downfield than the higher-field doublet, when the concentration of TOPO is increased from 0.622 to 1.306 M. Since TOPO is probably bonded to the OH(e) group, H(d) is closer to the coordination site than H(c), and one would expect therefore that the signal of H(d) would be shifted further downfield. We therefore conclude that the lowest multiplet in I is due to a superposition of the H(d) and H(c) signals, and that H(d) has the lower frequency of the two.

The frequencies of the various protons are given in the following table.
In the absence of TOPO, there is intramolecular hydrogen bonding involving OH(e). Since H(d) is closer to the coordination site also, its signal lies further downfield than H(c). This assignment is in agreement with the order given by Spectrum No. 185 of the Varian Associates High Resolution NMR Spectra Catalog (1962), in which H(c) and H(d) are listed as 7.73 and 7.82 p.p.m., respectively, in CDCl₃. It is interesting to note that for the compound

\[
\text{Spectrum No. 320 also lists } H(d) \text{ further downfield than } H(c): 7.70 \text{ and } 7.62 \text{ p.p.m., respectively. In the Spectra Catalog however, no reason is given of the order of assignment. We have shown here a quick method of making frequency assignments by observing the downfield shifts caused by the presence of an electron donor in hydrogen-bond formation.}
\]

On addition of 2-propanol, which itself is a strong hydrogen donor to TOPO, the latter may be removed from bonding with TTA. If this is the case, then one might expect that when excess alcohol is added to a CCl₄ solution containing TTA and TOPO, the two doublets in II or III might coalesce to form a multiplet, as in I. This has been observed. In separate experiments, we have also shown that in the absence of TOPO, 2-propanol does not affect the signals of the thiophene ring protons of TTA.

The IIT NMR Newsletter has been very helpful, and we regret the delay in sending in our contribution. The excuse is that one of us has only recently returned from a six-month sabbatical leave, which was spent as a Visiting Professor in Taiwan.

Sincerely,

Norman C. Li

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

Dear Barry:

As our contribution to IIT Letters, we would like to announce the availability of an IBM 7040 program for calculating high resolution NMR spectra of the type $A_nB$. The nuclei are all spin $\frac{1}{2}$ and $n_A \leq 13$ (all the A nuclei must be magnetically equivalent). The program is based on the recursion formulas for this case derived previously (P. L. Corio, Chem. Rev. 60, 363 (1960)), and was coded by the computer center at Socony Mobil.

Some of the general NMR programs now available can be used for calculating spectra of this type, but, occasionally, the large degeneracies that occur in such a system cause erroneous results. In these cases, or when the number of nuclei in the $A_nB$ system is very large, the above program should be quite useful.

IBM 7040 listings of the program are available by writing to us.

Sincerely,

R. C. Hirst

P. L. Corio

/trs
The sixth Experimental NMR Conference (6th ENC) will be held on Thursday, Friday and Saturday, February 25, 26 and 27, 1965, at Mellon Institute, Pittsburgh, Pennsylvania. The Conference is devoted to new developments in advanced instrumentation and experimental techniques; it does not compete with Workshops or courses offering an introduction to this field.

Sessions will consist largely of invited papers. A limited number of contributed papers will be accepted, and manuscripts or applications to give a paper should be sent to the appropriate Session Chairman or to the Chairman of the Conference (see enclosed instructions for Speakers and Contributors).

Sessions planned and chairmen are:

**Multiple Resonance:**
(2 sessions)

**Field/Frequency Control Methods:**
(1 session)

**Signal-to-noise Improvement:**
(2 sessions)

**Superconducting Solenoids:**
(1 session)

**Variable Temperature Equipment and Methods:**
(2 sessions)

**Pulse Techniques and Relaxation:**
(1 session)

**NMR of "Uncommon" Nuclei:**
(1 session)

**Spectral Analysis Techniques:**
(2 sessions)
NOTE: Additional information and the application to attend 6th ENC may be obtained only by returning the enclosed post-card (Don't forget to put a stamp on the post-card!) or by otherwise informing either the Chairman or the Sec'y-Treas. of your interest. Please be sure to do this promptly -- certainly no later than December 15 -- if you contemplate attending; it may be necessary to limit attendance because of restricted physical facilities.

The 1965 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will feature a full day of invited and contributed magnetic resonance papers on Monday, March 1.

Interest has been expressed in having an informal session on the teaching and instruction (both theoretical and experimental) of NMR, in both academic and non-academic environments. Please indicate on the attached post-card if you are interested in attending such a session. If adequate interest is expressed, a Chairman will be acquired and an informal session planned.

Instructions for Speakers and Contributors

I. Lengths of invited and contributed papers will be assigned by Session Chairmen so as to leave ample time for discussion in each session.

II. Abstracts and supplementary material (figures, tables, etc.) in no case exceeding 6 pages should be sent, by February 1, to:

Dr. A. A. Bothner-By
ENC Arrangements
Mellon Institute
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213

They will be printed and distributed to the conferees. Additional material, either too long or too late to have been printed, may be reproduced by the author and arrangements will be made to distribute it at the Conference. A distribution center will also be provided for commercial material of possible interest to the conferees. Authors are urged to submit detailed abstracts and drawings, schematics, spectra, etc., if at all possible. Participants in past conferences have found such a printed record to be quite valuable. In addition, the presentation of undigestible masses of data, complicated schematics, etc., on slides or blackboard is obviated, saving time and easing communication.

III. Abstracts and details of post-deadline papers and of contributions not accepted for formal presentation will be printed in a Supplementary Program and may be discussed at any appropriate session if time permits. The deadline and length limitations are the same as for contributed papers.

IV. Projectors for 3-1/2 x 4 inch and 2 x 2 inch slides will be available at all sessions. Unusual requirements of any sort should be transmitted to the Session Chairman.

"Structure of Rudiflorine, a Naturally Occuring Isomer of Ricinodine" R. Macberrie and A. Chatterjee Chem. Ind. 1964 (1964)

"Total Synthesis of dl-Acamidine" P. M. Quan, T. K. E. Karm and L. B. Quin Chem. Ind. 1953 (1964)


"1-Methyl-3,l-methylene-1,4-dihydroquinolin-2-one(s), Derivatives of a new ring system, the 1-M-cycloprop(2) quinolines" B. Levy, M. P. Korensha and K. M. Grader Chem. Ind. 1710 (1964)

"Aromatic Ring Synthesis via the Michael Reaction" C. E. Glassick, W. J. Flank and G. B. Post Chem. Ind. 1711 (1964)

"Long Range Proton Spin Coupling over Four Bonds" E. K. Erlich, Jr. Chem. Ind. 1712 (1964)

"X-Ray Diffraction Studies of the Conformation of Polymer Molecules in Solution. I. 1,1-Isodopolystyrene" G. W. Brady and N. Salovey J. Am. Chem. Soc. 56, 2999 (1964)


"A 2,3-Diacyclocapropane (Di-1-butylaziridines)" F. R. Greene and J. E. Toddell J. Am. Chem. Soc. 86, 3569 (1964)

"Proton-13C Spin-Spin Coupling. V. Inadequacy of Correlation of Proton-13C Coupling with δ-character" G. J. Karabatsos and C. E. Green J. Am. Chem. Soc. 87, 3774 (1964)

"Substituent Effects. III. Correlation of 13C-1 and 1H-1 Couplings by Pairwise Interactions" E. R. Malinowski and T. Vladimiroff J. Am. Chem. Soc. 87, 3775 (1964)

"Ring Inversion and Bond Shifts in Cyclononatetraene Derivatives" P. A. L. Ame, A. J. R. Bourn and Y. S. Lih J. Am. Chem. Soc. 87, 3776 (1964)


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"New Methods of Introducing the Carboxy-1-butoxy Amino-Protec-


"The Reaction of Horborne with 1-Butyl Hypochlorite and the Stereoeconomic 2,3-Chlorohydroxybicyclo[2.2.1]heptanes" E. Toher, D. R. Balle and R. J. Foster J. Org. Chem. 82, 2834 (1964)

"The Reaction of Horborne with Polyalcohets and the Behavior of the Adduct towards Acid and Base" E. Tober and R. J. Foster J. Org. Chem. 82, 2835 (1964)


"Cyclodehydration Reactions of Tryptamine Derivatives with Acetone" J. B. Bester, Jr. J. Org. Chem. 82, 2864 (1964)

"The Structure of Amides" C. L. Bell, C. N. Y. Hermus and L. Bauer J. Org. Chem. 82, 2873 (1964)


"Thermal Cleavage of 1,1-Diacetyl-1,1,4,4-"Tetrahydro-


"The Synthesis of 2,4,6-Trisubstituted Pyridine-2,5-Pyrimidines from 2-Amino-3,5-Pyrimidinediones" B. N. Halvey, S. G. calf and G. Diederich J. Org. Chem. 82, 2903 (1964)

"Preparation and Properties of 2- and 3-Bromo-1-methylcyclo-

hexanes" R. R. Marvell and R. Sexton J. Org. Chem. 82, 2919 (1964)

"The Structure and Reactions of the 11 Adduct of Benzeno-

sulfonfyl, Amide and Bicyclo[2.2.1]heptane" J. E. Fae, C. Ouch and W. N. Dietrich J. Org. Chem. 82, 2928 (1964)
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5-Deoxy-4-endo-5-Hexene Acid” R. L. Roberts J. Org. Chem. 29, 2765 (1964)


"Steric Course in Cycloaddition of Chlorotrifluoroethylene"
V. C. Solomon and L. A. Dee
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"A Reinvestigation of the Condensation of Ethyl Trimethyl-
late with Benzaldehyde"
J. R. Wiseman
J. Org. Chem. 29, 2793 (1964)

"The Preparation of Parahalene Acids from 1,1,3-Trisubstituted
Ureas via a Homann Elimination Reaction"
P. J. Stoffel
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"Derivatives of 1,4-Xylene-2,5-diboronic Acid and 1,4-Xylene-
5-boronic Acid"
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