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Prunas ✓

Illinois
Institute of
Technology
N−M−R
Newsletter

No. 74
NOVEMBER, 1964

Deadline for Next Issue:
18 December 1964

Glaxo · Research Limited

Greenford · Middlesex

TELEPHONE: BYRON 3434   TELEGRAMS: Glaxotha, London, Telex   CODE: New Standard, Bentleys

Please address reply to: Dr. J.E. Page   2nd October, 1964.

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 $33-34^\circ$; 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

THE PHYSICS LABORATORIES

UNIVERSITY OF KENT AT CANTERBURY

18th September 1964.

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

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

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,

$$\frac{H_1}{T_1} \approx 0.01 \quad \text{(For liquids } T_1 \approx T_2\text{)}.$$

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 (Muirhead 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 Bunsengesellschaft fur
          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.

THE UNIVERSITY OF LIVERPOOL

Coupling Constants in Rotamers of Cis and Trans iC$_3$F$_7$CH = CHF.

N. Boden, J.W. Emsley, J. Feeney and L.H. Sutcliffe.

Recently we have measured the temperature dependence of $\langle J_{H_2F_3} \rangle$ in cis and trans iC$_3$F$_7$CH = 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 $\langle J_{H_1F_3} \rangle$, $\langle J_{F_1F_3} \rangle$ and $\langle J_{F_1(CF_3)} \rangle$ and the data were found to be in accord with the above results.

The large long range coupling constants $J_{F_1F_3}$ in IA and $J_{F_1(CF_3)}$ in IIA are between spatially close fluorine nuclei; however, a large spin-spin interaction also exists between widely separated F$_1$ and F$_3$ 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.

– – – – – – – –

IA

IIA

IB

IIB
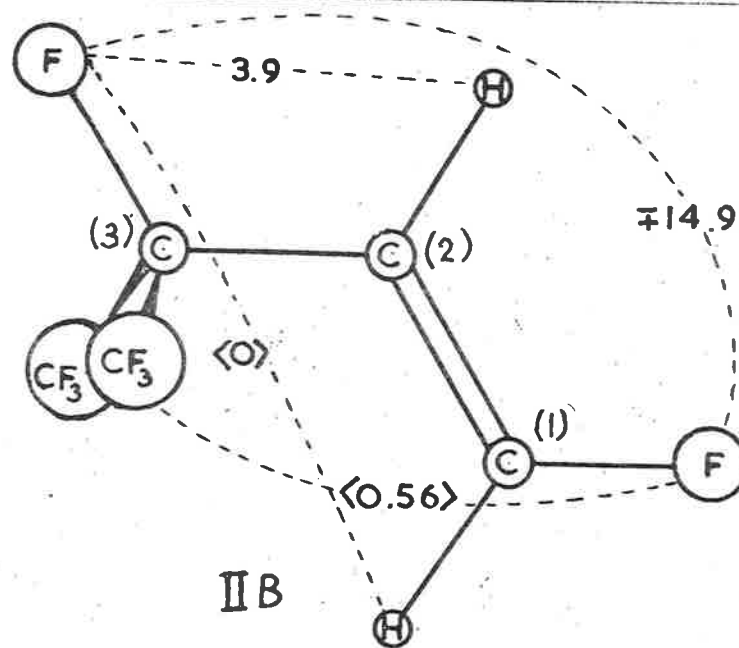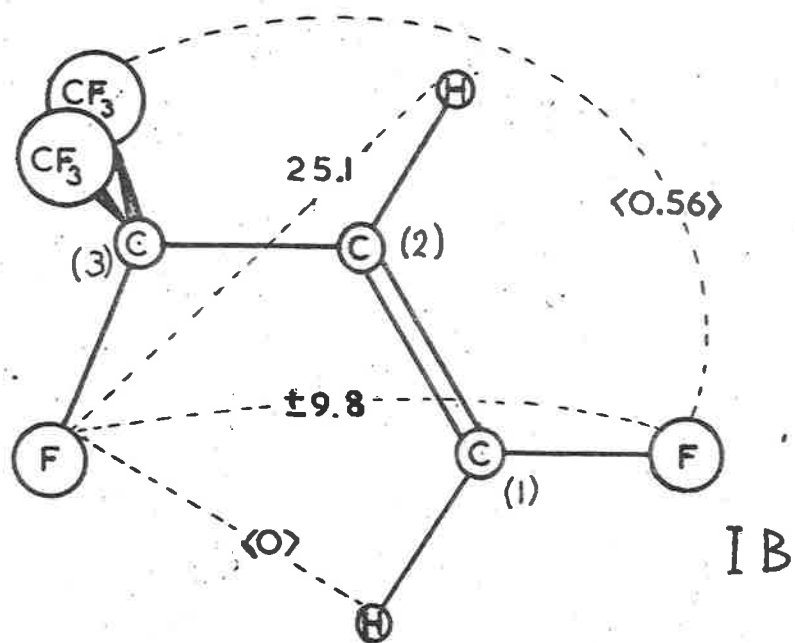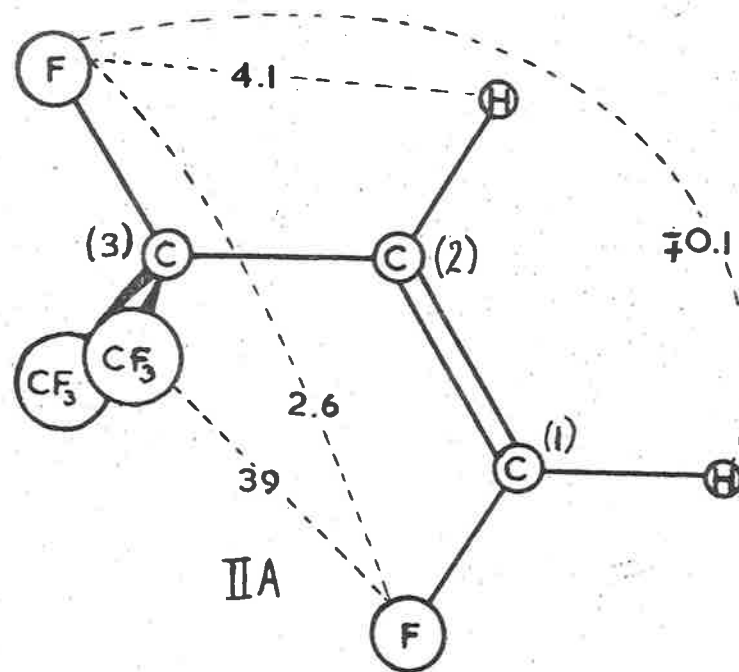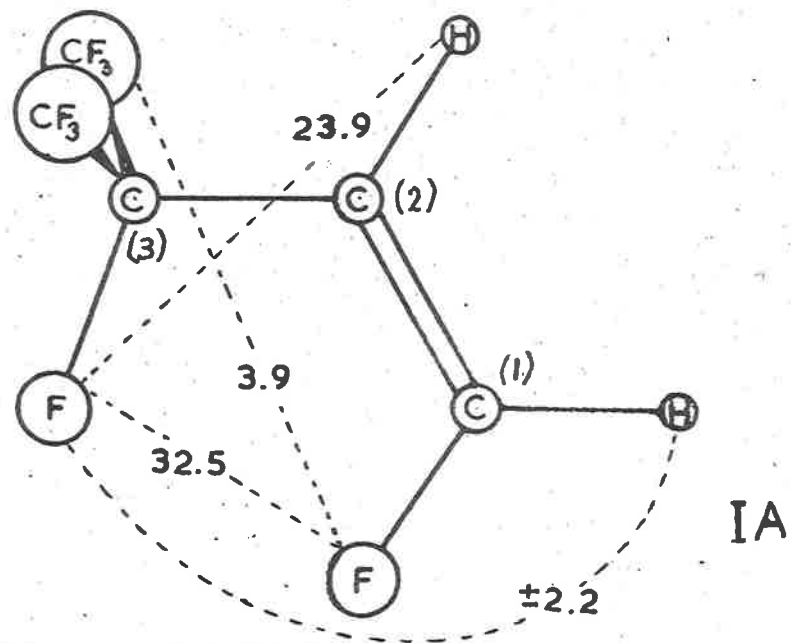
THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

P. O. BOX 39175
CINCINNATI 39, OHIO

October 22, 1964

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 O/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 (V0666) 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 L9 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 V0279.

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

Sincerely,

THE PROCTER & GAMBLE COMPANY
Research & Development Department
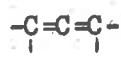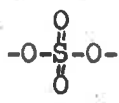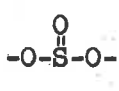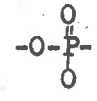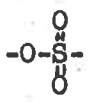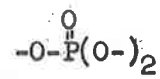
T. J. Flautt
Research Division

cw

Enc.

*N*M*R* SPECTRA INDEX

MAIN	FUNCTIONAL	FUNCTIONAL	FUNCTIONAL	GROUPS	*T* VALUE	SPECT. NO.
3	B /E	E	O /B		4.37	V0075
(3)	(C /A B)	(D /A C J)	(L /H L)		7.40	V0666
1	L9/A B H				8.32	V0279
1	L9/B H B				8.38	V0279
21	SULFUR	B /L			8.10	V0101
1	S2/D				6.87	TIERS

Additional Functional Group Codes

Code	Structure	Code	Structure
B1	$\overset{\displaystyle\mid}{B}$	P8	$-\overset{O}{\overset{\|}{\underset{\mid}{P}}}O-$
B2	$-\overset{\mid}{\underset{\mid}{B}}{}^{-}-$	P9	$-\overset{O}{\overset{\|}{P}}O-$
L4	$-\overset{\mid}{C}=C=\overset{\mid}{C}-$	S1	$-\overset{O}{\overset{\|}{S}}-$
L9	$-\overset{\mid}{C}=\overset{\mid}{C}-$	S2	$-\overset{O}{\overset{\|}{\underset{\|}{\underset{O}{S}}}}-$
P1	$-\overset{\mid}{\underset{\mid}{P}}-$	S3	$-\overset{O}{\overset{\|}{\underset{\|}{\underset{O}{S}}}}O-$
P2	$-\overset{O}{\overset{\|}{\underset{\mid}{P}}}-$	S4	$-O-\overset{O}{\overset{\|}{\underset{\|}{\underset{O}{S}}}}O-$
P3	$-\overset{\mid}{\underset{\mid}{P}}{}^{+}-$	S5	$-O-\overset{O}{\overset{\|}{S}}O-$
P4	$-O-\overset{O}{\overset{\|}{\underset{\|}{\underset{O}{P}}}}-$	S6	$-O-\overset{O}{\overset{\|}{\underset{\|}{\underset{O}{S}}}}-$
P5	$-O-\overset{O}{\overset{\|}{P}}(O-)_2$	Z1	Si
P6	$-O\overset{O}{\overset{\|}{P}}-$	Z2	Al
P7	$-\overset{S}{\overset{\|}{\underset{\mid}{P}}}-$		

ROHM & HAAS COMPANY

REDSTONE ARSENAL   RESEARCH DIVISION

HUNTSVILLE, ALABAMA 35807

October 6, 1964

Dr. B. L. Shapiro
Department of Chemistry
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois 60616

Dear Dr. Shapiro:

Recently we examined the ^1H and ^{19}F spectra of some
"alkyl fluoroazoxy" compounds (N-alkyl-N^1-fluorodiimide-N-
oxides). The proton spectra (Fig. Ia, R = benzyl; Fig. IIa,
R = β phenylethyl) show two and four peaks, respectively,
in the region of 4-4.5 δ 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 φ. 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 $J_{HF} \cong 0$.

$$\begin{array}{cc} \overset{\displaystyle O}{\underset{\displaystyle \quad}{\uparrow}} \ \overset{\displaystyle F}{|} & \\ R - N = N & \end{array} \qquad\qquad \begin{array}{c} \overset{\displaystyle O}{\uparrow} \\ R - N = N \\ \quad\quad\quad | \\ \quad\quad\quad F \end{array}$$

        A   B
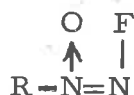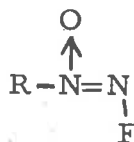
I   - R=benzyl

II - R=β phenylethyl

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. Ib) on simultaneous irradiation of ^{19}F at
37.650 Mc. Similarly the quartet of IIa collapses to a slightly
perturbed triplet in Fig. IIb.

Dr. B. L. Shapiro — -2- — October 6, 1964

Shift and coupling data are summarized in Table I.

Table I

NMR of Alkyl Fluoroazoxy Compounds

alkyl	methylene δ	fluorine ϕ	J_{HF} cps
benzyl	5.02, 5.14	-46.9 ϕ	7.1
phenyl ethyl	4.10, 4.22, 4.32, 4.44	-47.7 ϕ	~7.0
neopentyl	3.83, 3.95	-46.4 ϕ	7.2

Our conclusions are in agreement with similar work by Frazier, Holder and Worden,[1] who find J_{CF_3-F} = 7.1 cps for the related $CF_3-\overset{\overset{O}{\uparrow}}{N}=NF$. 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

bac

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[1] J. W. Frazier, B. E. Holder and E. F. Worden, J. Inorg. Nucl. Chem., <u>24</u>, 45 (1962).
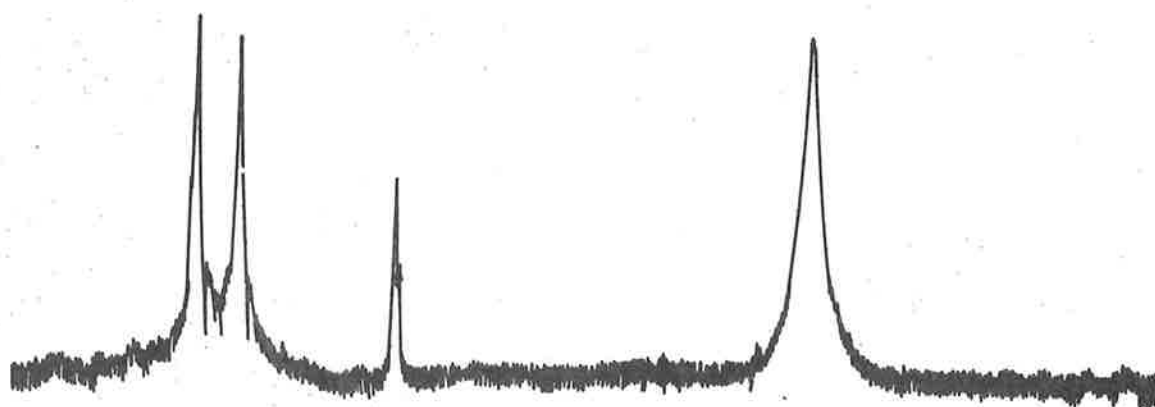
NORMAL
SPECTRUM
FIG Ia.

DECOUPLED
SPECTRUM
FIG. Ib

Proton n.m.r. spectrum of $\phi CH_2 NONF$ before (left) and after (right) radio frequency irradiation.
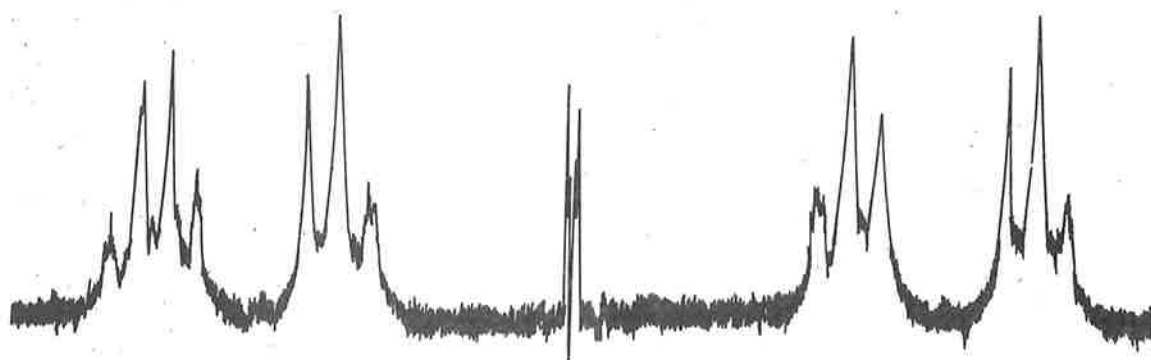
NORMAL
SPECTRUM
FIG. IIa

DECOUPLED
SPECTRUM
FIG. IIb

Proton n.m.r. spectrum of $\phi CH_2 CH_2 NONF$ before (left) and after (right) radio frequency irradiation.

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.
October 22, 1964

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

Dear Prof. 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 tetramethylsilane (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 $\gamma H_2/2\pi \simeq 1$ 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 $C_4O_2H_8$: C_6H_{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[1]) 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 occured 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 should 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

- 3 -

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 inter-
action of the form $J(t)I(1)\cdot I(2)$ 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 w_o of $\Delta m = 0$ flip-flop
transitions arising from this mechanism is given by

$$w_o = 2\pi^2 J^2 \frac{\tau_c}{1+\{\omega(1)-\omega(2)\}^2 \tau_c^2}$$

where τ_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 $T_1 \simeq 10$ sec of the components of the mixture, the
observed magnitude of the effect requires $w_o > 1$ sec^{-1}. Such
a magnitude can only be reached with $\sqrt{J^2} \simeq 10$ cps for
$\tau_c = \{\omega(1)-\omega(2)\}^{-1} \simeq 10^{-3}$ sec for the cases investigated.
Both values appear rather implausible.

One might then suppose that the required inter-
molecular 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 intemolecular Overhauser effect.

STALEMATE![5]

Sincerely yours,

R. Kaiser

REFERENCES

1. J. H. Noggle, Rev. Sci. Instr. 35, 1166 (1964).

2. A. Abragam, Phys. Rev. 98, 1729 (1955).

3. I. Solomon, Phys. Rev. 99, 559 (1955).

4. I. Solomon and N. Bloembergen, J. Chem. Phys. 25, 261
   (1956).

5. Private comments in addition to those already received
   from J. D. Baldeschwieler and J. Waugh will be
   gratefully accepted and not disclosed.

(a)   (b)

Fig. 1

Fig. 1: Repeated scans through cyclohexane resonance
      (a) with irradiation $\gamma H_2/2\pi \simeq 1$ cps applied
          50 cps off dioxane resonance

      (b) with irradiation $\gamma H_2/2\pi \simeq 1$ cps centered
          on dioxane resonance.

INSTITUT NATIONAL DE RECHERCHE CHIMIQUE APPLIQUÉE

(I. R. CH. A.)

12, QUAI HENRI-IV - PARIS-4ᵉ

N°

(à rappeler dans la réponse)

OBJET :

Pr. Bernard L. SHAPIRO
Department of Chemistry
Illinois Institute of Technology
CHICAGO, Illinois 60616
USA

Paris, 22 octobre 1964

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. $\underline{61}$ 1190, (1964)). From a simple Hückel model, it is possible to estimate roughly the electron distribution in molecules such as R_3PO, $(RO)_3PO$, $(R_2N)_3$ PO 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=) O electronic charge (in electron units).

.../...

	$\delta \ P_{31}$		electronic charge
$(CH_3CH_2O)_3 \ PO$	$- \ 22$	$(RO)_3 \ \underline{PO}$	.200
$(CH_3(CH_2)_3O)_2 \ P(O) \ (OCH_3)$	$+ \ 29$		
$(CH_3O)_2 \ P(O)H$	$+172$	$(RO)_2 \ R\underline{PO}$	.247
$(CH_3CH_2O)_2 \ P(O)CH_2 \ CH_3$	$+177$		
$(CH_3O) \ P \ (O) \ [(CH_2)_3 \ CH_3]_2$	$+340$	$(RO) \ R_2 \ \underline{PO}$	$\sim .310$
$[CH_3 \ (CH_2)_7]_3 \ PO$	$+830$	$R_3\underline{PO}$	.367

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

With all best regards of

G. MAVEL

FAIRCHILD 300 ROBBINS LANE, SYOSSET, L.I., NEW YORK 11791 · 516 WE 1-4500 · TWX:516 433-9121 · CABLE FAIRCAM SYOSSET NEW YORK

SPACE AND DEFENSE SYSTEMS
A DIVISION OF FAIRCHILD CAMERA
AND INSTRUMENT CORPORATION

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 Cl^{35},
Cl^{37}, Br^{79}, Br^{81} and I^{127}. In this work it is convenient for us to work at
different fields. The frequency stability of the Varian 4210A is not suffi-
cient 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 nec-
essary to boost the output below ten Mc with an Instruments for Indus-
try Model 500 Wide Band Amplifier. With the amplifier we can synchron-
ise 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 integrater 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

FAIRCHILD CAMERA AND INSTRUMENT CORPORATION

-2-

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

JEL/mi

THE UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
RIVER CAMPUS STATION
ROCHESTER, NEW YORK 14627

DEPARTMENT OF CHEMISTRY

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 coup-
ling constants of cis-1-methoxy-1-buten-3-yne

$$HC \equiv \underset{4}{C} \underset{3}{} \quad \underset{2}{C} = \underset{1}{C} \quad OCH_3$$
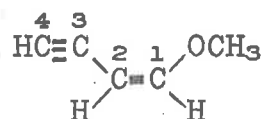
by the double resonance method described by Freeman and Whiffen.[1]
Our apparatus was described in an earlier newsletter.[2] Chemical
shifts and coupling constants with their relative signs are as
follows:

Chemical shift (τ)		Coupling constants (c/s)	
CH_3	6.28	$J_{1-2} \pm$	6.4
H-1	3.68	$J_{1-4} \pm$	0.9
H-2	5.61	$J_{2-4} \mp$	2.5
H-3	7.05		

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 corres-
ponding coupling constant in vinyl acetylene is also negative.
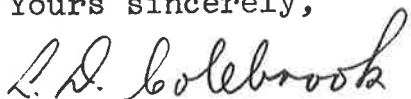
The chemical shift of the acetylene proton showed a signi-
ficant concentration dependence, moving to higher field as the
concentration in carbon tetrachloride was decreased. Evidently
this proton is involved in weak intermolecular hydrogen bonding.

Preliminary dilution studies (CCl$_4$ 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[4] for this compound and our own values to such a solvent effect.

1. R. Freeman and D. H. Whiffen, Molecular Physics, <u>4</u>, 321 (1961).
2. L. D. Colebrook, MELLONMR, <u>53</u>, 8 (1963).
3. E. I. Snyder, L. J. Altman and J. D. Roberts, J. Am. Chem. Soc., 84, 2004 (1962).
4. R. C. Hirst and D. M. Grant, J. Am. Chem. Soc., <u>84</u>, 2009 (1962).

Yours sincerely,

L. D. Colebrook

LDC/pn

^{11}B-Kernresonanz von Borsäureestern

Wir haben die ^{11}B-Kernresonanz einer Anzahl von Borsäureestern
und Boraten im Hinblick auf die Koordinationszahl des Bors
untersucht (15,o8 MHz, 11o1o G, 1o 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 $\Delta\nu_{1/2}$ stark vom
Lösungsmittel abhängig. Wir deuten die besonders große Breite
in H_2O 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,
was 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 25° kann daher gerade so groß sein, daß sie das
^{11}B-Signal bereits verbreitert, das ^{1}H-Signal aber noch nicht.

I   II   III
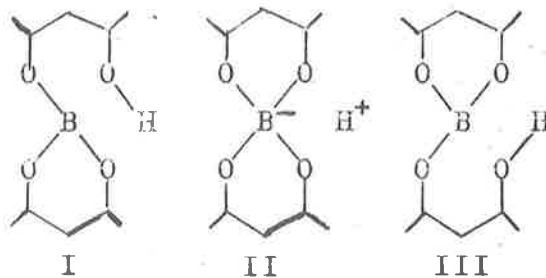
Im K-Disalicyltriborat, dessen Struktur nicht genau bekannt ist,
sind BO_3 - und BO_4-Konfiguration nebeneinander nachweisbar. Eine
Ausnahme in unserer Reihe ist der Borsäuretrimethylester, der
zwar die für eine BO_3-Konfiguration charakteristische chemische
Verschiebung, nicht aber die erwartete Breite 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.

	δ (ppm)	$\Delta\nu_{1/2}$ (sec^{-1})
Ebene BO_3-Koordination (sp^2):		
Borsäuredi-2,4-pentandiolester (H_2O)	-17	218
" ($HCCl_3$)	$-14,9$	200
" (CH_2Cl_2)	$-16,3$	82
Borsäuretrimethylester (Äther)	$-16,4$	28
Borsäure (H_2O/HCl)	$-15,1$	64
K-Disalicyltriborat (CH_3OH)	$-15,1$	54
Bortrichlorid	$-46,0$	75
Tetraedrische BO_4-Koordination (sp^3):		
Na-Metaborat (H_2O)	0	16
K-Dihydroxodifluoroborat (CH_2Cl_2)	2,5	23
Na-Di-2,4-pentandioxoborat (H_2O)	0	27
Na-Disalicylatoborat (CH_3OH)	0,1	31
K-Disalicyltriborat (CH_3OH)	0,55	32
Na-Dimethoxo-o-phenylendioxoborat (CH_3OH)	$-5,7$	31
Acetylacetonato-o-phenylendioxoboran ($CHCl_3$)	$-6,8$	25
Acetylacetonatodiacetoxoboran ($CHCl_3$)	0	33
Acetylacetonatodifluoroboran ($CHCl_3$)	0,95	18
Bortrifluorid-Diäthylätherat	$-3,3$	20

D.Imbery   E.Funck

Institut für physikalische Chemie
78 Freiburg i.Br., Deutschland
Hebelstrasse 38

College of Pharmacy · Department of Chemistry

UNIVERSITY OF ILLINOIS AT THE MEDICAL CENTER, CHICAGO

833 South Wood Street · Chicago, Illinois 60612 · Telephone 663-7245

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:

<u>Thursday, December 17</u> - 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

<u>Friday, December 18</u>

"Interpretation of More
Complicated Spectra"

Dr. LeRoy F. Johnson
Varian Associates

"Double Resonance Techniques"

Dr. Ray Freeman
Varian Associates

"Geminal Coupling and
Rotational Isomersim"

Dr. Bernard L. Shapiro
Illinois Institute of
Technology

<u>Saturday, December 19</u>

"Structure Elucidation of
Natural Products by Use of NMR

Dr. G. Slomp
The Upjohn Company

"Conformational Analysis and
Equibria

Dr. Frank A.L. Anet
University of California
at Los Angeles

(continued)

UNIVERSITY OF ILLINOIS

2.
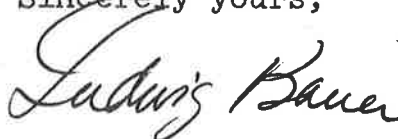
"Conformation of Aliphatic   Dr. G.J. Karabatsos
   Aldehydes and Carbonyl Compounds"   Michigan State University

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

LB/sf

THE MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY

(Faculty of Technology in the University of Manchester.)

MANCHESTER 1 · TELEPHONE CENTRAL 3266

Department of Chemistry

2nd November, 1964.

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 in our contribution.

Recently a series of perfluoroarylphosphorus 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.

Compound.	J_{PF} c/s		
	ortho F	meta F	para F
$(C_6F_5)_2P-NMe_2$	51·0	1·7	1·3
$C_6F_5PMe_2$	30·1	1·7	∼0
$C_6F_5PCl_2$	63·2	0·8	1·0
$(C_6F_5)_3P$	29	3·0	1·7
$C_6F_5PH_2$	4·0	1·7	∼0

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.

CONTINUATION

Dr. B. L. Shapire
Illinois Institute of Technology.   2nd November, 1964.

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.,69, 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 $\diagup^O$ but for the sake 12(RC-OF), 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 $-CF_3$ = a,α; $-CF_2-$ = β, β; $-CF-$ = Υ,γ; (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 $-CF_3$ and $-C(CH_3)_3$ (e.g. in $CH_2F\cdot CH_2 \cdot CF_3$ and $CH_2F \cdot CH_2 \cdot C(CH_3)_3$) 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 = ∅, and suggest also silicon = σ.

   (c) The definition of group y = 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,

                    R. Fields. (R. Fields)

                    m green. (M. Green)

The University of Strathclyde

Formerly the Royal College of Science and Technology

GLASGOW, C.1. TEL: BELL 4400

Chemistry Department,

28th October, 1964.

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:-
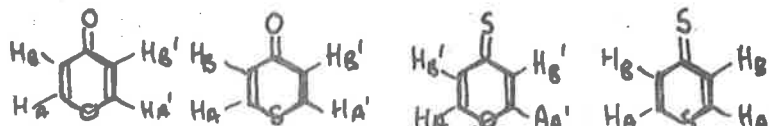
Chemical shifts (τ values)

H_A	2.08	2.15	2.48	2.10
H_B	3.62	2.95	2.85	2.40

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,

Dr. Peter Bladon.

Université Libre de Bruxelles   Bruxelles 5, le **November 5, 1964.**

FACULTE DES SCIENCES
Avenue F-D. Roosevelt, 50
—
Service : Organic Chemistry
Dir.: Professor R.H.MARTIN

(A rappeler dans la réponse)

LONG—RANGE SPIN-SPIN COUPLING BETWEEN AROMATIC
PROTONS LOCATED IN DIFFERENT RINGS OF A MONOSUB-
STITUTED 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 aro-
matic 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.

I
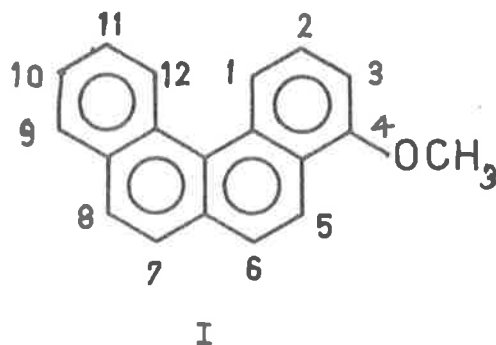
As anticipated, the OCH_3, which comes out as a <u>sharp</u> singlet
(240 c/s 60 Mc), has a shielding effect on H3 (ortho) and H1 (para),

and a deshielding effect on H5 (peri) (fig.1).

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

$\underline{H1}$ must be coupled with H2 ($J_{1,2}$ = 8.4 c/s) and H3 ($J_{1,3}$ = 0.8 c/s) and with $\underline{two}$ other protons ($J \sim 0.8$ 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).

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

As far as we are aware, this is the first example of well resol 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 commun 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) mentionned in this letter are the coupling constants mesured on the spectrum.

Fig. 1
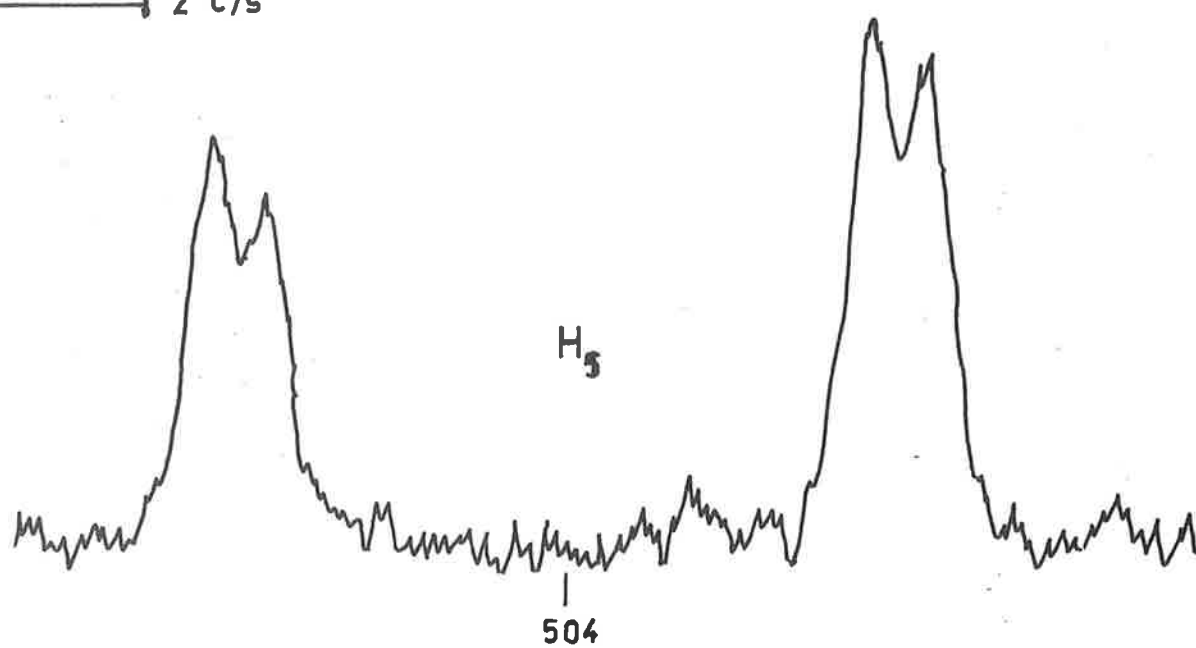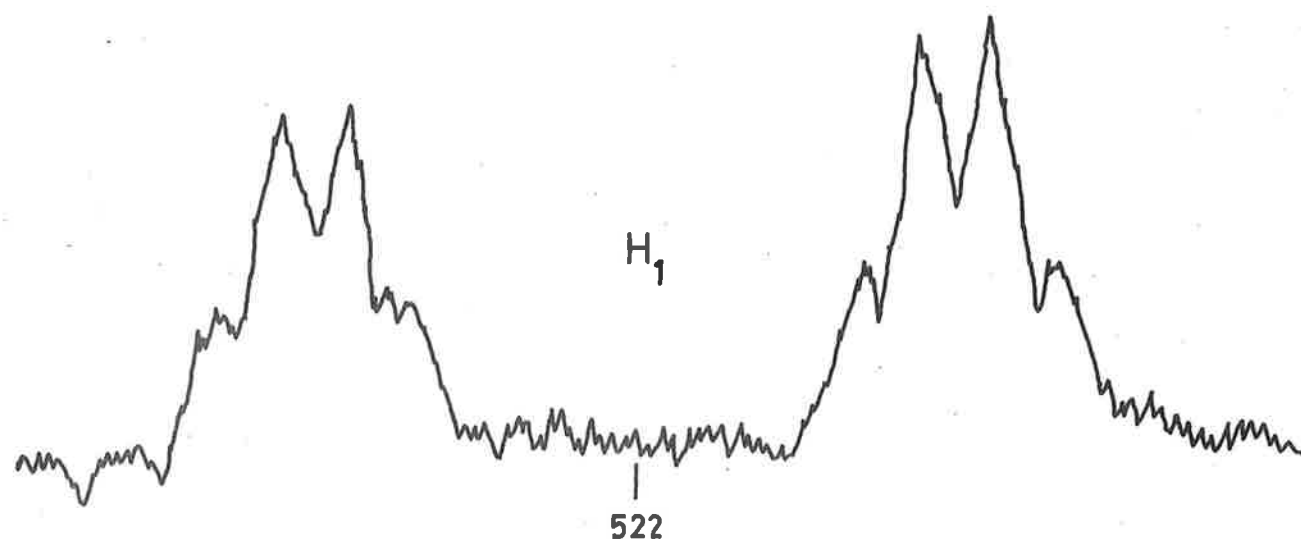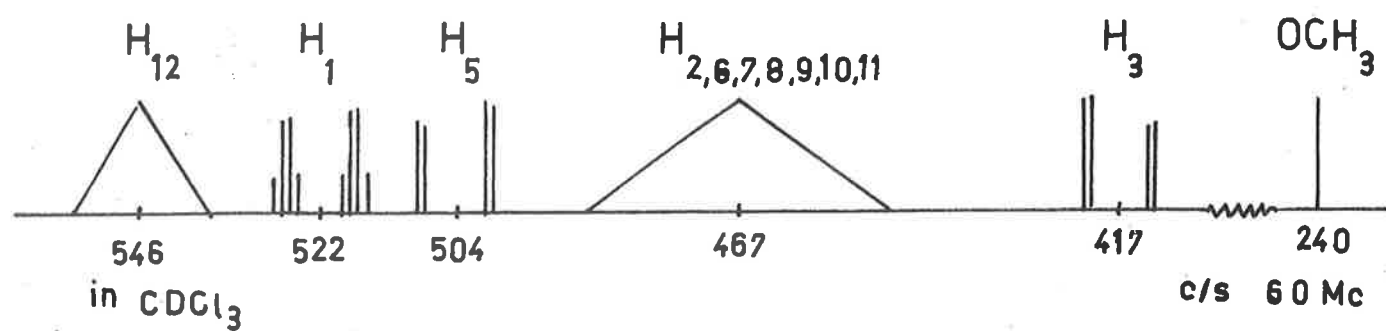
TATA INSTITUTE OF FUNDAMENTAL RESEARCH

National Centre of the Government of India for Nuclear Science and Mathematics

Telegrams: ZETESIS   COLABA, BOMBAY 5   Telephone: 2 1 3 6 6 6

November 3, 1964

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 $C^{13}-F^{19}$ coupling constants are being studied. The solvent effects on these coupling constants 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 character 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

Dr. B.L. Shapiro   3.11.1964

molecular association in aromatic compounds.

We have also recently started some work on the proton magnetic reso-
nance 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 reads

List of publications from Nuclear and Electron Magnetism Group, TIFR

1. High resolution nuclear magnetic resonance spectroscopy
   S.S. Dharmatti, 'Symposium on Spectroscopy', edited by Dr R.K. Asundi and published by the Bihar University. 5, 20-25, 1958

2. Nuclear magnetic moment as a tool for detection, analysis and structure of chemical compounds
   S.S. Dharmatti, C.R. Kanekar and S.C. Mathur, Proc. of the Second International Conference on the Peaceful Uses of Atomic Energy 28, 644-651, 1958. Published by the United Nations

3. Construction and working of a wideline NMR spectrometer and the measurements of some chemical shifts
   S.S. Dharmatti, K.J. Sundara Rao and R. Vijayaraghavan, Il Nuovo Cimento, 11, 656-669, 1958

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
   S.S. Dharmatti, Curr. Sci., 29, 165-170, 1960

7. Nuclear magnetic resonance in halogen complexes of mercury
   S.S. Dharmatti, C.R. Kanekar and S.C. Mathur, Proc. Symp. Chem. Co-ordination Compounds published by the National Academy of Sciences, India, II, 152-156, 1960.

8. Nuclear magnetic resonance study of co-ordination compounds of trivalent cobalt
   S.S. Dharmatti, C.R. Kanekar and S.C. Mathur, Proc. Symp. Chem. Co-ordination Compounds II, published by the National Academy of Sciences, India, 157-161, 1960

9. Proton magnetic resonance study of hydrogen bonded systems
   S.S. Dharmatti, G. Govil, C.R. Kanekar and Y.P. Virmani, Bull. Ampere, (Colloque de Pise, 1960) 480-494, 1960

10. Electron spin resonance studies of the free radicals derived from tetraphenylhydrazine,
    B. Venkataraman, A.V. Patankar and M.R. Das, Bull. Ampere, 9th Year p.260, 1960.

11. Varenna Summer School on radiofrequency spectroscopy
    C.R. Kanekar and B. Venkataraman, Curr. Sci., 30, 7-8, 1961

12. Nuclear magnetic resonance spectra for a system ABC of spin $\frac{1}{2}$ nuclei and their linewidths
    S.S. Jha, Proc. Ind. Aca. Sci. 44, 13-23, 1961

13. Proton magnetic resonance in sesamin and asarinins
    G. Govil, C.R. Kanekar and C.L. Khetrapal, Curr. Sci., 30, 252-254, 1961

14. Proton magnetic resonance spectrum of coumarin
    G. Govil, C.R. Kanekar, C.L. Khetrapal and Y.P. Virmani, Curr. Sci.,
    30, 331, 1961

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PROFESSOR DR. F. BOHLMANN
ORGANISCH-CHEMISCHES INSTITUT
TECHNISCHE UNIVERSITÄT BERLIN

Berlin-Charlottenburg 2, den 5.11.1964
Straße des 17. Juni Nr. 115
Fernruf: 32 51 81/252   Prof.B./Ra

Professor
Bernard L. Shapiro
Illinois Institute of Technology
Technology Center
Department of Chemistry

C h i c a g o 60616

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 1oo. As we were able to get a signal to noise ratio of 1 : 8o

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.
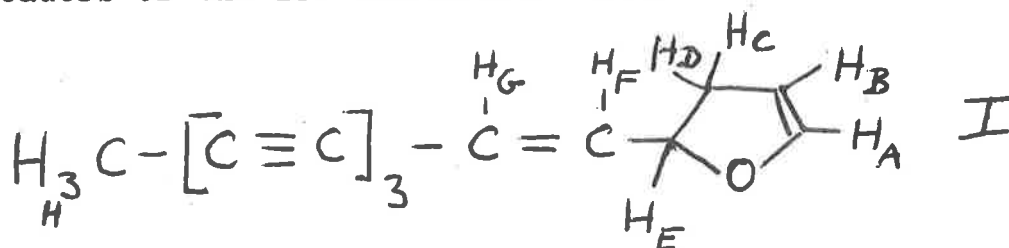
H_A ddd   3.57 ($J_{AB}=J_{AC}=J_{AD}=2.5$)

H_B ddd   4.98 ($J_{AB}=J_{BC}=J_{BD}=2.5$)

H_C dddd 7.66 ($J_{CD}=16$; $J_{CE}=8$; $J_{AC}=J_{BC}=2,5$)

H_D dddd 7.o2 ($J_{CD}=16$; $J_{DE}=11$; $J_{AD}=J_{BD}=2.5$)

H_E dddd 4.42 ($J_{CE}=8$; $J_{DE}=11$; $J_{EF}=8$; $J_{EG}=1.5$)

H_F dd   3.5o ($J_{FG}=11$; $J_{EF}=8$)

H_G dd   4.26 ($J_{FG}=11$; $J_{EG}=1,5$)

H_H s   7.98

$$H_3C\!-\![C\equiv C]_2\!-\!C$$
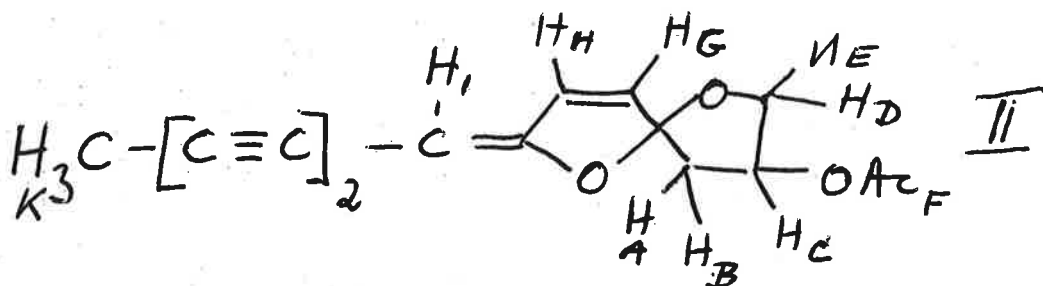
H_A dd 7.82 $(J_{AB}=14;\ J_{AC}=3)^{+)}$

H_B dd 7.32 $(J_{AB}=14;\ J_{BC}=6.6)$

H_C dddd 4.68 $(J_{AC}=3;\ J_{BC}=6.6;\ J_{CD}=4.8;\ J_{CE}\sim 2)$

H_D dd 5.76 $(J_{CD}=4.8;\ J_{DE}=10.1)$

H_E dd 6.14 $(J_{DE}=10.1;\ J_{CE}\sim 2)^{+)}$

H_F s 7.97

H_G dd 4.00 $(J_{GH}=5.5;\ J_{GI}\ 1)$

H_H d 3.89 $(J_{GH}=5.5)$

H_I (dq) 5.46 $(J_{IK}\sim 1.2;\ J_{GI}\ 1)$

H_K d 7.99 $(J_{IK}\sim 1.2)$

+) These signals are broadened, therefore a coupling

of H_A and H_E should be present

The only surprising point in the spectrum of II is the chemical
shift of H_C. The only explanation we could find is the possible
effect of the double bond and perhaps of a free electron pair
on the ringoxygen. In models with a special conformation this
could be understandable. But perhaps one of your readers can
give a better explanation.

- 3 -

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 1oo MHz.
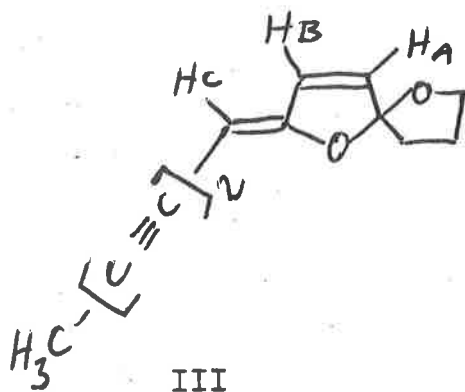
III   IV

H_A dd 3.94 (J_{AD}=5.8; J_{AC}=o.7) H_A dd 3.87 (J_{AB}=5,o; J_{AC}=1.6)

H_B d 3.81 (J_{AB}=5.8) H_B dd 3.39 (J_{AB}=5,o; J_{BC}=o.5)
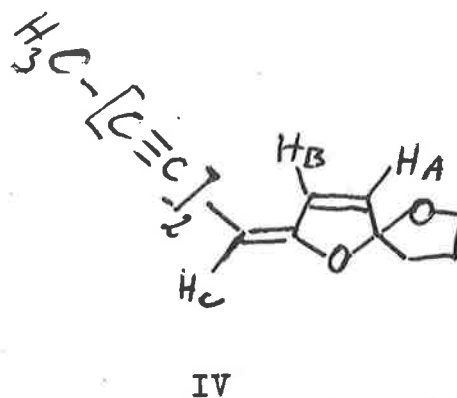
H_C m(dq) 5.55 H_C m(dq) 5.21

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,

F. Bollman

University of Durham

10th November, 1964

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 π-electron charge densities, in
accord with the theories of Karplus and Das [2], and Prosser and Goodman [3],
except when the fluorine nucleus has a neighbour other than fluorine. In
the latter case the ^{19}F shift can be at much lower applied fields than one
would expect from the dependence on π-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 $-B\Delta\langle E^2\rangle$,
where $\Delta\langle E^2\rangle$ 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 $(42-49)\times10^{-18}$ esu. $\langle E^2\rangle$ is given
approximately by

$$\langle E^2\rangle = 3\alpha I/r^6 \qquad\qquad\qquad (1).$$

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

The term $\langle E^2\rangle$ is particulary large for large, polarisable atoms such
as iodine, and because of the dependence on r^{-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 to-
gether than neighbouring ^{19}F's in hexafluorobenzene, consequently the
resonance peaks
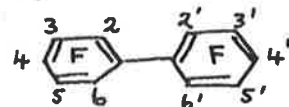
should be at lower applied field than those at positions 4 and 4' where the
π-electron density is similar in magnitude. The observed shifts from C_6F_6
are (2) 24.03, (3) 1.52 (4) 12.01 ppm, all to low field.

/The two....

Professor Shapiro.

The two rings will not be coplanar and θ , the angle of twist, has been calculated from the nmr data in two ways.   Firstly by calculating the π-electron density at positions 4 and 4' as a function of θ 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 $-B\Delta\langle E^2\rangle$.   The two methods give for θ 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}F shifts.   We are at the moment extending this work to other molecules containing sterically hindered fluorine nuclei.

Yours sincerely,

Jim Emsley.

J.W. Emsley.

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

MELLON INSTITUTE

4400 FIFTH AVENUE

PITTSBURGH, PA. 15213

November 10, 1964

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 F^{19} 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

John J. Burke

JJB:jal

Enclosure

MAR. 1, 1965   PENN-SHERATON HOTEL

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

Terrace Room

Monday Morning---   Bernard L. Shapiro, Presiding

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

Terrace Room

Monday Afternoon---   John J. Burke, Presiding
                                           Herbert L. Retcofsky, Presiding

1:00   (   )   NMR Spectra of Aluminum Alkyls--
                                           Kermit C. Ramey, James F. O'Brien and
                                           Alfred E. Borchert, The Atlantic Re-
                                           fining Company

1:20 ( )

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

1:40 ( )

An NMR Study of Proton Exchange in Methyl Substituted Guanidinium Salts--James U. Lowe, Jr., R. Barefoot and A. S. Tompa, U. S. Naval Propellant Plant

2:00 ( )

The Nuclear Magnetic Spectra of Acyclic Linear Terpenes I--Seymour Lemberg, Bernard M. Mitzner, E. T. Theimer and M. Jacobs, International Flavors and Fragrances, Inc.

2:20 ( )

The Nuclear Magnetic Spectra of Cyclic Bicyclic Terpenes II-- Seymour Lemberg, Bernard M. Mitzner, E. T. Theimer and M. Jacobs, International Flavors and Fragrances Inc.

2:40

Recess

3:00 ( )

Identification and Estimaton 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

3:40 ( )

A Study of Some Important Chlorinated Pesticides and Metabolites by Nuclear Magnetic Resonance--P. R. Datta and M. J. Nelson, Food and Drug Administration.

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 Pri-
               marily for Education and Training--
               Leonard Eisner and Frederick Engel,
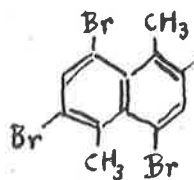   Barnes Engineering Company

Department of Chemistry
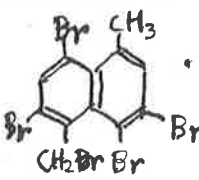Kobe University
Kobe, Japan
Nov. 9, 1964

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

(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 CH_2Br, 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 CH_2Br resonance is a single line. Consequently we in-ferred that II must be . To confirm this inference we reduced II ($CH_2Br \longrightarrow CH_3$) 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

A. Saika

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge 38, Massachusetts, U.S.A.

November 10, 1964

"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-½ observed with a weak rf field H_1 of frequency ω_1 in the presence of a strong rf field H_2 of frequency ω_2 consists of two resonances – one above the line and one below the line. Bloch[1] 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 $A = v_0 + \dfrac{\omega_2}{2\pi}$, $v_0 = \dfrac{-\gamma H_0}{2\pi}$, and $v_2 = \dfrac{-\gamma H_2}{2\pi}$.[2,3] A double resonance spectrum of the proton of $CHCl_3$ obtained by sweeping ω_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 ω_1 equals the irradiating frequency ω_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![1,3] If the resonances in Fig. 1 occur at values of $\omega_1 = \omega_1'$ and ω_1'', 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 ω_1 and detection of the response of the system only at ω_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 ω_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 ω_1, but referencing the synchronous detector to a third frequency ω_3. By sweeping ω_3 for fixed values of ω_1 and ω_2 it is possible to scan the output of the spectrometer for all the signals present for any stimulating frequency ω_1. Such an experiment is straightforward, for example, with the popular frequency-sweep double resonance system[4,5] 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 ω_1, and that the molecule does not perceive ω_3. Since ω_3 is of course not coherent with either ω_1 or ω_2, all phase information is lost, and the phantom signal will appear only as a beat pattern.

A spectrum obtained by sweeping ω_3 with $\omega_1 = \omega_1'$ is shown in Fig. 2. Three beat patterns at $\omega_3 = \omega_1'$, ω_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 ω_3, as well as ω_1 and ω_2. An incredible spectrum results, including four signals coherent with ω_3 (two up and two down) beat patterns at ω_1 and ω_2, and at least two phantom resonances. Are we really obligated to understand everything it is possible to do to a single spin-½?

Best regards,
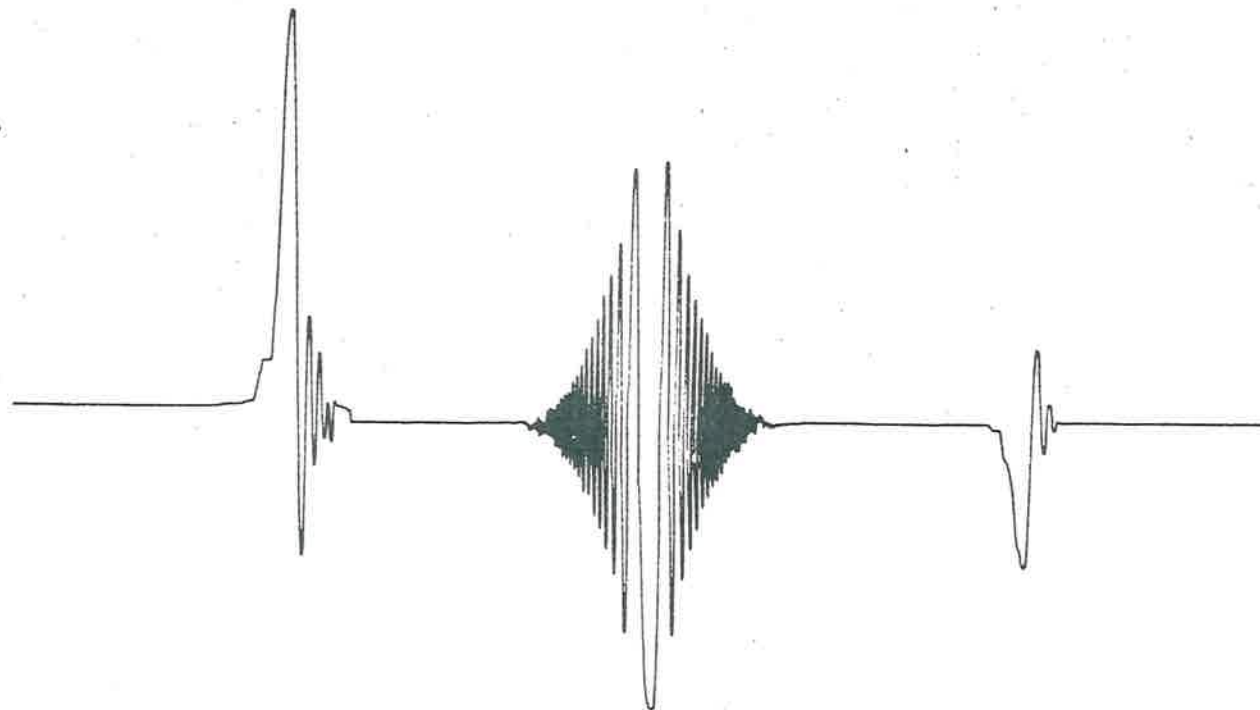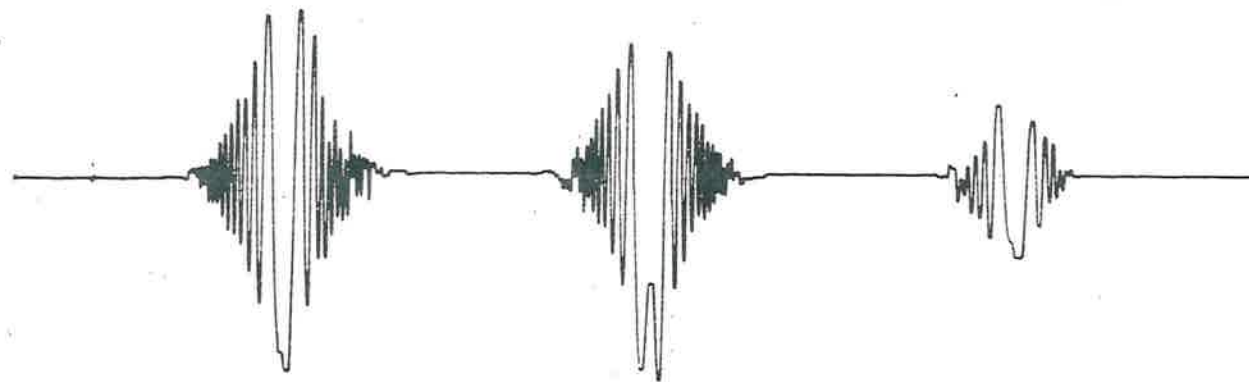
Leslie R. Anders
John D. Baldeschwieler

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1.

2.

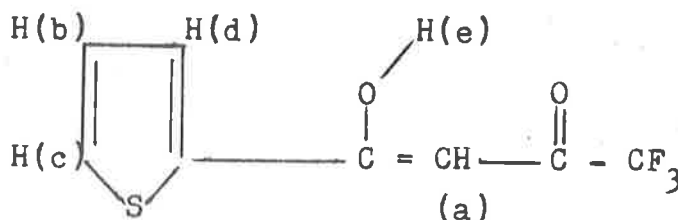W_1' W_2 W_1''

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

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.

- 2 -

Solution	Spectrum	H(a)	H(b)	H(c)	H(d)	H(e)
0.350M TTA	I	6.42	7.22	7.77	7.80	13.93
0.35M TTA, 0.622M TOPO	II	6.55	7.08	7.82	7.98	14.22
0.35M TTA, 1.306M TOPO	III	6.77	7.08	7.95	8.25	14.37

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 $CDCl_3$. It is interesting to note that for the compound
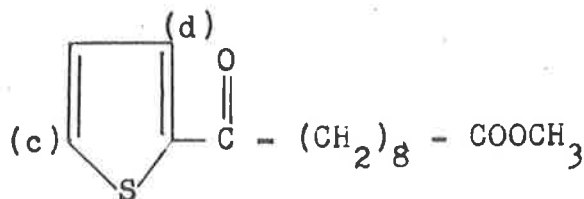
Spectrum No. 320 also lists H(d) further downfield than H(c): 7.70 and 7.62 p.p.m., respectively. In the Spectra Catalog however, no reason is given of the order of assignment. We have shown here a quick method of making frequency assignments by observing the downfield shifts caused by the presence of 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 CCl_4 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.
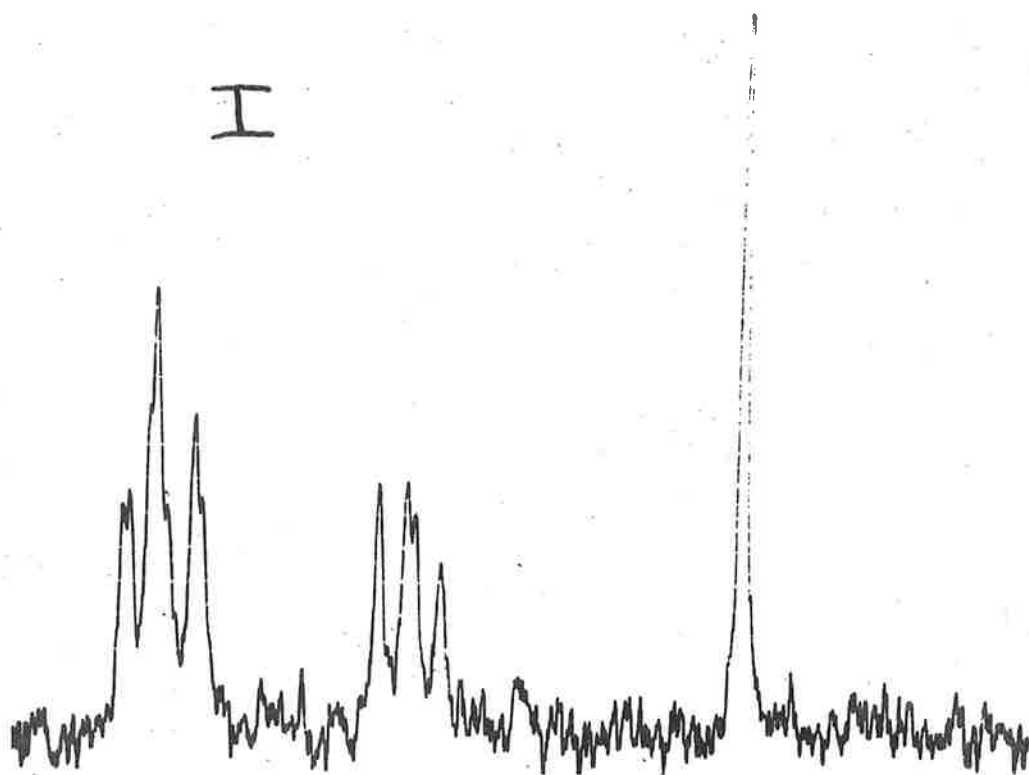
The IIT NMR Newsletter has been very helpful, and we regret the delay in sending in our contribution. The excuse is that one of us has only recently returned from a six-month sabbatical leave, which was spent as a Visiting Professor in Taiwan.

Sincerely,

Norman C. Li

George Pukanic

I

II

III

8.5   8.0   7.0   δ ppm   6.0
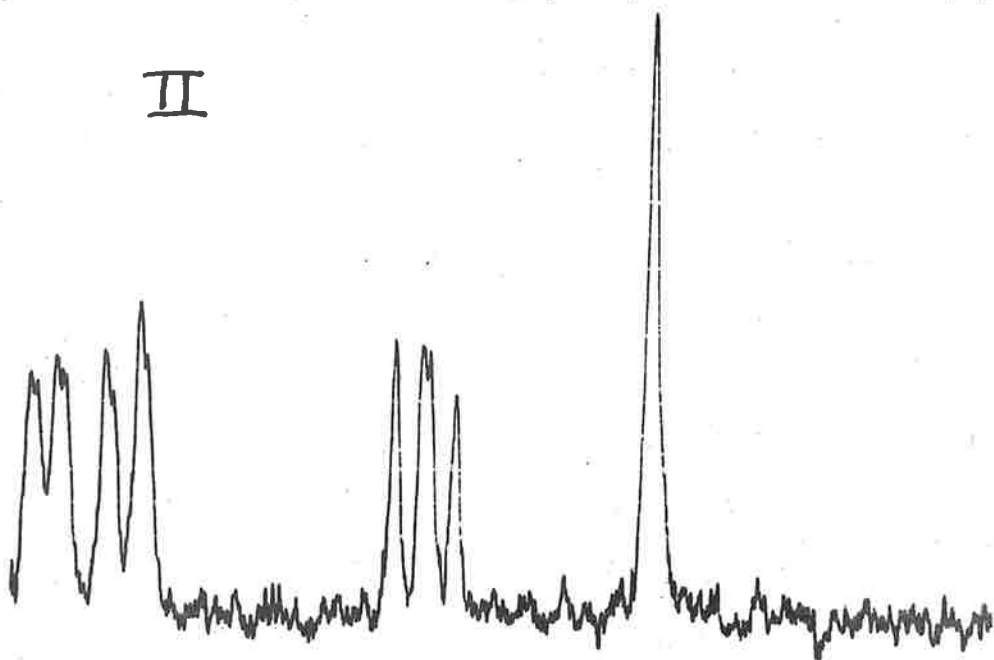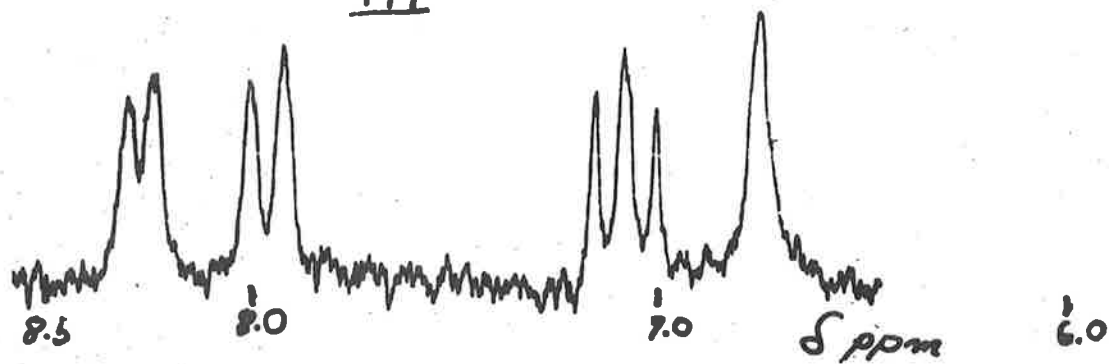
Mobil

Socony Mobil Oil Company, Inc.

PRINCETON, NEW JERSEY 08534
BOX 1025

RESEARCH DEPARTMENT
CENTRAL RESEARCH DIVISION LABORATORY

November 17, 1964

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 $A_{n_A} B$. 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. $\underline{60}$, 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 $A_{n_A} B$ 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

6th ENC (E X P E R I M E N T A L   N M R   C O N F E R E N C E)

6th ENC Committee

C. A. Reilly, Chairman
B. L. Shapiro, Sec'y-Treas.
P. C. Lauterbur, ex officio
A. A. Bothner-By, local arrngmnts
M. M. Crutchfield
J. E. LuValle
P. R. Shafer

Address correspondence to:

Dr. C. A. Reilly
Chairman, 6th ENC
Shell Development Co. **or**
4560 Horton Street
Emeryville, Calif. 94608

Dr. B.L. Shapiro
Sec'y-Treas., ENC
Dept. of Chemistry
Ill. Inst. of Tech.
Technology Center
Chicago, Ill. 60616

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)
F.A.L. Anet, Department of Chemistry, Univ. of California, Los Angeles, 405 Hilgard Ave., Los Angeles, California, 90024

Field/Frequency Control Methods:
(1 session)
S.L. Manatt, Jet Propulsion Laboratory, Calif. Inst. of Tech., 4800 Oak Grove Drive, Pasadena, California, 91103

Signal-to-noise Improvement:
(2 sessions)
C.H. Sederholm, Department of Chemistry, Univ. of Calif. at Berkeley, Berkeley, California, 94720

Superconducting Solenoids:
(1 session)
D.D. Elleman, Jet Propulsion Laboratory, Calif. Inst. of Technology, 4800 Oak Grove Drive, Pasadena, California, 91103

Variable Temperature Equipment and Methods:
(2 sessions)
P.R. Shafer, Department of Chemistry, Dartmouth College, Hanover, New Hampshire, 03755

Pulse Techniques and Relaxation:
(1 session)
D.W. McCall, Bell Telephone Laboratories, Inc., Post Office Box 261, Murray Hill, New Jersey

NMR of "Uncommon" Nuclei:
(1 session)
P.C. Lauterbur, Department of Chemistry, State Univ. of New York at Stony Brook, Stony Brook, Long Island, New York

Spectral Analysis Techniques:
(2 sessions)
D.M. Grant, Department of Chemistry, Univ. of Utah, Salt Lake City, Utah, 84112

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 limitation 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.

"Synthesis of Branched-chain Amino-sugars"
S. W. Gunner, W. G. Overend and N. R. Williams
Chem. Ind. 1523 (1964)

"Structure of Nudiflorine, a Naturally Occuring Isomer of
   Ricinidine"
R. Mukherjee and A. Chatterjee
Chem. Ind. 1524 (1964)

"Total Synthesis of dl-Anatabine"
P. M. Quan, T. K. B. Karns and L. D. Quin
Chem. Ind. 1553 (1964)

"Reaction of Acyl Azides with Norbornylene"
L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat and R. L. Hale
Chem. Ind. 1556 (1964)

"Absolute Configuration of Dendrobine"
Y. Inubushi, E. Katarao, Y. Tsuda and B. Yasui
Chem. Ind. 1689 (1964)

"1-Methyl-3,4-methylene-3,4-dihydroquinolin-2-one(s).
   Derivatives of a new ring system, the 1-H-cycloprop(c)
   quinolines"
B. Loev, M. F. Kormendy and K. M. Snader
Chem. Ind. 1710 (1964)

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

"Long Range Proton Spin Coupling over Four Bonds"
E. W. Garbisch, Jr.
Chem. Ind. 1715 (1964)

"X-Ray Diffraction Studies of the Conformation of Polymer
   Molecules in Solution. I. p-Iodopolystyrene"
G. W. Brady and R. Salovey
J. Am. Chem. Soc. 86, 3499 (1964)

"The Boron-11 Nuclear Magnetic Resonance Spectrum of $B_{20}H_{18}^{2}$
   at 60 Mc./sec."
R. L. Pilling, M. F. Hawthorne and E. A. Pier
J. Am. Chem. Soc. 86, 3568 (1964)

"A 2,3-Diazacyclopropanone (Di-t-butyldiaziridinone)"
F. D. Greene and J. C. Stowell
J. Am. Chem. Soc. 86, 3569 (1964)

"Proton-^{13}C Spin-Spin Coupling. V. Inadequacy of Correlation
   of Proton-^{13}C Coupling with s-Character"
G. J. Karabatsos and C. E. Orzech, Jr.
J. Am. Chem. Soc. 86, 3574 (1964)

"Substituent Effects. III. Correlation of ^{13}C-F and ^{29}Si-H
   Couplings by Pairwise Interactions"
E. R. Malinowski and T. Vladimiroff
J. Am. Chem. Soc. 86, 3575 (1964)

"Ring Inversion and Bond Shift in Cyclooctatetraene Deriva-
   tives"
F. A. L. Anet, A. J. R. Bourn and Y. S. Lin
J. Am. Chem. Soc. 86, 3576 (1964)

"The Amount of   -Bonding in Phosphorus-Oxygen and Sulfur-
   Oxygen Bonds"
P. Haake, W. B. Miller and D. A. Tyssee
J. Am. Chem. Soc. 86, 3577 (1964)

"Photochemical Cycloaddition as a Device for General Annelation"
H. Hikino and P. DeMayo
J. Am. Chem. Soc. 86, 3582 (1964)

"1-Dicyanomethylene-2,3-diphenylvyclopropene ("1,1-Dicyano-
   3,4-diphenyltriafulvene")"
E. D. Bergmann and I. Agranat
J. Am. Chem. Soc. 86, 3587 (1964)

"The Tropylium-Iron Tricarbonyl Cation"
J. E. Mahler, D. A. K. Jones and R. Pettit
J. Am. Chem. Soc. 86, 3589 (1964)

"New Methods of Introducing the Carbo-t-butoxy Amino-Protect-
   ing Group. Preparation and Use of t-Butyl Cyanoformate and
   t-Butyl Iminodicarboxylate."
L. A. Carpino
J. Org. Chem. 29, 2820 (1964)

"Alkaline Degradation of 1,1-Disubstituted Sulfonhydrazides.
   Synthesis of a Pair of Cyclic, Benzylic Hydrazines Derived
   from Acenaphthene and Acenaphthylene"
L. A. Carpino and S. Göwecke
J. Org. Chem. 29, 2824 (1964)

"The Reaction of Norbornene with t-Butyl Hypochlorite and the
   Stereoisomeric 2,3-Chlorohydroxybicyclo[2.2.1]heptanes"
E. Tobler, D. E. Battin and D. J. Foster
J. Org. Chem. 29, 2834 (1964)

"The Reaction of Norbornene with Polyhalomethanes and the
   Behavior of the Adducts towards Acid and Base"
E. Tobler and D. J. Foster
J. Org. Chem. 29, 2839 (1964)

"Trimethylsilyl-Substituted Norbornenes, Norbornanes, and
   Nortricyclene"
H. G. Kuivila and C. R. Warner
J. Org. Chem. 29, 2845 (1964)

"Cyclodehydration Reactions of Tryptamine Derivatives with
   Acetone"
J. B. Hester, Jr.
J. Org. Chem. 29, 2864 (1964)

"The Structure of Amidoximes"
C. L. Bell, C. N. V. Nambury and L. Bauer
J. Org. Chem. 29, 2873 (1964)

"Hydrogenation in the Pyridine Series. I. Catalytic Reduc-
   tion of the Isomeric Acetylpyridines"
M. Freifelder
J. Org. Chem. 29, 2895 (1964)

"Thermal Cleavage of 1,1'-Diacetyl-1,1',4,4'-tetrahydro-
   4,4'-bipyridine"
A. T. Nielsen, D. W. Moore, J. H. Mazur and K. H. Berry
J. Org. Chem. 29, 2898 (1964)

"The Synthesis of 2,4,6-Trisubstituted Pyrido[2,3-d]pyrimi-
   dines from 2-Amino-3,5-Dicyanopyridine"
D. M. Mulvey, S. G. Cottis and H. Tieckelmann
J. Org. Chem. 29, 2903 (1964)

"Preparation and Properties of 2- and 3-Bromo-1-methylcyclo-
   hexanes"
E. N. Marvell and H. Sexton
J. Org. Chem. 29, 2919 (1964)

"The Structure and Reactions of the 1:1 Adduct of Benzene-
   sulfonyl Azide and Bicyclo[2.2.1]heptene"
J. E. Franz, C. Osuch and M. W. Dietrich
J. Org. Chem. 29, 2922 (1964)

"The Reactions of Sulfonamides with Oxalyl Chloride"
J. E. Franz and C. Osuch
J. Org. Chem. 29, 2592 (1964)

"The Furanoquinoline Alkaloids. II. Synthetic Approaches
to Demethoxylunacrine"
J. W. Huffman and L. E. Browder
J. Org. Chem. 29, 2598 (1964)

"Furazan Oxides. IV. Extensions of the Scope of the Halo-
alkoxy Substitution Reaction"
F. B. Mallory, C. S. Wood and B. M. Hurwitz
J. Org. Chem. 29, 2605 (1964)

"Terpenes. XIV. The Reaction of Pulegone with Lead Tetra-
acetate"
L. H. Zalkow and J. W. Ellis
J. Org. Chem. 29, 2626 (1964)

"The Isotopic Substitutions of 4-Pyrone"
P. Beak and G. A. Carls
J. Org. Chem. 29, 2678 (1964)

"Exchange Reactions of 4-Pyrone and 4-Pyrone Derivatives"
D. W. Mayo, P. J. Sapienza, R. C. Lord and W. D. Phillips
J. Org. Chem. 29, 2682 (1964)

"A Comparison of Alkylpotassium and Alkylsodium Reagents in
Metalation of α-Olefins"
C. D. Broaddus
J. Org. Chem. 29, 2689 (1964)

"Coordination in Solutions. II. Acid Dissociation Constants
in Water and Structural Reassignments of the Isomeric
Chlorosalicylaldehydes"
C. Postmus, Jr., I. A. Kaye, C. A. Craig and R. S. Matthews
J. Org. Chem. 29, 2693 (1964)

"The Addition of Dimethyl Sulfoxide Anion to Olefins and the
Pyrolysis of Sulfoxides"
C. Walling and L. Bollyky
J. Org. Chem. 29, 2699 (1964)

"The Chlorination of Active Hydrogen Compounds with Sulfuryl
Chloride. II. Esters, Nitriles, Nitro Compounds, and Alde-
hydes"
D. P. Wyman, P. R. Kaufman and W. R. Freeman
J. Org. Chem. 29, 2706 (1964)

"The Action of Alumina on α- and β-Amyrin Sulfonate Esters"
F. Kohen, B. K. Patnaik and R. Stevenson
J. Org. Chem. 29, 2710 (1964)

"1H-2,1,3-Benzothiadiazin-4(3H)-one 2-Oxides"
A. A. Santilli and T. S. Osdene
J. Org. Chem. 29, 2717 (1964)

"The Chemistry of 4-Benzyl-2H,3H-thieno[3,2-b]pyrrol-3-one.
I. Reactions with N-Bromosuccinimide and with Aldimines"
E. T. Holmes and H. R. Snyder
J. Org. Chem. 29, 2725 (1964)

"Synthesis of Substituted 2,2'-Bipyrroles"
H. Rapoport and J. Bordner
J. Org. Chem. 29, 2727 (1964)

"Steroids. CCLXI. Microbiological Hydroxylation of Estrane
Derivatives with Fusarium moniliforme"
P. Crabbé and C. Casas-Campillo
J. Org. Chem. 29, 2731 (1964)

"The Preparation of Allylic Alcohols from Citral a and Citral
b. A Study of Their Dehydration Reactions"
P. B. Venuto and A. R. Day
J. Org. Chem. 29, 2735 (1964)

"Reaction of Cyclohexene with a "Thermal Dichlorocarbene" from
Chloroform"
F. E. Kung and W. E. Bissinger
J. Org. Chem. 29, 2739 (1964)

" gem-Dimetallic Compounds. Ethane-1,1-diboronic Acid and
Ethylidenedimercuric Chloride"
D. S. Matteson and J. G. Shdo
J. Org. Chem. 29, 2743 (1964)

"Preparation of Tetracyclines by Photooxidation of Anhydro-
tetracyclines"
M. Schach von Wittenau
J. Org. Chem. 29, 2746 (1964)

"Restricted Internal Reorientation in Large-Ring N-Methyl-
lactams as Evidenced by Nuclear Magnetic Resonance"
R. M. Moriarty
J. Org. Chem. 29, 2748 (1964)

"Synthesis and Structures of α-Tolyl- and α-Xylylisobutyric
Acids"
J. L. Adelfang, Ellis K. Fields and E. M. Banas
J. Org. Chem. 29, 2753 (1964)

"The Products of Treatment of Acetylandromedol and 10-Deoxy-
acetylandromedol with Cupric Sulfate in Acetone"
W. H. Tallent
J. Org. Chem. 29, 2756 (1964)

"Photochemical Transformations. XVII. The Photochemistry of
Palustric Acid"
W. G. Dauben and R. M. Coates
J. Org. Chem. 29, 2761 (1964)

"Ketene Acetals. I. A New Synthesis of Ketene Acetals and
Ortho Esters"
W. C. Kuryla and D. G. Leis
J. Org. Chem. 29, 2773 (1964)

"The Synthesis of Certain 16α-Substituted Derivatives of the
3-Methyl Ethers of 16β-Cyanoestrone and 16β-Cyanoestradiol"
R. E. Schaub, H. M. Kissman and M. J. Weiss
J. Org. Chem. 29, 2775 (1964)

"Substituted γ-Lactones. XV. Condensation between
Phthalide and Benzaldehyde"
H. Zimmer, R. D. Barry and F. Kaplan
J. Org. Chem. 29, 2778 (1964)

"Unsaturated Lactams from Ketones and Acrylonitrile"
J. J. Vill, T. R. Steadman and J. J. Godfrey
J. Org. Chem. 29, 2780 (1964)

"Preparation of the γ-Lactone and γ-Lactam of 5-Methyl-4-
oxo-2-hexenoic Acid"
D. L. Roberts
J. Org. Chem. 29, 2785 (1964)

"On the Occurrence of the Santolinenones. Terpenes. XV."
L. H. Zalkow, D. R. Brannon and J. W. Uecke
J. Org. Chem. 29, 2786 (1964)

"The Rearrangement of 2-Methylcyclohexylidene"
J. W. Wilt and W. J. Wagner
J. Org. Chem. 29, 2788 (1964)

"The Reactions of 1,1-Di(1-piperidinyl)ethylene with Isocyanates and Isothiocyanates"
D. H. Clemens, A. J. Bell and J. L. O'Brien
J. Org. Chem. 29, 2932 (1964)

"Chemistry of gem-Dihalocyclopropanes. II. The Reaction of Dienes with Dibromocarbene"
L. Skattebøl
J. Org. Chem. 29, 2951 (1964)

"The Reaction of Tetramethyl-1,3-cyclobutanedione with Triphenylphosphinemethylene"
E. A. LaLancette
J. Org. Chem. 29, 2957 (1964)

"Azohydrazone Conversion. II. The Coupling of Diazonium with β-Diketones"
H. C. Yao
J. Org. Chem. 29, 2959 (1964)

"Geometric Isomers of 2,3-Dimethyl-5-aryl-2,4-pentadienoic Acids. The Steric Factors Favoring 2-cis Formation"
R. H. Wiley, C. E. Staples and T. H. Crawford
J. Org. Chem. 29, 2986 (1964)

"The Meerwein Arylation of Vinyl Sulfones"
W. E. Truce, J. J. Breiter and J. E. Tracy
J. Org. Chem. 29, 3009 (1964)

"Synthesis and Study of Pseudo-Aromatic Compounds. II. The Synthesis of Indeno[5´,6´-4,5]-2,7-dicarboethoxytropone"
D. J. Bertelli
J. Org. Chem. 29, 3032 (1964)

"Aziridines from Diazomethane and Fluorine-Substituted Imines"
A. L. Logothetis
J. Org. Chem. 29, 3049 (1964)

"Dianhydrophenylosazone Acetates from Isomaltose and Gentiobiose"
H. El Khadem
J. Org. Chem. 29, 3072 (1964)

"Phenylcyclobutane Amino Acids"
A. Burger and W. E. Coyne
J. Org. Chem. 29, 3079 (1964)

"Conformations of Bicyclo[3.3.1]nonanes. 3-Methyl-2,4-dioxabicyclo[3.3.1]nonane"
E. N. Marvell and S. Provant
J. Org. Chem. 29, 3084 (1964)

"The Structure of 1,3-Naphthalenediol Anion"
E. Smakula Hand and R. M. Horowitz
J. Org. Chem. 29, 3088 (1964)

"Conformational Analysis of a Disultone"
J. H. Markgraf and R. W. King
J. Org. Chem. 29, 3094 (1964)

"Monochloro Products from Camphene. Identification of Camphenol as 6-Hydroxycamphene"
H. G. Richey, Jr., T. J. Garbacik, D. L. Dull and J. E. Grant
J. Org. Chem. 29, 3095 (1964)

"Nitrene Chemistry. An Analysis of the Products from the Pyrolysis of 2-Butylazidobenzene"
G. Smolinsky and B. I. Feuer
J. Org. Chem. 29, 3097 (1964)

"A Stable Intermediate in the Hantzsch-Beyer Reaction"
K. L. Marsi and K. Torre
J. Org. Chem. 29, 3102 (1964)

"1,5-Dibromoadamantane-2,6-dione Synthesis and Rearrangement to Tricyclo[3.3.0.0^{3,7}]-octane-1,3-dicarboxylic Acid"
O. W. Webster and L. H. Sommer
J. Org. Chem. 29, 3103 (1964)

"The Preparation and Nuclear Magnetic Resonance Spectrum of the Cyclic Sulfite of 1,1-Dimethylol-3-cyclopentene"
E. J. Grubbs and D. J. Lee
J. Org. Chem. 29, 3105 (1964)

"Proton Magnetic Resonance and Stereochemistry of 2-o-Tolyl-3-(2-hydroxyethyl)cyclohexanol and Related Compounds"
D. C. Staiff and A. C. Huitric
J. Org. Chem. 29, 3106 (1964)

"Photochemical Rearrangements of Cross-Conjugated Cyclohexadienones. V. A Model for the Santonin Series"
P. J. Kropp
J. Org. Chem. 29, 3110 (1964)

"Diels-Alder Reactions of Acyclic Fluoro Ketones"
W. J. Linn
J. Org. Chem. 29, 3111 (1964)

"Fluoro Ketones. II. Reaction of Amides with Fluoroacetones"
P. E. Newallis and E. J. Rumanowski
J. Org. Chem. 29, 3114 (1964)

"A New Bicyclic Thiete Sulfone"
D. C. Dittmer and F. A. Davis
J. Org. Chem. 29, 3131 (1964)

"Synthesis, Proton Magnetic Resonance, and Stereochemistry of Certain o-Tolylcyclohexanediols"
J. B. Carr and A. C. Huitric
J. Org. Chem. 29, 2506 (1964)

"Ketenes. III. Cycloaddition of Ketenes to Acetylenic Ethers"
R. H. Hasek, P. G. Gott and J. C. Martin
J. Org. Chem. 29, 2510 (1964)

"The Addition of Silicon Hydrides to Olefinic Double Bonds. X. Addition to Phenylalkenes. The Nuclear Magnetic Resonance Proton Spectra of (Phenylalkyl)silanes"
M. C. Musolf and J. L. Speier
J. Org. Chem. 29, 2519 (1964)

"Stereochemical Studies of Octahydrophenanthrenes. I. "
Z. G. Hajos, K. J. Doebel and M. W. Goldberg
J. Org. Chem. 29, 2527 (1964)

"Sesquiterpene Lactones. Coronopilic Acid"
T. A. Geissman and R. J. Turley
J. Org. Chem. 29, 2553 (1964)

"Enamine Chemistry. VIII. Reactions eith Miscellaneous Carbonyl and Active Hydrogen Compounds"
K. C. Brannocl, R. D. Burpitt, H. E. Davis, H. S. Pridgen and J. G. Thweatt
J. Org. Chem. 29, 2579 (1964)

"Phenylcyclobutane Amino Alcohols and Amino Ketones"
A. Burger and H. H. Ong
J. Org. Chem. 29, 2588 (1964)

"Steric Course in Cycloaddition of Chlorotrifluorethylene"
W. C. Solomon and L. A. Dee
J. Org. Chem. 29, 2790 (1964)

"A Reinvestigation of the Condensation of Ethyl Tricarbally-
  late with Benzaldehyde"
J. R. Wiseman
J. Org. Chem. 29, 2793 (1964)

"The Preparation of Parabanic Acids from 1,1,3-Trisubstituted
  Ureas via a Hofmann Elimination Reaction"
P. J. Stoffel
J. Org. Chem. 29, 2794 (1964)

"Phenolic Metabolite of "Low-Iron Fermentation" of Streptomy-
  ces griseus. Characterization of 2,3-Dihydroxybenzoic Acid"
J. R. Dyer, H. Heding and C. P. Schaffner
J. Org. Chem. 29, 2802 (1964)

"1-Methoxy- and 1-Ethoxyazulene"
L. L. Replogle
J. Org. Chem. 29, 2805 (1964)

"The Reaction of Diethyl Malonate with Styrene Oxide"
C. H. DePuy, F. W. Breitbeil and K. L. Eilers
J. Org. Chem. 29, 2810 (1964)

"Derivatives of 1,4-Xylene-2,5-diboronic Acid and 1,4-Xylene-
  2-boronic Acid"
J. F. Cairns and H. R. Snyder
J. Org. Chem. 29, 2810 (1964)