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Newsletter

FILE

No. 174

March, 1973

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All Newsletter correspondence, etc. should be addressed to:

Bernard L. Shapiro
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Texas A&M University
College Station, Texas 77843

(ii)

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MILL HILL,
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23rd February 1973

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

Dear Professor Shapiro,

^{13}C relaxation times in n-alkanes

Now that ^{13}C T_1 measurements are (relatively) straightforward, we, in common with many other people, are interested in using them to study segmental motion in biological systems - such as amino-acid sidechains in proteins, and hydrocarbon chains in lipid bilayers and membranes (1). Using an extension (2) of the method of Wallach (3), we have used the ^{13}C T_1 values measured in lipid bilayers to estimate the rates of motion about individual bonds of the hydrocarbon chains in these systems (4).

One of the interesting questions about the motion of hydrocarbon chains in a bilayer is the extent to which they are modified by chain packing. As an approach to this problem, Drs. Lee, Birdsall and Metcalfe have measured the ^{13}C T_1 's of all the resolved resonances in a series of n-alkanes from C6 to C18. The values for C6-C10 (for which all the carbon resonances can be resolved) are given in Table 1; the dominant relaxation mechanism appears to be the ^{13}C - ^1H intramolecular dipolar interaction. From these values we have calculated the individual rotational diffusion constants, using an extension of our earlier method to take account of the anisotropic motion of these molecules. We assumed that the alkane molecules behaved as prolate ellipsoids, with $D_z > D_x = D_y$ (where D_n is the diffusion coefficient about the n th molecular axis), and that the ratio D_z/D_x is given by the ratio of moments of inertia about these axes. Initially, we assumed that the diffusion coefficients for motion about the bonds (D_i) were constant along the chain. Somewhat to our surprise, we found that this crude model was able to give a good fit to the data for all the carbons except the terminal methyl; we had to introduce faster motion about the terminal bond. The values of the various diffusion coefficients obtained are given in Table 2. We were gratified to find that only a $\pm 15\%$ variation in these diffusion coefficients was possible if the T_1 values for all the

carbons were to be fitted to within the experimental error. This encourages us to believe that T_1 measurements of this sort will indeed be very valuable for quantitative studies of internal motion in a variety of systems. In the alkanes it is striking that an appreciable gradient of T_1 values along the chain is seen, even though the motion about the bonds is slower than that about the long axis of the molecule.

Comparison of the diffusion coefficients D_i found for hexadecane with those in a dipalmitoyl (C16) lecithin bilayer shows that the rates of motion about bonds near the terminal methyl are closely similar in the two systems, but the rates for bonds close to the glycerol group in the bilayer are more than an order of magnitude slower than for the alkane. Chain packing thus has a substantial effect at the glycerol end, but little or no effect at the terminal methyl end of the chains in the bilayer.

Yours sincerely,



G. C. K. Roberts

- (1) Levine, Birdsall, Lee & Metcalfe. Biochemistry, 11, 1416 (1972)
Metcalfe, Birdsall & Lee. FEBS Symposium, in press.
- (2) Levine, Partington & Roberts. Molecular Physics, in press
(March, 1973)
- (3) Wallach. J. Chem. Phys., 47, 5258 (1967)
- (4) Levine, Partington, Roberts, Birdsall, Lee & Metcalfe.
FEBS Letters, 23, 203 (1972).

Table 1. ^{13}C T_1 values (seconds) in alkanes

	Carbon number ^a				
	1 ^b	2	3	4	5
Hexane	21.22 \pm 0.69	14.78 \pm 0.99	15.87 \pm 0.92		
Octane	12.76 \pm 0.14	10.94 \pm 0.38	10.11 \pm 0.30	9.58 \pm 0.22	
Decane	8.74 \pm 0.14	6.64 \pm 0.11	5.71 \pm 0.10	4.95 \pm 0.07	4.36 \pm 0.29

a Counting from the terminal methyl as carbon 1

b Multiplied by 3/2 to facilitate comparison with the other values
 T_1 values were measured at 25.2MHz on a Varian XL-100-15 using
the standard 180°-t-90° sequence. Samples were degassed, and the
probe temperature was 31°C.

Table 2. Rotational diffusion coefficients (all 10^{11} sec^{-1})

	D_z	$D_x = D_y$	D_i	D_ω^a
Hexane	2.6	0.35	0.20	0.9
Octane	1.4	0.113	0.17	0.3
Decane	1.0	0.064	0.115	0.3

a Diffusion constant for motion about the bond to the terminal
methyl

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Feb. 8, 1973

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

Dear Dr. Shapiro;

CHEMICAL SHIFT PAIRWISE INTERACTION PARAMETERS: APPLICATION TO DONOR-ACCEPTOR INTERACTIONS:

In our studies of halogen redistribution in tetrahedral boron compounds we have become interested in explaining the trends in ^{19}F and ^{11}B nmr parameters of the mixed boron trihalide adducts. It turns out that the ^{19}F and ^{11}B chemical shifts and ^{11}B - ^{19}F coupling constants can be correlated by pairwise additivity parameters (1), but not by direct additivity parameters. Thus, for example, the ^{19}F chemical shift can be expressed as $\delta^{19}\text{F} = \sum \eta_{i,j}$; where $\eta_{i,j}$ is a parameter associated with substituents i and j and independent of all other substituents. The sum is taken over all boron substituents, except the nucleus being observed in the nmr experiment. Therefore, for the adduct $\text{D.BF}_2\text{Cl}$

$$\delta^{19}\text{F} = \eta_{\text{D},\text{F}} + \eta_{\text{D},\text{Cl}} + \eta_{\text{F},\text{Cl}}.$$

The table shows donor-halogen ^{19}F chemical shift pairwise parameters $\eta_{i,j}$ determined from a number of mixed and unmixed boron trihalide adducts. The halogen-halogen parameters are practically identical to those reported previously for the mixed tetrahaloborate anions (2). The donor-halogen parameters show interesting trends. For the "hard" oxygen and nitrogen donors the parameters show a pronounced decrease in the order $\eta_{\text{D},\text{F}} > \eta_{\text{D},\text{Cl}} > \eta_{\text{D},\text{Br}}$, whereas the reverse order is found for the "soft" donors Me_2S and Me_3P . Donors of intermediate hardness (e.g. 4-methylpyridine) show small variations in the parameters over the series F, Cl, Br. Interpretation of this trend, and of others which occur in the ^{11}B chemical shift and ^{11}B - ^{19}F coupling constant pairwise interaction parameters, should indicate something about changes in the nature of the donor-acceptor bond between hard and soft donors.

It is also of interest that oxygen donors give rather similar differences between $\eta_{\text{D},\text{F}}$ and $\eta_{\text{D},\text{Cl}}$ and (where data is available) between $\eta_{\text{D},\text{Cl}}$ and $\eta_{\text{D},\text{Br}}$, which are distinct from the differences in these terms when any other donor atom is involved. Thus the pairwise parameters seem to provide an indication of the donor site when the Lewis base has more than one possible donor atom. The data is consistent with the already established oxygen donation in tetramethylurea (3) and dimethylacetamide, and indicates oxygen donation in MeC(O)SMe in accord with other evidence which we hope to publish shortly. It should be possible to develop these parameters so that they give a reliable indication of donor site, and thus are of empirical use in adduct systems.

Yours Sincerely,

Steve Hartman *Jack M. Miller*
J.S. Hartman and J.M. Miller
Assoc. Prof. Assoc. Prof.

References

- (1) T. Vladimiroff and E.R. Malinowski; J. Chem. Phys., 46, 1830 (1967).
 (2) J.S. Hartman and G.J. Schrobilgen; Inorg. Chem., 11, 940 (1972).
 (3) J.S. Hartman and G.J. Schrobilgen; Can. J. Chem., 50, 713 (1972).

TABLE

PAIRWISE SUBSTITUENT PARAMETERS $\eta_{i,j}$ for ^{19}F CHEMICAL SHIFTS: *(A) η halogen, N-donor

	Me_3N	4-Mepy	CH_3CN
F	56.45	45.48	45.60
Cl	50.59	43.67	43.70
Br	47.12	41.86	

(B) η halogen, O-donor

	Me_2O	MeOEt	acetone	MeOAc	EtOAc
F	53.78	52.66	48.84	49.37	49.27
Cl	42.46	42.31	39.80	40.33	40.21
Br	38.69	-	-	36.74	37.56

	Me_3PO	TMU	DMAC	MeC(O)SMe
F	47.24	49.46	48.96	48.78
Cl	36.95	37.41	39.37	39.49
Br	-	-	-	36.84

(C) η halogen, Soft donor

	Me_3P	Me_2S	Me_3PS	MeC(S)OMe
F	43.32	43.96	33.84	41.2
Cl	51.41	45.91	33.10	-
Br	55.29	-	-	-

*Chemical shift data: ppm to high field of internal CFCl_3 .

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February 12, 1973

Professor B. L. Shapiro
Texas A & M University
College of Science
College Station, Texas 77843

Title: CAT Trigger for Use with the Varian HALOOD NMR Spectrometer

In these laboratories we have developed a method of using the CAT which requires neither internal trigger compounds nor the movement of the carriage to trigger the CAT. This method makes use of the BCD output taken from the V-4315A frequency counter which is applied through thumbwheel switches to a multiple input gate and produces a trigger pulse on completion of the flyback sweep of the CAT.

Since the V-4315A is not provided with a BCD output it is necessary to bring out wires from the input to the readout modules as shown in Fig. 1. Four wires for each of the five decades plus one each for ground and HOLD are required. The BCD outputs are connected to the inputs of five 7475 Quad Latches (one for each decade). The HOLD output is connected through one input of a 7430 eight input NAND gate (the other seven inputs are paralleled and connected to a voltage divider across the power supply) which feeds the paralleled inputs of a 7440 dual four input NAND buffer, the outputs of which drive the enable terminals of the quad latches, Fig. 2. The outputs of the latches (BCD plus complement) are connected to the corresponding terminals of five GE Type CR 103FX 11 CC, BCD with complement thumbwheel switches, through germanium computer type isolating diodes. The common terminal of each switch goes to an input of a 7430 NAND Gate. The output of this gate drives a saturated switch consisting of R_3 , R_4 , and Q_1 ; the collector of Q_1 is capacitively coupled to the external trigger input of the CAT. An operational amplifier (Analog Devices Type 233J) connected in the inverting mode with provisions for adjustable negative gain (Fig. 3) is inserted between the CAT ramp output and the VCG input of a function generator (Wave-Tek 115). The adjustable amplitude sine wave output from the front panel of the 115 is connected to the SWEEP OSC OUT J-1307 (really sweep osc. in) BNC jack on the rear of V-4354A, and also to the EXT OSC binding posts on the left-hand side of the Mode Selector

Panel V-4391. Polarity must be observed in making these connections. It is necessary to operate the CAT in controlled flyback mode at the slowest flyback rate (FLYBACK control in extreme clockwise position). To do this with an external trigger the search ramp must be disabled by removing cards number 56 and 57 from the CAT. The trigger requires about 200 mA. at 5V. An Analog Devices Model 903 (5V @ 500 mA.) or equivalent may be used. We chose to build our own on the same printed circuit board. It is also possible that the V-4315A might handle the load.

Calibration - With the recorder carriage set on the left-hand index of the recorder paper (1000 Hz at 1000 Hz sweep width), the thumbwheel switches at some value greater than 3500 Hz, note the value of the internal sweep oscillator (3500 Hz) by reading the frequency counter with SIG MON on SWEEP FREQ. Set the SIG MON to EXT and adjust the output frequency of the function generator (Wave-Tek) to match that of the internal oscillator (3500 Hz) with a 1-volt output. When the thumbwheel switches are set to this exact value (3500 Hz) the CAT should trigger and scan to the right. The 10-turn pot on the op. amp. should be adjusted so that the end of trace occurs at 2500 Hz. It may be necessary to repeat adjustments at each end more than once to obtain perfect agreement at both ends. If the function generator output is off by as little as 1 Hz from the setting on the thumbwheel switches, no trigger pulse will be obtained.

A brief description of the operation of the HALOOD/CAT combination follows. To set up an experiment: First on the CAT - Set the FLYBACK control in the full clockwise setting and set EXT TRIG. Then considering the area of interest in the spectrum set up the required sweep time controls and all other controls for normal CAT operation.

On the HALOOD, first to avoid triggering, set the thumbwheels that control the CAT/trigger at some number downfield from the starting point for the CAT Scan (+1000 is a convenient point). Move the SIG MON to SWEEP FREQ and set the sweep starting point using the frequency counter and moving the pen bridge to the starting frequency. (if the sweep width for the experiment includes the lock signal, offset about -50 Hz to avoid losing the lock). Turn the SIG MON to EXT and set the Wave-Tek output at 1 volt with ATTEN KNOB - (same as INT SWEEP FREQ), then set the Wave-Tek oscillator to exactly the same reading on the frequency counter as obtained for the pen position; these readings must be the same or the lock will be lost.

After achieving an exact match we check homogeneity via RCVR and tweak up if necessary, then flip the AUTO SHIM to ON.

To start the CAT: Turn the SIG MON to SWEEP FREQ and the SWEEP FREQ SWITCH to EXT and move the thumbwheel for the CAT trigger - 1000 (regain original reading). We must now have identical readings for INT SWEEP FREQ, EXT SWEEP FREQ and the thumbwheels on the CAT trigger.

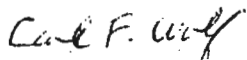
To stop the CAT scan for any reason, reverse the last two steps: Move the thumbwheel off +1000 while the CAT is scanning, wait until the frequency counter returns to the starting point and then move the SWEEP FREQ switch back to INT (can lose the lock otherwise).

At this point the CAT controls can be manipulated for examination of the memory contents, or for readout, etc.

As pointed out by C. A. Glass⁽¹⁾ the HALOOD recorder does not go flying back and forth all night and in addition with our trigger any sample can be summed via the CAT with out any trigger signal being added to the sample.

The system is stable and adds coherently over a fourteen hour summation with no appreciable line broadening.

Very truly yours,



Carl F. Wolf

CFW:jw

(1) IIT NMR Newsletter 117-14 (1968).

Please credit this to Dr. John E. Lancaster's account

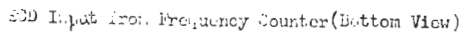
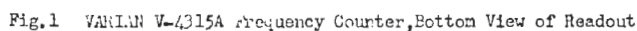
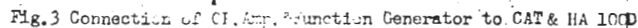


Fig. 2 TRIGGER



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Boîte postale 296/R 8
Prof. J.M. LEHN

Dr. J.P. KINTZINGER

Professor B.L. SHAPIRO
Department of Chemistry
Texas A & M University
COLLEGE STATION, Texas 77843

U.S.A.

High Resolution ^{14}N NMR Spectroscopy

Dear Barry,

As one may expect, the introduction of F.T. in ^{14}N NMR Spectroscopy opens new fields of investigation.

For example, the chemical shifts of ammonium salts were difficult to measure accurately because of the absence of field-frequency lock stabilization and the low sensitivity of the nucleus.

We wish to illustrate here some results obtained with our XL-100-15 spectrometer equipped with a Fourier Transform accessory, ^1H noise decoupling and deuterium lock facilities.

The enclosed figure is the spectrum of a mixture of quaternary ammonium salts (concentration 0.2 M for each species, 12mm o.d. sample tube, $t=50^\circ\text{C}$, $\text{H}_2\text{O}/\text{D}_2\text{O}$ (2/1) solution, deuterium lock, proton noise decoupling).

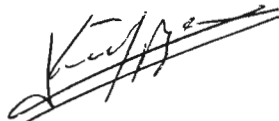
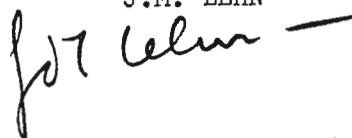
anion : bromide
cation: a: tetramethylammonium
cation: b: dimethylmorpholinium
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cation: d: hexamethonium
cation: e: dimethylpiperidinium
cation: f: dimethyldiethylammonium
cation: g: methyltriethylammonium
cation: h: diethylazetidinium
cation: i: tetraethylammonium
cation: j: dimethylpyrrolidinium

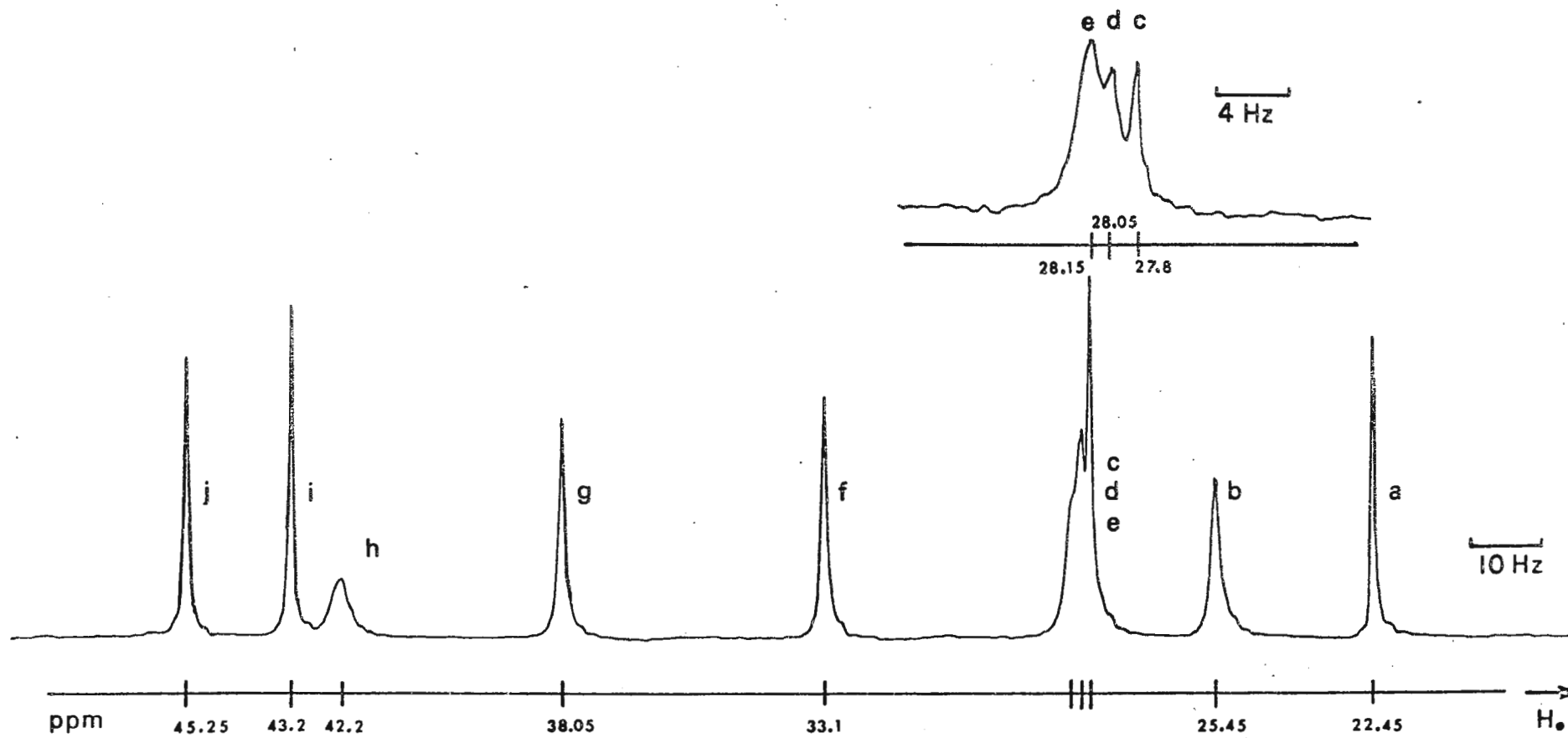
The chemical shifts are given with respect to the resonance of internal NH_4^+Br^- . The spectrum was obtained by accumulating 4000 F.I.D.'s of four seconds following $\pi/4$ pulses (total duration: 10 hours). However a satisfactory spectrum (signal/noise ≥ 20) may be obtained in 200 seconds (200 F.I.D.'s; A.T. = 1 sec.). Further N-14 studies are in progress.

Cordially yours,

J.P. KINTZINGER

J.M. LEHN



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Prof. Dr. P. Diehl

Basel, February 20, 1973/ho

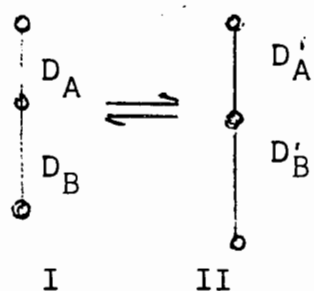
Professor B.L. Shapiro
Department of Chemistry
Texas A. & M. University
College Station, Texas 77843 /USA

"is oriented NMR helpful in conformational analysis?"

Dear Barry,

As Norman Sheppard pointed out long ago (IITNM 109,20,1967), the possibility of studying conformational problems in liquid crystal spectroscopy is limited. In fact, even if the geometries of all the conformers are known, only the quantities $p_i S_i$ can be measured, where p_i = proportion of conformer i and S_i = degree of orientation of that conformer. In spite of this warning an increasing number of papers has appeared lately, in which a determination of concentration p_i was seemingly achieved. (Tetrahedron Letters 38,3497,1971; Mol.Phys. 24, 673,1972; J.C.S. Perkin II 755,1972, Chem.Phys. Letters 15,396, 1972; J.Chem.Phys. 56, 1290, 1972).

These papers have been based on the following arguments:



S, p

$S', (1-p)$

We have two conformers I and II with direct couplings D_A, D_B respectively D'_A and D'_B , concentrations p and $(1-p)$ and orientations S and S' .

In principle, due to the conformational equilibration, we observe averages:

$$\bar{D}_A = pD_A + (1-p)D'_A = G_A \cdot S \cdot p + G'_A S' (1-p)$$

$$\bar{D}_B = pD_B + (1-p)D'_B = G_B \cdot S \cdot p + G'_B S' (1-p)$$

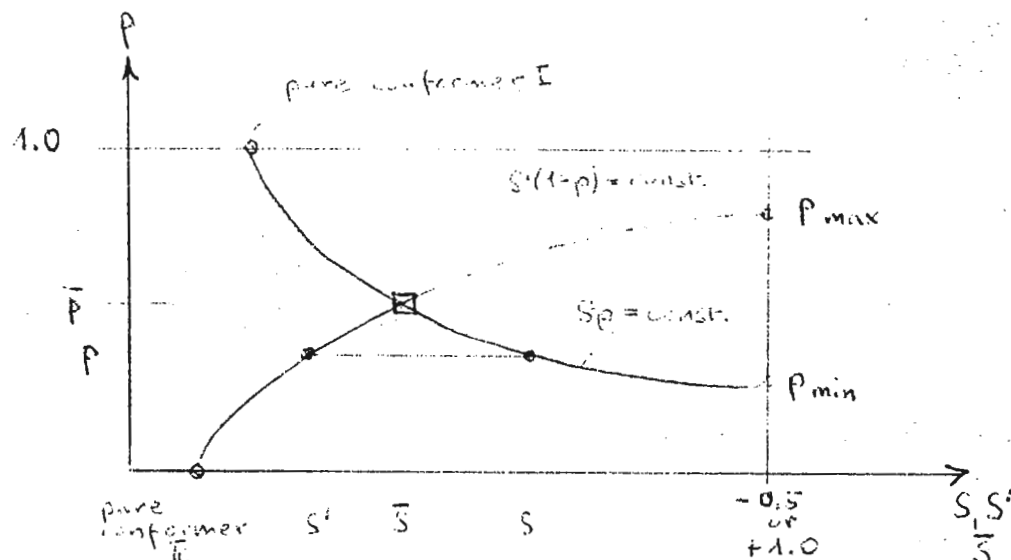
Obviously such equations only provide the values of $S \cdot p$ and $S' (1-p)$ if the G 's (functions of the molecular geometry) are known.

If, however, it is assumed that the system has an average orientation \bar{S} we obtain

$$\bar{D}_A = [G_A \bar{p} + G'_A (1-\bar{p})] \bar{S}$$

$$\bar{D}_B = [G_B \bar{p} + G'_B (1-\bar{p})] \bar{S}$$

and the two unknown \bar{p} and \bar{S} can be derived. Graphically these two different approaches can be represented as follows:



With two different orientations S and S' there is an infinite number of solutions. However, there are upper and lower limits for p , because S and S' must be in the range between $-0,5$ and $+1,0$.

With an "average" orientation there is a "unique" solution \bar{p} with \bar{S} .

How do we find out, which approach is correct? In the system presently discussed there is no way of telling. In more complex systems there are several independent S -values i.e. many pairs of curves and crossing points like the one shown in the figure. If all these crossing points have equal \bar{p} , we feel that it is safe to say that an average orientation exists, even though the other solutions cannot be excluded. If there are several values of \bar{p} , there is danger, because it turns out that the RMS error of the fit is not a good criterium. Obviously the RMS error for any pure conformer must be large because the corresponding points only fulfil the conditions of one of the two curves. In the literature (Mol.Phys. 24, 673, 1972) we have found a case where one set of curves gave a conformer concentration of 45%, another of 76% and the published value of 61% ($\frac{1}{2}(45+76)$) seems to produce a reasonable RMS error of the fit.

In conclusion we still think that hands should be kept off such "conformational analysis" or the data should be much more critically analysed.

Yours sincerely,

Peter W. Niederberger

P. Diehl W. Niederberger

International Society of Magnetic Resonance

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FIFTH INTERNATIONAL SYMPOSIUM ON MAGNETIC RESONANCE

We are pleased to announce that the Fifth International Symposium on Magnetic Resonance will be held at the Tata Institute of Fundamental Research in Bombay, India, January 14-18, 1974, under the chairmanship of Prof. A. K. Saha, Calcutta, India and Prof. V. Venkataraman, Bombay, India.

The program will be devoted to basic aspects of Nuclear Magnetic Resonance, Electron Spin Resonance and their applications of Physics, Chemistry and Biology. The following topics will also be discussed:

Quadrupole Resonance; Cyclotron Resonance; Ferromagnetic Resonance; Acoustic Magnetic Resonance. The program will include papers presented by invited lecturers followed by contributed papers and discussion.

A final scientific program will be mailed to registered participants at a later date.

Contributions - Abstracts of proposed papers should be submitted prior to July 1st, 1973, and the contributed papers not later than September 1st, 1973.

Information - Further details on the symposium and registration forms may be obtained upon request.

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February 16, 1973

Dr. Bernard Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Dr. Shapiro:

Nuclear Quadrupolar Relaxation of ^{79}Br Bromide with DNA Polymerase Using the XL-100-FT System.

For studies with DNA polymerase, which is a Zn containing enzyme (1,2) we have used the "halide ion probe" method introduced by Baldeschwieler (3), and first used by Ward with other Zn metalloenzymes (4). These authors observed ^{35}Cl . We are looking at ^{79}Br using the Varian XL-100-FT system set up to observe ^{13}C locking on ^2H , with minor modification. We here explain a way of doing this trick. The outlines of the method were inspired by Dr. Paul Ellis of the University of South Carolina and (of course) Charlie Peters of Varian. We have recently also observed $^{81}\text{Br}^-$, a narrower resonance, which can also be studied by this method.

Normally the ^2H lock frequency is provided by the 15.4 MHz master oscillator, but in our case we needed a slightly different field so that ^{79}Br would resonate at the standard ^{13}C frequency. We therefore used an external oscillator, namely the spin decoupler. The frequency provided by the spin decoupler was made to be higher than the standard 15.4 MHz by pushing the appropriate Gyrocode buttons. A 50 ohm line (see figure 1) was run from J1000 of the spin decoupler unit to the lock r.f. attenuator input, which we provided with a BNC connector for convenience. The original line was terminated with 50 ohms to load the buffer amplifier. A 100 ohm resistor tapped a signal into the mixer input of the Lock Local Oscillator, provided with a BNC instead of going in via P213-A2. The original line here was also terminated with 50 ohms.

Here are some of the settings which may not be obvious. It should be mentioned that the ^{79}Br resonance is very broad (700 Hz), allowing high r.f. power in the cw mode and .01 sec acquisition times and no pulse delay in Fourier. We used a 5 mm sample tube in a 12 mm outer tube containing D_2O . We observed the downfield ^{79}Br resonance while locking on the upfield ^2H resonance. A 2M KBr sample and 10 transients with a sensitivity enhancement = .01 sec gave a signal/peak-to-peak noise of 15.

Experiments with DNA polymerase (2), exemplified in figure 2, were carried out at 0.2 M KBr and took 10 minutes per spectrum. The enzyme broadens the $^{79}\text{Br}^-$ resonance and this broadening is partially reversed by the DNA analog (dT)₆₋₉ suggesting that DNA displaces Br^- from the enzyme-bound Zn. We will publish details of the enzyme experiments in the near future.

J. L. Engle
J. L. Engle

R. Abramson
R. Abramson

C. F. Springgate
C. F. Springgate

L. A. Loeb
L. A. Loeb

A. S. Mildvan
A. S. Mildvan

ASM/lvm

1. Slater, J. P., Mildvan, A. S., and Loeb, L. A. Biochem. Biophys. Res. Commun. 44, 37 (1971).
2. Springgate, C. F., Mildvan, A. S. and Loeb, L. A. Fed. Proc. 1973, in press.
3. Stengle, T. R., and Baldeschwieler, J. D. Proc. Nat. Acad. Sci. 55, 1020 (1966).
4. Ward, R. L., Biochemistry 8, 1879 (1969).

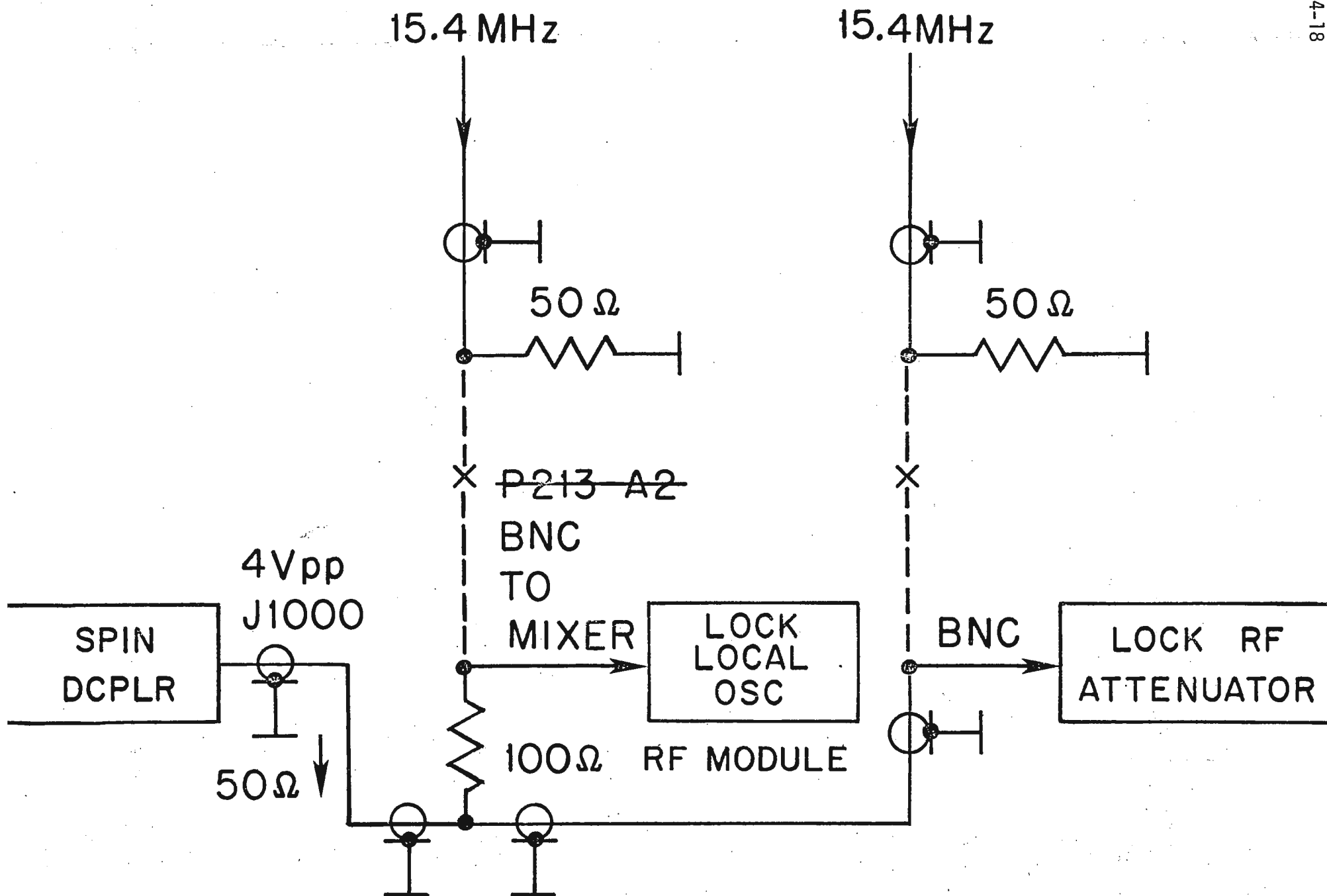


FIGURE 1: Cable Connections for Locking on D₂O while observing ⁷⁹Br NMR with XL-100.

0.2 M Bromide

+ DNA Polymerase (55 μ M)

+ DNA Polymerase (46 μ M)

+ (dT)₆₋₉ (77 μ M)

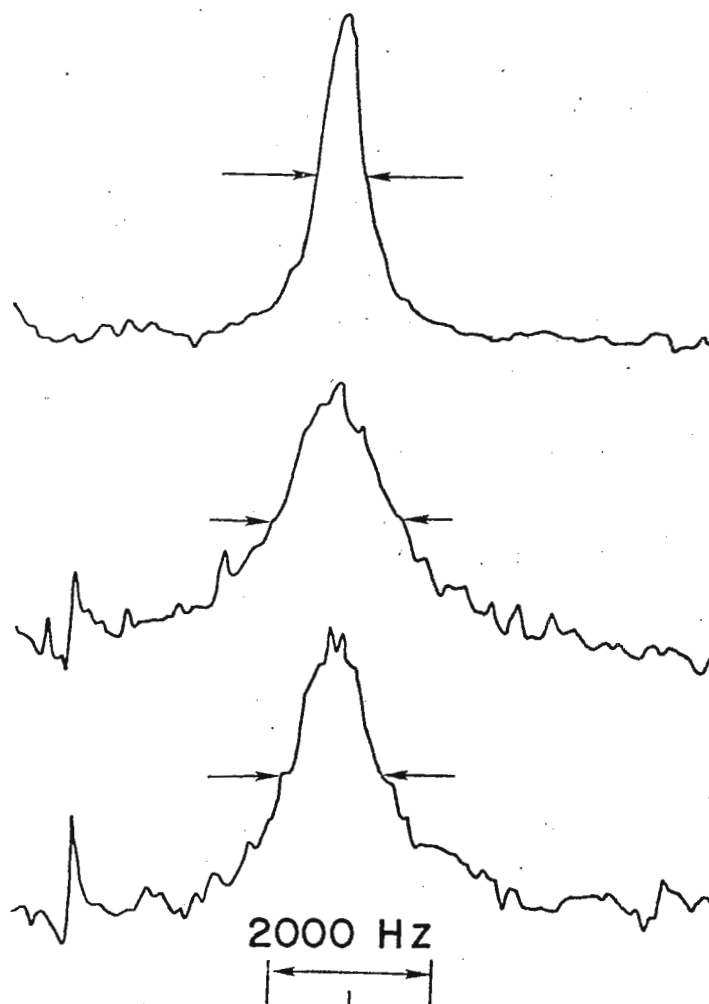


FIGURE 2: ⁷⁹Br Nuclear Quadrupolar Relaxation

Conditions: Volume 0.2 ml.

Decoupler Mode: HETERO

Hetero Power: Lo

Gyrocode: A 2, 4, 5; B 1, 2, 3, 4, 5;; C 2, 4; D 2, 3

DCPLR attenuator: 105dB

DCPLR offset: 79991

Lock Attenuator: 90dB

Sweep Offset for Fourier: 34241

Spec. Width for Fourier: 10000

Acq. Time: .01 sec

Sens. Enhancement: .01 sec

No. of Transients: 20K

DOW CORNING

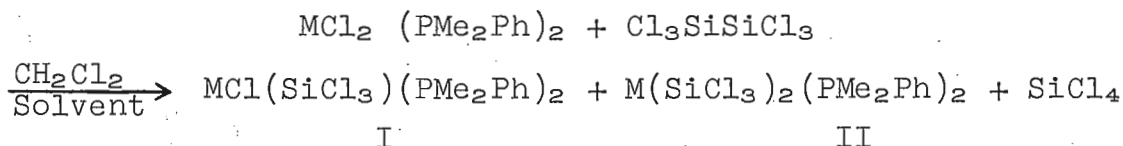
February 19, 1973

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

Dear Barry:

Subject: Anomalous ^1H NMR of silylpalladium and
 silylplatinum phosphine complexes

Recent work in our laboratories has involved the synthesis of silylpalladium and silylplatinum phosphine complexes by the following reaction (1):



We found that ^1H NMR of the methyl group provided a good way to monitor the reaction since complex I is about .27 ppm downfield while complex II is about .43 ppm upfield from the starting material. We also expected to be able to determine the stereostructure since the diagnostic value of the methyl absorption of such complexes is well established (2,3); i.e.:

1. a. cis: $J_{\text{PP}} = 0-18$, so the usual doublet ($^2J_{\text{PH}} \approx 11$) with doublet fine structure ($^4J_{\text{PH}} = 0-1$) is observed. Minor "inner" and "outer" peaks are also observed when $J_{\text{PP}} \neq 0$.
- b. trans: $J_{\text{PP}} \approx 550$, so a 1:2:1 triplet [separation = $(^2J_{\text{PH}} + ^4J_{\text{PH}})/2 \approx 3.5$] is observed due to virtual coupling (4) to both P nuclei. The central peak may be broadened due to "incomplete virtual coupling" at lower values of J_{PP} .
2. a. Cis Pt complexes: $^3J_{\text{PtH}} = 32-38$
- b. trans Pt complexes: $^3J_{\text{PtH}} = 21-31$.

3. In most cases, the absorption for the cis complex is about .15-.30 ppm upfield from that of the corresponding trans complex, although occasionally they are coincident.

Unfortunately, our results were not so simple. For the isolated platinum complex I, a triplet with a separation of 3.9 Hz and $^3J_{PtH} = 27.8$ was observed, as expected for the trans configuration. However, platinum complex II (in a mixture of I and II cooled to -20°C to suppress broadening and exchange between these two complexes) showed a doublet with $^2J_{PH} = 10.5$ (indicating cis) but with $^3J_{PtH} = 23$ (indicating trans).

The palladium complexes displayed other anomalies. Although isolated complex I at -20°C showed a triplet with a separation of 3.5 Hz, as expected for trans, as the temperature was raised the methyl resonance gradually shifted upfield and collapsed to a single relatively sharp peak ($\Delta\nu_{1/2} \leq 3$ Hz at 55°C). Both this change and an accompanying color change from colorless to intense yellow were reversible, indicating that some new species was being formed at higher temperatures which was in rapid equilibrium with the initial complex. The major puzzle is, how could the phosphine methyl band be a singlet?

The palladium complex II displayed a third anomaly. This material in a mixture with complex I again cooled to -20°C to suppress broadening and exchange between these two compounds, showed a splitting pattern intermediate between doublet and triplet ($J_{PP} \approx 75$) which became more doublet-like at lower temperatures. Possibly this observation indicates that both the cis and trans forms of palladium complex II are present in rapid equilibrium with each other.

We intend to continue studies of these complexes to resolve some of these structural uncertainties and to identify some of the chemical processes that are occurring.

Very truly yours,



Dwight E. Williams



Gary N. Bokerman

- (1) G. N. Bokerman and W. H. Atwell, submitted to J. Organometal. Chem., 1973.
- (2) J. M. Jenkins and B. L. Shaw, J. Chem. Soc. A, 1966, 770.
- (3) D. A. Duddell et al., J. Chem. Soc. A, 1969, 2134.
- (4) R. K. Harris, Can. J. Chem., 1964, 42, 2275.

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LEIDEN, 26th febr. 1973

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

CHEMICAL SHIFTS OF FLUORO-NITRONAPHTALENES

Dear Professor Shapiro,

In connection with the investigation of the fotosubstitution pattern of substituted naphthalenes some fluoro-nitronaphthalenes were prepared. Some compounds were synthesised via the Schiemann reaction of the corresponding amines, and some by nitration of fluorinated derivatives. As the directive effects in these compounds are not yet completely understood, the identification of the compounds was an important point. NMR spectroscopy appeared to be a useful tool in this case too.

Although six out of the seven spins in these systems have a chemical shift between 7 and 8.5 ppm, and can give therefore rather complex spectra, these systems have some features which facilitate the analysis of these spectra very much.

1. Protons at positions ortho to the fluorine substituent get an upfield shift, so these protons have to be found in the high-field part of the spectrum.
2. Protons ortho or peri to the nitro group are shifted downfield by 0.6 to 0.8 ppm. Consequently these protons absorb at the low-field part of the spectrum.
3. Protons at positions meta to the fluorine substituent have a coupling constant $^4J_{H,F}$ of 4-6 Hz. In these systems no other coupling constants lie in this range, so the presence of a coupling constant of this magnitude unequivocally identifies this type of protons.
4. Peri- and antiperiplanar coupling constants (Fig. 1) mostly are smaller than 1.5 Hz. When in some absorption line broadening is observed (as a result of the presence of small couplings) this is a strong indication that the proton concerned occupies an alpha position. Moreover, by this fact the spectra can be divided in two very weakly coupled parts; the protons in each ring can be handled as separated three- or four-spin systems.

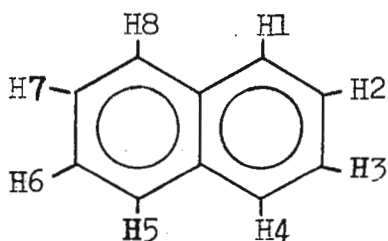


Fig. 1

H_1, H_8 and H_4, H_5 have a peri-relationship
 H_1, H_5 and H_4, H_8 have an anti-periplanar relationship.

In this way six fluoro-nitronaphtalenes could be analysed completely with the aid of the computerprogram LAME. As seven-spin systems have a very large number of lines, the iterative procedure is very laborious and there are many possibilities of wrong line number assignments. Therefore, the assignments are made by visual comparison of calculated and observed spectra. The data are collected in table 1. and table 2.

Table 1. Chemical shifts (in ppm from TMS) of some nitro-fluoro-naphtalenes measured in CDCl_3 at 100 MHz.

naphtalene derivative	chemical shift							
	$\delta 1$	$\delta 2$	$\delta 3$	$\delta 4$	$\delta 5$	$\delta 6$	$\delta 7$	$\delta 8$
1-fluoro, 4-nitro-	--	6.93	8.01	---	8.33	7.52	7.39	7.83
1-fluoro, 6-nitro-	--	7.27	7.49	7.71	8.62	--	8.13	8.07
1-fluoro, 8-nitro-	--	7.23	7.45	7.62	7.90	7.45	7.63	--
2-fluoro, 5-nitro-	7.40	--	7.35	8.46	--	8.09	7.46	7.94
2-fluoro, 6-nitro-	7.39	--	7.52	8.02	8.69	--	8.22	7.88
2-fluoro, 8-nitro	8.33	--	7.42	7.96	8.12	7.49	8.33	--
1-chloro, 8-nitro	--	7.62	7.44	7.79	7.66	7.47	7.94	--

Ref.1

Table 2. Coupling constants(in Hz) of some nitro-fluoro-naphtalenes measured in CDCl_3 at 100 Mhz

naphtalene derivative	coupling constant													
	J12	J13	J14	J15	J23	J24	J34	J48	J56	J57	J58	J67	J68	J78
1-fluoro, 4-nitro-	9.04	7	-	1.88	7	-	-	x	7.51	1.5	x	6.71	1.28	4
1-fluoro, 6-nitro-	9.14	70.51	51.57	11.07	31.1	--	2.5	x	--	--	--	--	--	8.7
1-fluoro, 8-nitro-	11.74	5	x	1.67	41.47	9	-	7.91	1.6	-	7.1	--	--	--
2-fluoro, 5-nitro-	8.22	70.4	--	8.65	79.6	x	--	--	--	--	7.50	87.8	--	--
2-fluoro, 6-nitro-	8.22	4	x	x	8.65	18.6	x	--	2.8	x	--	-	-	8.9
2-fluoro, 8-nitro-	11.52	50.5	x	8.06	09.0	x	7.91	1.0	-	7.5	-	--	--	--

x Not observable

1. W. Brügel, Nuclear Magnetic Resonance Spectra and Chemical Structure Vol. I, p.129, Academic Press, New York-London 1967.

The chemical shift values of 1-fluoro,8-nitronaphtalene need some comment. From the reaction pathway follows that the compound could be either 1-fluoro,8-nitro- or 1-fluoro,5-nitronaphtalene. The dipole moment (4.8 D) indicated that it was the 1-8 derivative. As compared to protons in a similar environment the chemical shift of the proton ortho to the nitro group seems to be surprisingly low, and one could ask whether or not the assignment is correct. Indeed, in many spectra of α -nitronaphtalenes the chemical shifts of protons ortho and para to the nitro group can be interchanged without any observable influence on the spectra, especially in cases where peri and antiperiplanar couplings are small. In this compound however, these coupling constants are readily observable. The signal at 7.90 ppm appears as two triplets with a separation of about 8 Hz. In each triplet two couplings of about 1.8 Hz are present. One of them clearly is an antiperiplanar coupling with the fluorine substituent (Observed also in the ^{19}F spectrum of the compound). A coupling constant of this magnitude between a fluorine atom at C1 with a proton at C6 or C7 never has been observed, so the assignment of the resonance at 7.90 ppm to the proton on C5 seems to be quite sure. A possible explanation of the relatively high-field resonance of the proton next to the nitro group could be the loss of resonance of the nitro group with the aromatic ring caused by steric interaction with the fluorine substituent. The same effect is expected to be present also in 1-chloro-8-nitronaphtalene. As shown in table 1 the effect in this compound is just the other way around. It should be born in mind however that in these compounds the chemical shifts of H5 and H7 could be interchanged. As pointed out above the assignment of this type of protons can be very difficult in the absence of peri- or antiperiplanar couplings. At least an antiperiplanar coupling cannot be present in this compound and peri couplings are mostly unobservably small. The effect we found in 1-fluoro-8-nitronaphtalene clearly needs further investigations and we are preparing now other 1-8 derivatives.

Sincerely Yours,

C. Erkelens.

J. Lammers

A. J. de Hoog

Department of Chemistry


YORK
UNIVERSITY

FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW 463, ONTARIO

15 February 1973

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

Dear Dr. Shapiro:

^{13}C - Workshop, $J_{11\text{B}} - ^{13}\text{C}$

York was recently host to a ^{13}C NMR Workshop arranged by Varian Associates. An NV-14 multinuclear instrument was temporarily installed for CW proton and FT/CW ^{13}C NMR. Within four hours the instrument was giving adequate ^{13}C spectra in FT mode. This time included the positioning and unpacking of the instrument and a short coffee break. The instrument was interfaced with a Varian 620L 16K computer, and operates at 15MHz with an 8mm insert for ^{13}C . Subsequently the instrument pulsed (some 3.5 million pulses) through countless spectra. The results were uniformly satisfactory. On comparing the spectra of identical samples run on both the NV-14 and the XL-100 (courtesy of Professor J.B. Stothers, Western Ontario) there seemed little to choose between them. This in part may reflect the difference between the 16K and the 8K computer, however the NV-14 performance was certainly impressive. Its ease of operation was also a delight to a newcomer to FT NMR. A pen shaking routine in the computer programme provided light relief and kept the drawing ink flowing.

Naturally, we reached for the shelf and put what we could find of interest through the routine. Stimulated by a blue letter, we report a brief item on boron-carbon coupling.

Sodium tetraphenylboron has been previously investigated¹ and ^{11}B -C coupling reported for the directly-bonded carbon and the meta-carbon. No other couplings were seen. Our spectrum is shown below. We also observe the directly-bonded coupling, but in addition all the other carbons are doublets with a varying bumpy plateau in the middle. We were unable at this time to perform variable temperature studies. However, it seems reasonable that the structure is due to partially resolved ^{11}B -C coupling. The line shapes are then not unlike that obtained in the ^{19}F spectrum of

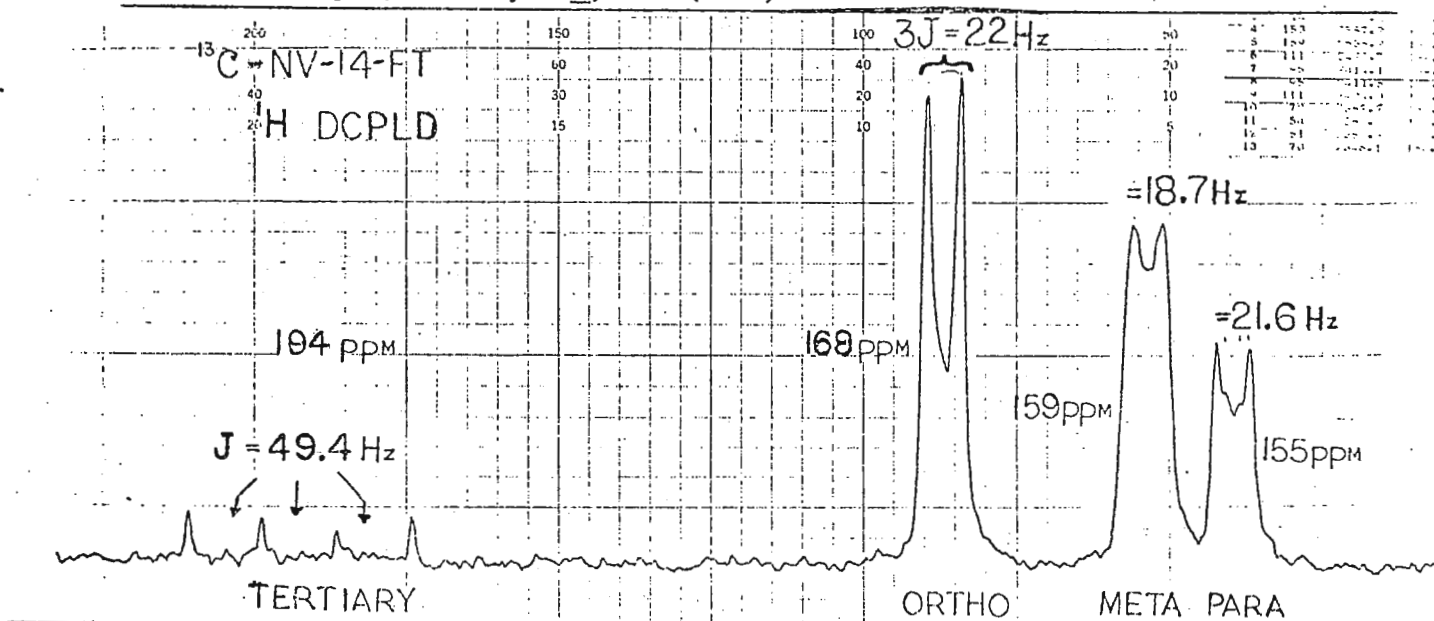
the NbF_6^- ion, where fluctuating electric field gradient causes broadening of the inner lines of the multiplet. Unfortunately, the theory² predicts that all four components of coupling due to ^{11}B should be of equal shape. This is almost observed for the directly-bonded case. Since the nuclear g-factors of ^{11}B and ^{13}C are comparable and not particularly small, and that of proton is large, magnetic dipole relaxation mechanisms are probably important for the boron nucleus. The observed line shapes could be due to this, each doublet structure being the outer lines of a quartet. On this basis we present the proposed $^{11}\text{B} - ^{13}\text{C}$ coupling for the ring carbons. Similarity with other $\text{X}-^{13}\text{C}$ ring couplings are then evident.

$J_{\text{B-C}}$ Hz, direct 49.4; ortho 7.3; meta 6.2; para 7.2

Sincerely,

D. E. Axelson *A. J. Oliver* *C. E. Holloway*
D. E. Axelson A. J. Oliver C.E. Holloway

1. F.J. Weigert & J.D. Roberts, J.Am.Chem.Soc. 91, 4940 (1969) and Inorg.Chem. 12, 313 (1973).
2. J.A. Pople, Mol.Phys. 1, 168 (1958).



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Herrn

Prof. Bernard L. Shapiro

Department of Chemistry

Texas A&M University

College Station, Texas 77843U.S.A.

IHR ZEICHEN

IHRE NACHRICHT VOM

UNSER ZEICHEN
Ho/FrDATUM
20.2.1973

E.G. Hoffmann and W. Stempfle

Setup of a PDP-11-Computer for FT-NMR-Spectroscopy.

Sehr geehrter Herr Shapiro!

In Eile, den rosa Mahnbrief vor Augen, schreibe ich in Deutsch eine Mitteilung, damit meine TAMUNN LETTER-Subskription nicht verloren geht. Wie in unserem Bericht Angewandte Chemie, Int. Ed. 11, 375ff, 1972 ausgeführt, kann eine im Timesharing-Modus arbeitende Großrechenanlage nur 1 schnelle Datenaquisition flexibel genug ausführen, so daß Fourier-Transform-NMR CAT-Läufe nicht rationell zu fahren sind. Wir haben deshalb unser Spektrometer an einen 16 K-PDP 11/20-Computer angeschlossen. Als Interface benutzen wir das im Euratom-Bereich standardisierte CAMAC-Modularsystem, das sich leicht mit der PDP 11 verbinden läßt. Die Programmierung im PAL-Assembler ist nicht so zügig fertiggestellt worden, wie dies Herres und Ziessow in TAMUNN Nr. 171 beschrieben haben, weil wir nur ein Tape-Device als Massenspeicher investieren konnten und ohne Disc arbeiten mußten. Wir können jetzt unseren Pulscyclus von 10 sec-Intervallen auf Intervalle von 1 sec oder weniger reduzieren. Für die FFT steht uns der Großcomputer (PDP 10) zur Verfügung, und wir können so den größten Teil des Speichers der PDP 11 für die Datenaquisition ausnützen.

- Übrigens lassen sich mit einem von der PDP 10 übermittelten LAOCOON Part 1-Programm, das wir für 5 Kerne reduzierten,

auf dem Kleincomputer in Verbindung mit einem Sichtgerät
leicht Spektren für Unterrichtszwecke simulieren. -

Ich hoffe, bald über ein Problem berichten zu können, das
für die Freunde der TAMUNN-Letters interessanter ist. Bis
dahin bleibe ich

mit herzlichen Grüßen

Ihr

Ernst Hoff —

DIVISION OF CHEMISTRY
DIVISION DE CHIMIE



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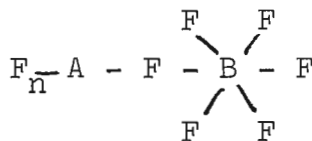
19 February 1973.

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

Chemical Shifts in Complex Fluoroanions

Dear Barry:

For some time we have been trying to understand the relative stability, chemical shifts and spin coupling constants of complex fluoroanions with structure I.



I

In the cases where B is tantalum or niobium and A is Mo, W, Nb, Ta or Sb one can use the chemical shifts of the equatorial or terminal fluorine atoms as a measure of the electron withdrawing ability of the AF_n species. The only exception found thus far is when A is molybdenum and B is niobium. A summary of these results are shown in the accompanying table.

Best wishes,

S. Brownstein

S. Brownstein.

SB:jes
Attach.

Measuring Nucleus	Chemical Shift with Binary Fluoride				
	MoF ₅	WF ₄	NbF ₅	TaF ₅	SbF ₅
Equatorial F on Tantalum	-58.6	-65.6	-69.4	-72.0	-78.6
Terminal F on Tantalum	-89.9	-94.6	-108.7	-115.1	-125.7
Equatorial F on Niobrium	-161.1	-138	-145.5	-149.4	-156.6
Terminal F on Niobrium	-194.4		-191.3	-197.4	-205

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Feb. 21st, 1973

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

Dear Prof. Shapiro:

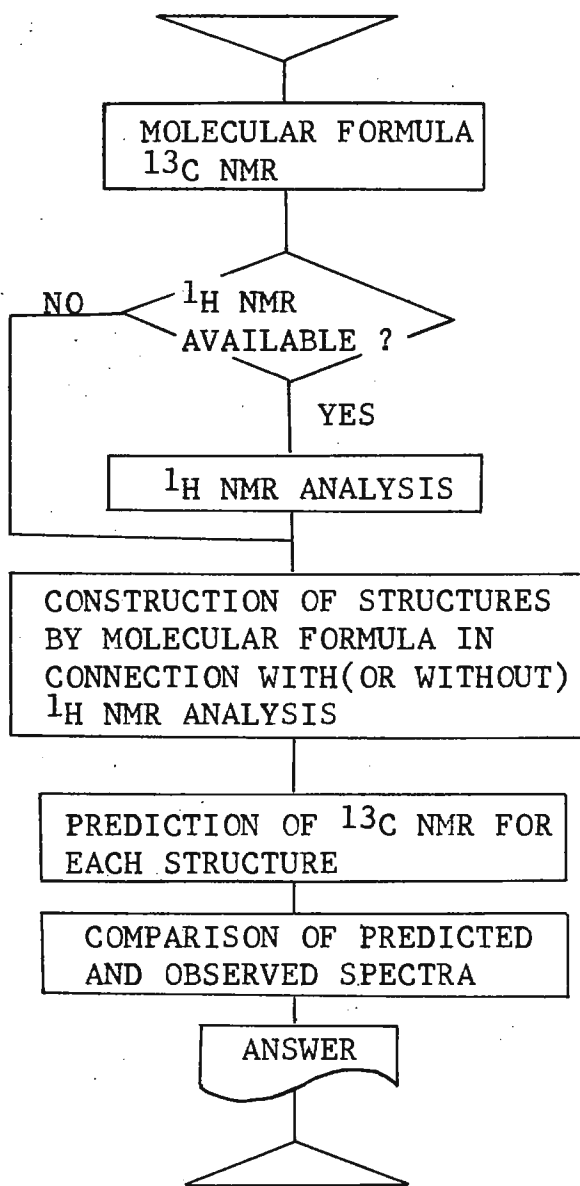
The automated identification of alkanes and alkenes by feeding the molecular formula and the proton decoupled ^{13}C NMR spectrum of sample alkane or alkene has already been reported by us (Japan Analyst, 21, 916 (1972)).

The same kind of experiment for the identification of alcohols has been carried out. In this computation (see flowdiagram), the molecular formula and the ^{13}C NMR spectrum of sample alcohol are essential input data, and the digitized ^1H NMR spectrum, if available, is very useful to make the responded results accurate.

First, all possible isomeric structures are computed based on the molecular formula and the components, CH_3 -, $-\text{CH}_2$ -, $-\dot{\text{C}}\text{H}$ -, $-\dot{\text{C}}$ -, and $-\text{OH}$, in referring with (or without) the ^1H -NMR analysis. Then the chemical shift of each carbon in every isomeric structure is calculated by the aid of parameters prepared by us. Finally, a structure(s) whose predicted spectrum is consistent with that of sample within the limit of $\pm 5\text{ppm}$ is typed out as the most plausible candidate(s). This computation system was applied to

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Flowdiagram for alcohol-
identification

38 alcohols and one correct answer was given for 25 alcohols, two answers containing a correct one for 4 alcohols, three for 3 alcohols, four for 4 alcohols, and five for 2 alcohols.

The detail will be contributed to the Analytical Chemistry in the nearest future.

Sincerely yours,

S. Ochiai

Shukichi Ochiai
JEOL Limited
Tokyo, Japan

S. Sasaki

Shin-ichi Sasaki
Miyagi University of
Education
Sendai, Japan

Mereside Alderley Park
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Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station
TEXAS 77843

Pharmaceuticals
Division

Your ref

Our ref
DG/RB

Tel ext
7-462

Date
26 February 1973

CMR OF METHYL CATECHOL DERIVATIVES

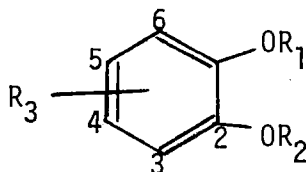
Dear Professor Shapiro,

Mono ethylation of 4 methyl catechol would produce 2 isomers designated as the 4 and 5 methyl derivatives (compounds I and II in table). The c.m.r. spectrum of the isomeric mixture showed separation of all aromatic carbon signals and by calculations using substituent parameters for $-OH$, $-OC_2H_5$ and $-CH_3$ groupings together with several reference compounds, assignments have been made. The proportions of the 4 and 5 methyl isomers was roughly equal in the phenol. Introduction of a further different alkyl group (methyl morpholine) to the free phenol group still showed definite doubling of all aromatic carbon signals, now in the ratio 2:1 - these chemical shifts are shown as the major and minor isomers in the table. Attempts have been made to try and assign these signals to determine which isomer (4 or 5) is the predominant one. Because of the similarity of the two alkyl groups and because the right reference compounds are not to hand we have found it impossible to do this but take consolation from the fact that c.m.r. was the only technique that showed clearly a mixture of compounds, g.l.c., t.l.c. and p.m.r. all failing to do this.

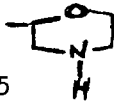
Please contribute this to the account of Dr. G. R. Bedford.

Yours sincerely,

D. Greatbanks.



¹³C Chemical shifts relative to TMS

	$R_1 = H$ $R_2 = C_2H_5$ $R_3 = CH_3$ (4)	$R_1 = H$ $R_2 = C_2H_5$ $R_3 = CH_3$ (5)	$R_1 = CH_2$  $R_2 = C_2H_5$ $R_3 = CH_3$	
			major	minor
C ₁	-143.9	-143.9	-147.1	-146.8
C ₂	-145.9	$\xleftrightarrow{a)}$ -145.8	-148.8	-149.1
C ₃	-111.9	-112.8	-114.7	-115.3
C ₄	-129.3	-120.2	-130.8	-121.3
C ₅	-121.6	-131.0	-122.1	-131.6
C ₆	-114.4	-115.6	-116.3	-115.6

a) Assignments can be reversed

TELEPHONE
34 0484

TELEGRAMS
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University of Melbourne

DEPARTMENT OF ORGANIC CHEMISTRY

Parkville, Victoria 3052

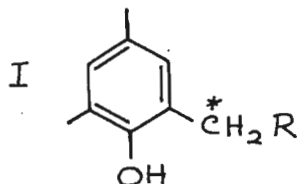
20th February, 1973.

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

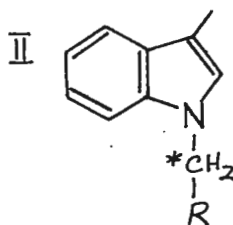
Dear Dr. Shapiro,

We have been investigating the use of ^{13}C chemical shifts for the identification of the formaldehyde derived $-\text{CH}_2-$ groups in formaldehyde cross linked proteins and peptides.¹ A number of amino acids have been proposed as the sites of cross linking, including tyrosine, tryptophan, lysine, glutamine and others. Using 2,4-xyleneol and 3-methylindole as models for tyrosine and tryptophan respectively, Shao Wei Let has shown by proton NMR that crosslinking occurs between aryl carbon and nitrogen (e.g. I) and between two nitrogen atoms (e.g. II).² Since the methylene protons were often partly obscured by the solvent peak (HOD) and in expectation of other overlapping methylene absorptions in higher molecular weight systems, we turned to ^{13}C NMR to identify the formaldehyde residue.

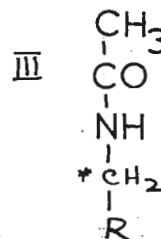
The chemical shifts of the formaldehyde derived carbons (marked *) illustrating $\text{N}-\text{CH}_2-\text{C}$, $\text{N}-\text{CH}_2-\text{N}$, $\text{N}-\text{CH}_2-\text{S}$ and $\text{N}-\text{CH}_2-\text{O}$ linkages, are given here, accurate to ± 0.1 ppm downfield from TMS.



R = alanine 50.0
glycine 50.5

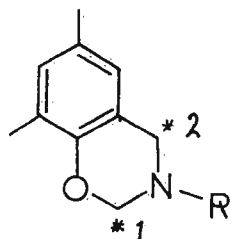


59.7
-



51.4
-

IV

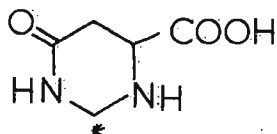
R = CH₃

1	2
83.5	52.2

R = C₂H₅

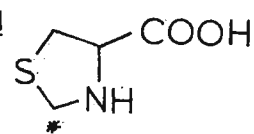
81.6	50.0
------	------

V



56.0

VI



53.6

The spectra were recorded in the FT mode on a Bruker HX-90 spectrometer at the Bruker agents in Australia³. Our own instrument, an HA-60 interfaced to a PDP 15/20 computer is being modified for FT operation by Digilab.

Please credit this contribution to Dr. M.L. Heffernan (Monash University).

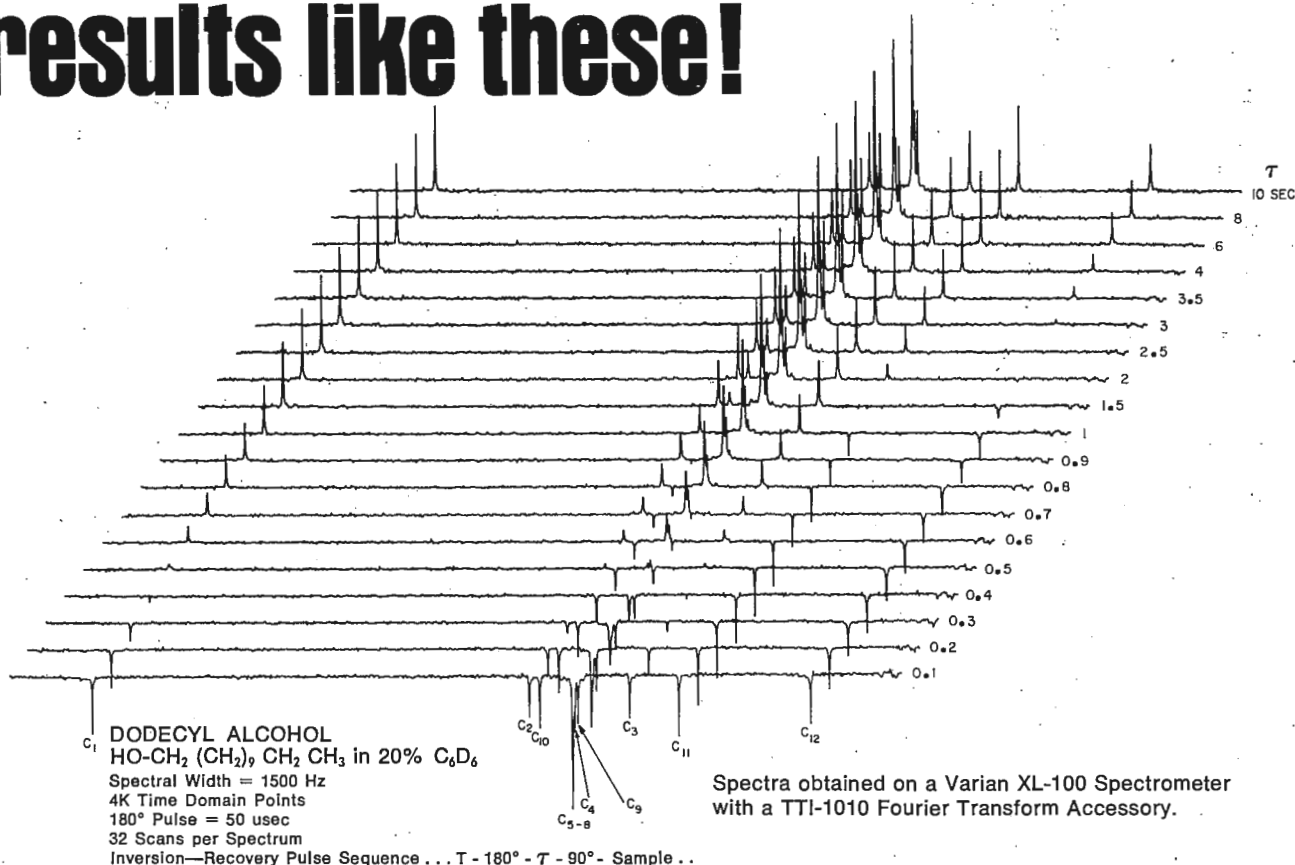
Yours sincerely,

M.K. Dewar.
D. P. Kelly.

1. M.K. Dewar, R.B. Johns, Shao Wei Let and D.P. Kelly, unpublished results.
2. Shao Wei Let, Ph.D. thesis, University of Melbourne, 1970.
3. H.B. Selby and Co., Notting Hill, Victoria; Mr. H. Hollenweger

Title: ¹³C Shifts of Formaldehyde Derived Methylene Groups

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Spectra obtained on a Varian XL-100 Spectrometer with a TTI-1010 Fourier Transform Accessory.

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The above spectra of dodecyl alcohol were obtained using the Nicolet automatic T_1 program, which utilizes the $[180^\circ - \tau - 90^\circ - (\text{sample}) - T_1]_n$ inversion recovery¹ or PRFT² pulse sequence. In this experiment, the value of the inter-pulse interval τ is varied from a time much less than the shortest T_1 to a time about 5 times longer than the longest T_1 in the sample. Data are signal averaged at each value of τ and stored on the Nicolet 600,000 word cartridge disk memory.

For $\tau \ll T_1$, nuclear magnetization will still be inverted when

the 90° pulse is applied, leading to inverted peaks in the transformed spectrum. For $\tau \approx T_1 \ln 2$, a null will be observed, since at this time the magnetization is just passing through zero when the 90° pulse is applied. Finally, when $\tau \gg T_1$, the nuclei will have returned to their usual precession about the $+z$ axis before the 90° pulse is applied, and the experiment reduces to the usual single pulse Ft nmr experiment.

After all spectra are obtained, they are processed all at once and displayed or plotted as shown. The spin-lattice relaxation times of each line can be estimated from the plots or calculated using a least squares treatment, from the equation $A = A_0 [1 - 2 \exp(-\tau/T_1)]$. This calculation is performed directly by the program upon command.

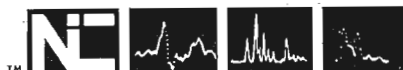
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1. R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.* **48**, 3831 (1968).
2. A. Allerhand, D. Doddrell, V. Glushko, D. W. Cochran, E. Wenkert, P. J. Lawson and F. Gurd, *J. Am. Chem. Soc.* **93**, 544 (1971).

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

Your ref

Our ref

Date 23 Nov 72

Dear Dr.Shapiro,

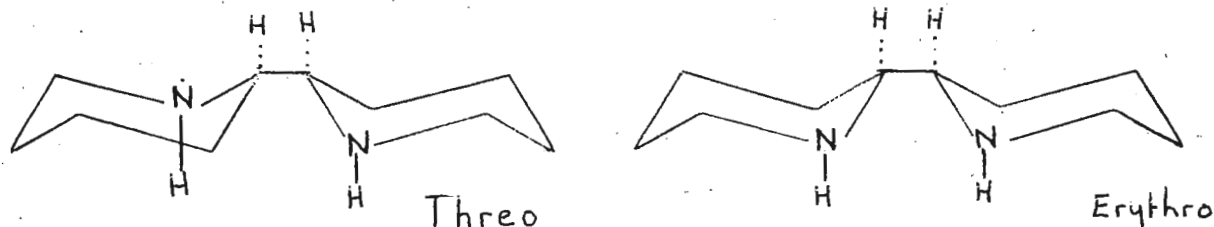
^{13}C NMR SPECTRA OF BIPYRIDYLS AND BIPIPERIDYLS

We have been interested for some time in the identification and estimation of components in mixtures of isomers in the bipyridyl and bipiperidyl series. Using 100 MHz proton spectroscopy, all the bipyridyl positional isomers give quite distinct characteristic spectra in the aromatic region. The quantitative analysis of the main components, the 2,2' and 4,4'-isomers is straightforward, but the analysis becomes increasingly difficult as more of the minor components e.g. 2,3', 2,4', 3,3' and 3,4' isomers, have to be dealt with. The bipiperidyl positional isomers all give complicated spectra in the aliphatic region and little can be done in quantitatively analysing mixtures of the positional isomers due to the extensive overlap of the spectra.

Now that ^{13}C NMR has become established, we have taken a preliminary look at these types of compounds. (Thanks are due to our colleagues Geoff Bedford and David Greatbanks of ICI Pharmaceuticals Division, Alderley Park, for running some of the ^{13}C spectra on their ^{13}C FT modified HA100D and allowing us spectrometer time to run others ourselves). The ^{13}C spectra of 2,2' and 4,4'-bipyridyl are straightforward, with proton coupled spectra allowing easy assignment of peaks. The proton decoupled spectra are not overlapped at all and we feel confident that this will be so for the other positional isomers, which we hope to run soon. As yet, we have not investigated the quantitative aspects of mixture analysis by ^{13}C NMR.

The ^{13}C spectra of 2,2' and 4,4'-bipiperidyl also allow ready distinction of the isomers and again extension to include the minor positional isomers and possible quantitative analysis of mixtures in this series can be anticipated. The ^{13}C NMR spectrum of 2,2'-bipiperidyl proved of additional interest in that doubling up of the expected five peaks in the proton decoupled spectrum was found. This is shown on the diagram attached, together with the shift positions relative to TMS.

We believe that this doubling is due to the presence of two components. If it is assumed that both piperidyl rings have the chair configuration and that the NH protons are most likely to be axially orientated (1), then the two species involved could be the two diastereoisomers



We have some evidence that these species may be separable by GLC and a recent Russian publication (2) indicates that separation by TLC is possible also. If we can separate and collect fractions, then we would hope to assign the two sets of bands to the two species.

All ^{13}C spectra were obtained from CDCl_3 or dioxan solutions, with $^{13}\text{CH}_3\text{I}$ as lock and TMS as reference.

Yours sincerely,

P. HAMPSON*

A. MATHIAS

A. M. WILDE.

P. Hampson

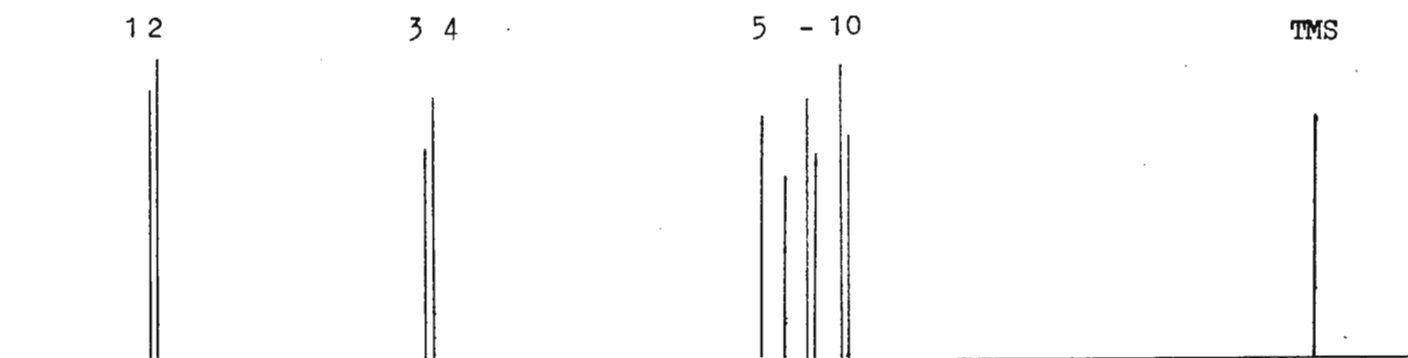
A. Mathias

A. Margaret Wilde

- (1) Eliel, Allinger, Angyal and Morrison; Conformational Analysis, Interscience, 1965 p.244.
- (2) Forostyan, Efimova and Soroka, J. Org. Chem. USSR 7, 2198, 1971 (p. 2282 in English Translation).

*Present address:- ICI Pharmaceuticals Division, Hurdsfield Works, Macclesfield.

<u>Carbon Lines</u>	<u>Shift (ppm)</u>	
1	-61.9	
2	-61.6	
3	-47.4	
4	-46.9	
5	-29.3	
6	-28.2	
7	-27.0	
8	-26.7	
9	-25.0	
10	-24.8	
TMS	0.0	reference



^{13}C NMR Spectrum of 2,2'-Bipiperidyl (proton decoupled).

Oklahoma State University

Department of Chemistry / (405) 372-6211, Ext. 7215 / Stillwater, Oklahoma 74074

February 21, 1973

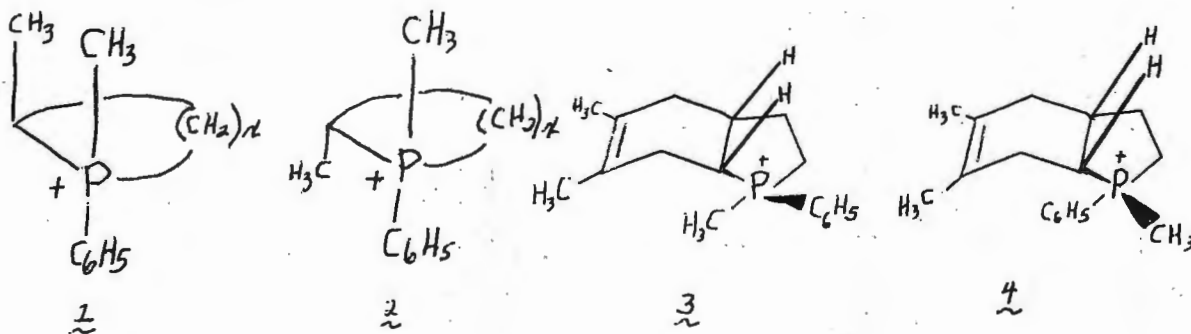
Dr. B. Shapiro
 Department of Chemistry
 Texas A & M University
 College Station, TEXAS 77843

Dear Dr. Shapiro:

Bicyclic C-P Heterocycles

The stereochemistry of cis and trans alkyl substituted carbon-phosphorus heterocycles 1 and 2 has been examined using simple chemical shift difference^{1,2}, Lanthanide shift reagents³, and J_{PCH} coupling constants⁴.

We have determined the overall stereochemistry of 3 and 4 via pmr analysis. The configurational assignment was based, in part, on the chemical shift of the $P-CH_3$ group. The lower field methyl was assigned to 3 ($\delta 2.18$ for 3 in $DCCl_3$) in analogy with cis-2-methyl-1-phenylphospholene-1-methyliodide² (compared to $\delta 2.12$ for 4 in $DCCl_3$).



The reported assignment² for the methyl iodide salt is logical because of the deshielding effect on the cis P -methyl group, but supporting evidence would appear lacking. Fortunately, the methyl groups on the six-membered ring of 3 and 4 [$CH_3(A)$ and $CH_3(B)$] permit a more definitive assignment. These methyl groups appear as two singlets ($\delta 1.31, 1.51$) for 3 at higher fields

than for 4 (δ 1.58, 1.68), which would be expected based on their proximity to the phenyl group, i.e., exo in 3 and endo in 4. The J_{PCH} coupling for the CH_3 protons is normal at 13.5 Hz in either isomer. Work is continuing on C-P-heterocycles.

Sincerely yours,

K. D. Berlin

K. D. Berlin
Regents Professor

Don L. Morris

Don L. Morris
Research Associate

- (1) L. D. Quinn and T. P. Barket, *J. Amer. Chem. Soc.*, **92**, 4303 (1970).
- (2) K. L. Marsi, F. Burns, and R. T. Clarks, *J. Org. Chem.*, **37**, 238 (1972).
- (3) B. D. Cuddy, K. Treon, and B. Walker, *Tetrahedron Lett.*, 4434 (1971);
J. R. Corfield and S. Trippett, *Chem. Comm.*, 721 (1971).
- (4) J. P. Albrand, D. Gagnaire, M. Picard and J. Robert, *Tetrahedron Lett.*, 4593 (1970).

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DEPARTMENT OF CHEMISTRY

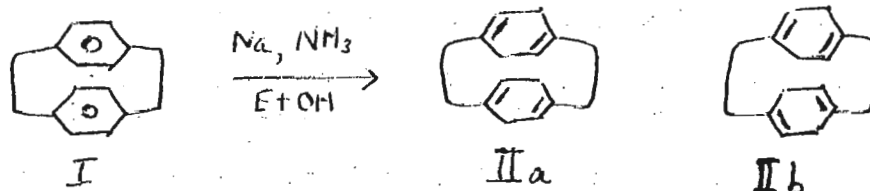
February 26, 1973

Title: Eu(fod)_3 as a tool for elucidating stereochemistry of olefins
(via the epoxides).

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

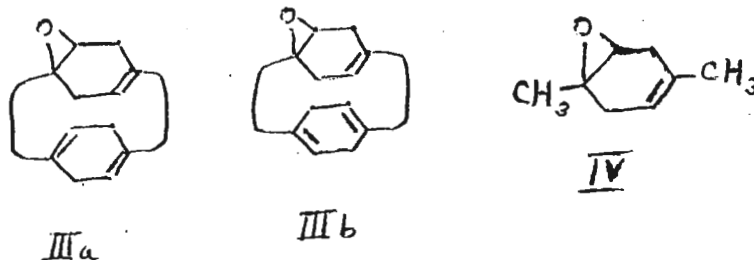
Dear Barry:

We have previously determined that the Birch reduction of [2.2]paracyclophane (I) gives the 2,5,2',5'-tetrahydro product (II) [Tetrahedron Letters, No. 10, 757 (1971)]. At that time we were aware that two stereoisomers were possible -- meso (IIa) and d,l (IIb) -- but we had no way to determine if our product was IIa, IIb, or a mixture of both.

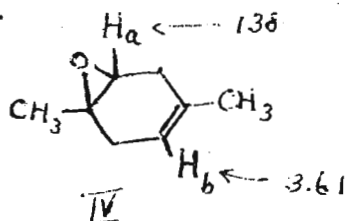


Subsequently, we recorded the carbon magnetic resonance spectrum of II. This spectrum exhibited four signals, indicating that the product was one stereoisomer and not a mixture. Further attempts to elucidate the stereochemistry (e.g., photochemical studies, resolution of diastereomeric salts) were unsuccessful.

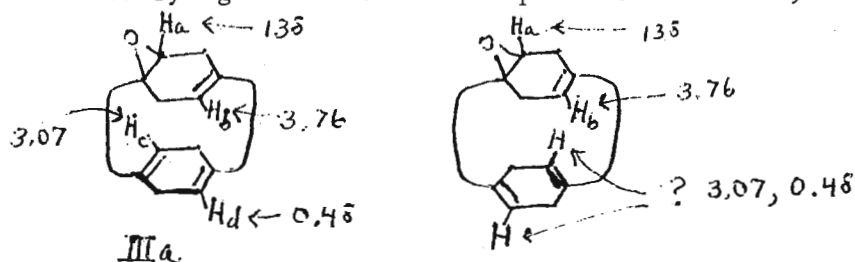
Finally, an Eu(fod)_3 shift study [by the method of B. L. Shapiro *et al.*, J. Amer. Chem. Soc., **93**, 3281 (1971)] of III -- the monoepoxide of II -- was conducted. For a model compound for III we synthesized IV, the monoepoxide of 2,5-dihydro-p-xylene.



The chemical shift observed for an equivalent amount of $\text{Eu}(\text{fod})_3$, $\Delta\delta/\rho$, was determined by plotting the observed chemical shifts as increasing amounts of $\text{Eu}(\text{fod})_3$ were added. Good linear plots were thereby obtained. The results for IV are shown below: the epoxide proton H_a experienced a shift of $\Delta\delta/\rho = 138$, while the olefinic proton H_b experienced a much smaller shift of 3.61.



We next determined the $\Delta\delta/\rho$ values for III. The epoxide proton H_a experienced a shift of 138, while the three olefinic protons experienced shifts of 3.76, 3.07, and 0.48. The 3.76 value was assigned to H_b on the basis of the shifts for the model compound IV (this assignment was substantiated by agreement of the respective $\Delta\delta$ values). Assignment of the



two remaining $\Delta\delta/\rho$ values could be done only for the stereoisomer IIIa: the H_b and H_c protons lie almost equidistant from the Eu atom, leading to similar $\Delta\delta/\rho$ values of 3.76 and 3.07; the more remote H_d proton has the smaller $\Delta\delta/\rho$ value of 0.48. When one tries to assign the H_c and H_d protons for the other stereoisomer IIIb, one cannot explain why these two protons -- both equidistant from the Eu atom -- have such different $\Delta\delta/\rho$ values.

The conclusion is that the monoepoxide is IIIa and that the tetrahydro product of [2.2]paracyclophane is the meso stereoisomer IIa.

Sincerely yours,

James L. Marshall
Associate Professor

JLM:hs

3737 BELLAIRE BOULEVARD
HOUSTON, TEXAS

February 27, 1973

MAILING ADDRESS
P. O. BOX 481
HOUSTON, TEXAS 77001

Some ^{12}C - ^{13}C Isotope Shifts

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

Dear Barry:

Perhaps I can get this to you in time to forestall your sending me one of your nasty letters.

I recently had occasion to measure ^{13}C - ^{13}C coupling constants and ^{12}C - ^{13}C isotope shifts in some hydrocarbons. The enclosed figure is representative of the kind of results I have obtained. The coupling constant of 34.9 ± 0.1 Hz between adjacent carbons is not unexpected. However the observation of a small difference in isotope shift (see Table) depending on the location of the carbon in the molecule has, to my knowledge, not yet been reported.

Species I	Species II	$\delta_{II} - \delta_I$
$-\text{}^{12}\text{CH}_2-\text{}^{13}\overset{*}{\text{CH}}_3$	$-\text{}^{13}\text{CH}_2-\text{}^{13}\overset{*}{\text{CH}}_3$	0.06 ppm
$-\text{}^{12}\text{CH}_2-\text{}^{13}\overset{*}{\text{CH}}_2-\text{}^{12}\text{CH}_2-$	$-\text{}^{13}\text{CH}_2-\text{}^{13}\overset{*}{\text{CH}}_2-\text{}^{12}\text{CH}_2-$	- 0.06 ppm
$-\text{}^{13}\text{CH}_2-\text{}^{13}\overset{*}{\text{CH}}_2-\text{}^{12}\text{CH}_3$	$-\text{}^{12}\text{CH}_2-\text{}^{13}\overset{*}{\text{CH}}_2-\text{}^{13}\text{CH}_3$	0.12 ppm

(Starred C is the one being observed).

If anyone knows of published data on such ^{13}C isotope shifts, I would appreciate hearing about it.

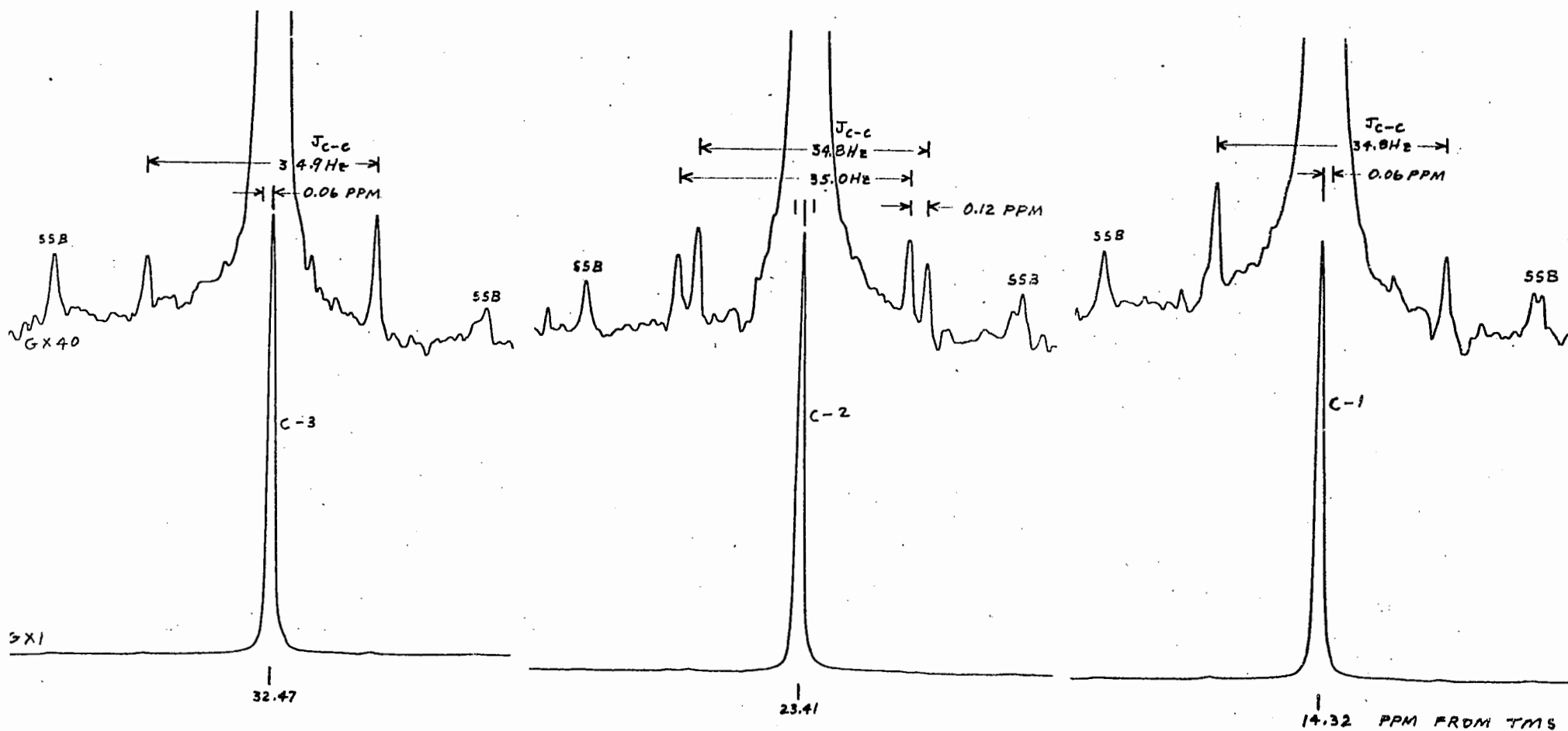
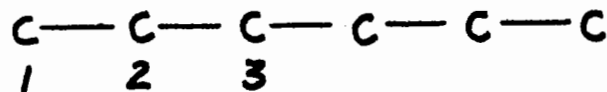
Sincerely yours,

Charlie

C. A. Reilly

CAR:pcr
Attachments

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PROGRAM FOR SYMPOSIUM ON NMR SHIFT REAGENT CHEMISTRY

To be held at the Spring National Meeting of the
American Chemical Society

Dallas, Texas
April 9, 10, 11, 1973

SPONSOR: DIVISION OF ANALYTICAL CHEMISTRY
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MONDAY AFTERNOON

Symposium on NMR Shift Reagent Chemistry
Robert E. Sievers, Presiding

- 2:00 Robert E. Sievers. Introductory Remarks.
- 2:05 C.C. Hinckley, W.A. Boyd, F. Behbahany, and G.V. Smith.
Chemistry of Lanthanide Shift Reagents: Secondary Deuterium
Isotope Effects.
- 2:35 Discussion
- 2:40 R.E. Sievers, J.J. Brooks, J.A. Cunningham, D.S. Dyer, and
R.E. Rondeau. Interactions of Nucleophiles with Lanthanide NMR
Shift Reagents.
- 3:10 Discussion
- 3:15 William DeW. Horrocks, Jr., James P. Sipe, III, and Daniel
Sudnick. Magnetic Anisotropy and Dipolar Shifts in Shift Reagent
Systems.
- 3:45 Discussion
- 3:50 Harlan L. Goering. Direct Determination of Enantiomeric Com-
positions with Optically Active NMR Shift Reagents.
- 4:20 Discussion
- 4:25 R. Burton Lewis and E. Wenkert. Structural Elucidation of
Natural Products.
- 4:55 Discussion

TUESDAY AFTERNOON

Symposium on NMR Shift Reagent Chemistry
Ernest Wenkert, Presiding

- 2:00 G.E. Hawkes, C. Marzin, D. Leibfritz, S.R. Johns, K. Herwig,
R.A. Cooper, D.W. Roberts, and J.D. Roberts. Lanthanide Shift
Reagents and C-13 NMR Spectroscopy.
- 2:30 Discussion

- 2:35 Raymond E. Davis and M. Robert Willcott. Assessment of the Pseudo Contact Model via Agreement Factors.
- 3:05 Discussion
- 3:10 M. Robert Willcott and Raymond E. Davis. Configurational Assessment of Conformationally Mobile Molecules by the LIS Experiment.
- 3:40 Discussion
- 3:45 D.A. Sweigart, L.E. Ford, C.M. Dobson, and R.J.P. Williams. The Structure of the Cholesterol · Ln(III)(DPM)₃ Complex in CDCl₃.
- 4:15 Discussion
- 4:20 G.P. Moss and E.W. Randall. Some Investigations of Lanthanide Induced Shifts in NMR.
- 4:50 Discussion

WEDNESDAY AFTERNOON

Symposium on NMR Shift Reagent Chemistry
Charles S. Springer, Jr., Presiding

- 2:00 B. L. Shapiro, M.D. Johnston, Jr., A.D. Godwin, H.L. Pearce, T.W. Proulx, M.J. Shapiro and F.A. Reilly. Some Applications of Lanthanide Induced Shifts to Organic Structure Problems. Discussion
- 2:25
- 2:30 Tobin J. Marks, J.S. Kristoff, R. Porter, and D.F. Shriver. Organometallic Aspects of Shift Reagent Chemistry.
- 2:55 Discussion
- 3:00 Joachim Bargon. Chemically Induced Dynamic Nuclear Polarization in the Presence of Paramagnetic Shift Reagents.
- 3:25 Discussion
- 3:30 C.S. Springer, Jr., A.H. Bruder, S.R. Tanny, M. Pickering, and H.A. Rockefeller. Ln(fod)₃ Complexes as NMR Shift Reagents: The Effects of Water, and Changes of the NMR Time Scale.
- 3:55 Discussion
- 4:00 I.M. Armitage, L.D. Hall, A.G. Marshall, and L.G. Werbelow. Use of Lanthanide NMR Shift Reagents for Determination of Molecular Configuration.
- 4:25 Discussion
- 4:30 Jacques Reuben. Effects of Chemical Equilibrium and Adduct Stoichiometry in Shift Reagent Studies.
- 4:55 Discussion



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Department of Chemistry • TEL. (603) 646-2501

February 27, 1973

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

Re: Postdoctoral Position

Dear Barry:

We are seeking an "nmr research associate" with a strong background in nmr research and instrumentation to supervise and maintain our nmr laboratory for 12 months while I am on leave. He or she could begin as early as late May.

Our present nmr facility consists of an HA-60IL (^1H , ^{19}F , ^{13}C , ^{11}B) equipped for decoupling, signal-averaging, variable-temperature, and pulse operations; of a Perkin-Elmer R-24 for routine use; and of a DEC Lab 8/E Computer.

The specific duties for this position will be:

- 1) to assist and instruct students and faculty in the ordinary and specialized operations of the nmr.
- 2) to assist two or three faculty members in the nmr phase of specific research projects.
- 3) (depending on abilities and interest) to help extend the computer interfacing of our nmr facility.

The person involved would have the remaining time for his own research or for a more involved interaction with one of the faculty.

Interested persons should send resume and list of references as soon as possible, so that a decision can be made before mid-May.

Sincerely yours,

Paul R. Shafer
Professor of Chemistry

PRS/blw

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March 1, 1973

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

Dear Barry:

SUBJECT: Positions Open

This is to inform your readers that we have two positions open which we hope to fill as soon as possible:

- 1) An R & D position in NMR, ESR. A background in electronics and instrumentation would be very helpful. The ability and willingness to work with people is also essential.
- 2) A position in our Service Department. A complete, broad-knowledge of electronics and instrumentation is absolutely essential.

Both positions are located in our Cranford office. The salary will be commensurate with the training and experience of the person hired. Anyone interested should contact me at the above address.

Very truly yours,

JEOL U.S.A., INC.



Thomas C. Farrar
Director of Research & Development

TCF/rmh

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 ^{13}C NMR of Alkyl Substituted Phenols

Dear Professor Shapiro,

For some time we have been interested in the identification of polyalkyl substituted phenols by NMR. Although proton NMR is very useful for the identification of the alkyl substituents the analysis of the aromatic proton region does not lead to an unambiguous assignment for the numerous possible positional isomers. We have therefore obtained the C-13 spectra of nearly 60 mono-, di-, and tri-methyl, iso-propyl or tert-butyl phenols and derived a set of direct (S_d) and indirect (S_i) shielding parameters.

The Direct Effect of Alkyl Substitution on the
Carbon-13 Chemical Shift in Phenols

Relation to Hydroxy Group	Substituent		
	Methyl	<u>iso</u> -Propyl	<u>tert</u> -Butyl
Ortho	-9.0 (-6.6)	-19.4	-20.4
Meta	-9.7 (-6.5)	-20.2	-19.8
Para	-9.0 (-5.7)	-20.1	-21.1

For the methyl substituent two values were found, indicating that the S_d are affected by a further introduction, at the ortho position to the methyl group considered, of a second or third methyl group. The bracketed values refer to phenols having at least two methyl groups ortho to each other and are examples of "crowding" constants observed by many workers both in the ^1H and ^{13}C spectra of polysubstituted benzenes.

The Indirect Effects of Alkyl Substitution on the
Carbon-13 Chemical Shifts in Phenols

Effect	Position of Substituent Relative to Hydroxy Group	Substituent											
		Methyl				<u>Iso</u> -propyl				<u>Tert</u> -butyl			
		Ring Carbon Position				Ring Carbon Position				Ring Carbon Position			
		s	<u>o</u>	<u>m</u>	<u>p</u>	s	<u>o</u>	<u>m</u>	<u>p</u>	s	<u>o</u>	<u>m</u>	<u>p</u>
Ortho	<u>o</u> -	1.4		-1.4		2.6		3.5		0.3		2.7	
	<u>m</u> -		-0.9		-1.1		2.8		2.4		2.6		3.3
	<u>p</u> -			-0.4				2.3				3.3	
Meta	<u>o</u> -		-0.3		-0.1		0.0		0.1		0.4		0.9
	<u>o</u> -		(0.9)		(1.0)								
	<u>m</u> -	0.2		0.4		0.1		0.5		0.1		0.6	
	<u>p</u> -		-0.5				0.0				0.6		
	<u>p</u> -		(-0.6)										
Para	<u>o</u> -			2.8				3.2				2.6	
	<u>m</u> -		3.1				2.8				2.6		
	<u>p</u> -	2.2				1.8				2.5			

The bracketed values indicate substituted ring carbons.

The derived S_d and S_i parameters were applied in an additive manner to the calculation of the ring carbon chemical shifts of a number of mixed alkyl phenols (Me,Pr^1 ; Me,Bu^t ; $\text{Me}_2\text{,Bu}^t$; Me,Bu_2^t) and reproduced the observed values with an averaged absolute deviation of 0.46 ppm, the maximum deviation, being 1.5 ppm. Typical examples for tert-butyl-methylphenols are given below.

Observed and Calculated Carbon-13 Chemical Shifts
for tert-Butyl-Methyl Phenols

Phenol	Carbon Number					
	1	2	3	4	5	6
2- <u>tert</u> -Butyl Obser.	41.2	57.0	65.8	63.6	65.8	76.4
4-Methyl Calc.	40.9	56.9	65.5	63.0	65.4	77.9
2- <u>tert</u> -Butyl Obser.	39.1	60.0	66.2	72.0	56.7	76.0
5-Methyl Calc.	38.9	60.7	66.3	70.8	56.1	77.5
2- <u>tert</u> -Butyl Obser.	40.2	57.6	68.4	73.1	65.0	70.2
6-Methyl Calc.	40.1	58.5	68.7	72.8	64.4	69.9
3- <u>tert</u> -Butyl Obser.	38.3	83.3	43.1	74.5	54.6	79.8
5-Methyl Calc.	38.7	83.7	43.8	74.2	54.1	79.7
4- <u>tert</u> -Butyl Obser.	42.0	69.6	65.4	50.6	69.8	78.4
2-Methyl Calc.	42.3	69.6	65.1	51.9	69.3	78.3

Chemical Shifts in ppm from internal CS₂

H. Pyszora

H. PYSZORA

INSTITUTE OF ORGANIC CHEMISTRY
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GERHARD BINSCH
PROFESSOR OF THEORETICAL ORGANIC CHEMISTRY

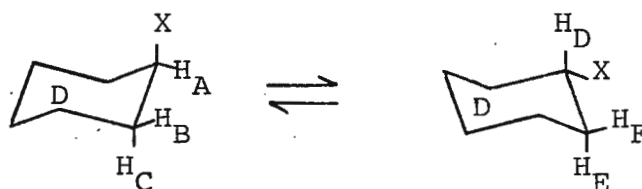
February 26, 1973

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

Non-Mutual Exchange of Three-Spin Systems

Dear Barry:

One of my former coworkers at Notre Dame, Susan A. Lesko, did her thesis work on non-mutual exchange of tightly-coupled three-spin (proton) systems. Since we couldn't find suitable model compounds that showed all the effects we were looking for, we decided to prepare a few ourselves. In addition to the molecules *a* - *d* we also investigated the dnmr spectra of octadeuteriocyclohexane, a sample of which was kindly supplied by Ed Garbisch. There is nothing particularly remarkable about the latter compound, except that the AA'BB' \rightleftharpoons BB'AA' spectra suffer from the usual drawback of collapsing to a singlet on fast exchange.



- a*, X = CN
- b*, X = Cl
- c*, X = Br
- d*, X = OCD₃

We were fortunate in that the deuterium-decoupled slow-exchange as well as the fast-exchange spectra were nicely complicated in all four cases, yet simple enough to be completely analyzable without difficulty. The point of doing work of this kind is, of course, to obtain thermodynamic and kinetic information *simultaneously*. Since in addition to the temperature dependence of the conformer populations in the range from -130° to -85° we have also managed to obtain reliable equilibrium data around ambient temperature, the precision and accuracy of our thermodynamic numbers far exceed even high standards proclaimed by Jensen and Bushweller. The exchange-broadened spectra were, however, analyzed by visual comparison with computed band shapes. I have decided to delay publication of the details of this work until we have completed a full least-squares analysis, since I now tentatively believe to have an idea as to how to overcome the mathematical and computational obstacles of such an approach in an elegant and efficient manner. Whether this turns out to be feasible remains to be seen. We are cooperating on this project with Josef Heinzer at the ETH Zürich, who has already incorporated a brute-force least-squares procedure into DNMR3. Hopefully we will have something to say about the progress of our joint venture by the time the next blue letter arrives.

Sincerely yours,

Gerhard

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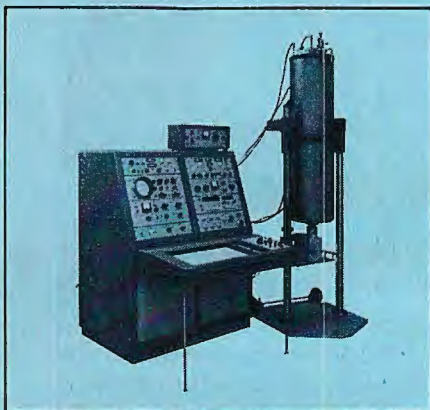
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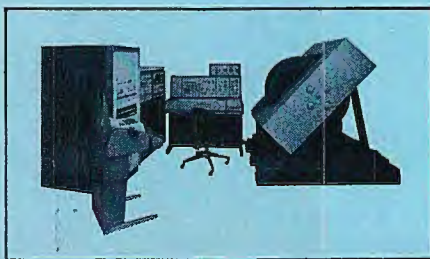
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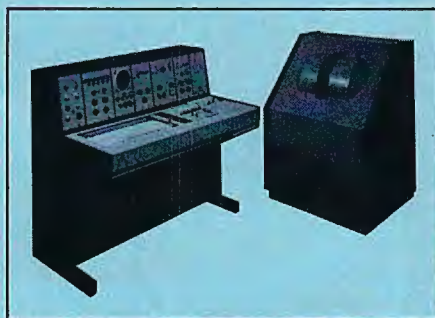
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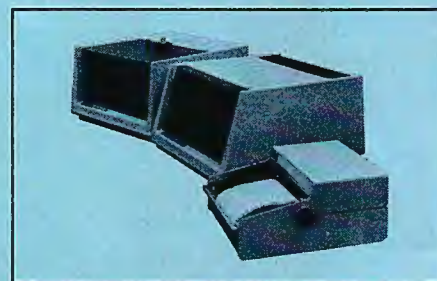
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