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Newsletter

No. 179

Rec. 8/27/73

August, 1973

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Deadline Dates: No. 180: 3 September 1973 No. 181: 1 October 1973

All Newsletter correspondence, etc. should be addressed to:

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

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STATE UNIVERSITY OF NEW YORK AT STONY BROOK

DEPARTMENT OF CHEMISTRY

STONY BROOK, N.Y. 11790

June 28, 1973

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

How to Change the Shutter Speed of the NMR Camera

Dear Professor Shapiro:

We have recently carried out some experiments designed to help deal with problems, often encountered in DNMR work, caused by the magnitude of the <u>difference</u> of the resonance frequencies of exchanging nuclei in the absence of exchange $(\Delta\nu_{\infty})$. When $\Delta\nu_{\infty}$ values are quite small or zero, traditional DNMR experiments are difficult and fraught with error or impossible. The selective nature of the isotropic hyperfine shifts caused by the lanthanide shift reagents (LSR) are very useful in this regard.

Figure 1 shows the $^{\perp}H$ NMR spectrum of trimethyl carbamate (TMC) in CCl $_{ll}$ solution at 32°C (60 MHz). Although there is known to be hindered rotation about the carbonyl carbon-nitrogen bond, the NCH $_3$ groups exhibit only a single resonance. This must occur because either the rate of rotation is fast on the NMR time-scale, or because $\Delta\nu_{\infty}$ is zero under these conditions (the latter turns out to be the case). Incremental addition of the shift reagent Eu(fod) $_3$, which interacts at the carbonyl oxygen atom, causes a broadening, splitting and then resharpening of the N-CH $_3$ resonances. The 0-CH $_3$ resonance shows only a slight, continuous, paramagnetic broadening with ρ (the mole ratio of Eu(fod) $_3$ to TMC). All peaks continuously move downfield as expected.

The shift reagent has two effects. First, it continuously changes $\Delta\nu_{\infty}$ (the <u>cis</u> NCH₃ group is closer to the coordinated europium ion than the <u>trans</u> NCH₃ group) and, thus, the NMR time-scale through the exchange-sensitive region. The rate of exchange between free and coordinated TMC is considerably larger than the rate of rotation. Second, the acidic Eu(fod)₃ slows down the reaction by increasing the double bond character of the carbonyl carbon-nitrogen bond and by steric hinderance.

We have used an uncoupled two-site exchange program to totally analyze the line shapes of the N-CH3 resonances. The program requires, as input parameters, a value for $\Delta\nu_{\infty}$ and a value of the line width, both in the absence of exchange. The observed $\Delta\nu$ was used as $\Delta\nu_{\infty}$ and the width of the 0-CH3 resonance was used as the input width at each value of ρ . The line shape fittings were quite good and values of the pre-exchange lifetime, $\tau_{\rm Obs}$, were obtained for each value of ρ .

Figure 2 shows a plot of $k_{\rm obs}(1/2\,\tau_{\rm obs})$ for the rotation as a function of σ , the fraction of TMC coordinated to Eu(fod)3. Disregarding the two points at lowest σ (where the peaks are still coalesced and a good estimate of $\Delta\nu_{\infty}$ can not be made) a good straight line is observed over 90% of the saturation fraction (σ). Extrapolating to either end, we can see that $k=33\pm4$ sec $^{-1}$ for the free TMC in CCl4 at 27°C. This corresponds to a value of $\Delta G^{\ddagger}_{300}$ of 15.5 \pm 0.1 kcal/mole, in excellent agreement with a literature value obtained in another solvent (CDCl3) where the traditional DNMR experiment is possible. The value of k for the complexed TMC is zero within experimental error. This would not have to be true in order for the method to work.

A compound which changes either the NMR time scale ("shutter speed") or the lifetime of a reactant involved in a rapid equilibrium might be called a DNMR reagent. The proton, in the elegant Saunders-Yamada method for studying the inversion of amines, acts as a DNMR reagent mostly by altering the lifetime. The LSR acts as a DNMR reagent, in this case, in both modes.

The details of this work will appear in a November issue of the Journal of the American Chemical Society.

Sincerely yours,

Charles S. Springer, Jr.

Assistant Professor of

Chemistry

Stephen R. Tanny Pre-doctoral Research

Associate

Miles Pickering
Post-doctoral Research

see de lei al III

Associate

P.S. Please credit this contribution to Paul Lauterbur's subscription.

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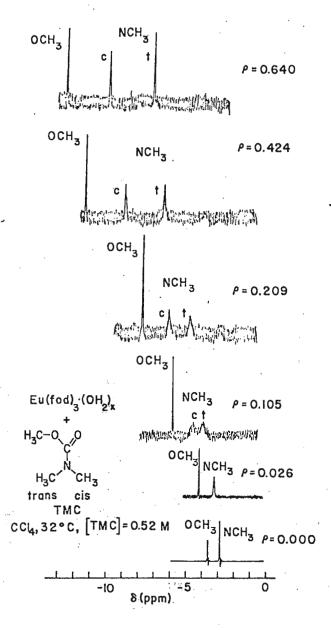


Figure 1. The proton NNR spectrum of TMC in CCl_h with varying mole ratios (ρ) of Eu(fod)₃·(OH₂)_x(x <1/2). [TMC] = 0.52 \pm 0.02 M, T = 32°C. The spectrum was recorded with differing values of the spectrum amplitude setting for different values of ρ .

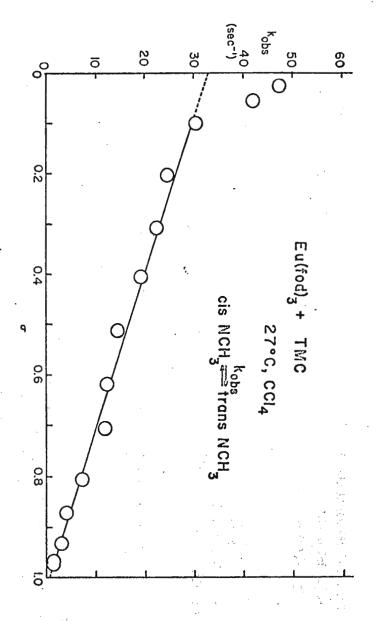


Figure 2. The dependence of the observed rate constant for isomerization of TMC, $k_{\rm obs}$, upon the saturation fraction, the fraction of TMC coordinated to Eu(fod)₃, σ .

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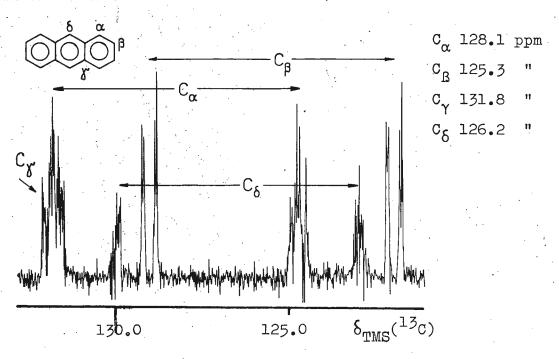
Prof.Dr.H.Gunther

5 KOLN, June 25, 1973 ZULPICHER STRASSE 47 TELEFON: 470 3263

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

Assignments for Carbon-13 Resonances

Dear Barry, Since our last letter^[1] ¹³C-NMR-work with our Bruker HX-90 FT-spectrometer has steadily increased and a number of research programs have already been completed^[2,3]. In many cases we found the undecoupled ¹³C-spectra very useful for the assignment of ¹³C-resonances. For systems containing symmetrically 1.2-disubstituted benzene rings typical fingerprints are observed that characterize the C_{α} - and C_{β} -resonances^[4]. An example is given with the spectrum of anthracene:



This experiments also demonstrates that the earlier assignment for the C-9,10 resonances (δ 132.8 ppm^[5]) has to be revised.

Often characteristic differences found for one bond ¹³C, ¹H-coupling constants are useful, as in the case of compound I,

where the previous assignment for C-8 (J \sim 125 Hz) and C-10 (J \sim 160 Hz) that was based on substituent effects [6] must now be reversed.

Sincerely yours,

H. Gunther

TABLE 1 (numbering of compounds as in [6]).

<u>6</u> 130.6 122.2 128.8 40.1 24.6

7 125.9 127.7 130.3 130.8 137.2 26.6

<u>8</u> 123.0 124.6 130.8 49.4 31.1 27.3

<u>3</u> 37.7 129.0 119.2 32.3 19.7* 15.3*

9 49.4 123.0 124.3 35.7 25.4

<u>10</u> 47.3 123.9 124.4 37.9 25.8 49.2

<u>11</u> 22.9 28.6 31.5 131.1 132.7 125.9 126.6 127.2 182.0 128.0

TABLE 3

<u>13</u> 120.4 128.5 135.7 26.9 34.0 39.6 40.1

<u>14</u> 125.6 133.2 25.9 32.0

<u>15</u> 124.4 20.2 12.8 32.0

^[1] The receipt of several reminders is gratefully acknowledged.

^[2] H. Günther, H. Schmickler, H. Königshofen, K. Recker, and E. Vogel, Angew. Chem. <u>85</u>, 261 (1973); Angew. Chem. Int. Ed. 12, 243 (1973).

^[3] H. Günther and G. Jikeli, Chem. Ber. 106, 1863 (1973).

^[4] H. Günther, H. Schmickler, and G. Jikeli, J. Magn. Resonance, in print.

^[5] R. J. Pugmire, D. M. Grant, M. J. Robins, and R. K. Robins, J. Amer. Chem. Soc. 91, 6381 (1969).

^[6] H. Günther and T. Keller, Chem. Ber. 103, 3231 (1970); the chemical shifts given in this paper are too large by 2.4 % does to an error in the conversion factor. The corrected data have been given recently in ref. [3] and are as follows:

^{*}reversal of assignment as discussed above

School of Chemistry

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Cantock's Close Bristol England BS8 ITS

26th June, 1973.

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

Dear Professor Shapiro,

Effect of P-P coupling in methyl complexes and determination of its sign by ¹H{³¹P} INDOR

Your blue note confirms my suspicion that it was some time ago that we sent our last contribution. Our studies on trimethylphosphine complexes have thrown up a couple of things that may be of interest to newsletter readers.

Whilst measuring the platinum shift of some methyl complexes, the proton spectrum of cis $PtMe_2(PMe_3)_2$ attracted our attention. The methyl part of the spectrum of complexes of the type cis $MMe_2(PR_3)_2$ have previously been described as of the $\begin{bmatrix} AX_3 \end{bmatrix}_2$ system but not analysed. A little thought shows that the spectrum, Figure 1, cannot be analysed on this basis. The complete spin system is $\begin{bmatrix} AR_0X_3 \end{bmatrix}_2$ for which Harris and coworkers have recently published an analysis assuming $J_{RR} = J_{XX} = J_{RX} = 0$. The important difference from $\begin{bmatrix} AX_3 \end{bmatrix}_2$ is that the R nuclei split the X spectrum into 19 (i.e. 2t+1) subspectra of the $\begin{bmatrix} ax_3 \end{bmatrix}_2$ type even though $J_{RX} = 0$. The series of doublets have separation.

$$\left[\left\{ \Omega L_{AR} + \chi L_{AX} \right\}^{2} + J_{AA}^{2} \right]^{\frac{1}{2}} \quad \pm \quad \left[\left\{ \Omega L_{AR} + (\chi - 1) L_{AX} \right\}^{2} + J_{AA}^{2} \right]^{\frac{1}{2}}$$

where $L_{AR} = J_{AR}$, etc., Ω takes integral values from -9 to +9 and χ takes values 1, 2 and 3. We have been able to analyse the spectrum on this basis and the resulting calculated spectrum is in good agreement. Because $L_{AX}^{9-2}L_{AR}$, a number of transitions approximately coincide e.g. the related inner and outer features marked o and i in Figure 1 have components from $(\chi,\Omega) = (1,0)$, (1,2), (2,2), (2,2), (2,4) and (3,4). In the absence of such a simplifying relationship there are likely to be so many weak features that analysis will not be possible. This example points to the dangers of describing or more particularly analysing a spectrum 'by parts'.

The value of $^2\mathrm{J}_{PP}$ here is only 2Hz less than that of the related iodide whereas Jptp is nearly half, which leads one to wonder if there might have been a sign change. This brings me to my second topic, the determination of the sign of $^2\mathrm{J}_{PP}$ by $^1\mathrm{H}\{^{31}\mathrm{P}\}$ INDOR. The previously used methods are not easily applied to these systems as $^2\mathrm{J}_{PP}$ is small compared with the width of the phosphorus spectrum (due to coupling with the protons). We had noticed that the 1H(31p) INDOR spectra obtained from the two strong proton lines were asymmetric and mirror images of each other requiring the measurement of both to find the true centre. This inconvenience turned into an advantage when I realised it must contain the sign information on $^2\mathrm{J}_{pp}$. The INDOR spectrum obtained from one of the strong lines consists of only half the $^{31}\mathrm{P}$ spectrum and the result calculated on this basis agrees well with the observed spectrum except that the 'outer' lines (more forbidden transitions) are relatively more intense in the latter. This is illustrated in Figure 2 for cis PtCl₂[P(OMe)₃]₂ (which is more soluble than the PMe₃ analogue and hence gives better pictures!) By this means, we have shown that 2Jpp is negative in all the cis PMe3 and P(OMe)3 complexes of platinum(II) that we have examined.

We hope to get our JEOL PS 100 FT system set up within a month when we shall discover for ourselves the difficulties of going from a CW only system to an FT only one.

Yours sincerely.

Robin Goodflow

R.J. Goodfellow.

1. G. Hägele, R.K. Harris and J.M. Nichols, J.C.S.Dalton, 1973, 79.

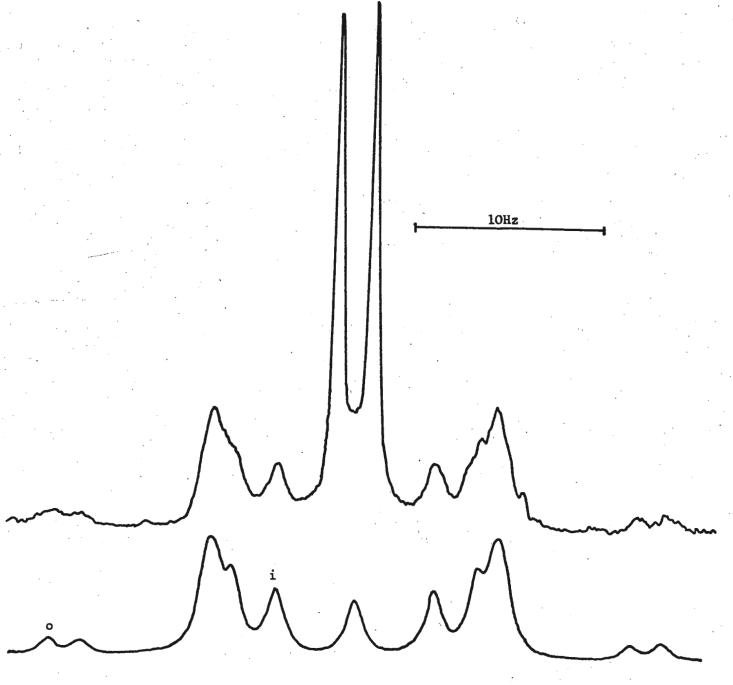


FIGURE 1 1 H n.m.r. spectrum of the platinum bonded methyl groups of <u>cis</u> PtMe₂(PMe₃)₂ with (below) spectrum calculated for 2 J_{pp} = -12.0, 3 J_{pH}(<u>cis</u> = +9.1, 3 J_{pH}(<u>trans</u>) = -7.3, 2 J_{pH} = -8.1₅ and 4 J_{pH} = +0.1₅Hz (the strong doublet has been omitted). Other parameters are:- $^{\tau}$ Me(Pt) = 9.69, 2 J_{ptH} = -65.4, $^{\tau}$ Me(P) = 8.58, 3 J_{ptH} = 20.1, $^{\delta}$ p̄ = 23.8p.p.m., J_{ptP} = +1790Hz and $^{\delta}$ pt = +22p.p.m.

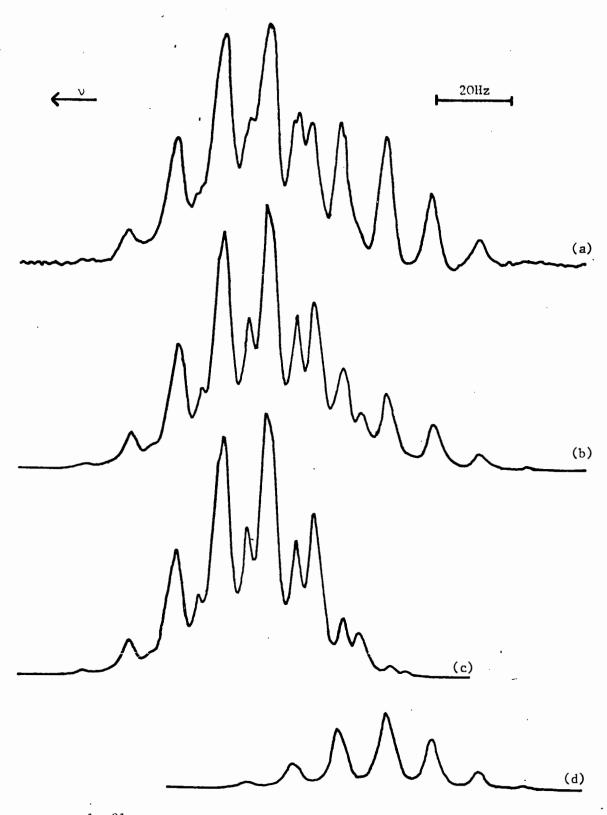


FIGURE 2. 1 H{ 31 P} INDOR spectrum of <u>cis</u> PtCl₂[P(OMe)₃]₂. (a) spectrum observed, monitoring high frequency line, $\alpha\alpha(m,p)$ (b) total calculated spectrum of transitions to $\alpha\alpha(m,p)$ for 2 Jpp negative.

- (c) calculated inner lines
- (d) calculated outer lines

 $[^{2}J_{PP} = -17.8, ^{3}J_{PH} = +12.7_{5} \text{ and } ^{5}J_{PH} = -0.0_{5}Hz]$



(formerly Fabri-Tek Instruments, Inc.)

July 2, 1973

Dr. B. L. Shapiro TAMUNMR Newsletter Texas A&M University College of Science College Station, TX 77843

Dear Barry:

TITLE: TIME SHARED HOMONUCLEAR DECOUPLING

We have been experimenting with a variation on time shared homonuclear decoupling which allows the time sharing frequency to be completely variable. One of the more common methods for the implementation of time sharing is by simply allowing the decoupling frequency to be turned on between spectral data points and turned off while the computer is sampling the fid. This does lead to the unnecessary restriction that the time sharing frequency must be equal to the sampling frequency. Since this may cause harmonics within the spectrum in some instances, we devised a somewhat different method.

In our method, the pulsing frequency as well as the time sharing frequency are selected using the NIC-293 controller, which allows the loading of six timers with independent pulse widths and delays. The mode in which the timers are triggered is controlled by a patch panel.

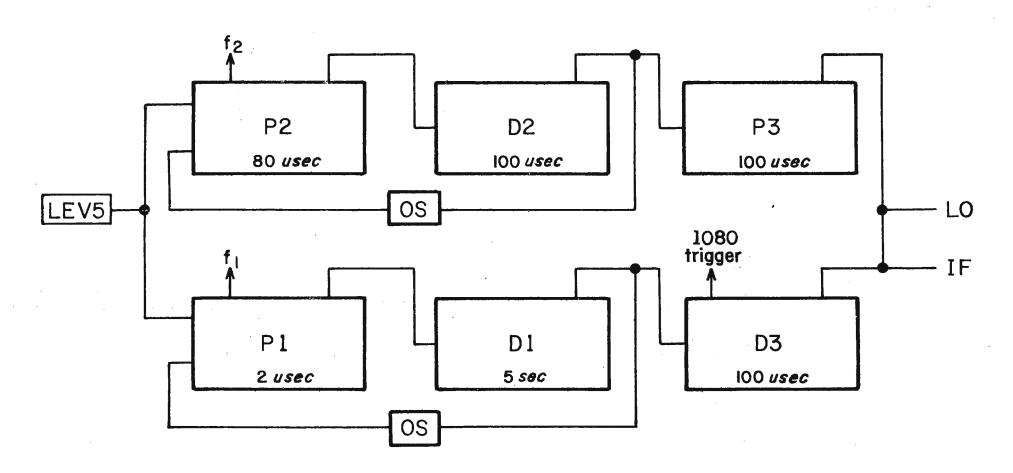
The attached Figure 1 shows timers P1 and D1 representing the 90° pulse and repetition rate of 2 µsec and 5 seconds respectively. Timers P2 and D2 represent the time that the time sharing pulse is on and off, being 80 and 100 µsec, respectively. Timers P3 and D3 are set to 100 usec each and are triggered by the onset of the rf pulse or the time sharing pulse, so that a 100 µsec pulse is produced whenever P1 or P2 is triggered. The 100 usec pulse is then used to gate the receiver so that neither rf pulse will reach the data system. As a result, the time sharing pulse repetition rate is entirely independent of the sampling rate and can be varied to produce optimum decoupling.

We ran these experiments on a Bruker HX-90E connected to a 1080 data system and show a typical example of time shared decoupling in Figures 2 and 3, where ethylbenzene, that favorite of spectroscopists for years, is shown undecoupled and decoupled. The sample was 50% v/v in CDC13 and the spectrum was obtained in 4 scans of 8K time domain points.

James W. Cooper

C. H. Bradley, University of Wisconsin

Please credit this to JWC's subscription.



NIC-293 PATCH PANEL DIAGRAM FOR HNFT EXPERIMENT

Figure 1.

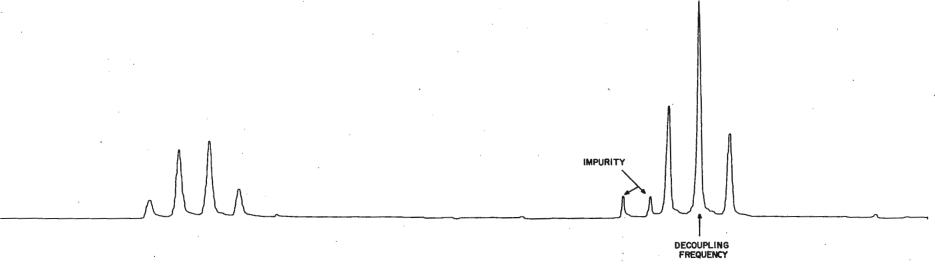


Figure 2.

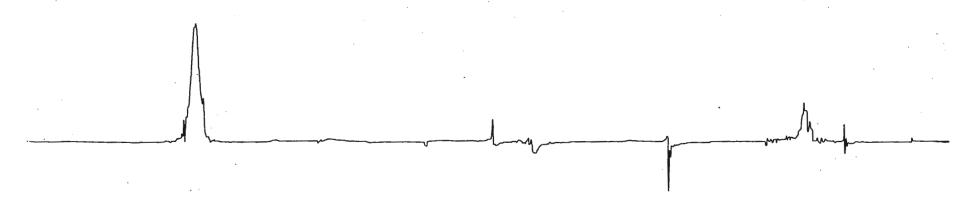


Figure 3.

DOW CORNING

July 5, 1973

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

TITLE: HA-60 IL for sale; Yb shift reagents

Dear Barry,

We wish to sell a Varian HA-60 whose cost when purchased in 1966 was \$00,000 including accessories. It is in good operating condition and is equipped for 1H, 19F, 29Si NMR with heteronuclear and homonuclear decoupling, wide sweep offset, variable temperature, and 5 and 15 mm spinning sample tubes. Those interested in acquiring this spectrometer at a relatively nominal cost should contact me at the below address.

As you know, we have been involved for some time in the use of shift reagents to analyze intractable mixtures. Recent publications suggest that the Yb reagents, particularly Yb(DPM)3, may be more suitable for this purpose since they may exhibit simpler stoichiometry. If anyone has preprints or unpublished data that bears upon this question, I would be most grateful to hear from them.

Very truly yours,

Dwight E. Williams

Mail No. 27

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Midland, MI 48640

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HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

12 Oxford Street

Cambridge, Massachusetts 02138

U.S.A.

July 2, 1973

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

Dear Barry:

As a part of a study of the binding of isonitriles to hemoglobin Barbara Manuck and I have been measuring T_2 's using high resolution Fourier transform techniques. Typical T_2 measurements are shown in the enclosed Figure; both in the presence (A) and absence (B) of ^{14}N decoupling. These measurements were made on an Varian XL-100 using a $T-\pi/2-\tau-\pi-\tau$ spin echo pulse sequence. While the τ 's are fairly long the resolution was good ($\Delta v^* \lesssim 0.2 Hz$) so that we feel spin diffusion was not significantly hurting us. We are indebted to Dr. George Gray for loaning us the ^{14}N decoupler.

Best regards,

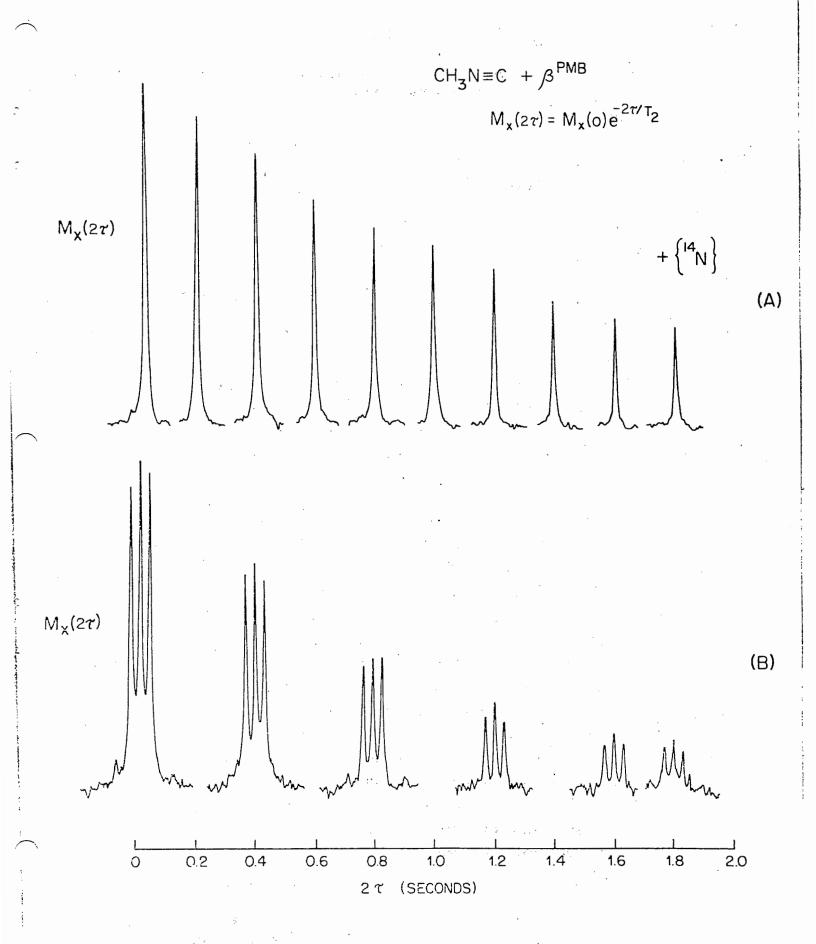
Buan

Brian D. Sykes

P.S. Who's Lisa?

Enc:

BDS:bam



THE CITY COLLEGE

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DEPARTMENT OF CHEMISTRY

(212)621-7402

July 9, 1973

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

Subject: Spin Coupling Between Directly-Bonded 15N Nuclei

Dear Barry,

Recently, we have been investigating coupling between directly bonded $^{15}\text{N-}^{15}\text{N}$ nuclei in a variety of molecules. Our efforts have largely centered on using double-labeled materials (>95% enrichment) and some of the preliminary data that have been accumulated are summarized in the accompanying table.

Several observations can be made. Firstly, the range of values is rather small - less than about 20 Hz. Secondly, the data seem to parallel the s-characters of the nitrogen atoms involved suggesting the importance of the Fermi Contact term. For example, a comparison of the observed $^{15}\mathrm{N}-^{15}\mathrm{N}$ coupling in phenylhydrazine (6.7 Hz) with that found in the p-nitrobenzaldehyde phenylhydrazone (10.7 Hz) shows a significant increase (4 Hz) in the coupling. This, presumably, arises from the incorporation of the terminal nitrogen of phenylhydrazine in a imine bond. In trans-azoxybenzene or p-hydroxyazobenzene where both nitrogen atoms may be taken as sp² hybridized, the coupling is even larger. Finally, in the case of dibenzylnitrosamine, where there is much evidence for substantial $p-\pi$ bonding between the nitrogens, the largest coupling (19 Hz) to date has been found. On this basis the phenyl diazonium ion might be expected to exhibit even larger coupling, but this value is presently unknown.

Sincerely,

Theodore Axenrod

Some Directly Bonded ¹⁵N-¹⁵N Coupling Constants

1- ¹⁵ N), Hz	Approximate Hybridizations in N-N bond
(DMSO)	sp ² -sp3
(DMSO)	sp^3-sp^2
(ether)	$\operatorname{sp}^2 - \operatorname{sp}^2$ $\operatorname{sp}^2 - \operatorname{sp}^2$
(acetone)	sp ² -sp ²
(DMSO)	sp^2-sp^2
7	N- ¹⁵ N), Hz 7 (DMSO) 7 (DMSO) 7 (ether) 0 (acetone) 0 (DMSO)

⁽a) G. Binsch, J. D. Lambert, B. W. Roberts and J. D. Roberts, J. Amer. Chem. Soc., 86, 5564 (1964).

⁽b) N. N. Bubnov, K. A. Bilevitch, L. A. Poljakova and O Yu Okhlobystin, Chem. Commun., 1058 (1972).

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THE OHIO STATE UNIVERSITY

Professor Bernard L. Shapiro Department of Chemistry Texas A & M University July 5, 1973

College Station, Texas 77843

SLOW INVERSION IN TETRAHEDRAL ADDUCT OF AMIDE

Dear Barry:

Bender's report of 1952 that tetrahedral alcoxide adducts of esters (when R is perfluoro) could in some cases be isolated, (1)

induced us to investigate the behavior of an amide adduct with nmr.

Addition of potassium t-amyloxide to N,N-dimethyltrifluoracetamide in iso-octane establishes the equilibrium (2).

(2)
$$CH_3 OK$$
 $CH_3 OK$ $CH_3 CH_2 COK CH_3 CH_3 CCH_3 CCH$

The N-methyl proton resonance of this solution at 30° consists of two quartets, $(J_{\rm H,F}=2{\rm Hz})$ for the free amide, indicating slow rotation and a sharp singlet 0.5 ppm to higher field ascribed to adduct I. This latter line disappears when water is added to the solution. Only N,N-dimethyltrifluoracetamide and t-amyl alcohol are obtained on hydrolysis and there is no evidence for dimethylamine. These results also show the equilibrium (2) to be slow on the nmr time scale.

As the temperature is lowered from 10° to -20° the N-methyl resonance of I progressively broadens and finally splits into an equal doublet, 2Hz. Careful comparison of the shift with respect to internal standards and of the line-shape itself reveals that these effects come from an exchange process. Tentatively we propose the N-methyl non-equivalence to come from the asymmetry at C* in I, and its averaging to nitrogen inversion. Why inversion in species I should be so slow must have something to do with the electronegativity of the substituent together with the possible complexation of both oxygen and nitrogen in I to potassium, that is, the potassium holds the nitrogen rigid, II. We tested this hypothesis by testing the effect of added crown ether (dicyclohexyl-18-crown-6). In fact this increases the inversion rate.

We are hoping to clear up some of these questions with kinetic measurements of inversion. For the usual reasons coalescence temperatures will not be discussed.

With best wishes,

Sincerely, Cideon Frachkel

FACULTÉ DES SCIENCES DE MARSEILLE - SAINT-JÉROME 13 - Marseille (13%)

TÉL.: 50-31-61

DÉPARTEMENT DE CHIMIE ORGANIQUE LABORATOIRE DES ORGANOMÉTALLIQUES PROFESSEUR J. C. MAIRE

July 6, 1973

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

Title: INFLUENCE OF SiMe_3 GROUP ON THE ALLYLIC COUPLINGS

Dear Professor Shapiro,

Thank you for your blue and red reminders and my apologies for the delay in replying you. My contribution concerns the effect of $-\mathrm{SiMe}_3$ group on allylic coupling constants.

In 1970, the allylic coupling constants of compounds of the type:

$$H_{1}^{2}C = C_{1}^{CH_{3}}$$

ham been studied by D.G. KOWALEWSKI[1]. He obtained a linear correlation between the two allylic coupling constants (Cis and trans) and the Y electron gativity.

Therefore, we synthesized and studied some similar compounds with Y = $SiMe_3$ and Y = CH_2 - $SiMe_3$ with the aim of determining the inductive or resonant effect of $SiMe_3$ group.

In fact, refering to the propene, the SiMe substituent gives a I effect and the CH_-SiMe_3 a I effect. In the second case, the -CH_2 group forbids any conjugation between the double bond and the empty 3d orbitals of the silicon atom. The results found in the litterature give us a ratio I /I = 1.6. So, if the allylic couplings are related to the Y electronegativity, their variations, refering to the propene, must be in the ration 1.6:1. The following table collects our results and those found in the litterature for the propene:

Y	$J_{\text{CH}_3}\text{-H}_1$ (cis)	J CH $_3$ -H $_2$ (trans)
SiMe ₃	1.35	2.0
Н 3	1.33	1.75
CH ₂ -SiMe ₂	0.9	1.35
$\begin{array}{c} \text{CH}_2-\text{SiMe}_3 \\ \text{CH}_2-\text{SiMe}_3 \end{array}$	$J_{\text{CH}_2}^{-\text{H}_2} : 0.9$	J_{CH_2} - $H_1:0$

One can se, we do not have any inductive effect because -CH₂-SiMe₃ and -SiMe₃ are working in opposite directions. If we first use the $\sigma-\pi$ picture for the allylic coupling, it is hard to see how the -SiMe₃ group could increase the coupling. The only possible non-inductive electronic effect is a $d\pi-p\pi$, pushing the π electrons into the silicon atom and decreasing the $\sigma-\pi$ conjugation (i.e the allylic

Coupling constants). So, we do not agree with D.G. De KOWALEWSKI[1], thinking that conformational effects (c.f. Dreiding models corresponding to compounds $\underline{1}$, $\underline{2}$ and $\underline{3}$) are, at least, as important as the electronic effects of the substituent in the study of allylic coupling constants.

[1] This newspaper, 1970, 143-4

R. GASSEND

II. Journal

Y.LIMOUZIN

y way

J.C.MAIRE

14.

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA 93106

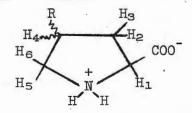
July 12, 1973

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

"Conformational Analysis of 4-Fluoroprolines"

Dear Barry:

L-Proline (Ta) and 4-hydroxy-L-proline (Tb) are the only cyclic α-imino acids to commonly appear in protein sequences and, as a result, the conformational properties of these molecules have been of particular interest. We have completed a study of cis and trans 4-fluoroproline (Ic) in an effort to learn



Ia R = H

b R = OH

c R = F

more about these properties in this five-membered ring. The presence of the fluorine atom spreads out the proton spectra to the extent that a complete spectral analysis of the ABCDEFX systems is possible - the only requirements for the analysis being infinite patience and a nearly matching amount of money for the ever-hungry computer.

A local version of the IAOCN3 program was used. About 100 lines were assigned in each case; the chemical shift and coupling constant parameters so obtained reproduced these lines to within an error of 0.1 Hz or less. A discussion of the relative signs of coupling constants and the assignment of the various groups of resonances to particular nuclei of the structures are given in a paper that will appear in J. Amer. Chem. Soc. For the present it is sufficient to state that the vicinal H-H and H-F coupling constants are accurately known.

These coupling constants were used in conjunction with a version of the Karplus equation to define the dominant solution-state conformations of these species. The three-dimensional structure of an arbitrary five-membered ring can be specified

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by the five bond lengths and by four angles which can be any combination of bond angles or dihedral angles (1). We assumed all bond lengths to be 1.52Å, an average based on crystal structure data. The computer was then used search through the conformations defined by the angles. At each step of the way a least-squares fit of observed coupling constants to the Karplus equation was made. The best fit was assumed to be that obtained from the dominant conformation. The procedure converged cleanly for both sets of data; the best-fit conformation selected for each isomer is shown below.



trans

cis

The interesting thing is the tendency of the fluorine atom to take up an axial orientation (It has often been found that fluorine prefers to be axial in sixmembered rings.) and in this respect, the fluoroprolines appear to have the same conformational properties as the corresponding hydroxyprolines (2).

Sincerely yours,

R. S. McLeod

, 6000

J. T. Gerig

References

- 1. J. B. Hendrickson, J. Amer. Chem. Soc. 83, 4357 (1961).
- 2. R. J. Abraham and K. A. McLauchlan, Mol. Phys. 5, 513 (1962).

Prof.Dr.G.Hägele Institut für Anorganische Chemie der Universität Düsseldorf Düsseldorf, 25.6.73 Moorenstrasse 5

to
Prof.Dr.B.Shapiro
Texas A & M University
College of Science
College Station
Texas 77843
USA

Dear Professor Shapiro!

I would very much like to join the readers of TAMU NMR Newsletters with the following contribution: Protonresonance spectra of $[CH_3(t-C_4H_9)P(X)]_2Y$, (X= free electron pair, 0, S; Y= direct bond, 0, S), may be trated as R- and X-spectra of $[AR_tX_n]_2$ spinsystems $^1)$, ore more generally as $[AX_n]_2 - \text{systems}^2$. Corresponding phosphorus spectra can be calculated as series of overlapping [ab] -subspectra obeying the following equations::

- 1) if the usual definitions for [AB] -systems are adopted: $C = \sqrt{\Delta \nu^2 + J^2} , \quad s_i = C J , \quad s_o = C + J ,$ $\nu_c = (\nu_A + \nu_B)/2 , \quad \text{Int}_i = 1 + C/J , \quad \text{Int}_o = 1 C/J$ Totalintensity = 4 , and
- 2) the $[A \sum_{i,i}^{i} J_{2} System$ is given by:

 2 z groups with n_{i} spins of I = 1/2,

 all longrange couplings $J_{X^{i}X^{i}}$, $J_{X^{i}X^{j}}$, $J_{X^{i}X^{j}}$ ære zero, $N_{AX}i = [J_{AX}i + J_{AX}i']$, $L_{AX}i = [J_{AX}i J_{AX}i']$, k_{i} , k_{i} = integer parameters from 0 to n_{i} , than
- 3) there are $\prod_{i=1}^{t} (n_i + 1)^2$ [ab] -subspectra for the A-resonances

$$\Delta v = \sum_{i=1}^{2} (k_i - k_i) * L_{AX}^i$$

$$v_c = v_A + 0.5 * \sum_{i=1}^{2} (k_i + k_i, -n_i) * N_{AX}^i$$

$$J = J_{AA}^i$$

and a statistical weight for each [ab] -subspectrum of

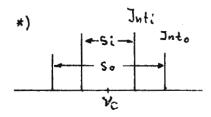
$$ST = 4 \times \left[\begin{array}{c} t \\ ki \end{array} \right] \star \left[\begin{array}{c} n_i \\ k_i \end{array} \right] \star \left[\begin{array}{c} n_i \\ k_i \end{array} \right]$$

deceptively simple singuletts with:

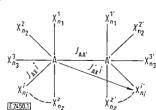
$$Y = V_A + 0.5 * \sum_{i=1}^{2} (2k_i - n_i) * N_{AX}i$$

$$Int = 4 * \bigcap_{i=1}^{2} \binom{m_i}{k_i}^{2}$$

- 1) G.Hägele, R.K.Harris and J.M.Nichols; J.C.S.Dalton, 1973,79
- 2) G.Hägele, R.K.Harris; Ber.der Bunsenges. 76, 910 (1972)



+)



Yours sincerely

T-40, fell

Gerhard Hägele

Announcement

FIFTH INTERNATIONAL SYMPOSIUM ON MAGNETIC RESONANCE

AΨ

TATA INSTITUTE OF FUNDAMENTAL RESEARCH HOMI RHABHA ROAD, BOMBAY 400005, INDIA

From

Monday, January 14, 1974

To

Friday, January 18, 1974

1. PROGRAMME

The scientific programme at the above symposium will consist of contributed papers and invited papers devoted to basic aspects of magnetic resonance and its applications to Physics, Chemistry and Biology. Besides electron paramagnetic and nuclear magnetic resonance, the programme will include nuclear quadrupole resonance, cyclotron resonance, ferromagnetic resonance and acoustic magnetic resonance. The language of the Symposium will be English.

2. SPONSORSHIP

The Symposium is held under the auspices of the International Society of Magnetic Resonance and Association of Magnetic Resonance Spectroscopists (India) and is sponsored by the Indian National Science Academy, International Union of Pure and Applied Chemistry and the Tata Institute of Fundamental Research. Applications for sponsorship have also been made to International Union of Pure & Applied Physics, International Union of Biological Sciences, and the International Union of Pure and Applied Biophysics.

3. ABSTRACTS

Abstracts of proposed papers should reach the Chairman, Local Organizing Committee by September 1, 1973. The abstracts should be submitted on quarto paper (8" x 11") leaving a 1" margin on all 4 sides and should not exceed one page. It is preferable to use an electric typewriter. The name of the author presenting the paper at the conference should be underlined.

4. REGISTRATION FEE

(i) US \$ 45 for participants (ii) US \$ 15 for students and accompanying persons (iii) US \$ 30 for members of the International Society of Magnetic Resonance.

All requests for further information should be addressed to Prof. Balu Venkataraman, Chairman, Local Organizing Committee, Fifth International Symposium on Magnetic Resonance, Tata Institute of Fundamental Research, Bombay 400005, India.



NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

6110-316:WBM:pls 17 July 1973

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

Low Cost 100W 25 MHz Amplifier and Driver

Dear Barry:

We have obtained very satisfactory results using a simple and inexpensive final rf power amplifier for our 25 MHz C-13 FT system. It consists of a ham type mobile linear amplifier with 100W P.E.P. output for 10W drive. We chose a Lafayette Model HA-250A (about \$100), but there appear to be several other manufacturers of equivalent units. Simple wiring changes bypass the rf sensing circuit so that the B⁺ and antenna (output) circuits are always activated. The overall tuning range is 20 - 54 MHz, and output loads from 40 to 600 ohms can be matched. We also purchased a Model HA-255 power supply (about \$40), which allows operation of the HA-250A from 117 VAC. The two units together occupy less than a cubic foot.

The drive to the HA-250A is supplied by a Lakeland transistor amplifier. (Lakeland Instruments Laboratory, RR2, Box 52-A, Angola, Indiana 46703). This unit also costs about \$100, and supplies 30W out at 25.1 MHz for 1-3W drive, with 50 ohm input and output impedances.

Sincerely,

W. B. MONIZ

Physical Chemistry Branch Chemistry Division Until recently, if you wanted broadband RF power, you had to settle for bulky tube-type power amplifiers. No more. Starting at the top, we developed a full line of all-solid-state Class A power amplifiers, covering the frequency spectrum of 10 kHz to 560 MHz, with power outputs ranging from 300 milliwatts to over 1000 watts. And we're still climbing.

tuned, our highly linear units will ampilfy inputs of AM, FM, SSB, TV and pulse modulations with minimum distortion. Although all power amplifiers deliver their rated power output to a matched load, only ENI power amplifiers will deliver their rated power to any load regardless of match.

We also designed our amplifiers to be unconditionally stable and failsafe-you need never fear

put meter. Ruggedized amplifiers capable of operating under severe environmental conditions are available.

To find out more about our RF power amplifiers write: ENI, 3000 Winton Road South, Rochester, New York 14623. Call 716-473-6900, TELEX 97-8283 ENI ROC.



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Stauffer Chemical Company

1200 South 47th Street / Richmond, California 94804 / Tel. (415) 233-9361

July 19, 1973

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

Dear Barry:

Re: Long-range H-P Coupling Constants

We have observed long-range H-P coupling constants in various 2-phosphorylimino - 3-methyl-4-thiazolines. The magnitude of the H-P coupling in the H-C-N-C=N-P framework (1.67-4.89 Hz) is much larger than that in H-C-S-C=N-P (0.46 \sim 1.41 Hz). Both H-P coupling constants are sensitive to the substituents at the phosphorus atom. The five bond H-P coupling constants are listed in the table. The size of the coupling between P and $\rm H_4$ increases in the order of PO, PS, and P. No such relation was observed for the coupling between P and H_5 .

X	R	J _{PH₄(Hz)}	J _{PH5} (hz)
0	0C ₂ H ₅	1.67	1.22
S	0C ₂ H ₅	2.30	1.41
-	0C ₂ H ₅	3.82	0.46
-	C ₆ H ₅	4.89	0.65

Sincerely yours,

A. Mihailovski

PERKIN-ELMER



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

July, 1973

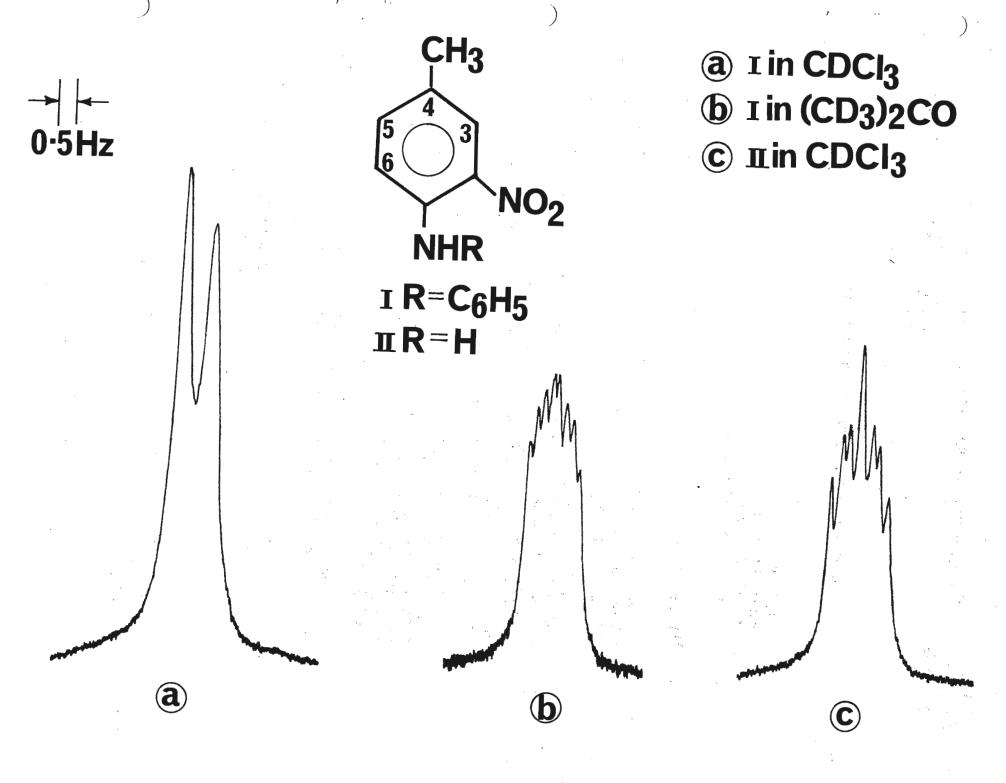
"Virtual Decoupling"

Dear Dr. Shapiro,

I hesitate to use the term deceptive simplicity in TAMUNMR as it has been applied so often to situations which would deceive none of your readers. Recently, however, I encountered an example which made me think twice, involving as it does coupling constants of opposite signs. The methyl signal of I at 90 MHz in CDCl₃ appears surprisingly as a doublet despite the presence of two ortho protons. In the aromatic region the signal H–3 only could be identified, and decoupling of this proton collapsed the CH₃ resonance to a singlet with 0.5 Hz linewidth. The explanation lies in the very small chemical shift difference between H–5 and H–6. Since the four and five bond coupling constants J_{45} and J_{46} have opposite signs the normal deceptive simplicity appears rather as a "virtual decoupling". This was confirmed by running the spectrum in $(CD_3)_2CO$ when there is a larger shift difference between H–5 and H–6, and also by looking at II which has a nearly first order spectrum in CDCl₃. The observed CH₃ multiplets are well reproduced by ABMX₃ calculations using J_{34} –0.8 Hz, J_{45} –0.4 Hz, and J_{46} +0.2 Hz. Incidentally, the values of J_{45} are unusually small.

Yours sincerely, for Perkin-Elmer Limited,

R.A. Spragg





THE UNIVERSITY OF NEW MEXICO

ALBUQUERQUE, NEW MEXICO 87106

DEPARTMENT OF CHEMISTRY TELEPHONE 505: 277-2821 20 July 1973

CHEMICAL SHIFTS IN SUBSTITUTED PHENAZINES

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

Dear Dr. Shapiro,

Over the past few months I have been looking at temperature and solvent effects on $^{13}\mathrm{C}$ chemical shifts. The work I would like to describe, however, is of a slightly different nature.

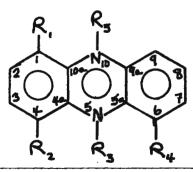
Dr. Ulrich Hollstein of this department has been preparing substituted phenazines. We have obtained chemical shifts for the carbons in several of these in various kinds of solvents. The assignments are not easy to make but we have made some guesses for them. I would like to present the data here with our fragmentary and tentative assignments in the hope that a reader might be able to help out. Very few of the assignments are really firm.

The Table presents the data we have gathered so far. Compound II was dissolved in D_2O as was compound III. All of the other compounds were dissolved to the point of saturation in D_2O -NaOD solutions. There will be significant solvent effects in some of the peaks (i.e. (1) in compound VI and (1) and (6) in compound V, etc.). The concentration of the solute was generally in the range of 1 mole%.

I should mention also that our graduate program in physical chemistry still has some openings for serious students.

Dr. Wm. M. Litchman

Thank you



SAMPLE	E I*	II	III	IV	V	VI	VII
R ₁	_	-	СООН	СООН	ОН	ОН	ОН
R ₂	<u>·</u>	-	_	-	_		-
R ₃	- ,	$CH_3^+, CH_3SO_4^-$		-	_	_	0
R ₄		-	-	СООН	ОН	<u> </u>	ОН
R ₅	_	_	_	_	-		0
_	16.02(4a)	-19.35(4a)	-38.66(R ₁)	-48.50(R ₁)	-37.01(1)	-37.86(1)	-6.01(1)
-3	3.20(1)	-14.84(2)	-16.59(10a)	-15.45(1)	-15.73(4a)	-16.95(4a)	-4.17(4a)
-2	2.23(2)	~7.90(9a)	-15.85(1)	-12.63(4a)	-12.72(5a)	-13.57(5a)	+15.37(2)
		-7.55(4)	-12.52(4a)	-12.31(5a)	-4.84(3)	-13.44(9a)	+27.71(4)
		-6.13(3)	-12.31(5a)	-2.92(4)	+15.64(2)	-12.48(10a)	
		+6.77(1)	-10.08(6)	-2.25(3)	+16.46(4)	-7.48(?)	2 peaks
		+69.88(Me)	-7.76(4)	-1.08(2)		-2.94(?)	missing
		•	-5.96(3)			-1.25(?)	
			-4.51(7)			-1.13(?)	
•			-3.00(9)	•		+0.92(?)	
			-2.63(8)			+16.41(2)	
		·	-0.58(2)			+17.54(4)	• •
			+2.65(9a)		·		

^{*} R. J. Pugmire and D. M. Grant, J. Am. Chem. Soc. <u>91</u>, 6381 (1969).



ICN Nucleic Acid Research Institute

A Division of International Chemical & Nuclear Corporation

24 July 1973

2727 Campus Drive Irvine, California 92664 Telephone 714: 833-2500 TWX: 910-595-1754

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

Dear Professor Shapiro:

I wish to bring some FT equipment to the attention of the Newsletter readers which I would like to sell. We have a 4K computer package consisting of a Nicolet 1074 averager interfaced to a Digital Equipment Corp PDP-8/e. An ASR-33 Teletype is included. An additional feature of this 1074 is a systems noise reduction program in the SD-72 ADC. This feature normally is present in Nicolet 1080 computers. This FT package listed for \$23,000 in 1971. We are asking \$10,000 (negotiable) or \$6,000 for the 1074.

Nicolet 1074 Noise Reduction Option

The normal analog to digital converter, Model SD-72 (or SD-72-I), supplied with the Nicolet 1074 computer portion of the 1074-PDP-8/e package, is adequate for transient accumulation up to $\sim 50,000$ scans. If this number of transients is exceeded on very weak samples, the systematic systems' noise of this converter becomes of comparable magnitude to that of the signal. The resulting Fourier Transform contained "spurious signals" as well as exhibited baseline problems.

The noise reduction option on the Model SD-72-A digitizer, designed and installed by Nicolet Instrument Corp., electronically averages the systematic noise of the digitizer to zero, yielding a true transient average. The noise reduction is accomplished by subjecting the input signal to a differential amplifier before the signal reaches the digitizer. This amplifier produces two signals, one normal and one inverted, which are alternately sampled. Simultaneously, the accumulator is being switched from add to subtract which results in the input signal always being added to the memory. The systems' noise of the digitizer is not being inverted and this noise is being averaged to zero because of the alternating add and subtract functions of the accumulator.

With this option, we have been able to obtain C¹³ spectra after 200,000 scans which do not show any "spurious signals" and exhibit a good baseline. This new option is clearly very useful for the accumulation of a very large number of transients. Although the quality of the spectra obtained from several thousand transients was acceptable for both digitizers, the S:N ration for the SD-72-A was approximately a factor of 2 greater than the SD-72-I for the same sample run under identical conditions.

Sincerely yours,

M. P. Schweizer, Ph.D.

Head, Biophysical Chemistry



University of Strathclyde

Department of Pure and Applied Chemistry

Thomas Graham Building, Cathedral Street, Glasgow, C1 Telephone: 041-552 4400

10th July, 1973.

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

Dear Barry,

Continuing our series of contributions which report the rediscovery of known facts, let me mention some observations we have recently made on nematic phase spectra.

In reading around on the subject of oriented spectra, it occured to me that permanent magnet spectrometers might be ideal in providing the thermal stability and uniformity necessary for producing good quality spectra using the low temperature nematic phases such as p-ethoxybenzylidene-p-butyl aniline (EBBA). Our R10 spectrometer has adequate resolution with a non-spinning sample tube, and the first experiment with benzene as solute produced results which matched those published in the literature. The example shown is of the spectrum of benzo-2,1,3 thiadiazole (I, X=S), 16.7% mole fraction in EBBA at 33.5°. Satisfactory spectra are obtained on a single scan but that shown is of 62. accumulated scans.

To achieve good results with accumulation techniques it was necessary to leave the sample in the spectrometer some hours to reach thermal equilibrium, thereafter the frequency separations of peaks at the extreme ends of the spectrum were constant to #in 2000 Hz. Line widths were 14Hz.

In the instrument used the sample was in contact with the magnet thermostatic system, I am not so sure that such good results would be obtained in those permanent magnet instruments which have separately controlled variable temperature sample systems.

The structures of benzo-2,1,3-thiadiazole and its oxaand selena- analogues (I, X=0,Se) are of some interest and they have already been examined by conventional proton n.m.r.¹ and microwave² methods and I am currently engaged in the necessary calculation from these oriented spectra results.

Kind regards,

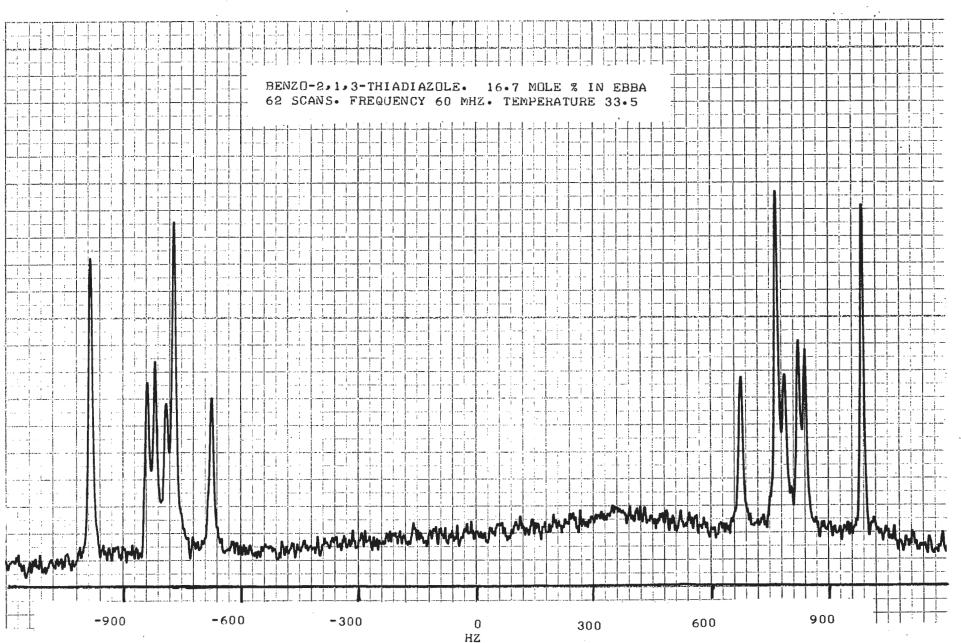
Yours sincerely,

Peter Bladon.

Dr. P. Bladon.

References

- N.M.D. Brown and P. Bladon, <u>Spectrochimica Acta</u>,
 1968, <u>24A</u>, 1869.
- N.M.D. Brown, D.G. Lister and J.K. Tyler,
 Spectrochimica Acta, 1970, 26A, 2133.



1/9-3

The University of Manitoba

Department of Chemistry Winnipeg, Manitoba Canada R3T 2N2



July 20, 1973.

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

Dear Dr. Shapiro:

In an attempt to convince the experimentalists here that we could really simulate an NMR experiment, we recently calculated the enclosed AB spin-1/2 spectrum, which is complete with a simulation of noise using a random number generator. Actually, only one-half of the spectrum is calculated, the other half being experimental. The discerning eye may be able to pick out the synthetic half, but we're not telling.

Please credit this note to Dr. Schaefer.

Yours sincerely,

Bruce Goodwin, Graduate Student.

/bf enc.

* Using the method we outlined in J. Magn. Resonance, 8, 41 (1972).



Continuous wave spectra of an AB system of spin-1/2 nuclei. One-half of the spectra is experimental; and one-half is a simulation, including simulated noise.



THE DOW CHEMICAL COMPANY

FOST OFFICE BOX 400
WAYLAND, MASSACHUSETTS 01778
617 · 235-5422
July 26, 1973

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

INDUSTRIAL POSITION - NMR SPECTPOSCOLIST

Dear Barry:

We would like to take advantage of the widely circulated Texas

A & M NMR Newsletter to announce that an opening exists in our
laboratory for a NMR Spectage conist. Interested applications should:

Have the Ph.D. Degree

Be applications orientated

Have a strong desire to learn and apply new techniques

Have a clear history of being a "problem solver"

Have electronic maintenance and servicing capabilities

Have some knowledge and appreciation of organic chemistry

Be capable of independent, aggressive research

The job would involve collaboration with resident organic natural product chemists in elucidating the structures of complex molecules, seeking out and applying NMR to the solution of a wide variety of company technical problems, and assuming part of the responsibility for the upkeep and maintenance of our NMR systems. Some time would be available for physical/analytical technical development that is often required to solve a non-routine NMR problem.

There are currently 28 professional people in our laboratory. Our primary charge is to develop new Dow chemistry that will ultimately result in new products or plant processes. Instrument-wise, we presently have three Varian NMR systems (A 56/60, NV-14 and HA-100) and a 16-62 MHz Bruker 3215 pulse spectrometer. The HA-100 and 321S instruments are interfaced to and completely supported by a 16K PDP 12/30 LDP Digital Equipment Corporation computer. The A 56/60 and NV-14 spectrometers are part of our self-service analytical system.

Applicants should write directly to me and enclose a resume, academic transcripts and Ph.D. thesis abstract (or associated publications). Dow is an equal opportunity employer.

Sincerely yours,

pat

cc: S. W. Tobey

J. J. Flynn

Don T. Dix Research Specialist

GEORGIA INSTITUTE OF TECHNOLOGY ATLANTA, GEORGIA 30332

CHEMISTRY

July 24, 1973

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

Dear Barry:

 ${\bf T}_1$ Measurements on a 4H-100 NMR Spectrometer

We have been trying to do T_1 measurements on organic liquids using a JEOL 4H-100 NMR spectrometer by recording recovery curves after inversion by adiabatic fast passage. While we could perform all room temperature measurements without any difficulty, we encountered a weird problem when we tried temperature variation experiments. These experiments require flow of nitrogen around the NMR sample tube, and we have noticed the following strange effects.

- (1) Whenever there is a gas flow around the sample tube, there is an abrupt shortening of the apparent relaxation time T₁ as measured by the recovery curves after inversion by adiabatic fast passage. This is noticeable even at room temperature, but is very marked when the temperature of the gas is different, even slightly, from room temperature. The apparent recovery curves are usually non-exponential, and reproducibility is poor.
- (2) The shortening of T_1 could be remedied to some extent by saturating the sample for a long time by a strong rf field (e.g. by performing successive adiabatic rapid passages until the signal amplitude decays to zero), and then monitoring the recovering of magnetization using a weak rf field. Using this technique, we could obtain reasonable relaxation times for low temperatures. However, this remedy did not seem to work for high temperatures.

Tentatively, we are trying to explain the phenomena as follows. The probe, being single coil, will affect only a very small volume of the sample in an adiabatic fast passage since the coil is only about 1.5 mm in height. Subsequently, the spins in the affected volume could be carried outside the range of the single coil (and the weak rf field) by thermal currents induced in the sample by the gas flow outside the sample tube. This will explain both observations (1) and (2).

We have tried winding irradiation coils outside the single coil so that a larger portion of the sample could be affected during a rapid passage. Our initial attempts failed, but we are still proceeding along this line. If any body else has encountered similar experiences on a JEOL 4H-100 spectrometer (or any other single coil spectrometer), and has found a remedy, please let us know.

Yours sincerely,

S. J. Gordon
S. L. Gordon

N. R. Lushua.

N. R. Krishna

SLG/NRK:1m



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FACULTEIT DER WISKUNDE EN NATUURWETENSCHAPPEN KATHOLIEKE UNIVERSITEIT NIJMEGEN, NEDERLAND

Professor Bernard L. Shapiro Department of Chemistry Texas A:& M University COLLEGE STATION, Texas 77843 USA

Uw kenmerk

Uw brief van

Ons kenmerk

Datum July 26, 1973

Onderwerp

Calculation of Fermi contact and pseudo-contact contributions to lanthanide-induced shifts in polyglycoldimethylethers from the temperature dependence of the shifts.

Dear Professor Shapiro,

In a recent publication (1) we investigated the temperature behaviour of the NMR spectra of 1:1 complexes of dimethoxyethane (DME) with $Pr(FOD)_3$, $Eu(FOD)_3$, $Pr(DPM)_3$, and $Eu(DPM)_3$. We found that the Eu^{3+} -induced shifts of the DME resonances were proportional to 1/T and the Pr^{3+} -induced shifts to 1/T², in agreement with Bleaney's theory of the pseudo-contact shift (2). However, though the intercepts of the shift versus $1/T^2$ plots for $Pr(FOD)_3$, DME (1:1) were small, the intercept for the CH_2 protons in DME significantly differed from zero. This points to a small Fermi contact contribution to the shift of these protons, since for the case of Pr^{3+} -induced shifts the Fermi contact contributions are proportional to 1/T, but the pseudo-contact contributions are proportional to 1/T. The experimentally observed Pr^{3+} -induced shifts, δ_{Pr} , can now generally be expressed as

$$\delta_{Pr} = \frac{a}{T} + \frac{b}{T^2}$$

a/T representing the Fermi contact and b/T^2 the pseudo-contact contribution. A quadratic least squares fit of the experimental Pr^{3+} -induced shifts

will then yield the values for a and b, from which we can calculate the Fermi

contact and pseudo-contact contributions to the shifts at any temperature. For the shifts for the CH_3 and the CH_2 protons of DME present in $Pr(FOD)_3$, DME (1 : 1) at 31.5°C we thus obtained:

$$\frac{\text{CH}_3}{\delta_{\text{pc}}} = \frac{\delta_{\text{Fc}}}{\delta_{\text{pc}}} = \frac{0.8 \pm 0.4 \text{ ppm}}{-26.0 \pm 0.5 \text{ ppm}}$$

$$\frac{\text{CH}_2}{\delta_{\text{pc}}} = \frac{\delta_{\text{Fc}}}{\delta_{\text{pc}}} = \frac{-5.0 \pm 0.5 \text{ ppm}}{-25.2 \pm 0.6 \text{ ppm}}$$

Clearly, for the ${\rm CH_3}$ proton shift the Fermi contact contribution can be neglected, but the ${\rm CH_2}$ proton shift originates for about 17% from this interaction.

Finally, it should be noticed that for the CH₂ proton shift the Fermi contact contribution reinforces the pseudo-contact contribution; this, together with the well established fact that Eu³⁺-induced Fermi contact shifts are of opposite sign and greater magnitude as those induced by Pr³⁺ (3), explains the low Pr/Eu shift ratios for these protons, which we reported in an earlier publication (4).

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Sincerely yours,

A.M. Grotens

J.J.M. Backus

4.00

E. de Boer

VIth INTERNATIONAL CONFERENCE ON MAGNETIC RESONANCE IN BIOLOGICAL SYSTEMS KANDERSTEG, SWITZERLAND, SEPTEMBER 16 — 21, 1974

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July 24, 1973

Dr.B.L. Shapiro
Dept. of Chemistry
Texas A+M University
College Station Texas
USA

Dear Barry,

I would like to ask you to include the following announcement in TAMUN.

The VI th International Conference on Magnetic Resonance in Biological Systems will be held in Kandersteg, Switzerland, from September 16 - 21, 1974.

The purpose of the conference is to bring together scientists of many disciplines who are concerned with the application of magnetic resonance in biochemistry, molecular biology, biophysics, pharmacology, and medicine. The program will include papers presented by invited lecturers, contributed communications, and discussion periods.

For further information write to:

Professor Dr. K. Wüthrich Institut für Molekularbiologie und Biophysik ETH-Hönggerberg CH-8049 Zürich

Best wishes

Sincerely yours,

West Without

P.S. Thank you for the blue reminder. We will answer it shortly.

DEPARTMENT OF CHEMISTRY

THE UNIVERSITY OF GEORGIA ATHENS, GEORGIA 30601

July 25, 1973

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

Dear Barry:

Title: LSR and Organophosphorus Compounds.

As my subscription contribution, I thought you might be interested in some of our work in the area of LSR and organophosphorus compounds.

A variety of LSR have been tried with trimethylphosphite and trimethylphosphite as model compounds. In terms of induced shifts (both ¹H and ³¹P), Pf(fod)₃ and Yb(fod) appear to be the best of LSR for organophosphorus compounds. It is clear from the data that there is a sizeable contact contribution to both the ¹H and ³¹P induced shifts and for some cases, it appears to be the dominate mechanism controlling the ³¹P induced shifts. Experiments with Gd(dpm)₃ have confirmed this.

The ^{31}P shifts of trimethylphosphate with the Pr LSR are interesting in that a change of the ligand from dpm to fod causes a reversal in the direction of the induced shift. It has been suggested that changing the ligand from dpm to fod increases the acidity of the lanthanide. Thus one would expect a strong complex with $Pr(fod)_3$ than with $Pr(dpm)_3$ and hence, a large contact contribution to the induced shift.

Several differences were noted for the LSR induced ³¹P shifts of trimethylphosphite compared to the phosphate: (1) the magnitude of the induced shift is smaller for the phosphite; and (2) the induced shift is in the opposite direction compared to the phosphate. These results can be accounted for if the pseudo-contact contribution dominates the induced shifts for the phosphite. This is reasonable since the phosphite is a softer base than the phosphate.

Similar results have been obtained for a variety of organophosphorus substrates. Finally, to date we have been successful in observing separate ¹H signals for enantomeric mixtures using optically active LSR. However, due to line broadening, enantomeric signals have not been observed in the ³¹P spectra.

Sincerely yours,

Richard H. Cox

Assistant Professor



University College of Swansea

Department of Chemistry

J. H. Purnell M.A. Sc.D. Professor of Physical Chemistry and Head of Department. A. Pelter Ph.D. Professor of Organic Chemistry.

SINGLETON PARK SWANSEA SA2 8PP UNITED KINGDOM TEL SWANSEA (0792) 25678

CWH/BH

25th July 1973

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

Dear Professor Shapiro,

Some thoughts on statistical aspects of least squares analyses of spectra in isotropic and anisotropic media

There have been numerous comments on the statistical estimates of the reliability of parameters (chemical shifts and isotropic and anisotropic coupling constants) obtained by standard computer programmes for isotropic 1-5 and anisotropic 6-10 media; for these are frequently a good deal smaller than would be expected, having regard to the reliability of experimental measurement of line positions. It is hoped that the following observations (which amplify and extend comments in ref.11) may clarify the relation between these two approaches, and suggest generally valid procedures. The background is explained very clearly in ref. 12.

After an iterative least squares procedure has converged, the variance of the k'th parameter x, is given, under the simplest assumptions, by

$$[\sigma(x_k)]^2 = s^2 A_{kk}$$
 (1)

Here A_{kk} is the appropriate diagonal element of the inverted normal matrix from the last iteration, and s^2 is the variance of the line positions. Now we have in principle two alternative estimates of this quantity s: the first one, based on the reproducibility of the spectra, we denote by sspec; the second, based on the precision of fit of the

calculation, by s^{fit}. Four cases may be distinguished.

(i) s^{fit} is significantly less than is spec. (The criterion of significance is given below.)

We deduce the model (here/spin Hamiltonian) can be fitted more precisely than the inherent accuracy of the data warrant; thus s^{fit} is a gross under-estimate of

the true s.

(ii) s^{fit} < s^{spec}, but not significantly.

(iii) s^{fit} ≥ s^{spec}, but not significantly.

sfit is significantly more than sspec. This means the model cannot be satisfactorily (iv)fitted to the data. The situation is unlikely to arise in isotropic studies, except in the case of a wrong assignment. In liquid crystal work, it would probably indicate an invalid assumption had been made. Clearly further investigation is required when this case is found to arise.

In case (iii) the computer's statistical estimates may be retained. In cases (i)

and (ii), the printed standard deviations or probable errors should be multiplied by (sspec/stit), where sfit is the printed R.M.S. line deviation. This procedure is included in the programme LEQUOR 11b, though not discussed in ref. 11a. The reader is reminded that $[x_k^{calc} - x_k^{true}]/\sigma(x_k)$ follows a Student's t distribution, available in all sets of statistical tables. The number of degrees of freedom is f = n - p, where n is the number of assigned lines to be fitted, and p the number of parameters to be refined. E.g., for a typical ABCD spectrum, if n=32 and p=10, and $\sigma(x_k)$ is 0.050 Hz, then the error limit 13a at the 95% oconfidence level is ± 0.104 Hz (scarcely different from the value of +0.098 Hz obtained from a Gaussian distribution with f infinite). Remember too that a probable error is 0.6745 times a standard deviation.

The Analysis of Variance yields the following results. Let m spectra be recorded; let y; be the i'th line position in the j'th spectrum. Then

$$\overline{y}_{i} = (1/m) \underbrace{\xi}_{i} y_{ij}$$
 (2)

is clearly the best estimate of the i'th line position. Now

$$(s^2)^{\text{spec}} = \{ (y_{ij} - \overline{y}_i)^2 / [m(n-1)] \}$$
 (3)

After the least squares calculation has converged,

The ratio of the larger to the smaller of these two variances follows Snedecor's F distribution, which is also readily available. The numbers of degrees of freedom are $v_1 = m(n-1)$, and $v_2 = f$. E.g. for $v_1 = 100$ and f = 24, tables show ^{13b} that a variance ratio as high as 2.33 would not, at the 95°/o confidence level, invalidate the null hypothesis that the two variances are measures of the same population. This is the criterion of significance mentioned earlier.

The statistics of the y_{ij} data can be used in the actual least squares calculation by introducing a weighting factor 14a, 12. This is incorporated 14 in my isotropic programmes LAME and LACX, and has recently been used in liquid crystal research, 8, 15. The variance of the i'th line position is estimated from

$$[\sigma(y_i)]^2 = (1/m) \stackrel{\checkmark}{=} (y_{ij} - \overline{y}_i)^2$$
 (5)

The appropriate (diagonal) weighting matrix W is defined by

$$W_{ii} = [\sigma(y_i)]^{-2} \tag{6}$$

The resulting algebra is displayed in ref.12. We need only note that now the estimates of the parameter variance-covariance matrix are:

$$\underbrace{\nabla^{\text{spec}}}_{\text{fit}} = \underbrace{\left(\underline{D'} \ \underline{W} \ \underline{D} \right)^{-1}}_{\text{J}} \qquad (7a)$$

$$\underbrace{\nabla^{\text{fit}}}_{\text{fit}} = \underbrace{\left(\underline{N'} \ \underline{W} \ \underline{N} \right) / \text{f}}_{\text{J}} \left(\underline{D'} \ \underline{W} \ \underline{D} \right)^{-1}}_{\text{J}} \qquad (7b)$$

$$V^{\text{fit}} = [(\underline{N'} \ \underline{W} \ \underline{N})/f] (\underline{D'} \ \underline{W} \ \underline{D})^{-1}$$
 (7b)

Here \underline{N} is a vector of line errors, with $N_i = \overline{y_i} - y_i^{calc}$; \underline{D} is a rectangular Jacobian matrix defined by

$$D_{ik} = \partial y_i / \partial x_k;$$

and

and a prime indicates a transpose. In (7b) the quantity in square brackets is a scalar, the (dimensionless) weighted mean square deviation of line positions; thus \bigvee^{spec} and \bigvee^{fit} are multiples of each other. The F-test therefore is to be applied to $[N^i \ \ N^i]$ or its reciprocal. Of course $\P(x_k)$ is now the square root of \bigvee^{i}_{k} . My experience with isotropic spectra is that different weighting schemes (or none) have surprisingly little effect on refined parameter values or even on their standard deviations; they can however cause some large changes in parameter correlation coefficients 4ac, 12, 16, and I now feel these are usefully quoted only to one decimal place. Segre and Castellano 15 also found weighting scarcely affected their anisotropic refinement.

We have so far made the common assumption that the raw data were uncorrelated. However, the still considerable difficulties in obtaining good spectra in nematic solutions could well lead to appreciable correlation between line-position errors. Equation (5) should then be supplemented by using the spectroscopic estimate of the variance-covariance matrix Z of line-positions, defined by

$$Z_{i|} = (i/m) \le (y_{i|} - \overline{y}_{i})(y_{i|} - \overline{y}_{i})$$
 (8)

Equation (6) should now be replaced by

a non-diagonal weighting matrix. The remaining algebra of ref.12 and our equations (7) is otherwise unaltered. In the light of the comments in my previous paragraph, it seems quite likely that the extra work in using this modification will scarcely be worthwhile, but someone might like to try!. After all, if one has gone to the trouble of recording and carefully calibrating twenty separate scans 10, detailed statistics of this kind do have some value.

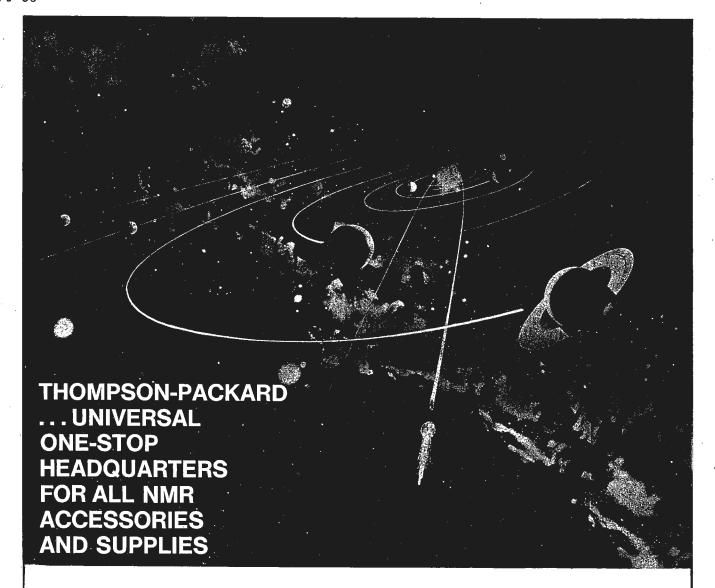
There is one closely related type of calculation in which the mathematics adumbrated in the last paragraph could have important repercussions. The chief aim of most liquid crystal NMR spectroscopists is to use the anisotropic coupling constants, part of the vector x of parameters, to determine the orientation parameters and inter-nuclear distances; and this is frequently accomplished in a second least squares calculation. Now in an anisotropic medium p is larger, other things being equal, so f is smaller; and the parameters are likely to be appreciably correlated to each other. Consideration of the analogue of (9) for our new calculation, and of (7a) – assuming case (i) or (ii) – shows that the correct weighting matrix for the anisotropic couplings in this second calculation is simply that square part of the normal matrix of the first least squares calculation which refers to the anisotropic couplings, including its off-diagonal elements. Ten words (only) in ref.11a indicate this method of calculation is currently being used at Basel; but the attention of all practicing nematic NMR spectroscopists is earnestly drawn to this crux.

It is a pleasure to acknowledge helpful conversations and/or correspondence with Professor Diehl and Dr. Kellerhals (Basel), Dr. Pachler (Pretoria), Dr. den Hollander (Leiden) and Dr. Fruchier (Montpellier).

Yours sincerely,

C. W. Haigh

- P.S. Another point arises in the common situation where experimentally discernable peaks contain more than one calculated transition. Consider first a simple situation like an $[A_2B_3]$ or $[AB_4]$ spin-system, handled (as in LAOCOON) without magnetic equivalence factorisation: clearly many lines will be identically degenerate. Let there be n^{spec} distinct lines, and let the i'th line contain n_i calculated transitions. Then equation (6) should be replaced by $W_{ii} = [\sigma(y_i)]^{-2}/n_i$, or if the experimental lines are not otherwise being weighted by $W_{ii} = 1/n_i$. Secondly, equation (7b), f should be replaced by the smaller quantity ($n^{spec} p$), resulting in larger standard deviations. Dr. den Hollander (leiden) and I have both shown that with these modifications, the LAME calculations using magnetic equivalence are all exactly reproduced. In more common cases where the degeneracy is not exact, analogous modifications should lead to more realistic conclusions. For certain types of problems, we both feel this may be a significant cause of the unrealistically low standard deviations discussed at the outset of this letter.
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University of Toronto FACULTY OF PHARMACY

19 Russell Street TORONTO, ONTARIO M5S 1A1

July 17, 1973

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

Dear Professor Shapiro:

After a recent failure of the compressed air supply that cools our XL-100 probe during high power decoupling we built a circuit to protect against possible damage. (The final version owes a lot to suggestions from Mits Yonemitsu and Wolfgang Panning of Chemistry electronics.) It needs no relays, and is somewhat more flexible than the circuit described by Rapper and Runsink in Newsletter 175.

A small 6.3V transformer is connected through a DPDT replacement for S401 (Fig. 1) to power the N₂ pilot lamp and pressure switch of the temperature controller at all times. Since the "N₂" bulbs don't last long in continuous service we soldered an LED plus an ordinary diode for the other half-cycle into the base from a burnt-out bulb as a direct replacement. The output, taken in parallel to the light, is about 2V AC, present only during normal gas flow.

This signal goes to a logic circuit (Fig. 2) which we have mounted in the auxilliary console. Resistor R₁ is selected to give a reliable output from the photo coupler U1 (which isolates the temperature controller) without turning off the "N₂" LED. As long as there is gas flow the coupler provides a constant string of trigger pulses to U2 and U3, keeping their pin 8 outputs at logical 1. An interruption of more than about 1 second lets U2 pin 8 go to logical zero, setting the latch (U4 pins 1-6). The warning light comes on and "accumulation interlock" (same as lock lost) is signalled to the computer. The decoupler is switched by U3 which has a longer delay time (about ten seconds) to allow completion of data collection from the current F.I.D. With the circuit in Fig. 2 the decoupler comes back on as soon as gas flow resumes but the light and computer interlock must be reset using a push button. If you want the decoupler to stay off until the

Professor B. L. Shapiro

button is pressed, connect pin 3 of U3 to pin 3 of U4 rather than to +5V. If you want the computer interlock to come back on immediately with gas flow (so that Reset affects only the warning light) take it from U2 pin 8 rather than U4 pin 3.

transport of the contract was the

The decoupler is switched off in the same way as for computer Gyro Gate control, so the interlock is effective in both high and low power modes. If you want to restrict it to high power, pass the Gyro Gate signal through a spare section of the LOW/HIGH switch 3705 on the way to 31026-13.

If you already have Gyro Gating installed simply put the Fig. 2 circuit into the line from computer to decoupler. If not, you may have to modify one decoupler card according to Fig. 3. The computer control line for Gyro Gate is taken from pin z (little z) of J4 of our old Mark I Digital to Analog Converter (DAC). For the Mark II DAC the corresponding connection is J1-EE, AA.

For most experiments the average power from the observe frequency pulses is not sufficient to damage the probe even with cooling gas off. However, if you are worried you can gate the RF pulse logic with the same signal used for computer interlock, as shown below.

Please credit this contribution to Murray Freedman's subscription.

Sincerely,

Alan Quirt

AQ:1d

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TIOIL

FROM J1817-26

FROM JI814-FF

1944 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945 - 1945

RF WIDTH

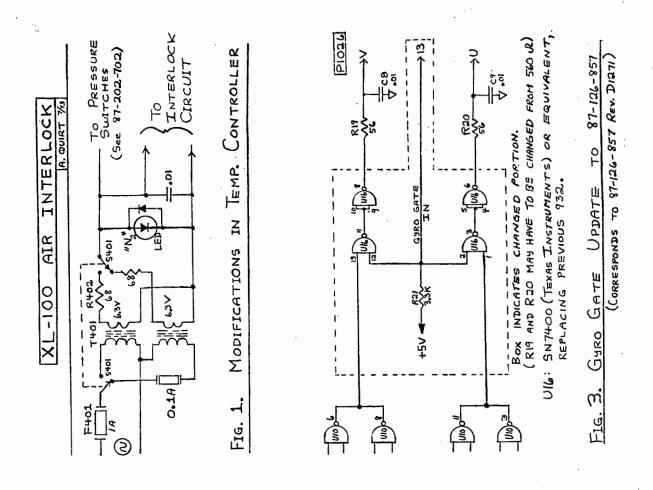
INTERLOCK

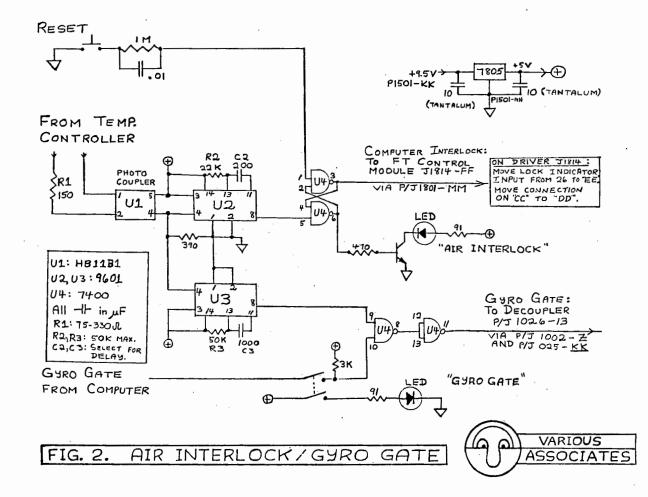
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TO J1815-1

PULSE INTERLOCK





Koninklijke/Shell-Laboratorium, Amsterdam



Shell Research B.V.

Uw ref.:

Onze ref.: FR-OC

Amsterdam, 17th July 1973 Postadres: Postbus 3003 Tel. via telefoniste (020) 20 91 11 Tel. rechtstreeks (020) Hr/Mw

Dear Professor Shapiro,

Measurement of ²J(¹⁹⁵Pt-¹⁹⁵Pt) in Pt₂I₄(PBu₃)₂

Although platinum has a naturally occurring isotope with a nuclear spin of one half (195Pt, 33.7 % abundant) and although many complexes containing two platinum nuclei are known¹, hitherto no platinum-platinum coupling has been reported. A complex of type A (L = tertiary phosphine, X = halogen)

exists as a mixture of three magnetic isomers containing 0, 1 or 2 magnetic (I = $\frac{1}{2}$) platinum nuclei. In the $3^{1}P$ NMR spectrum these three isomers give rise to A_{2} , AA'X and AA'XX' patterns, respectively. By careful examination of the $3^{1}P$ NMR spectrum of A with L = PBu₃ and X = I we have detected all the lines predicted for the three aforementioned magnetic isomers, see Figure. Previously, for this type of complex, with L = PBu₃ and X = Cl, only three of the expected 19 lines have been reported². From the positions of the AA'XX' lines 2J(195Pt-195Pt) is readily calculated³. Further, the finding that the most intense lines in the AA'XX' spectrum {i.e. at +1751 Hz and -1751 Hz centered about $\delta(PBu_{3})$ } fall inside the $\frac{1}{3}J(3^{1}P-195Pt)/\frac{1}{4}J(3^{1}P-3^{1}P)$ doublet of doublets +1764 Hz and -1764 Hz {relative to $\delta(PBu_{3})$ } indicates that $\frac{1}{3}J(3^{1}P-195Pt)$ are opposite in sign. The NMR data are listed in the Table.

These results demonstrate the possibility of measuring coupling constants abetween two metal nuclei for which direct observation might be difficult (e.g. 195Pt, 103Rh) by analysing the spectrum of an easily observed nucleus (e.g. 31P, 19F, 1H, 13C) which is also present in the complex.

 3^{1} P NMR data for Pt₂I₄(PBu₃)₂ from spectra recorded at ca. 40° in chloroform at 40.5 MHz.

1	shift and constants	Position of lines arising from AA'XX' pattern, centered about δ(PBu ₃) = 0			
δ(PBu ⁿ ₃) ^a 1 _J (31 _P _195 _{Pt}) 3 _J (31 _P _195 _{Pt}) 4 _J (31 _P _31 _P) 2 _J (195 _{Pt} _195 _{Pt})	+140.3 <u>+</u> 0.1 ppm 3528.0 <u>+</u> 0.1 Hz 26.0 <u>+</u> 0.1 Hz 5.1 <u>+</u> 0.1 Hz 380 <u>+</u> 1.0 Hz	<u>+</u> 1595 <u>+</u> 1600 <u>+</u> 1751 <u>+</u> 1975 <u>+</u> 1980			

a. Relative to P(OMe) 3.

Please credit this contribution to Dr. R. Prins.

Yours sincerely,

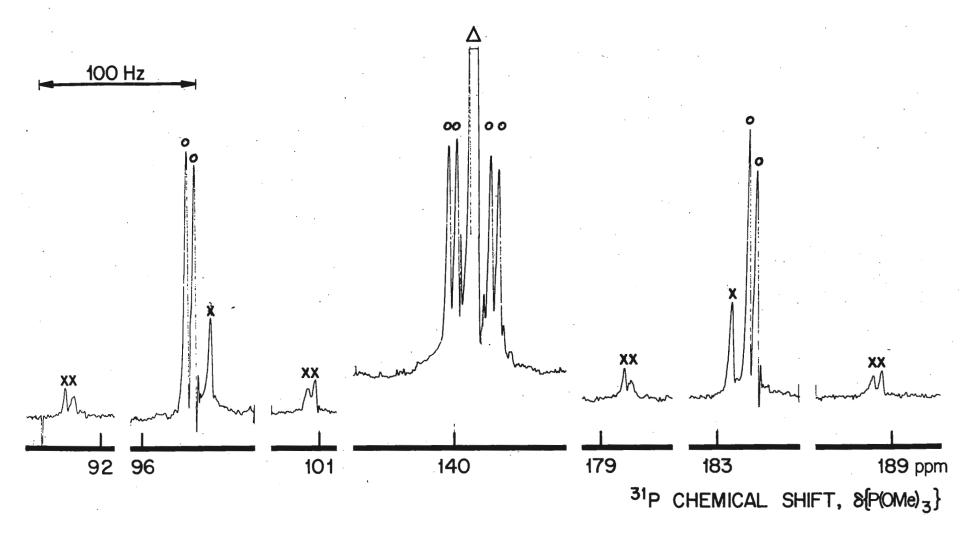
J.A.M. van Broekhoven

C. Masters

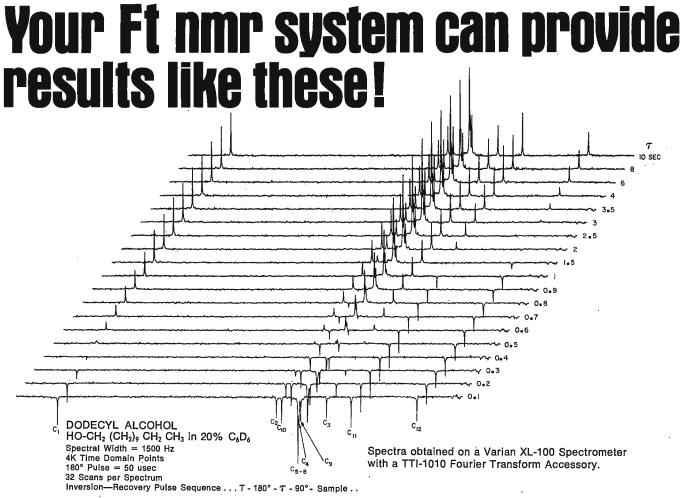
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 $^{31}\text{P NMR SPECTRUM OF }\text{Pt}_2\text{I}_4\text{(PBu}_3)_2$ LINES INDICATED BY Δ , o AND x ORIGINATE FROM COMPLEXES CONTAINING O, 1 OR 2 MAGNETIC ($\underline{\text{I}}=\frac{1}{2}$) PLATINUM ATOMS, RESPECTIVELY



It's easy using the Nicolet 1080 Data System. The 1080 incorporates unique concepts designed specifically for the scientific laboratory. It has two processing units—a wired one for acquiring data and a programmable one for processing data. Thus each unit performs the functions it does best. Signals are digitized and added to memory by the wired processor while it is displaying the entire averaged signal in a continuous, flicker-free display. This unique signal averager approach to data acquisition allows the display to continue regardless of the data acquisition rate (up to 100 kHz) so that the user can examine the input signal or the averaged signal, at any vertical or horizontal expansion, without interrupting the data acquisition process. This allows instantaneous inspection of the signal to noise as well as examination of the data for pulse feedthrough, decoupling power, and frequency offset.

The unique 20-bit word 1080 data processor not only allows more single-precision dynamic range than any other, but it also has a much more powerful instruction set. This permits faster and more efficient data reduction and programming simplicity.

The above spectra of dodecyl alcohol were obtained using the Nicolet automatic T_1 program, which utilizes the [180° - τ - 90° - (sample) - $\mathsf{T}]_n$ inversion recoveryl 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 $A = A_0 \left[1 - 2 \exp \left(- \tau / T_1 \right) \right]$. This calculation is performed di-

rectly by the program upon command.

This quality of data and ease of operation can be yours with the Nicolet 1080 Data System, including the 600,000, 20-bit word NIC-294 cartridge disk system and the NIC-293 Pulse Controller. This latter unit allows the production of up to eight computer-selectable times corresponding to rf pulses and pulse intervals. This unit is already in use measuring T₁'s, T₂'s, performing gated decoupling and homonuclear pulsed decoupling and providing the versatility for use in almost any definable experiment.

The Nicolet 1080 Data System has been successfully used with all major spectrometers and is also available with a complete Fourier pulse accessory package for the Varian XL-100 through Nicolet's affiliate, Transform Technology, Incorporated. Why not investigate the features of the 1080 Data System

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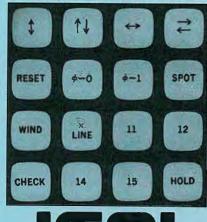
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