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Newsletter

No. 185

February, 1974

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All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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B. ROQUES

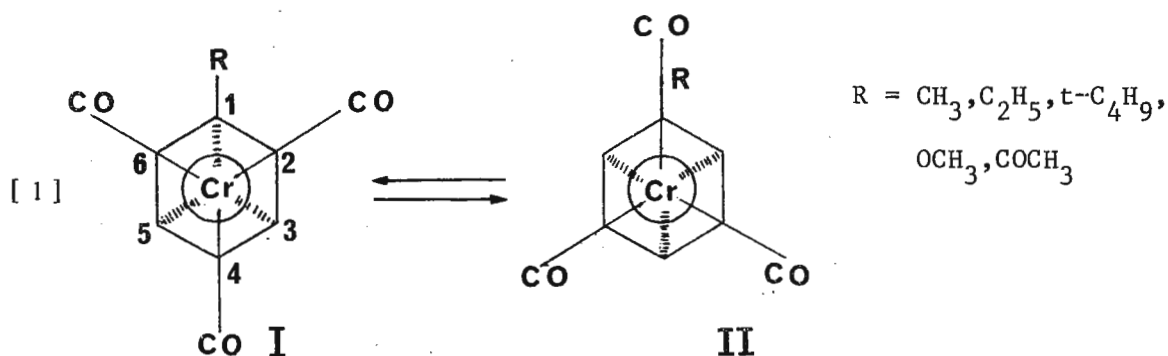
PARIS, le 10 Janvier 1974

Dr. Bernard L. SHAPIRO
 Department of Chemistry
 Texas A & M UNIVERSITY
 College Station, TX. 77843
 USA

Dear Dr. SHAPIRO,

^{13}C NMR OF SUBSTITUTED BENZENE CHROMIUM TRICARBONYL COMPLEXES

The bonding scheme in π complexes is very discussed and we think that ^{13}C NMR can be useful to bring additional informations in this field. The direct observation of the carbon atoms involved in the metal-ligand bond must provide some light on the modification of the σ and π systems under complexation and on the conformational equilibrium :



This latter is very hardly studied by ^1H NMR (1,2).

In a first step, we compare the carbon chemical shifts of free and complexed molecules at 25°C. The ring carbon resonances are shifted up-field from ca. 33 ppm under complexation. Such an effect can be attributed to changes either in hybridization and π mobile bond order or in the average excitation energy. This is actually under discussion.

According to NELSON and coworkers ⁽³⁾, a linear relationship is found between δ_{Cpara} and σ^+ Hammett constants, both in free and complexed benzenes. For the complexes, the best correlation is obtained when the ratio of conformers I and II is similar for all the derivatives (See figure).

Thus, the transmission of the electronic effect of substituent to the para carbon is unaffected by the complexation and this shows that the benzenic π system is only slightly modified by coordination.

Elsewhere a study of the complexes by variable temperature shows two opposite trends for the $C_{3,5}$ and $C_{2,4,6}$ resonances respectively. If R is electron-releasing, $C_{2,4,6}$ are shifted upfield and $C_{3,5}$ downfield with decreasing temperature while, if R is electron-withdrawing, an opposite behaviour occurs. No significant variation of ring carbon chemical shifts with temperature is observed for the t-butyl substituted complex.

These results are attributed to the fast equilibrium [1] : the localized bonds between Cr and ring carbons in the two conformers induce changes in electronic density and thus in carbon chemical shifts. So, the observed average chemical shift describes the equilibrium at a given temperature. We calculate then the ratio of conformers I and II, the equilibrium constants and the differences of enthalpy and entropy between I and II.

We may also calculate approximately the shielding of the protons attached to the carbons bonded to the metal. The result is in good accordance with the experimental values.

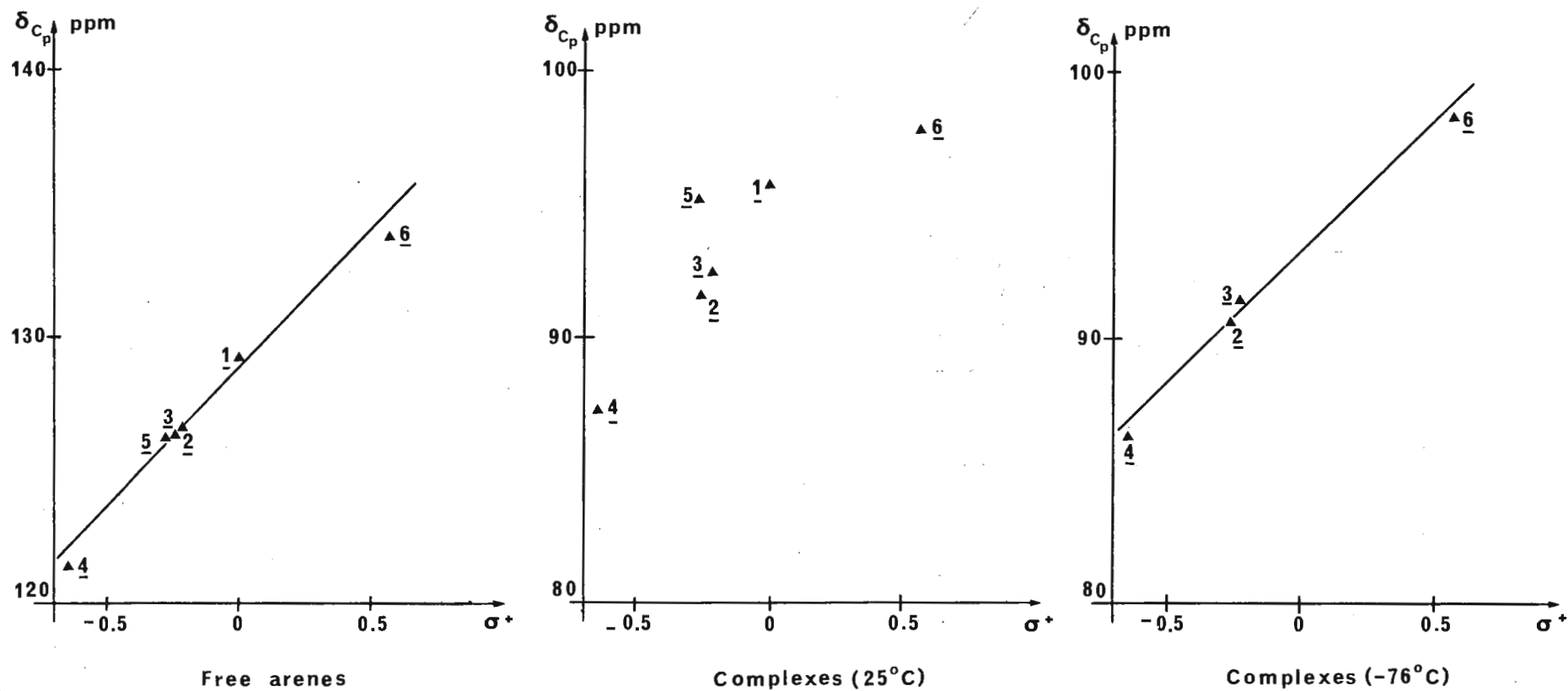
We hope that these preliminary results ⁽⁴⁾ will provide some light on the bond in π complexes.

Sincerely Yours.

B.P. ROQUES, C. SEGARD, S. COMBRISSE and F. WEHRLI.

- 1) - W.R. JACKSON, W.B. JENNINGS, S.C. RENNISON and R. SPRATT, J. Chem. Soc. (B), 1214, (1969).
- 2) - C. SEGARD, B. ROQUES, C. POMMIER and G. GUIOCHON, Anal. Chem. 43, 1146, (1971).
- 3) - G.L. NELSON, G.C. LEVY and J.D. CARGIOLI, J. Amer. Chem. Soc., 94 3089, (1972).
- 4) - B. ROQUES, C. SEGARD, S. COMBRISSE and F. WEHRLI, Manuscript submitted to the J. Organometallic Chemistry.

FIGURE



R	H	CH ₃	C ₂ H ₅	OCH ₃	t-C ₄ H ₉	COCH ₃
Nr	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>

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TELEX NO. 13-8840

October 2, 1973

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

TITLE: ^{13}C Homonuclear Decoupling

Dear Barry:

As usual, your cherry blossom colored reminder reached us as Tom Farrar is getting a suntan on Mt. Fujiyama.

We have noticed that more and more customers are submitting ^{13}C enriched samples. Some of the most interesting ones were submitted by S. Fermandjian (CEN, Saclay, France), and consisted of tyrosine, aspartic acid, and phenylalanine, 90% ^{13}C enriched in all positions! Needless to say, the standard ^{13}C spectra are quite complex and consist of a superposition of all possible combinations of the mono-di-tri-etc. labeled species. After spending a whole day devising a formula to account for all spectral lines, we decided to try some ^{13}C - ^{13}C homonuclear decoupling experiments.

Since the ^{13}C - ^{13}C coupling constants are on the order of 40-65Hz, a larger decoupling field must be used than in the analogous H-H decoupling experiment. Our first experiments were done with 25% ^{13}C dilabeled sodium acetate (Spectrum 1). After perfecting our technique, we sequentially decoupled all carbons of phenyl alanine, the results of decoupling the carbonyl carbon being shown in Spectrum 3.

We did encounter difficulty in irradiating the aromatic region using CW power and we could not appreciably sharpen the CH_2 peaks. However, by frequency modulating the irradiation power with a 125Hz random noise source, we did collapse the CH_2 group into a doublet, at the cost of increased noise in the baseline (see insert in Spectrum 3).

We are continuing our experiments on tyrosine and aspartic acid, however, even with 90% enrichment, the low solubility in D_2O (tyrosine, 1mg/ml, pH~7) still necessitates averaging for 10 - 20K scans for each experiment.

Sincerely,

V. J. Bartuska
V. J. Bartuska

K. Ishibitsu
K. Ishibitsu

/rmz
Encl.

• 100% TMS

IRRAD.

^{13}C Decoupled Spectrum

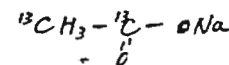
standard spectrum

$^{13}\text{C}=\text{O}$

$^{13}\text{CH}_3$

SPECTRUM 1

SPECTRUM NO. _____
SAMPLE _____



SOLVENT D_2O
CONC. _____
REFERENCE _____
TEMP. R.T. °C

OBSERVE ^{13}C
NUCLEUS _____
FREQ. 25.149536 MHz
PULSE: ☒ Sing. ☐ Multi. _____
WIDTH 26 u sec.
INTERVAL _____ SEC
REPETITION 23 SEC
DATA POINTS 8K
WINDOW EXPONENTIAL T.C. -3
MODE _____
SPECTRUM WIDTH 5 KHz
FILTER 5 KHz
AMPL. _____
NO. of SCANS 10

LOCK ☒ INT. ☐ EXT. _____
FREQ. 15.35740 MHz (CD)
SIGNAL D_2O
LEVEL RF 20dB AF _____

SPIN DECOUPLER
FREQ. 77.274 MHz (^{1}H)
POWER 10dB B.W. 25 KHz
MODULATION _____
☐ CW ☒ Noise ☐ EXT. _____

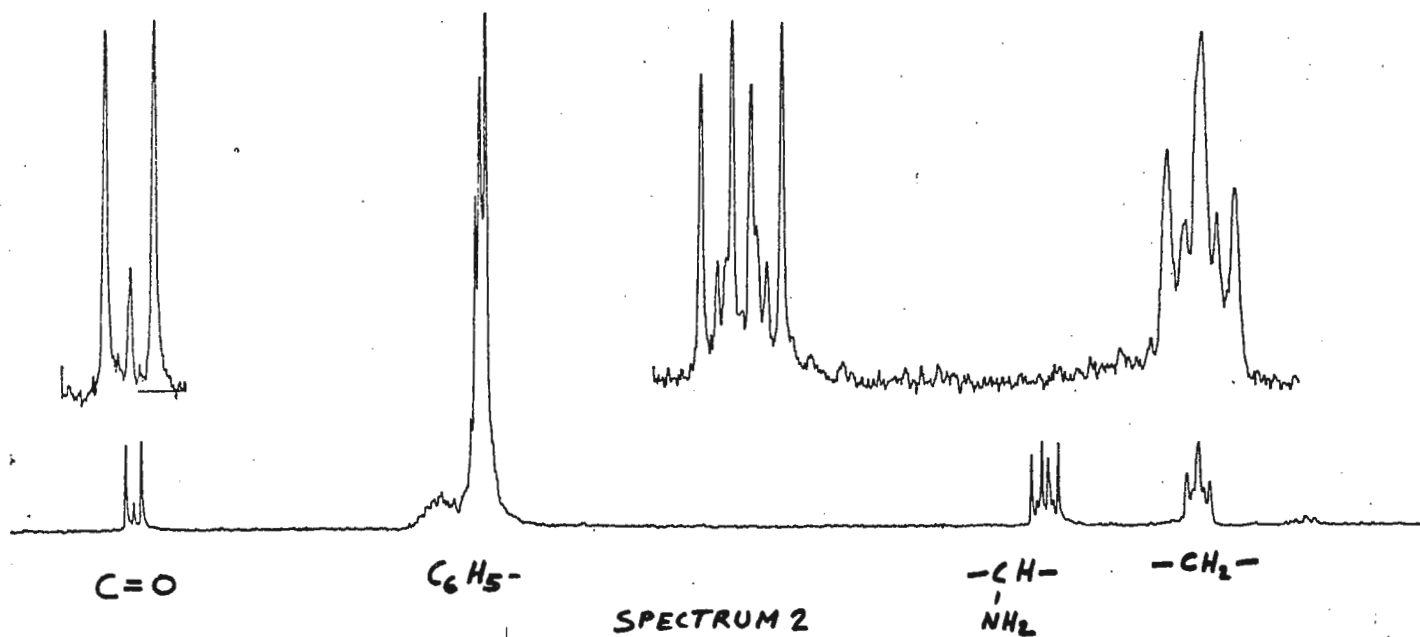
DATE July 9, '73
OPERATOR VJB K.I.

REMARKS:

185-5

JEOL

Standard ^{13}C spectrum of
90% ^{13}C enriched phenylalanine
($^*\text{C}_6\text{H}_5 - ^*\text{CH}_2 - \underset{\text{NH}_2}{^*\text{CH}} - ^*\text{COOH}$)



SPECTRUM NO. _____
SAMPLE _____

SOLVENT D₂O
CONC. _____
REFERENCE _____
TEMP. R.T. °C

OBSERVE *DC*

NUCLEUS _____

FREQ. _____ MHz

PULSE: ☒ Sing. ☐ Mult. _____

WIDTH *15* μ sec.

INTERVAL _____ SEC

REPETITION *5.1* SEC

DATA POINTS *10K*

WINDOW EXPONENTIAL *T.C. = 1*

MODE *Peak*

SPECTRUM WIDTH *5* KHz

FILTER *5* KHz

AMPL. _____

NO. of SCANS *1000*

LOCK ☒ INT. ☐ EXT. ☐
FREQ. 15.3500 MHZ. 12D
SIGNAL D.C.
LEVEL RF 20.15 AF

SPIN DECOUPLER
FREQ 99.936 HZ (14
POWER 500 B.W. 25 KH
MODULATION _____
☐ CW ☒ NOISE ☐ EXT. _____

DATE July 11, '73
OPERATOR K. J. WJB

REMARKS:

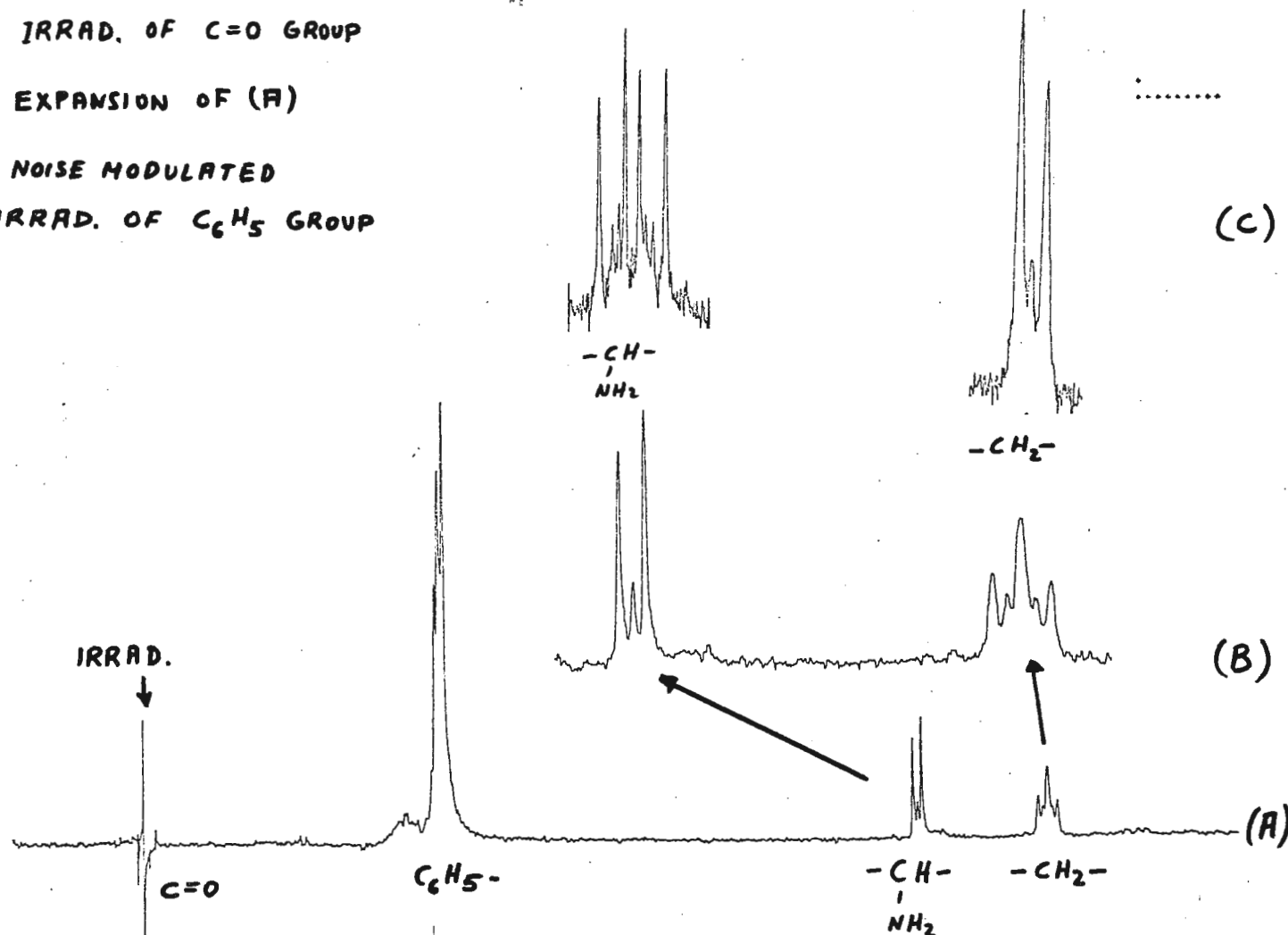


¹³C Homonuclear decoupling experiments
on 90% ¹³C enriched phenylalanine
(¹³C₆H₅-¹³CH(¹³NH₂)-¹³CH₂-¹³COOH)

(A) IRRAD. OF C=O GROUP

(B) EXPANSION OF (A)

(C) NOISE MODULATED
IRRAD. OF C₆H₅ GROUP



SPECTRUM NO. _____
SAMPLE C₆H₅-CH-CH₂-COOH
NH₂
SOLVENT D₂O
CONC. _____
REFERENCE _____
TEMP. RT °C
OBSERVE _____
NUCLEUS _____
FREQ. _____ MHz
PULSE: ☐ Sing. ☐ Mult. _____
WIDTH 21 μsec. (400)
INTERVAL _____ SEC
REPETITION 13 SEC
DATA POINTS 16K
WINDOW EXPONENTIAL T.C. 3
MODE REC
SPECTRUM WIDTH 5 KHz
FILTER 5 KHz
AMPL. _____
NO. of SCANS 500

LOCK ☒ INT. ☐ EXT. _____
FREQ. _____ MHz. (____)
SIGNAL _____
LEVEL RF _____ AF _____

SPIN DECOUPLER
FREQ. _____ HZ (____)
POWER max B.W. 2.5 KHz
MODULATION _____
☐ CW ☒ Noise ☐ EXT. _____

DATE July 10, 13
OPERATOR KI v. J. B.

REMARKS:
¹³C Homo
decoupling

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Unsere Zeichen

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464-

Ludwigshafen

Jan. 15, 74

Betreff

Do not always believe what computers tell you

Dear Barry,

exactly one year of experience with our Bruker WH-90 spectrometer exclusively running on 22 MHz is a good occasion for a short retrospect. We were more than satisfied with the performance of the spectrometer itself, however, I feel the software of the Nicolet / Bruker B-NC-12 still needs improvements. Severe problems with integration, base line manipulation, T₁-experiments were partially solved in the meantime. One observation we made recently should be pointed out to the newsletter readers, because it demonstrates the danger of using the spectrometer as black box without checking from time to time whether the computer output is reliable.

Lately we played more often with the spectral width SW in order to make optimum use of the resolution of our 8k-data memory. Thus we left the "allowed" value of SW = 5000 Hz for the survey scan, and used other (sometimes odd) frequencies SW - with the result that we found smaller chemical shifts-values δ with deviations Δ which were proportional to the chemical shifts itself:

$$\Delta = k \cdot \delta$$

This is demonstrated in table 1 for the resonance frequencies (relative to TMS int.) of a sample containing 30% CHCl₃ and 10% C₆H₁₂ in CDCl₃. The observed deviations from the mean value (cf. table 2) are considerably higher than the "resolution" R of the computer

$$R = SW / 4000 \text{ [Hz]}$$

and obviously connected to the dwell time DW

$$DW = 1 / 2 * SW \text{ [s]}$$

Empfänger

Unsere Zeichen

67 Ludwigshafen am Rhein

Blatt

Prof. Dr. B.L. Shapiro

WHE-WBr/Dr

Jan. 15, 74

Betreff

Our explanaiton is as follows: The operator enters the spectral width SW, the computer calculates the corresponding dwell time DW, cuts off the decimals and performs the pulse experiment with a modified dwell time DW_{eff} . However, when the spectrum is transformed and calculated, the old spectral width SW and not the correct value SW_{eff}

$$SW_{eff} = 1 / 2 * DW_{eff}$$

is employed. This leads to the observed deviations

$$\Delta = \frac{DW - DW_{eff}}{DW} \cdot \delta$$

It is understandable that the spectrometer is limited to discrete dwell times and that these values are automatically chosen. It is not sensible that the computer does not at least change the incorrect SW to SW_{eff} and it would be even better to give a message to the operator with the corrected value. Needless to say how dangerous this procedure is. Errors can amount to more than 1% with spectral widths larger than 5000 Hz, more than 0,5% with SW larger than 2500 Hz, while the operator expects only deviations in the order of 0,1%. How disillusioned he will be when he uses a "forbidden" frequency, believing the statement of the manual that only "round-off errors may occur".

By the way, what about the results of your survey on the accuracy of 1H -CW-NMR? I feel this is a good context to come back to Prof. Mavel's (uncensored) and may (censored) question already dating back to 1972.

Kindest regards,

Wolfgang Zolmer
(W. Bremser)

Enc.

SW	CHCl ₃	C ₆ H ₁₂	R	DW
[Hz]	[Hz]	[Hz]	[Hz]	[μ s]
10000	1750.5	615.2	2.5	50.0
8000*)	1734.4	609.4	2.0	62.5
6000*)	1741.7	610.8	1.5	83.3
5000	1750.5	614.0	1.2	100.0
4000	1750.0	614.3	1.0	125.0
3300*)	1744.3	612.3	0.8	151.5
3000*)	1742.4	611.6	0.7	166.7
2700*)	1747.5	613.7	0.7	185.2
2500	1749.3	614.0	0.6	200.0
2250*)	1747.9	613.0	0.6	222.2
2000	1750.0	614.3	0.5	250.0
1840*)	1744.8	612.7	0.4	271.7

Table 1 : Observed resonance frequencies for CHCl₃ and C₆H₁₂ relative to TMS under different experimental conditions, i.e. varying spectral widths. "Forbidden" spectral widths are marked with *) and rerun under appropriate conditions in table 2.

SW	CHCl ₃	C ₆ H ₁₂	R	DW
[Hz]	[Hz]	[Hz]	[Hz]	[μ s]
8064.52	1750.3	614.3	2.0	62
6024.10	1750.2	614.8	1.5	83
3311.26	1750.2	614.4	0.8	151
3012.05	1749.4	614.0	0.7	166
2702.70	1749.9	614.3	0.7	185
2252.25	1749.7	614.2	0.6	222
1845.02	1750.0	614.4	0.4	271
Mean value	1750.0	614.3		

Table 2 : Experiments with "allowed" spectral widths obtained by entering an integer for the dwell time DW. The mean value is the average over all 12 correct experiments (table 1 and 2).

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

January 4, 1974

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRYJOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

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

¹³C T₁ Measurements on Dioxane-D₂O
Solutions

Dear Barry,

Following our recent publication in TAMU Newsletters, we have discovered that the actual pulse width seen by the sample on our "Brukarian" spectrometer is 6 μsec longer than the value entered via the teletype. As it is common practice, prior to any T₁ measurement on our instrument, to determine the magnitude of the 180° pulse, this additional 6 μsec has introduced a 20% error in our T₁ values evaluated for a true 90° flip. For example, with our single-coil spectrometer, the 180° pulse width was routinely found to correspond to a teletype value of 22 μsec; therefore, a 90° value of 11 μsec was employed for the progressive saturation mode. In fact, the 180° flip was equal to 22 + 6 = 28 μsec and thus a 90° flip would correspond to a teletype value of 14 - 6 = 8 μsec and not 11 μsec.

Following this discovery, all T₁ values were recalculated by inserting the actual pulse angle (α = 110°) into the following equation:

$$\frac{S_a}{S_b} = \frac{1 - e^{-a/T_1}}{1 - e^{-b/T_1}} \cdot \frac{1 - \cos \alpha e^{-b/T_1}}{1 - \cos \alpha e^{-a/T_1}}$$

α = flip angle

The resulting T₁'s were found to be in excellent agreement with those redetermined with a correct 90° pulse.

This discrepancy in pulse width was measured using a precalibrated scope to monitor the pulse width picked up by a probe placed directly in the insert. Teletype values of from 2 μsec to 40 μsec were then entered and the actual magnitude determined. For each teletype entry, the observed pulse width was consistently 6 μsec longer. As the RF gate pulse was of the

ugh!

proper length, this additional 6 μ sec arises in the RF amplification stages.

Of perhaps more general interest, a similar study on a Varian XL-100-15, where a 90° flip corresponds to ca. 50 μ sec, showed an addition in pulse width of 3 μ sec, or an error of only 3% if unaccounted for. On a Varian HR-220 spectrometer, with a 90° pulse width of 35 μ sec, a 2 μ sec addition was observed.

With all said and done, the correct ^{13}C T_1 value for a 2:3 (v/v) solution of dioxane in D_2O is $6.2 \pm .6$ sec at 15.09 MHz, 30°C , and not $7.8 \pm .8$ sec, as was reported in November's issue of TAMU reports.

With all good wishes,

Very truly yours,

Ian M. Armitage

Ian M. Armitage

H. Huber

Hanspeter Huber

David Live

David Live

Jack

John D. Roberts

185-14 Dr. V.F. Bystrov
USSR Academy of Sciences
SHEMYAKIN INSTITUTE FOR CHEMISTRY OF
NATURAL PRODUCTS

Ul. Vavilova, 32
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January 3, 1974

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

Title: Request for NMR Data
on Peptide Systems

Dear Barry,

We are currently compiling data for a review on "NMR Spectroscopy of Peptide Systems" to be published in Progress of NMR Spectroscopy (Eds. J.W. Emsley, J. Feenly and M.L. Sutcliffe). The contents include the following:

1. ^1H , ^{13}C and ^{15}N Chemical Shifts in Peptides and related Compounds.
2. Coupling Constants ^1H - ^1H , ^1H -X and X-Y (X and Y = ^{13}C and ^{15}N) in Peptides and Related Compounds.
3. Signal Assignment in Peptide Spectra.
4. NMR Conformational Study of Synthetic and Natural Occuring Linear and Cyclic Peptides.

In order to be as comprehensive and up-to-date as possible, we would greatly appreciate reprints, preprints and correspondence regarding unpublished data on or related to the above. Any unpublished data will be kept strictly confidential until released by the author(s) if so desired. The deadline for inclusion is March 1, 1974; however, a limited amount of material may be added to the galley proof. For this work to be of maximum utility to everyone, we earnestly solicit your assistance.

Sincerely,


V.F. Bystrov


V.T. Ivanov

S.L. Portnova

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January 4, 197 4

Prof. Bernard L. Shapiro
Department of Chemistry
College of Science
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College Station
Texas 77843, USA

Dear Professor Shapiro,

Some experiments with stochastic resonance

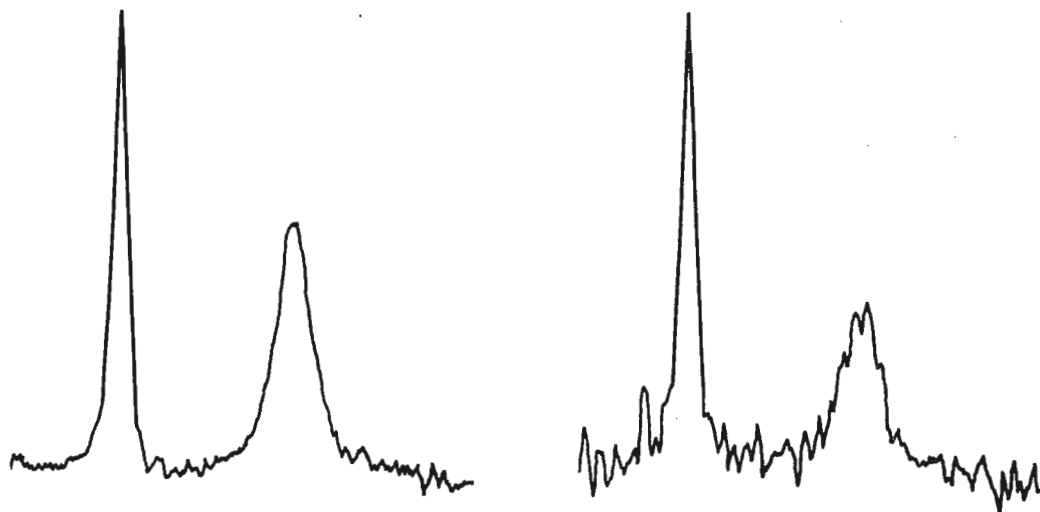
Please accept my apologies for the lateness of this contribution.

We have lately become interested in the possibilities of noise and stochastic resonance methods in high resolution NMR spectroscopy. At present we are measuring the spectra of as many nuclei as possible in any molecule being studied including the resonances of ^{13}C , ^{14}N , ^{15}N , ^{17}O , ^{31}P , ^{19}F , ^{11}B , ^{117}Sn , ^{119}Sn , and others, and using the conventional pulse Fourier transform technique and a Nicolet-1083 computer with a Kennedy 3112 tape unit for this purpose. Although the noise spectrometry does not permit a reduction of the measurement time below that of pulsed Fourier transform spectrometry, a significant reduction of the needed peak transmitter power is always useful, because with large shift ranges and broad lines one is easily short of peak *rf* power or overloads the pulse handling capacity of the input circuit, particularly at lower frequencies. Since in stochastic or noise spectroscopy the necessary power spectral density of excitation can be generated with many weak pulses instead of a single high-amplitude pulse, the use of peak *rf* power is much more economical [the second 'multichannel advantage' of Kaiser, see TAMUNN 181, 30 (1973)]. The much smaller dynamic range of the exciting pulses is paralleled by a similar reduction in the dynamic range of the stored data that leads to much better use of the core memory during data acquisition, though not in the subsequent processing. Also, since the noise sequence length determines the resolution and the measuring time determines sensitivity, both can be separately optimized.

Since complicated noise spectra with narrow gaps in it, as used by Tomlinson and Hill, are rarely needed in heteronuclear resonance and since our computer has only a limited (12 K) memory, we found the 1023-step binary pseudorandom noise generator to be the most convenient source of reasonably white noise with a frequency spectrum close to that of a single *rf* pulse in the sequence used. In the spectrometer layout time sharing with the receiver turned off (50%) during the *rf* pulse (25%) at a frequency in the 1 to 10 kHz range was the obvious choice. It leads to the use of short *rf* pulses, which is advantageous, because in stochastic resonance the pulses must be of the same length as in conventional FT spectroscopy although the amplitudes are small and the repetition rate is high. Unfortunately, any change to 1024 steps, needed for FFT, completely destroys the uniform power spectrum, making the noise unsuitable for spectrum excitation without gross distortions and considerable additional noise in the final spectrum.

A simple amplitude modulation, where the presence or absence of a *rf* pulse of constant phase, amplitude and width was determined by the pseudonoise generator, was used. Formation of the nuclear pulse response function through multiplication of the input and output noise samples was thereby simplified and could be carried out by a small subroutine in the FFT package, followed by zero filling, multiplication with a positive or negative exponential for resolution enhancement or S/N improvement, and fast Fourier transform after it. This way the memory use was as efficient as in the case of pulse FT, but with all the flexibility retained. The pseudonoise technique was successfully applied to the study of ^{13}C , ^2D , ^{11}B and ^{14}N NMR spectra, and was particularly successful with ^{14}N , where the use of too strong single *rf* pulses leads to excessive ringing in the input circuit and to loss of most of the free induction decay after the excitation pulse.


— α -Nitropyrrole ^{14}N FT spectra, registered with the same peak pulse power and the same total acquisition time in the stochastic (left) and single pulse (right) mode serve as an illustration.



Some small modifications in the NIC-1083 computer hardware were necessary. Those enabled it to pass one complete excitation cycle before any data were stored, to synchronize the computer sweep (1023 addresses) with that of the shift register cycle time, eliminated any time delay between sweeps and determined the correct timing of the receive period after each random excitation pulse.

With best regards,

Yours sincerely


E. Lippmaa


J. Past


J. Puskar



DEPARTMENT OF ORGANIC CHEMISTRY
ZERNIKELAAN, GRONINGEN
THE NETHERLANDS
TEL.: 050 - 11

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

Dear Professor Shapiro,

Gated Spin Tickling or GASP.

We recently applied a new NMR technique, that is basically a Gated SPin tickling technique and we called it the GASP-technique¹. In such a gated spin tickling experiment similar conditions as in homonuclear proton spin tickling are used, but the spin decoupler is only on during the pulse delay and off during acquisition of the FID. In this way coupling constants remain the same (as in gated noise decoupled spectra) whereas the line intensities are changed due to disturbances of the spin state populations involved (comparable to the theory of INDOR). We want to make some additional remarks on this technique.

By irradiating one ¹³C satellite in the proton spectrum, only the intensities of the absorptions due to the carbon atom bearing this proton are disturbed. For a CH group one observes on irradiating the low-field ¹³C satellite, a decreased intensity of the low-field part and an increased intensity of the high field part of the carbon doublet. The low-field part becomes even negative at slightly higher decouple power. The place of the ¹³C satellites is easily calculated if one knows the ¹³C-¹H coupling constants e.g. from non-decoupled ¹³C spectra. The accurate decouple frequencies are obtained in the usual way from a proton

spectrum, that is measured at exactly the same lock conditions as the ^{13}C spectrum. Less accurate decouple frequencies can be calculated without running the proton spectrum if one knows the spectrum and the decouple frequency of TMS. We used, as in homo decoupling experiments, the lower side band for irradiation².

We have used GASP to assign tertiary carbons in aromatic compounds. In one case we irradiated a ^{13}C satellite, caused by long-range ^{13}C - ^1H coupling, that was hidden under the normal proton signals. This resulted in asymmetry in the line heights of the long-range coupling pattern.

In spin tickling experiments without gating considerable splitting up of the ^{13}C absorptions was observed. It is clear that the selectivity is very good at the low decouple power used in these experiments.

Sincerely yours,



J. Runsink

¹J. Runsink, J. de Wit, W.D. Weringa, Tetrahedron Lett., in press.

²The instrument was a XL 100/15 with a 620/f computer (8k memory).

The gate used is the same as for gated noise decoupling.



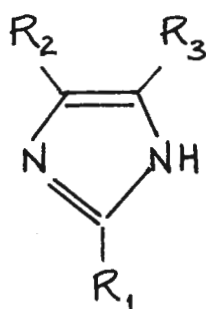
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
9000 ROCKVILLE PIKE
BETHESDA, MD. 20014

January 7, 1974

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

Dear Professor Shapiro:

We have recently studied the effect of neighboring formal charge on the ^{19}F and ^1H nmr titration curves of 2-fluoro-histidine(2) and 4-fluoro-histidine(4). As expected, the results indicate that the ^{19}F nucleus is more sensitive to change in the local electronic environment by at least an order of magnitude than the proton. Titrations of carboxyl group(from $-\text{COOH}$ to $-\text{COO}^-$) or amino group(from $-\text{NH}_3^+$ to $-\text{NH}_2$) shift the imidazole ring protons upfield by ca 0.15 ppm in 2 and 0.07 ppm in 4. Similar titrations, however, shift the fluorine nucleus upfield by ca 0.58 ppm in 2 and 1.74 ppm in 4.

		<u>R_1</u>	<u>R_2</u>	<u>R_3</u>
	<u>1</u>	F	H	H
	<u>2</u>	F	H	$-\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
	<u>3</u>	H	F	H
	<u>4</u>	H	F	$-\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$

Interesting, but anomalous, ^{19}F shifts are found in the titrations of the imidazole ring in 1-4. (Table 1) Conversion of the imidazole to either imidazole cation or imidazole anion shows a downfield shift in the 2-fluoro substituted compounds(1 and 2). By contrast, an upfield shift is found in the 4-fluoro substituted compounds(3 and 4). We are not able to interpret these puzzling anomalies at the present time.

Sincerely yours,

Herman J. Yeh *Jack S. Cohen*
Herman J. Yeh, Jack S. Cohen



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Table 1. ^{19}F Chemical Shift Changes

<u>Compound</u>	$\Delta\delta_1^a$, ppm (from neutr ^l to cation)	$\Delta\delta_2^a$, ppm (from neutral to anion)
<u>1</u>	3.91	2.66
<u>2</u>	4.49 ^b	2.15
<u>3</u>	-5.56	-5.74
<u>4</u>	-3.74 ^b	-5.11

a). A negative $\Delta\delta$ indicates an upfield shift. b). These values include the shift due to titration of the carboxyl group.

Title: ^{19}F Chemical Shift Anomalies in Ring-Fluorinated
imidazoles and Histidines.

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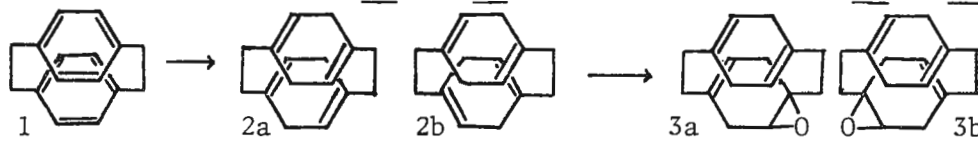
TITLE: Limitations of the LIS Method with Molecules of
Uncertain Geometry and Conformation --
Tetrahydro[2.2]paracyclophane Monoepoxide

January 10, 1974

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

Dear Barry:

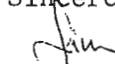
In our previous contribution to TAMNMR Newsletter [174-44] we proposed that the LIS method when applied to the monoepoxide (3) of the tetrahydro Birch reduction product (2) of [2.2]paracyclophane (1) suggested that the correct geometry was 2a, the meso diastereoisomer. We wanted to see if this contention would be supported by quantitative treatment of the PDIGM program [M. R. Wilcott, R. E. Lenkinski, and R. E. Davis, *JACS*, 94, 1742, 1744 (1972)]. We found that in fact agreement between the observed LIS curves and the PDIGM predicted values was not seen unless a rather strange geometry of the Eu-O bond was assumed, viz., a Eu-O distance of 2.0 Å and an orientation of the Eu-O bond suspiciously close to the rest of the molecule. To make a long story short, we began to play with various conformations of both 3a and 3b (the decks in either 3a or 3b could either



be directly above and below one another or could be skewed off with the bridging ethylene groups in a more or less staggered conformation), testing the PDIGM program with each conformation, and a clear preferred conformation and stereoisomer was not forthcoming. The tentative nature of our results may attest to the difficulties that may be anticipated with the LIS method when the exact geometries of the possible structures are not known or when a pseudo-contact mechanism may not be strictly operative. At least we found that in the present case with so many variables, no definite answer could be obtained.

Fortunately, we were able to ascertain the correct geometry of 2 by another method -- a complete nmr analysis of the tetraepoxide of 2 (and without utilizing the LIS method). The correct geometry was actually the dl isomer, 2b. These results will appear in JOC.

Sincerely,


James L. Marshall
Associate Professor



BROWN UNIVERSITY Providence, Rhode Island • 02912

DEPARTMENT OF CHEMISTRY

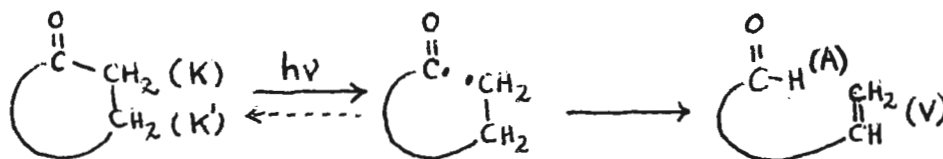
January 14, 1973

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

Field Dependent CIDNP from Photolyzed, Flowing Cyclooctanone Solutions

Dear Dr. Shapiro:

We are presently employing a high resolution nmr flow system recently constructed at Brown (1) to examine the magnetic field dependence of CIDNP spectra obtained during photolysis of cyclic ketones. Closs (2) has reported that the aldehyde proton (A) of the ring-opened product exhibits a magnetic field dependence consistent with the biradical intermediate shown in the reaction scheme below.



By using our flow system we have been able to record the entire CIDNP spectrum during the photolysis of cyclooctanone over a range of magnetic fields. Superimposed CIDNP spectra obtained from a chloroform solution of the ketone at three different fields are shown in the accompanying figure with letters identifying lines from protons in the above scheme. The maximum absolute intensity of all emission lines occurs when the photolysis is carried out in a field of ca. 5 kilogauss. Since the maximum in the field dependence should be correlated with the average electron-electron distance in the biradical (2) one can conclude that both the ring opened aldehyde and ring closure to give emission from the ketone occur from a common average geometry of the biradical intermediate.

The figure illustrates that the relative intensities of the CIDNP lines in this case are also field dependent. The effects are most pronounced in low fields and are only partly explainable by involving level-crossing of the kind responsible for some types of field effects in CIDNP generated by free radicals (3).

1. R. G. Lawler and M. Halfon, Rev. Sci. Instruments, January, 1974.
2. G. L. Closs and C. E. Doubleday, J. Amer. Chem. Soc., 95, 2735 (1973)
3. R. Kaptein and J. A. den Hollander, *ibid.* 94, 6269 (1972)

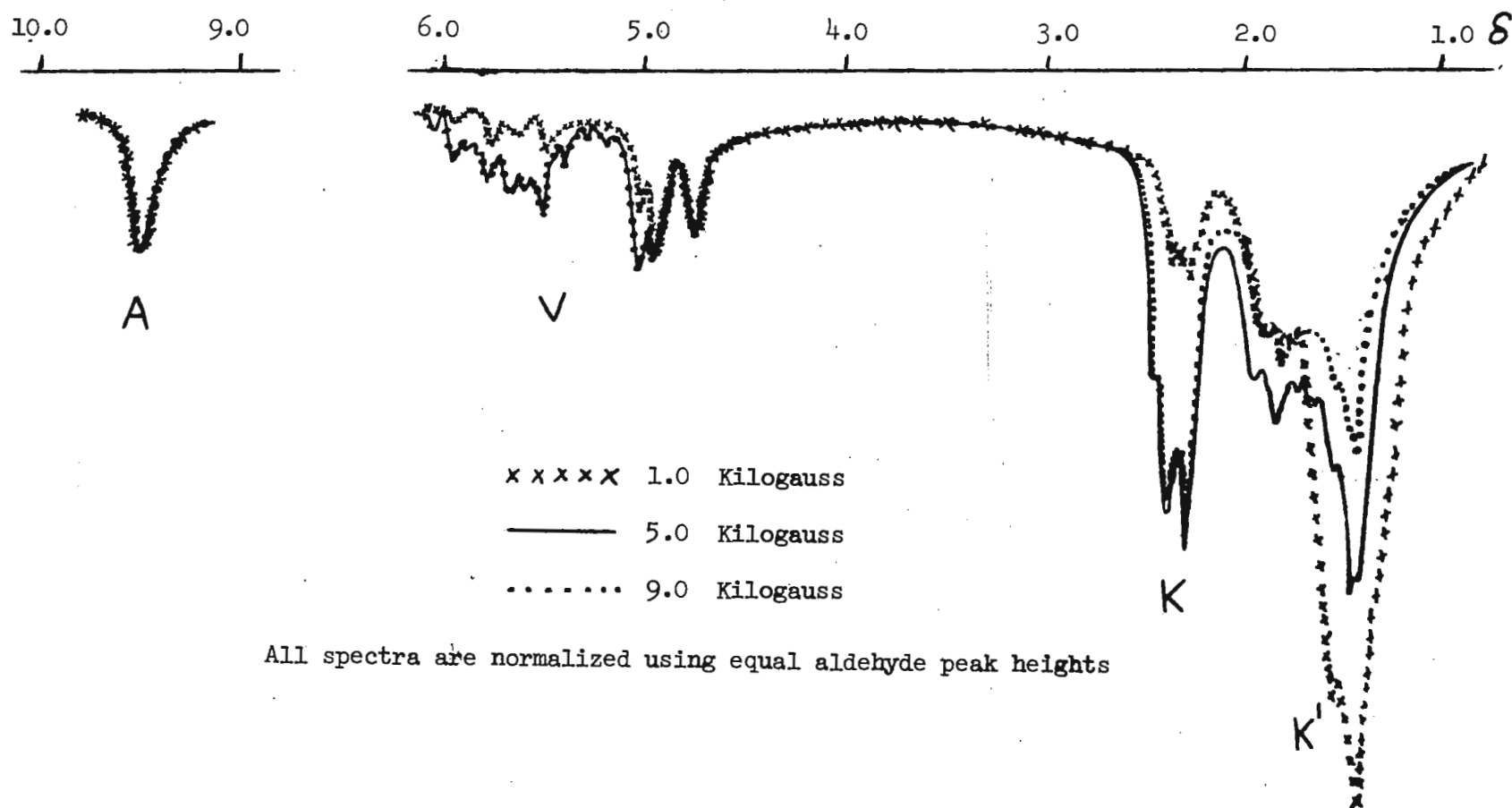
Sincerely yours,

Ronald G. Lawler
 Professor of Chemistry

Marc Halfon

RGL:jb

Photolysis of Cyclooctanone



All spectra are normalized using equal aldehyde peak heights

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

January 11, 1974

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77844

The Effect of Urea on Magnetic Relaxation in
Aqueous Solutions of Poly(Ethylene oxide)

Dear Professor Shapiro:

We have recently finished a PMR study of the PEO (poly(ethylene oxide))-urea-water system which included the measurement of T_1 and T_2 of PEO and the chemical shift between the PEO and water resonances. The measurements were made on a modified HA-60-IL spectrometer. The longitudinal relaxation times were measured by a 180° - 90° pulse sequence and the transverse relaxation time by a simple 90° - 180° pulse sequence. Translational diffusion did not contribute to the value of T_2 because of the small diffusion coefficient of 20,000 molecular-weight PEO.

This study was motivated by the observation of a rather sharp transition in the ultrasonic behavior of the PEO-urea-water system: a 50% decrease in the principal relaxation time between 2 and 4 molal urea.¹ Since the polymer and its immediate solvent environment are thought to be involved in the transition, we thought that measurements of T_1 , T_2 and the chemical shift might help to clarify the nature of the transition.

The measurements on dilute solutions of PEO in heavy water and d_4 -urea from 0 to 10 molal urea at 10° and 25°C revealed no transition but rather only a gradual change. The relaxation times were inversely proportional to the solvent viscosity and the small trend in the PEO-HOD chemical shift probably reflected exchange of protons between sites on water and urea. Thus within our experimental precision there is no NMR evidence for a transition in the equilibrium conformation of the polymer or its immediate solvent environment. The ultrasonic results remain unique. A more complete presentation of this work is being submitted to the Journal of Physical Chemistry.

Credit this letter to the account of P. R. Shafer who is on safari in Africa.

Sincerely,

Alan A. Jones
Alan A. Jones

Walter H. Stockmayer
Walter H. Stockmayer

1. G.G. Hammes and P.R. Schimmel, J. Am. Chem. Soc., 89, 422 (1967).



DEPARTMENT OF CHEMISTRY
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JWE/SR

14th January, 1974.

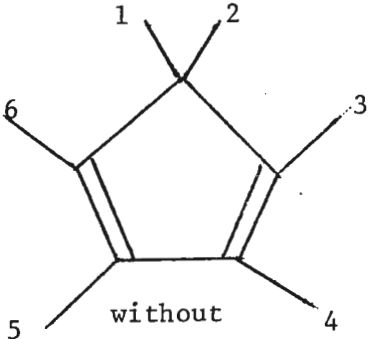
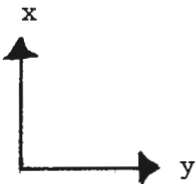
Professor B. L. Shapiro,
Department of Chemistry,
Texas A. & M. University,
College of Science,
College Station,
Texas 77843,
U.S.A.

Dear Barry,

Oriented NMR of cyclopentadiene and cyclopentadienyl complexes,
and the importance of vibrational averaging.

It is becoming apparent that dipolar coupling constants and orientation matrix elements can be strongly influenced by vibrational motion, and it is necessary to include such effects when trying to obtain accurate geometries of molecules. We have recently come across two examples of the magnitude of vibrational effects, and some of your readers may be interested in a preview of our results.

The first example concerns cyclopentadiene monomer, (J. W. Emsley, J. C. Lindon, M. C. McIvor and D. S. Stephenson, Mol. Phys., 1974) whose spectrum was obtained and analysed a long time ago. We have obtained ratios of inter proton vectors from the observed dipolar coupling constants with and without vibrational corrections, as follows:-

		
	without	with
r_{13}/r_{12}	1.510 ± 0.009	1.549 ± 0.009
r_{14}/r_{12}	2.253 ± 0.009	2.276 ± 0.009
r_{34}/r_{12}	1.460 ± 0.022	1.462 ± 0.022
r_{45}/r_{12}	1.526 ± 0.009	1.556 ± 0.009
r_{35}/r_{12}	2.439 ± 0.022	2.476 ± 0.022
r_{36}/r_{12}	2.501 ± 0.009	2.568 ± 0.009

Clearly, vibrational averaging is important if accurate structural data is required. The effect on the S values is also large. The vector r_{12} is chosen as the reference length, hence the value of S_{zz} is changed by the largest amount on averaging (-0.1477 to -0.1575), whilst the other two values change by smaller, but significant amounts i.e. S_{xx} (0.0650 to 0.0678) and S_{yy} (0.0827 to 0.0897).

Cyclopentadienyl ring protons in π Cp complexes have been studied several times by oriented NMR, and in some cases the ratio of dipolar coupling constants obtained differs significantly from the regular pentagon value of 4.236. Vibrational averaging reduces the theoretical value to 4.216, which agrees very well with the observed value for Cp NiNO of 4.211 ± 0.003 . The compound Cp NiNO C_{5v} symmetry, whereas CP Mn (CO)₃ for which a ratio of 4.11 ± 0.01 has been observed, does not. The NMR results indicate small deviations from a symmetric ring for the Mn compound? A more detailed account will be published soon (I. R. Beattie, J. W. Emsley and R. Sabine).

Best wishes,

Yours sincerely,

Jim Emsley.

J. W. EMSLEY.

UNIVERSITY OF DELAWARE
NEWARK, DELAWARE
19711

DEPARTMENT OF CHEMISTRY

January 17, 1974

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

TITLE: Improvement of FT baselines

Dear Barry:

Someone absconded to Switzerland with the University of Delaware subscription, so let this be the opening gun for renewal.

Glitches at the beginning of the FID are not uncommon in FT NMR and have an often disastrous effect on baselines and integrations. The usual method of dealing with this seems to be trapezoidal windows which are effective or ineffective, depending on how choosy you are.

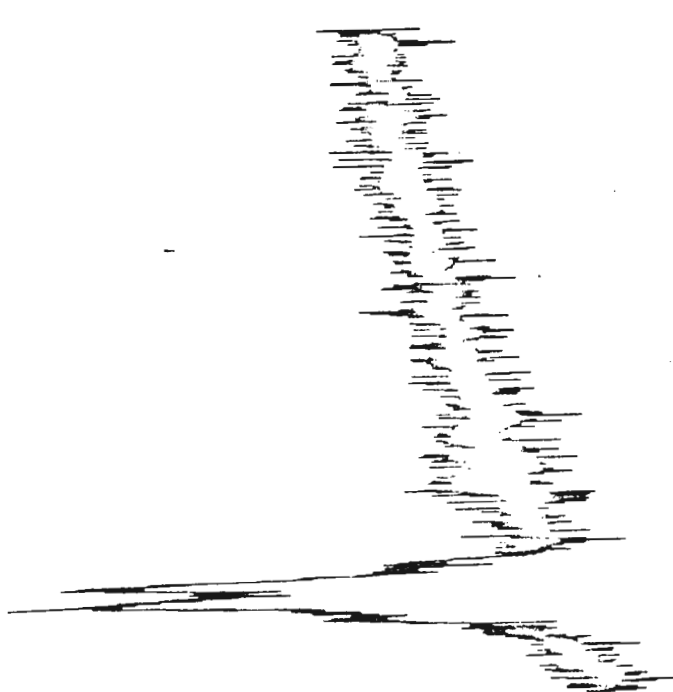
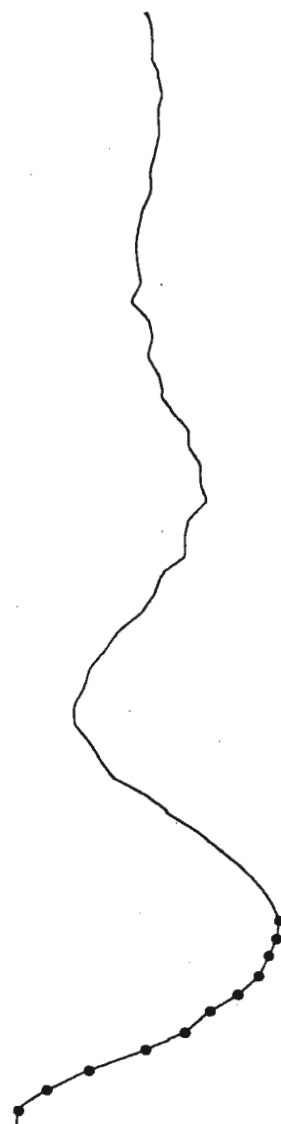
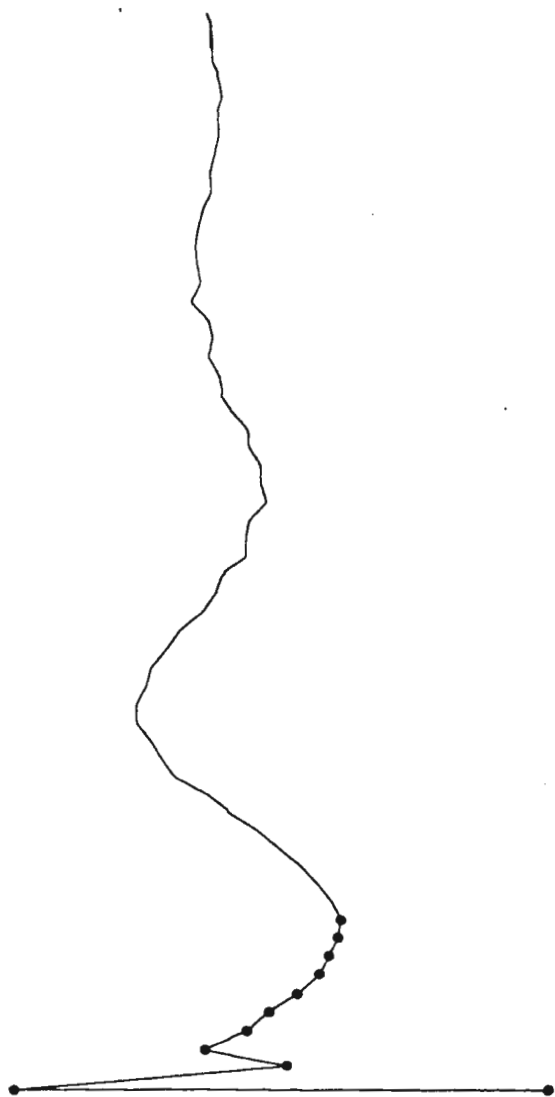
In some situations where a clear-cut pattern is observable in the FID, we are now using the "Dalrymple Massage", named after its inventor. This consists of filling in the first three or four distorted points on the FID to follow the pattern which is evident from the later and unaffected points. This is illustrated (see the pretty picture) on an N-15 quartet, both uncorrected (top) and corrected (bottom), in FID (right) and transformed spectrum (left). The effect is evident. Data points are the blackened dots; the first three were filled.

It is my educated* opinion that this is not cheating but merely furnishing the computer with information you have, but it doesn't, namely, Natura non facit saltus.



Joseph H. Noggle
David L. Dalrymple
Thomas K. Leipert

*After all, I did graduate.



Uppsala universitet
Fysiska institutionen

University of Uppsala
Institute of Physics OH/PÖ

1974-01-21



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

A very slow sweep on HA-60

In the investigation of high-resolution NMR line-shapes we found that it would be desirable to completely eliminate the effect of the sweep rate of the observing **rf** field. Even a sweep of 0.01 Hz/sec can in certain circumstances influence the line-shapes considerably. Therefore a simple electronic circuit was constructed which gives an almost "infinitely slow sweep".

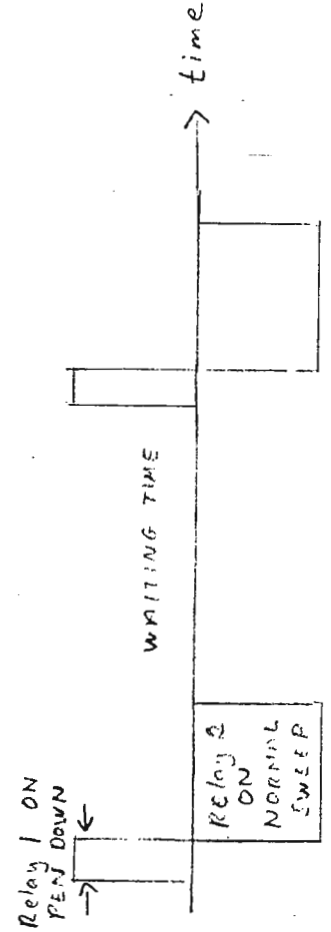
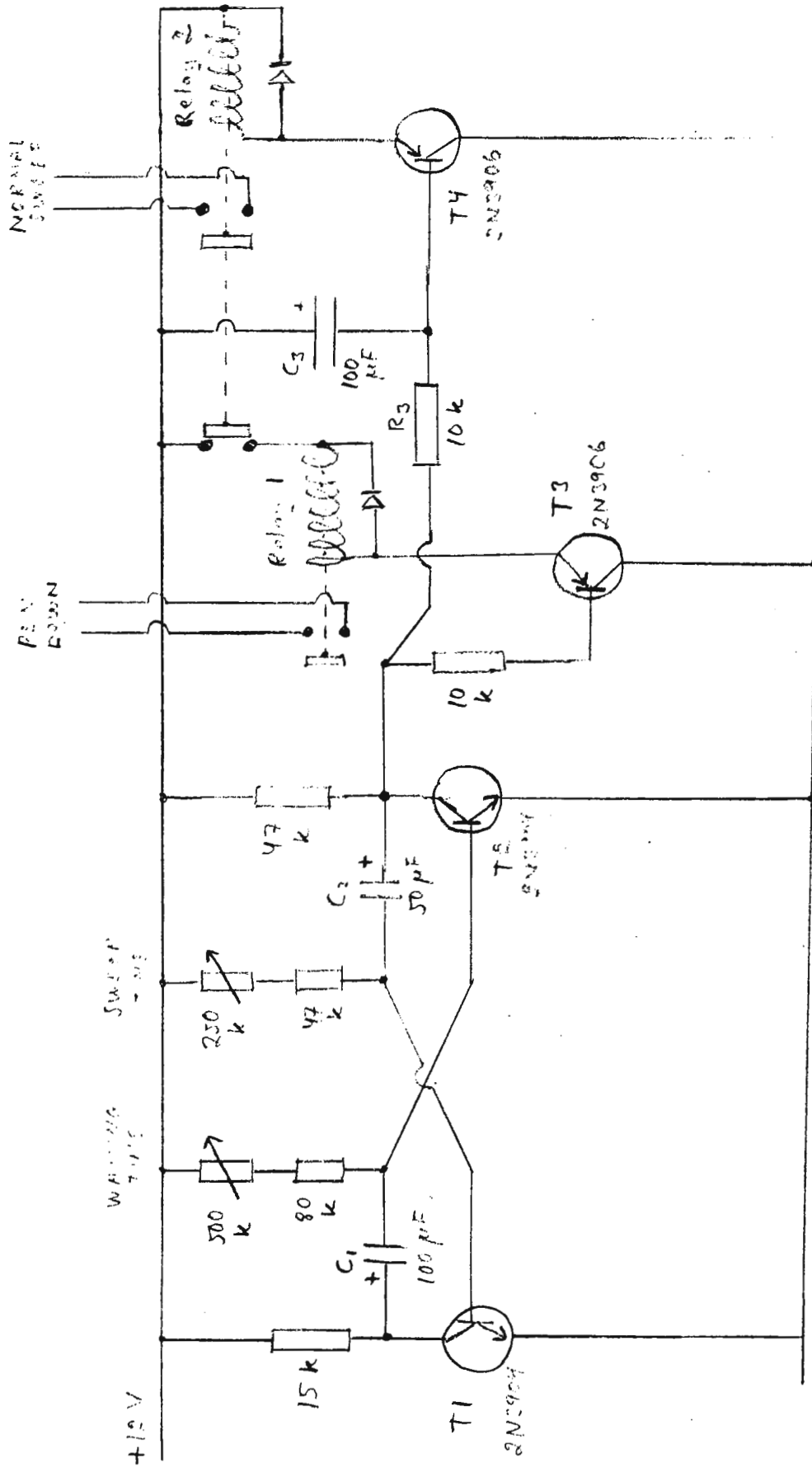
The function of the circuit is: the astable multivibrator with transistors T1 and T2 supplies time periods of 3 to 35 seconds. The transistors T3 and T4 allow the relays to be energized when the T2 transistor is "on". Capacitor C₃ together with R₃ delays the switching of relay 2 about 1 second. When relay 2 is energized relay 1 is cut off.

This gives the following sequence: The recorder sweep is activated for a few (3-12) seconds with the pen lifted. The recorder then stops and waits 5-35 seconds before the pen goes down for 1 second leaving a dot. The cycle is then repeated giving a spectrum of dots. At each point the spin system has relaxed towards equilibrium for 5 to 35 seconds, and the obtained spectrum can really be described as "steady state".

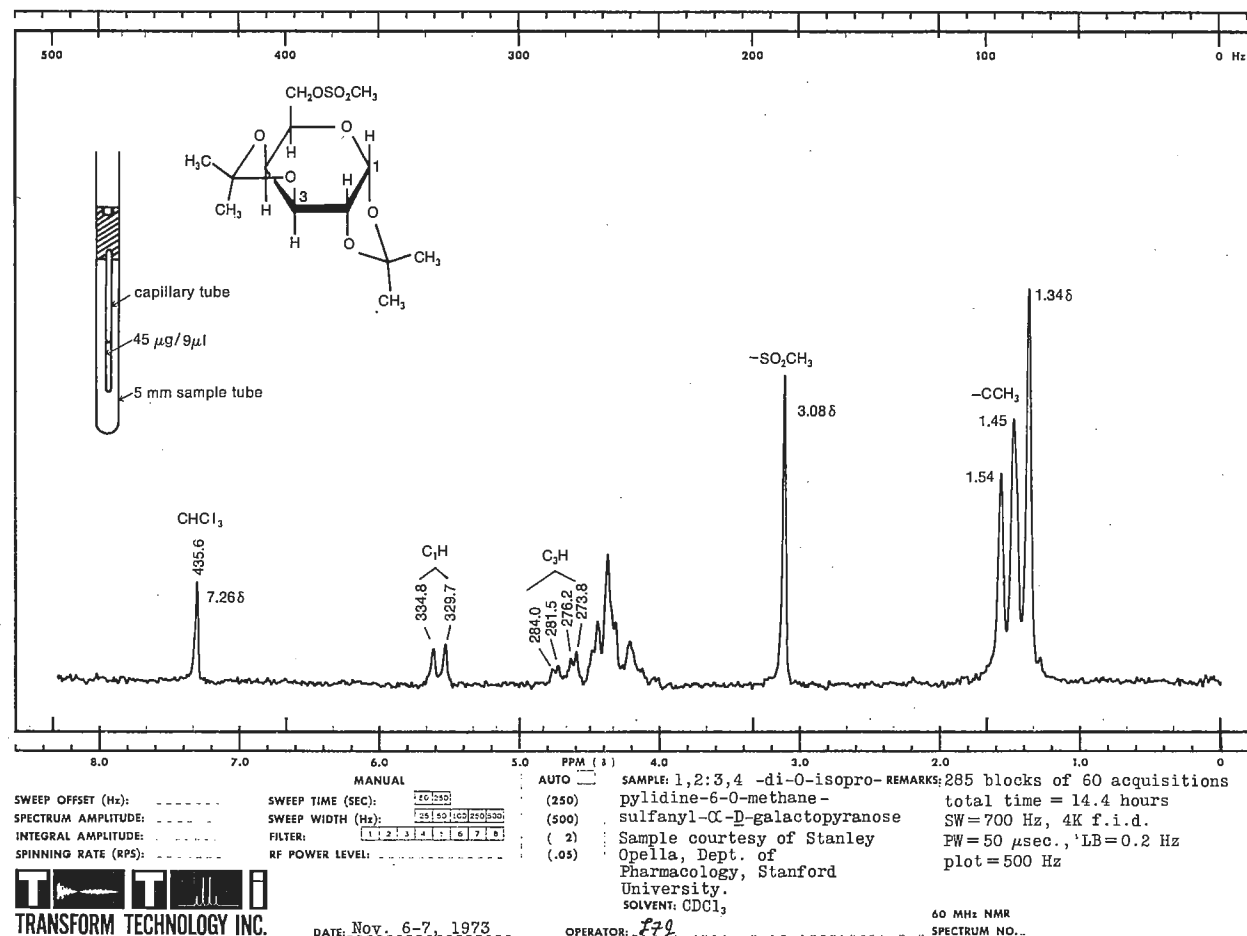
The overall sweep time for the spectrum is much longer than for a normally swept spectrum. A prerequisite for this experiment is naturally that the sweep frequency generator is in good shape.

Yours sincerely

Ola Hartmann



Relays = 12V 50mA



Analysis of very small samples is best done using a microcell approach. Here, 45 micrograms of a compound with molecular weight 338 was contained in a capillary tube of 1.0 mm I.D. The peak at 3.085, although weak after one block of acquisitions, served adequately for the peak register method, which effectively cancels long-term field drift. Signal frequencies and chemical shifts were copied from an oscilloscope display of peak positions using an assigned value of 435.6 Hz for the chloroform peak. The spectrum is very well defined, and demonstrates that overnight FT operation with a T-60A/TT-7 system is quite feasible and very useful for microsample analysis.

MICROSAMPLE ANALYSIS with a TT-7/T-60A System

The TT-7 pulsed RF Fourier transform accessory benefits NMR operation by dramatically increasing sensitivity over that obtained in the normal CW mode of operation. Typically, samples five to ten times smaller than those now being handled can be run in the same amount of analysis time. Signal input, accumulated free induction decay, or transformed spectra can be displayed on the TT-7's cathode ray tube for visual monitoring. The spectra can be

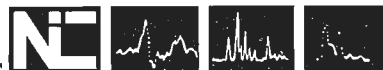
plotted using the T-60 recorder. Digital integrations of spectra can be viewed or plotted as well.

Not only will the TT-7 enhance the sensitivity and increase sample throughput of your T-60 but it will also provide an excellent Fourier transform training facility. Its ease of use is incomparable. In addition, spin-lattice relaxation times can be determined from a series of runs using the progressive saturation technique. Optional automatic T₁ mea-

surements are available using the inversion-recovery technique as well as other multi-pulse experiments. In addition to sensitivity improvement and T₁ measurement applications, the basic TT-7 system will provide computer calculations of theoretical NMR spectra of up to six spins (seven spins with 12K core memory and disk memory system).

Phone or write for more details.

NICOLET INSTRUMENT CORPORATION



5225 Verona Road, Madison, Wisconsin 53711
Phone: 608/271-3333



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

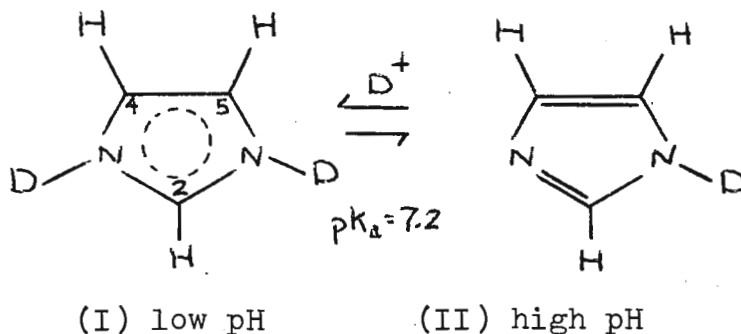
January 21, 1974

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

T_1 Values of Imidazole Protons and their Relevance
to NMR Studies of Proteins

Dear Barry:

Recently we have been interested in examining the potential of proton T_1 measurements as a probe in biological systems. To begin our study we examined the T_1 's of the C_2 and $C_{4,5}$ protons in imidazole as a function of pH. The results for the T_1 values of both C_2 -H and $C_{4,5}$ -H of freshly prepared solutions of imidazole (0.073 M) in 0.1 M NaCl in D_2O at $20^\circ C$ showed an unexpected distinct minimum around neutral pH. Histidine proton T_1 's showed a similar dependence on pH unrelated to the pK_a values. The T_1 results for



C_2 -H in degassed and undegassed samples of imidazole are shown in Figure 1. We carried out a number of obvious control experiments (concentration, salt effect) which did not explain the origin of the pH-dependence. However,

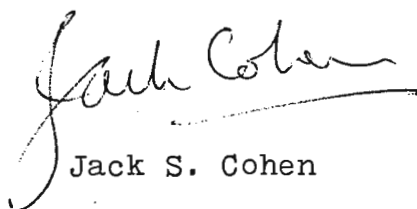
T_1 measurements in the presence of 10^{-4} M EDTA showed an increase at neutral pH. By contrast, the addition of Cu^{2+} at 10^{-4} to 10^{-6} M concentrations to the imidazole solutions resulted in an expected lowering of the T_1 values of the ring protons at neutral pH, but showed little effect in the acidic or basic solutions. (For example, in an undegassed imidazole sample at pH = 7 containing 7×10^{-5} M Cu^{2+} , the T_1 of $\text{C}_2\text{-H}$ was less than 0.2 sec. For this same undegassed sample at pH ≈ 0.7 the T_1 of $\text{C}_2\text{-H}$ was 22 sec).

These results indicate that the phenomenon of the minimum in the pH-dependence of the T_1 values of the imidazole protons arises from the binding of imidazole to paramagnetic metal ion impurities in the samples. At low pH values the positively charged metal ions would be displaced by D^+ (I), and at high pH values they would bind more strongly to deuterioxide ions (OD^-). Indeed, analysis of our samples using atomic absorption indicates copper concentrations of approximately 3×10^{-7} M, not an unusually high value.

In conclusion, we would like to stress that paramagnetic impurities at concentrations of approximately 10^{-7} molar can be sufficient to completely dominate relaxation rates for protons in some situations. Although it is obvious, it should be stressed that T_1 's are much more sensitive to the presence of paramagnetic ions than are line widths when $T_2^* > 1$ sec. Since the interpretation of line width variations has already led to erroneous conclusions because of paramagnetic interference (1, 2), even greater care must be exercised in the interpretation of proton T_1 data. Of course, the problem of trace amounts of paramagnetic impurities is less severe for protons that have intrinsically short T_1 's, or for groups which do not bind metal ions. Nor would such a large effect be expected

for the T_1 values of carbon nuclei with directly bonded proton(s). However, since proteins contain groups which are capable of binding paramagnetic metal ions, great care will be required in the interpretation of proton T_1 data in these systems (for example, see references 3 and 4).

Yours sincerely,



Jack S. Cohen

Reproduction Research Branch
National Institute of Child Health
and Human Development



Rod Wasylishen

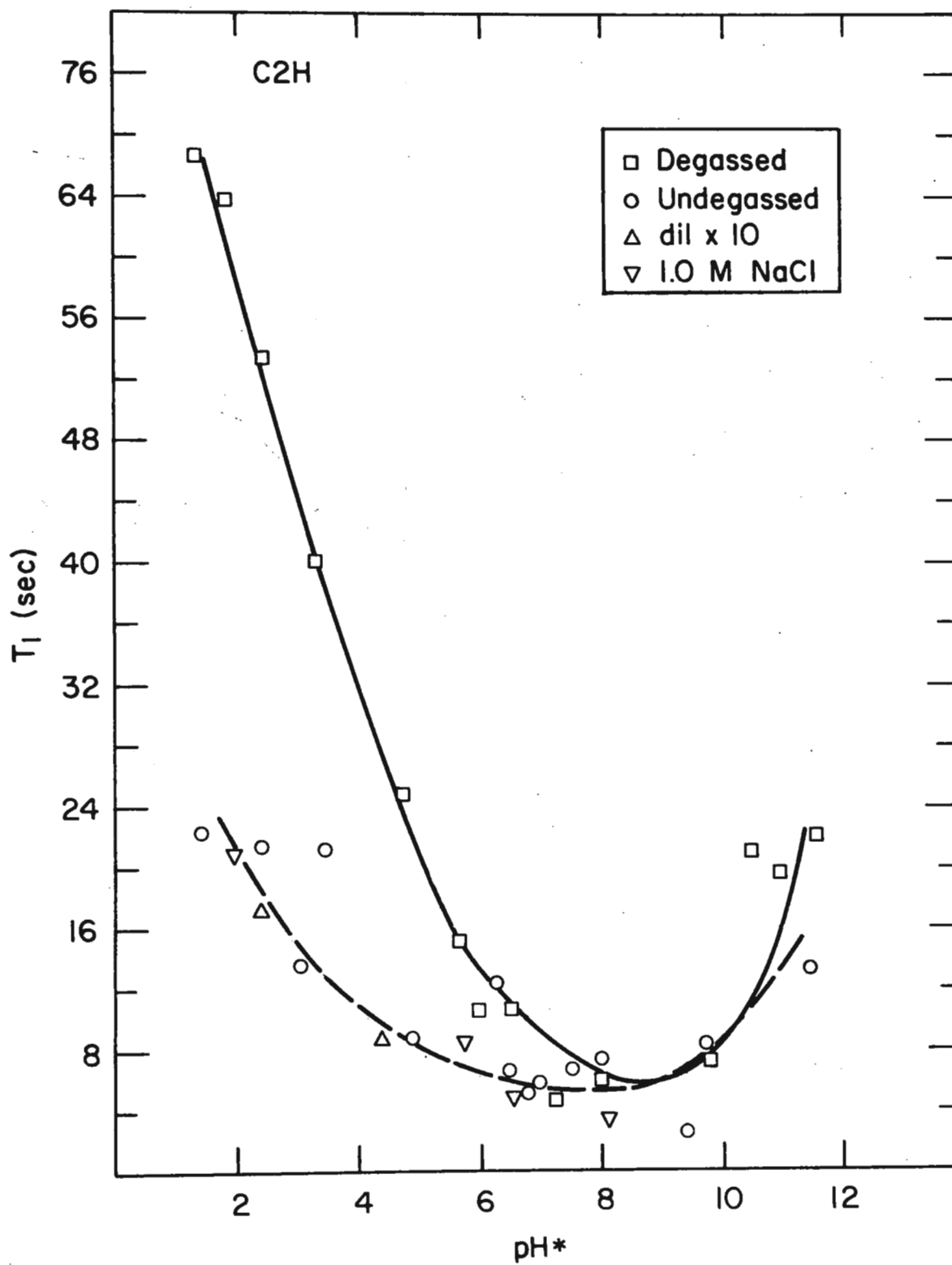
Laboratory of Chemical Physics
National Institute of Arthritis,
Metabolism and Digestive Diseases

RW/vw

References

1. Wong, Y.P. J. Am. Chem. Soc. 95, 3511 (1973).
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3. Benz, F.W., Roberts, G.C.K., Feeney, J., and Ison, R.R. Biochim. Biophys. Acta. 278, 233 (1972).
4. Arata, Y. and Jardetzky, O. Ann. N.Y. Acad. Sci. (in press).

P.S. Please note Jack's new address: Rm. B2-08, Bldg. 2
NIH, Bethesda Md. 20014





United States Department of the Interior

BUREAU OF MINES

4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

Pittsburgh Energy Research Center

January 14, 1974

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

Dear Barry:

We have been using the Mellon Institute high-field spectrometer to obtain

Correlation Mode ^{13}C NMR Spectra of Coal Extracts

at 62.8 MHz. The high sensitivity and rapid sweep capabilities of this instrument allow quantitative data for coal extracts to be obtained in very short periods of time. The free radicals normally present in coal proved to be a blessing in disguise; their effect on the carbon relaxation times are such that reasonably high r.f. power levels incident upon the sample can be used without saturating the resonances. Studies of a carbon disulfide extract of Pittsburgh coal yielded an aromaticity (aromatic carbon/total carbon) of 0.63 in excellent agreement with that estimated from the proton spectrum-- see H. L. Retcofsky and R. A. Friedel, in "Spectrometry of Fuels" (R. A. Friedel, ed.), Plenum Press, 1970. We have also examined other coal extracts as well as solvent extracts of "synthoil" to aid in the solution of engineering-type problems associated with the production of this potential "petroleum" from coal.

Without the aid and cooperation of two really "great" guys at Mellon Institute -- Joe Dadok and Rich Sprecher -- this work could not have even begun!

Dr. Frank Schweighardt has recently joined our staff as an NRC Fellow to explore the use of Nitrogen-14 NMR in energy research.

Sincerely yours,


R. A. Friedel


H. L. Retcofsky

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

22 January, 1974

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

MULTINUCLEAR CW or FT NMR SPECTROMETER

Dear Barry,


We have recently modified our Varian XL-100 FT-NMR spectrometer to permit observation of (in principle) any nuclear resonance, at a cost which is comparable to the commercial cost for adding just a single additional nucleus. Our scheme centers around an inexpensive frequency synthesizer and broad-band r.f. amplifier--all other components amount to about \$200 for each additional desired nucleus. By mixing the (continuous-wave) output of the external synthesizer with the (c.w. or pulsed) output of the existing 25 MHz carbon-13 transmitter, we can construct the (c.w. or pulsed) difference frequency to coincide with any desired nuclear Larmor frequency; a similar de-mixing step following the receiver preamp stage converts the nuclear response to a 25 MHz signal which can then be treated as usual by the existing carbon-13 receiver. In short, the spectrometer "thinks" it is irradiating and detecting carbon-13 as usual, while the NMR sample in the probe actually "sees" an arbitrarily-selected frequency excitation. The approach is equally adaptable to either CW or FT detection, as shown in Figure 1, and the principle should also apply to NMR spectrometers of other manufacturers.

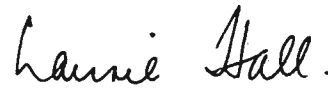
Advantages of the approach are: (1) overall cost is about the same as for commercial provision for just one nucleus; (2) there are no restrictions in the possible range of observable nuclear frequencies, with a cost of about \$200 for each additional nucleus after the first; (3) mainframe modifications for the Varian XL-100 consist of breaking a single cable; (4) performance of the device compares favorably with that of a commercial transmitter-receiver which is specially tuned for just one frequency; and (5) all existing spectrometer capability is retained, including decoupling, signal averaging, lock, and multiple-pulse sequences such as for T_1 -measurement.

A more complete report will appear shortly in J. Mag. Res., and further examples will be discussed in talks by A. G. Marshall at the 15th Experimental NMR Conference at Raleigh, 28 April-1 May, 1974, and by L. D. Hall at the Canadian Chemical Conference to be held in Regina, Sask., 2-5 June, 1974.

Please credit this contribution to the account of A. G. Marshall. Thank you.

Sincerely,


Alan G. Marshall


Laurance D. Hall

Continuous-Wave

Fourier-Transform (one transient)

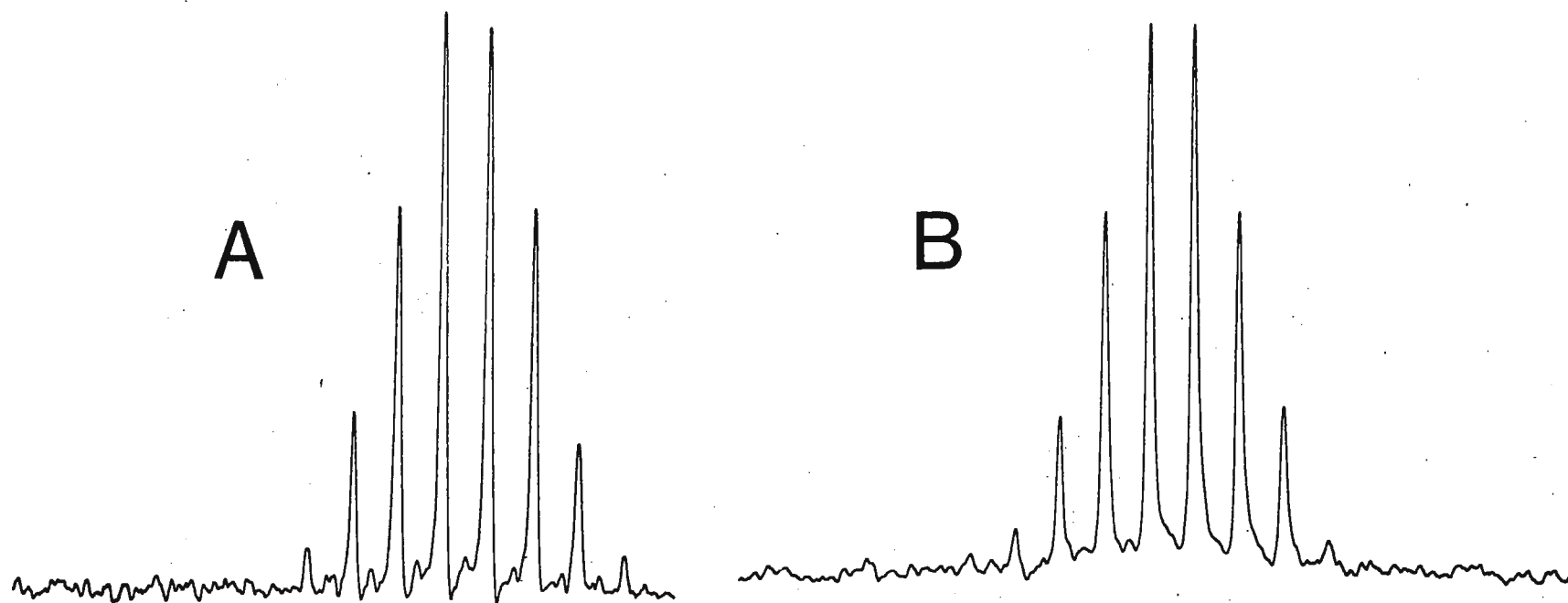


Figure. ^{31}P NMR spectra for Varian standard sample (6% TMS, 25% $(\text{CH}_3\text{O})_3\text{P}$ in C_6D_6). Both spectra were obtained using an existing 25 MHz transmitter-receiver in a Varian XL-100 FT-NMR spectrometer, in combination with an external frequency synthesizer as described on the previous page. Signal-to-noise for either spectrum, based on the Varian convention (height of left-most peak, divided by the maximum noise amplitude, then multiplied by 2.5) is 5:1, compared to the 6:1 specification for the same sample using the specially-tuned Varian ^{31}P transmitter-receiver network.

Department of Chemistry



FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW ~~xxx~~ ONTARIO M3J 1P3

January 29, 1974

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

Dear Dr. Shapiro:

Re: ^{13}C Correlations in Organotin Compounds

We would like to briefly report on a set of parameters we have obtained from a multiple regression analysis of ^{13}C shift data for a series of organotin derivatives. These parameters have been broken down into α , β , and γ contributions and subdivided into β and γ effects across either a carbon atom or a tin atom. These are denoted by β_X and $\beta_{\text{Sn}X}$ respectively. The marked attenuation of β and γ effects across a tin atom is noted (thus β_{SnC} is effectively zero and does not appear in the Table. The α -effect of the tin atom itself, α_{Sn} , has a value which is consistent with its electronegativity - the best correlation being observed with Sanderson electronegativities¹. Also interesting is the enhanced α -effects for carbon atoms near tin. The strange parameter ξ is applicable only to the tertiary carbon of the neophyl group and appears to be analogous to steric parameters which have been used elsewhere. The same parameter is required, along with the substituent parameters for organic compounds², to predict reasonable shifts for dineophyl itself.

We have also calculated corresponding parameters for the diamagnetically corrected shifts³. We do not find any significant change in the parameters (other than the α -effects of course), neither does the parameter ξ change appreciably despite the expectation³ that steric parameters are not necessary for diamagnetically corrected data.

The parameters have been used to predict shifts for a variety of organotin compounds with methyl, ethyl, isopropyl, t-butyl, t-amyl, neophyl, phenyl, benzyl and halogen substituents in various combinations and proportions. Most of the predicted results lie within 1ppm of observed shifts. An example is given (predicted results in parenthesis).

Dr. B.L. Shapiro
College Station, Texas 77843

January 22, 1974

A complete list of observed and calculated shifts for the 27 compounds studied are available from us - we don't intend to publish them because they can be calculated, within reason, from the parameters in the Table. The parameters also fit other published ^{13}C data for tetrahedral organotin derivatives.

We feel that systematic correlation of ^{13}C data in organometallic chemistry may be useful in the interpretation of the origins of ^{13}C shifts.

Sincerely,

C.E. Holloway & D.E. Axelson
Associate Professor

^{13}C Substituent Effects in Organotin Compounds

Substituent Effects	Coefficient
α_{C}	11.4
β_{C}	9.0
α_{Ph}	25.6
β_{Ph}	7.5
α_{Sn}	-5.2
β_{Sn}	4.0
γ_{Sn}	-0.3
β_{SnPh}	1.1
β_{SnI}	9.5
β_{SnCl}	7.4 [†]
γ_{SnCl}	-2.3 [†]
D	2.2
E	-22.7
Constant term	-3.16
Correlation Coefficient	.9951

[†] Obtained independently
from regression analysis.

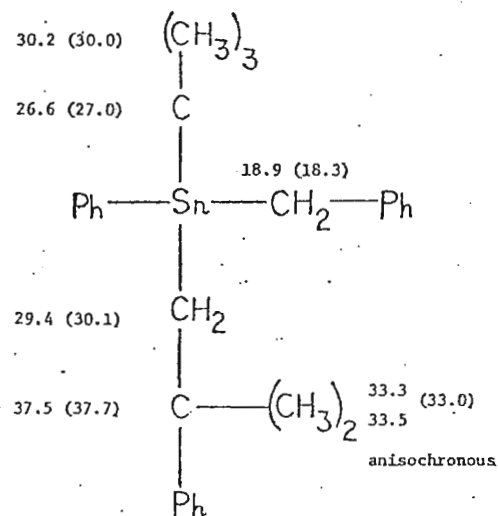
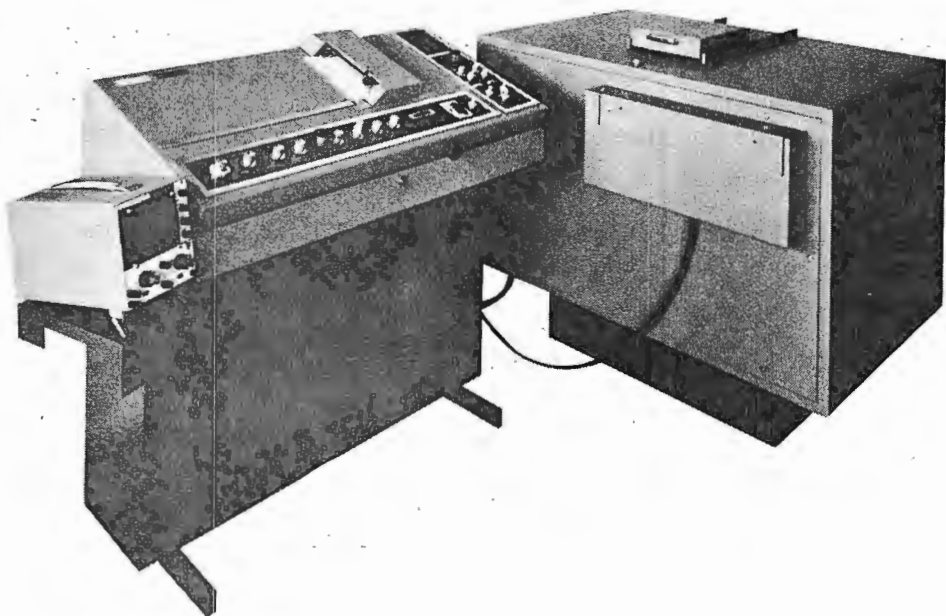


Fig. 1 Typical Fit of ^{13}C Data, Observed (Calculated)

1. R.T. Sanderson, J.Chem.Educ. 29, 539 (1952); 31, 238 (1954).
2. D.M. Grant and E.G. Paul, J.Amer.Chem.Soc. 86, 2984 (1964).
3. J. Mason, J.Chem.Soc.A, 2196 (1970).

A 100-watt bulb consumes as much power as the magnet in our NMR Spectrometers.



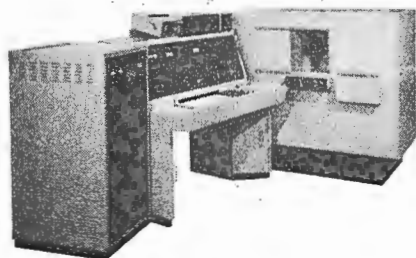
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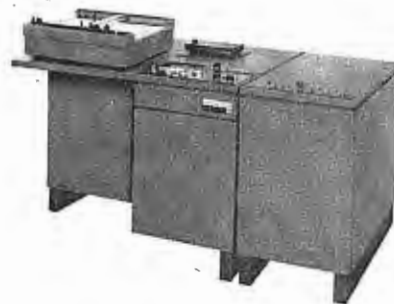
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DEPARTMENT OF CHEMISTRY

January 29, 1974

Havemeyer Hall

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

Dear Professor Shapiro:

Constancy of σ_{\parallel} in CH_3 Systems

Although the basic emphasis of the TAMU-NMR Newsletter is upon experimental aspects of NMR, theoretical considerations can often be very helpful in the interpretation of experimental results. From a number of recent experiments^{1,2} it has become evident that the quantity σ_{\parallel} (defined with respect to the C_{3v} symmetry axis) of carbon-13 of CH_3 groups remains fairly constant among a large number of variable systems.^{2,3} (See Table I.) No such trend is discerned among the quantity σ_{\perp} . Interestingly, the theoretical models of shielding have also shown a constancy of this quantity, although the numerical results are often incorrect. (See Table II.)

This phenomenon can be attributed to the fact that the bond between the carbon atom and its 4-th substituent (atom X) is co-linear with the symmetry axis. In the sum-over-states description of the paramagnetic part of the shielding, σ_{\parallel}^p , the effect of a magnetic field along the symmetry (z) axis is to change the spatial distribution of the occupied MO's by mixing them with the virtual orbitals, thereby changing the energy of the system. For a C_{3v} molecule, this mixing occurs only between E_x (occupied) and E_y^* (virtual) orbitals or vice versa and depends upon quantities such as $\langle E_x^* | M_z | E_y \rangle / \Delta E$, in which the energy denominators can be considered as weighting factors of the relative importance of various excitations (not an average energy). The shielding is the product of these weighted angular momentum matrix elements and similar terms involving the operator M_z/r^3 .

It has been shown⁴ for the molecule CH_3X , where atoms C and X

are along the z axis, that the integral $\langle E_x^* | M_z | E_y \rangle$ involves only the proton-centered 1s AO's, i.e. no contribution from the C or X AO's. It has also been found that the integrals $\langle E_y | M_z / r^3 | E_x^* \rangle$ have a very small dependence (0-5%) upon the X-centered AO's. Similar reasoning explains why the diamagnetic shielding along the symmetry axis σ_{\parallel}^d does not vary among CH_3X systems.⁴ The preceding arguments can in addition be extended to include orbitals of higher principal and azimuthal quantum number.

Although the derivation considered above is based on C_{3V} symmetry, the trend appears to be valid for systems without a true 3-fold axis of symmetry (See Table I). In addition it should be applicable to other CX_3 systems such as CCl_3 , CF_3 and SiH_3 . Although only limited data are available, preliminary studies seem to confirm such predictions in several cases.

The assumption of the validity of this trend allows the prediction of the shielding tensors in systems for which only an isotropic shift measurement is available. For example σ_{iso} of CH_3NH_2 is 180 ± 1 ppm with respect to CS_2 .² Assuming that $\sigma_{\parallel} = 192 \pm 8$ ppm, it is deduced that $\sigma_{\perp} = 224 \pm 6$ ppm. Such data could be used to compare with the theoretical calculations of the shielding tensor (e.g. Table II). It is also possible to evaluate the parallel and perpendicular components of the spin-rotation tensor for the analysis of this contribution to the spin relaxation time.

Sincerely yours,

Bernard Appleman
Bernard Appleman

1. A. Pines, M.G. Gibby & J.S. Waugh, Chem.Phys.Letters 15, 373 (1972).
2. B.R. Appleman & B.P. Dailey, Advan.Magn.Reson. 7 in press.
3. B.R. Appleman & B.P. Dailey, Proc. of Conf. on Critical Eval. of Phys. and Chem. Structure Information, to be published.
4. B.R. Appleman, T. Tokuhiro, G. Fraenkel & C.W. Kern, J.Chem.Phys. in press.
5. R. Ditchfield, D.P. Miller & J.A. Pople, J.Chem.Phys. 54, 4186 (1971); also unpublished data.
6. R. Ditchfield, see reference 3.

TABLE I. Experimental Carbon-13 Shielding of CH₃ Systems.^a

Molecule	$\sigma_{ }$	σ_{\perp}	Molecule	$\sigma_{ }$	σ_{\perp}
CH ₄	196	196	CH ₃ CHO	193	147 ^b
CH ₃ F	167	99	(CH ₃) ₂ CO	197	147 ^b
CH ₃ Cl	189	161	(CH ₃) ₂ SO	177	140 ^b
CH ₃ Br	185	185	(CH ₃ CH ₂) ₂ O	178	173 ^b
CH ₃ I	169	244	(CH ₃ CO) ₂ O	197	161 ^b
CH ₃ OH	190	124 ^b	(CH ₃ S) ₂	193	166 ^b
CH ₃ CN	196	191	CH ₃ CO ₂ H	197	162 ^b
CH ₃ C=CCH ₃	199	185	C ₆ H ₅ CH ₃	188	166 ^b
CH ₃ CH ₂ OH	189	169 ^b	C ₆ (CH ₃) ₆	173	173 ^b

a. See refs. 1 & 2; Units ppm.

b. Average of 2 \perp components.TABLE II. Theoretical Carbon-13 Shielding of CH₃ Systems.

Molecule	$\sigma_{ }$	σ_{\perp}	Molecule	$\sigma_{ }$	σ_{\perp}
BASIS A ^a	(Ref 4)		BASIS C ^c	(Ref 5)	
CH ₄	191	191	CH ₄	221	221
C ₂ H ₆	193	225	C ₂ H ₆	225	233
CH ₃ F	192	238	CH ₃ F	214	162
CH ₃ OH	193	223 ^d	CH ₃ OH	220	184 ^d
BASIS B ^b	(Ref 6)		CH ₃ NH ₂	223	208 ^d
CH ₄	205	205	CH ₃ C≡N	236	224
C ₂ H ₆	205	194	CH ₃ C≡CH	233	229
CH ₃ F	197	112	CH ₃ CHO	238	200 ^d
CH ₃ OH	201	138 ^d	(CH ₃) ₂ O	227	167 ^d
CH ₃ NH ₂	203	166 ^d	CH ₃ CH ₂ OH	223	234 ^d

a. Minimal Slater Type (STO).

c. Extended Gaussian Type (4-31G)

b. Gauge-Invariant Gaussian (4-31G). d. Average of 2 \perp components.

CENTRO DE INVESTIGACION DEL IPN

APARTADO POSTAL 14-740

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DEPARTAMENTO DE QUIMICA

January 30, 1974.

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

Dear Professor Shapiro:

About Calculation of NMR Spectra

A recent adaption (1) of the first part of the LAOCOON III program (2) to small 8K computers (IBM-1130) prompt us to improve the program to allow more versatile calculations. This was essentially achieved by changing the flow sheet of the program to the one shown in figure 1. For a given molecule, it is now possible to calculate spectra at several spectrometer frequencies and to construct many bar diagrams with various "resolution" values. The output can be compared directly with experimental spectra as illustrated in figure 2, which shows a P.E. R-32 90 MHz (through courtesy of Perkin Elmer de México) pmr plot of o-dichlorobenzene (ODCB). Interestingly this 90 MHz spectrum provides for ODCB the same information as 100 MHz measurements.

Satisfactory comparisons for ODCB were also made between experimental spectra obtained with Varian EM-300, A-60, HA-100 and HR-300 (this through courtesy of J.N. Shoolery, Varian) and computed ones obtained using a single set of input parameters in which chemical shifts are given in ppm and coupling constants in Hz.

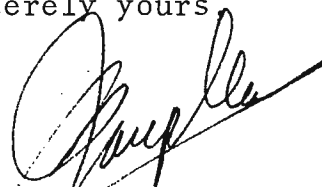
For the obtention of correct input parameters, the LAOCOON III program was compiled on an IBM-370-145 system and tested with the pyridine case (2). By assigning a working area of 100K of the central process unit and performing the scratch operations on temporary areas of a disk instead of on tapes as it is done clasically, the total execution time for the pyridine case was only 20.27 sec., the computer performed only 3 iterations instead of the 9 described, our RMS-error was 0.054 Hz instead of the published value of 0.070 Hz and all our probable error of the parameter sets were smaller than those reported. In addition on the 370 system the initial ODCB spectrum required 1.79 sec. cpu time and 4.92 sec. for the calculation with iterations.

The average execution times (in min.) for the 1130 calculations are:

No. of spins	3	4	5
First spectrum	5.5	7	15
Subsequent spectra	3.5	5	9
Studied example	Styrene	ODCB	Pyridine

Listings of the program and data input sequence are available upon request. The work was done with the assistance of graduate student J. Mares and has just been submitted for publication.

Sincerely yours



Dr. Pedro Joseph-Nathan
Professor of Chemistry

- (1) M. Bader, J. Chem. Educ., 48, 175 (1971)
- (2) A.A. Bothner-By and S.M. Castellano in "Computer Programs for Chemistry", D.F. Detar (Editor), W.A. Benjamin, Vol 1, pp. 10-53, New York (1968).

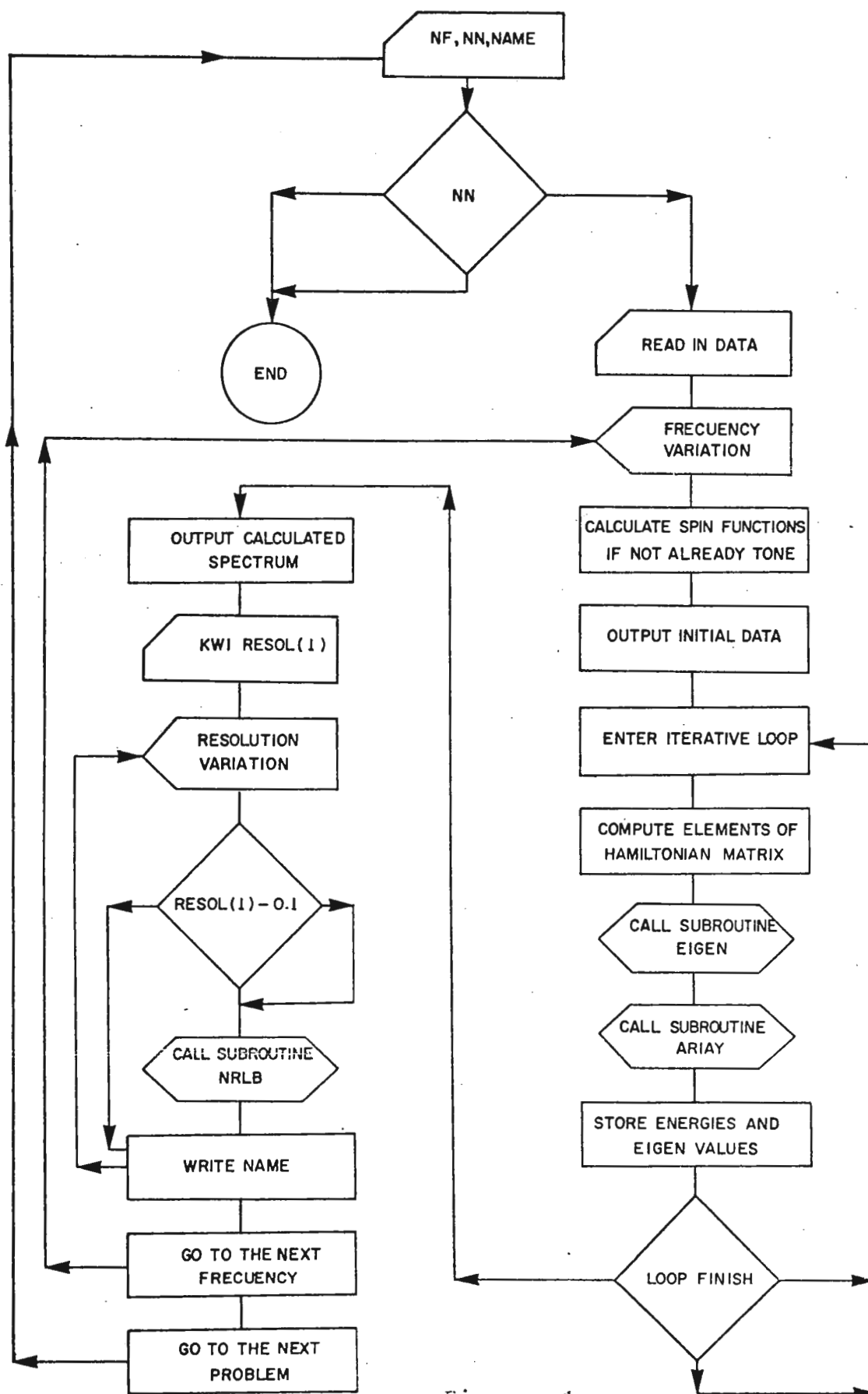
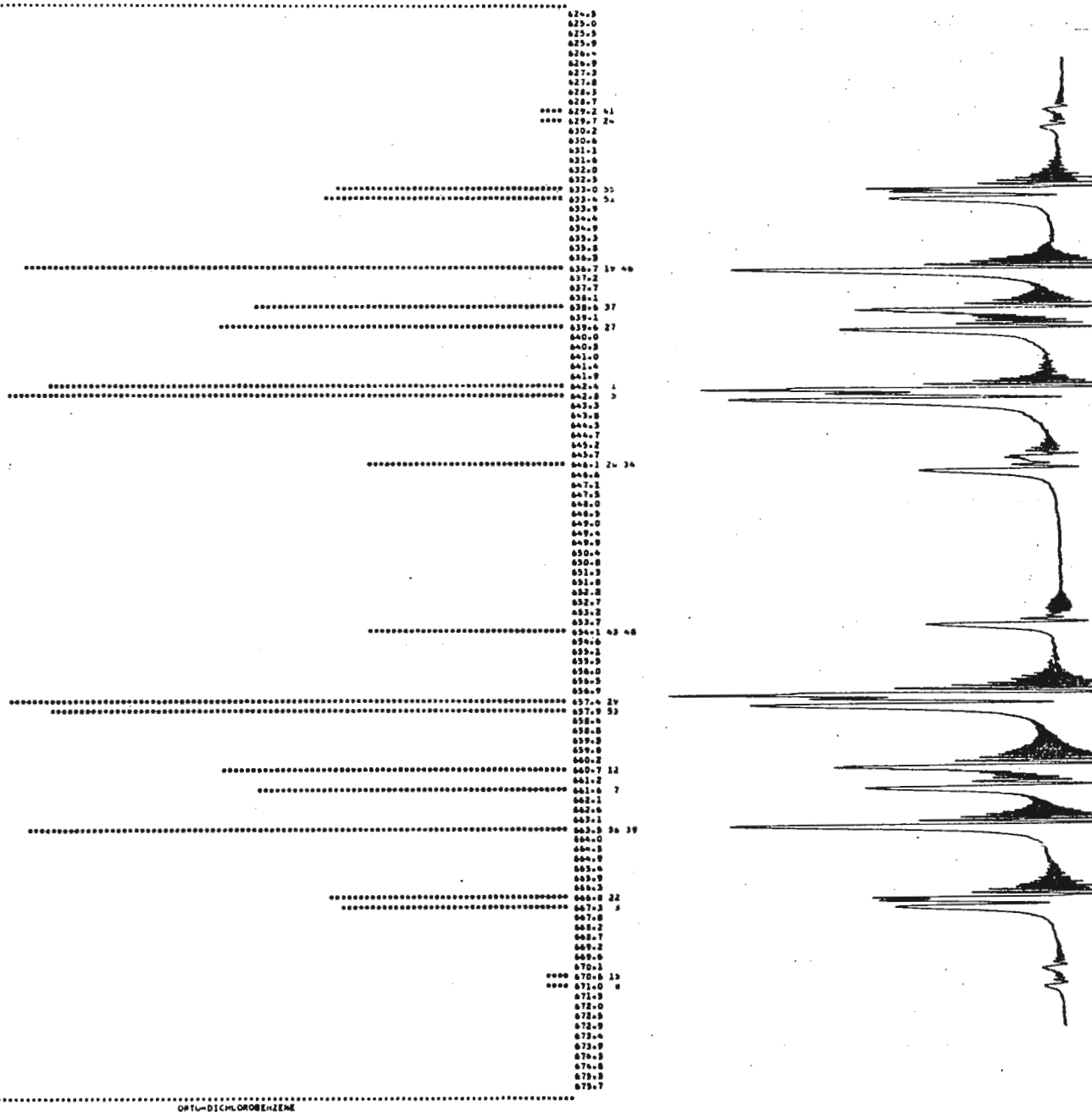


Figure 1

Figure 2.

PLOT OF INTENSITY VS. FREQUENCY RESOL = 0.670 MHz = 90.



TELEGRAMS:
MONASHUNI, MELBOURNE

MONASH UNIVERSITY

CLAYTON, VICTORIA. 3168

TELEPHONE:
544 0811

FACULTY OF SCIENCE

Department of Chemistry

OUR REF.

YOUR REF.

30th January, 1974

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

Dear Barry,

LIS before you Leap

The bicyclic lactone shown below provided two cautionary examples of the use of LIS reagents in easing degeneracies so that misleading second-order effects were removed.

One half of the AB pattern arising from the $-\text{CH}_2-\text{O}-$ protons was further split into triplets with $J = 1.0$ Hz. We had anticipated long-range coupling over the W pathway between H-4_{exo} and H-9_{exo} but the triplets suggested coupling to both of the C-9 protons. On addition of $\text{Eu}(\text{fod})_3$ to the CDCl_3 solution, however, the triplets were converted to doublets, $J = 1.4$ Hz, thus bolstering our faith in the doctrine of planar pathways.

In the normal spectrum, the H-1 signal is an apparent triplet with $J = 3.5$ Hz. Equal coupling of H-1 to each of the C-8 pairs would indicate the conformation with the bridging gem-dimethyls tilted over the lactone system. In the presence of the LIS reagent, the H-1 signal was a clean doublet of doublets, $J = 5.4$ and 1.9 , indicative of the conformation shown in which H-1 is unequally coupled to the C-8 protons. The geometry is really only apparent when one constructs a model.

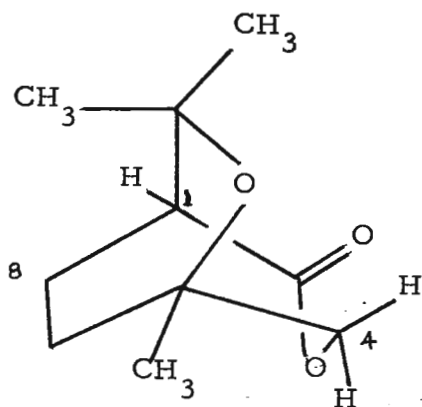
Not enough LIS reagent is added to completely resolve the $-\text{CH}_2-\text{CH}_2-$ system (we never managed that) but the changes in relative chemical shifts within the system were enough to remove the second-order effects before we leapt into print.

The ship bearing our Bruker WH-90 arrived in Melbourne last week and the pulse-FT era should commence at Monash within a week or so. Please credit this letter to Mike Heffernan's Monash subscription.

With kind regards,

Ian D. Rae

Ian D. Rae.



Michael L. Heffernan

Michael L. Heffernan.



Faculté
des sciences

UNIVERSITÉ
DE SHERBROOKE

Sherbrooke, Qué.

January 30, 1974.

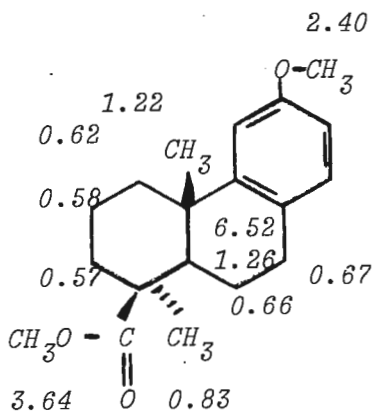
Professor B.L. Shapiro,
Department of Chemistry,
Texas A&M University,
COLLEGE STATION, TEXAS 77843, USA
An example of comparable T_1 values for CH_3 and CH_2 groups

Dear Professor Shapiro:

The application of C-13 T_1 data in organic structural analysis promises to be useful. One such application is to use T_1 values rather than off resonance decoupling for assigning a particular resonance to a C, CH, CH_2 or CH_3 - particularly in medium sized cyclic compounds. This of course is a result of the fact for isotropic motion

$$\frac{1}{T_1} = \frac{h^2 N \gamma_H^2 \gamma_C^2 \tau_C}{6 \gamma_{C-H}}$$

Thus it is simple to distinguish between a C, a CH, or a CH_2 . In compounds reported to date however, the T_1 for the CH_3 group has been longer than the CH, a consequence of at least one extra degree of freedom for the CH_3 group. This, however, cannot be considered a general criterion as can be observed from the diterpene type compound



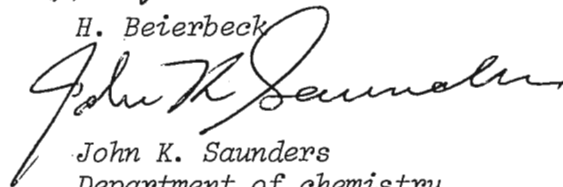
The axial CH_3 group has a value of T_1 similar to the CH moiety whereas the equatorial CH_3 gives a value close to that of the CH_2 groups. Thus utilisation of T_1 data in order to assign the CH_3 group relative to other carbons is not always possible.

The difference shown between axial and equatorial CH_3 groups appears to be quite general in terpene type compounds and is a ramification of different steric inhibition to rotation for the two groups.

Yours sincerely,



H. Beierbeck



John K. Saunders
Department of chemistry

JKS/mg



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Dpt. of Chemistry

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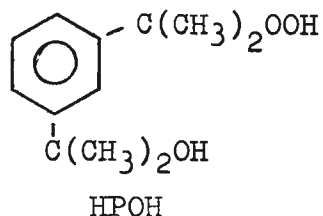
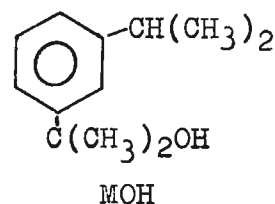
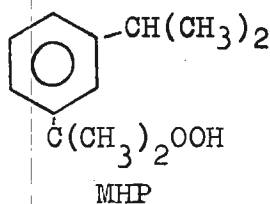
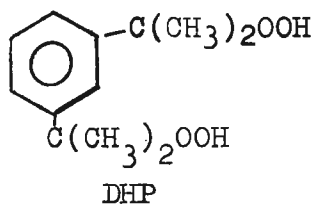
Sesto, 14.1.1974

da citare nella risposta LA/LC

Dear Prof. Shapiro,

this is the contribution to re-enroll me again as a TAMU NMR Newsletter subscriber since I moved to SIR Company. It is good to be back in the club.

We have just completed an NMR investigation of the oxidation products of m-diisopropylbenzene (m.DIB), the results of which can be of interest to someone of the NMR community. The catalytic oxidation of m.DIB gives, as main reaction products, the following compounds :



We worked directly with the crude reaction mixtures looking mainly at the β -methyl resonances. The best condi-

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tions to get sufficient separations of the β .methyl signals and to make accurate analysis of the amounts of the different components present in the crude reaction mixtures were obtained using CD_3COCD_3 as solvent. The definitive assignment in CD_3COCD_3 of the resonances could be stated with good confidence as follow :

Assignment		Chemical shift (Hz from TMS at 60 MHz)	
peroxides	$-\text{C}(\text{CH}_3)_2\text{OO}-$	94.3	E
D H P	$-\text{C}(\text{CH}_3)_2\text{OOH}$	93.1	A
M H P	"	92.2	B
H P O H	"	92 + 93	-
H P O H	$-\text{C}(\text{CH}_3)_2\text{OH}$	91.5	F
M O H	"	90.7	C
peroxides	$-\text{CH}(\text{CH}_3)_2$	ca. 73	D
M H P			
M O H			
m.DIB			

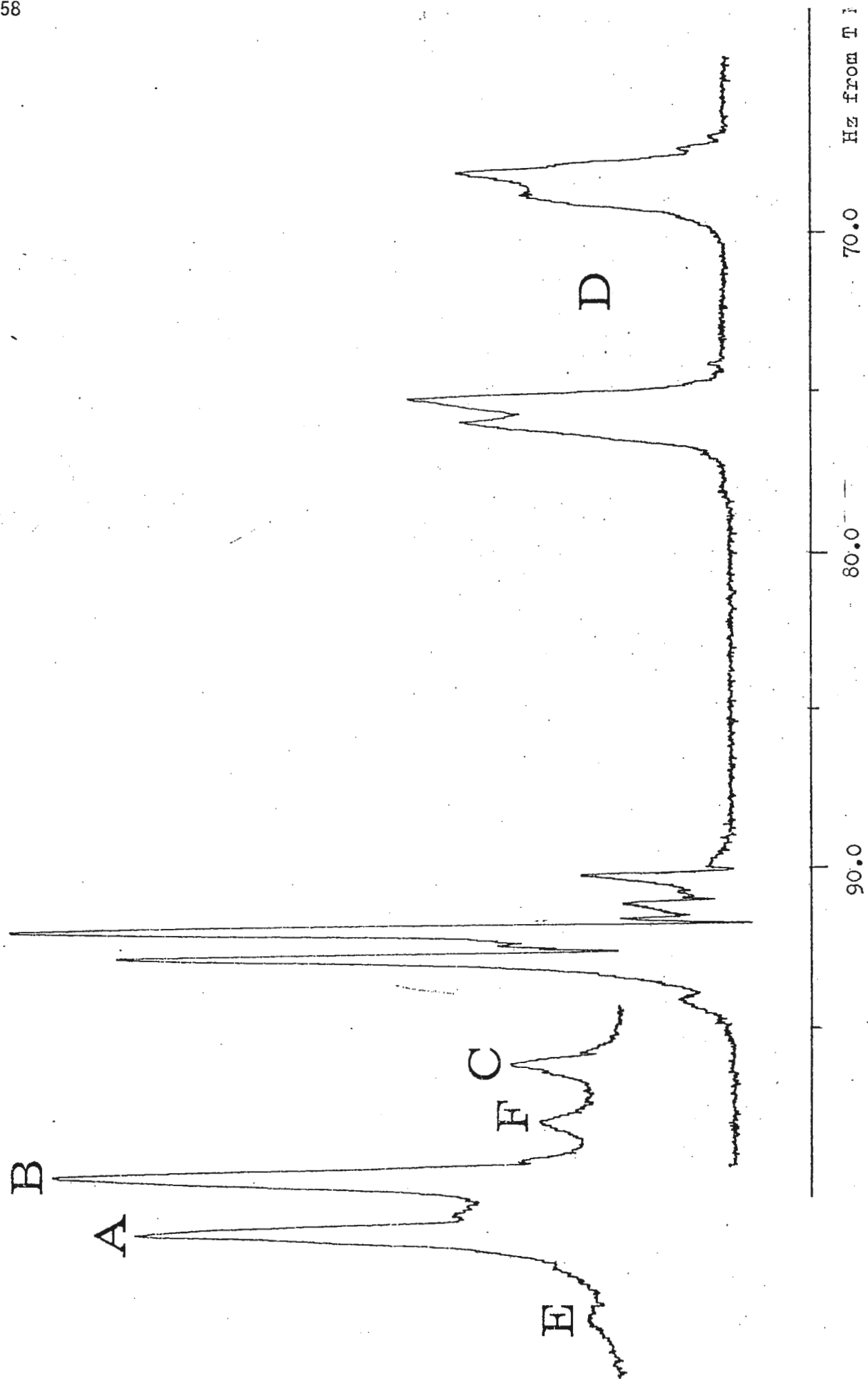
The Figure hereby attached shows the 60 MHz. NMR spectrum of a typical crude reaction mixture. The NMR Spectrum was recorded from diluted solution using a Jeol, JNM-C-6HL, spectrometer in the frequency-sweep mode.

Complete NMR data with details of the quantitative analysis of the crude m.DIB oxidation mixtures will be the subject of a forthcoming paper.

Yours sincerely,

SOCIETA' ITALIANA RESINE (Dr. L. Cavalli) (Dr. G. Cancellieri)

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