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Newsletter

No. 184

January, 1974

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Deadline Dates: No. 185: 4 February 1974 No. 186: 4 March 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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Carr Laboratory, Department of Chemistry

MOUNT HOLYOKE COLLEGE

South Hadley, Massachusetts 01075

Telephone 413 538-2214



28 November 1973

 $^{13}\text{C}$  Chemical Shift Parameters for Aliphatic Alcohols

We have recently had occasion to measure the  $^{13}\text{C}$  chemical shifts of all eighteen possible isomers of the saturated aliphatic monohydric alcohols containing six carbon atoms. The results of our regression analysis are given below. The very large parameters due to quaternary carbons adjacent to secondary and tertiary carbons are noteworthy.

## Regression Analysis of Chemical Shift Parameters in Six-Carbon Alcohols

Number of observations: 95

Number of independent variables: 15

Multiple correlation coefficient  $R$  squared: 0.9966Standard deviation in predicted chemical shifts:  $\pm 1.11$  ppmConstant term:  $0.64 \pm 0.91$  ppm

Variable and coefficients	Observations affected by variable, no.	Student T ratio
$\alpha$ $9.58 \pm 0.42$	95	22.8
$\beta$ $6.95 \pm 0.25$	95	28.2
$\gamma$ $-2.68 \pm 0.24$	76	11.1
Corrective terms:		
$\alpha$ $47.98 \pm 0.49$	18	98.7
$\beta$ $8.26 \pm 0.36$	20	22.9
$\gamma$ $-4.46 \pm 0.35$	26	12.9
$1^\circ(3^\circ)$ $0.61 \pm 0.38$	18	1.6
$2^\circ(3^\circ)$ $-1.09 \pm 0.47$	14	2.3
$2^\circ(4^\circ)$ $-4.20 \pm 0.71$	5	6.0
$3^\circ(2^\circ)$ $-5.95 \pm 0.76$	8	7.8
$3^\circ(3^\circ)$ $-9.49 \pm 0.80$	8	11.8
$3^\circ(4^\circ)$ $-13.27 \pm 1.10$	2	12.1
$4^\circ(2^\circ)^a$ $-11.84 \pm 1.30$	2	9.1
$4^\circ(2^\circ)^b$ $-18.97 \pm 1.33$	2	14.3
$4^\circ(3^\circ)$ $-19.35 \pm 1.33$	2	14.6

a) Quaternary carbon adjacent to three primary and one secondary carbon atoms

b) Quaternary carbon adjacent to two primary and two secondary carbon atoms

Sincerely yours,

Kenneth L. Williamson

Dale Clutter



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DEPARTMENT OF CHEMISTRY &amp;

Lawrence Berkeley Laboratory

BERKELEY, CALIFORNIA 94720

December 3, 1973.

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

Dear Barry:

- Re: 1. Dynamics of Polarization Transfer in  $^{13}\text{C}$ - $^1\text{H}$  Double-Resonance  
2. Postdoctoral positions available

An important problem in the design of efficient cross-polarization schemes for proton-enhanced nmr of  $^{13}\text{C}$  in solids (1) is the study of fluctuation dynamics of the cross coupling operator  $H_{IS}$  modulated by the pure abundant spin dipolar coupling  $H_{II}$ . We have studied this in organic solids by direct observation of the  $^{13}\text{C}$  cross-polarization from a demagnetized proton reservoir in the rotating frame, (2) to see whether the Lorentzian correlation function of Hahn, McArthur and Walstedt (3) shows up in  $^{13}\text{C}$ - $^1\text{H}$  double-resonance. Indeed, we find an exponential fluctuation spectrum for rotating  $H_1$  fields of up to 12 G applied at the  $^{13}\text{C}$  frequency. This is shown in figure 1, where I have plotted the inverse cross-polarization times vs.  $H_1$  in solid adamantane measured by my student Tom Shattuck. Hahn and Waugh tell me that they have separately observed similar behavior in other systems. A Lorentzian correlation function is extremely unusual and surprising; as yet, no theoretical basis has been advanced for this phenomenon.

By the way, I shall have some additional postdoctoral positions beginning in Spring and Fall, 1974. Anyone interested in working with me on one of several projects should write and have two letters of recommendation sent to me soon.

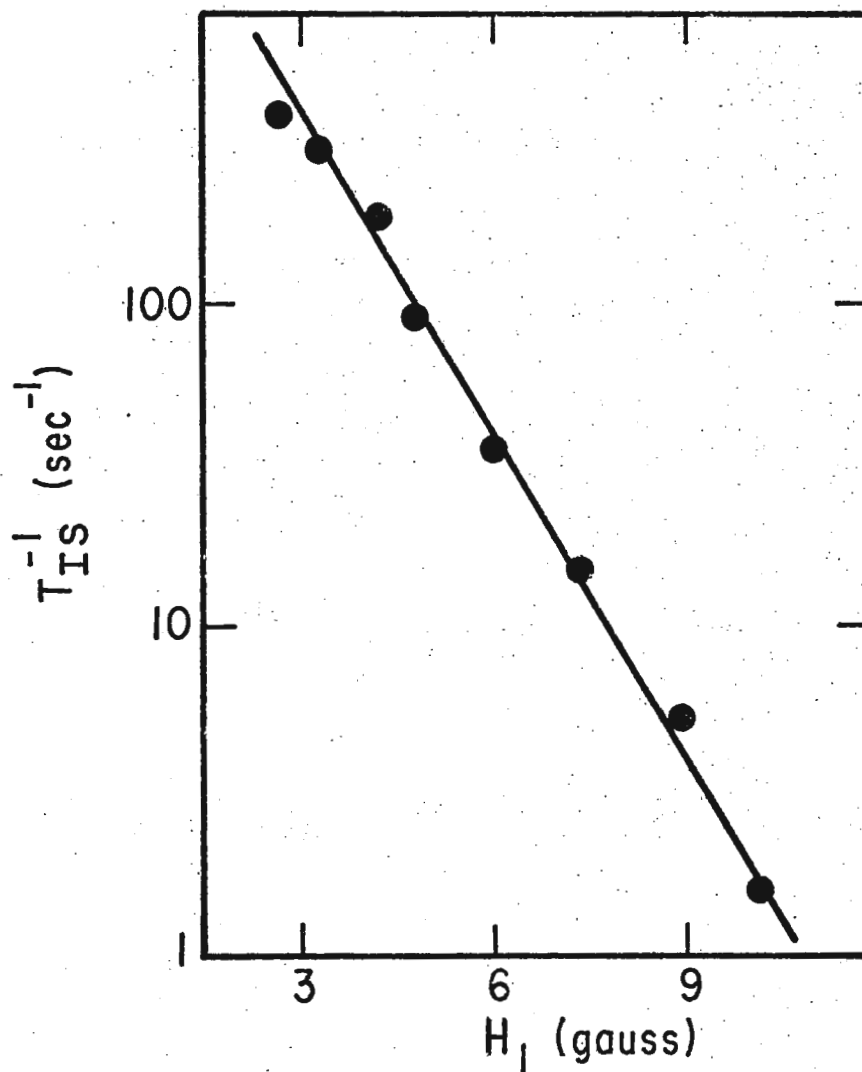
Best regards,

Alex Pines  
Assistant Professor

- (1) A. Pines, M. G. Gibby and J. S. Waugh, J. Chem. Phys. 59, 569 (1973).  
(2) A. Pines and T. W. Shattuck, to be published.  
(3) D. A. McArthur, E. L. Hahn and R. Walstedt, Phys. Rev. 188, 609 (1969).

Professor B. L. Shapiro  
December 3, 1973

Figure 1



*Dependence of inverse cross-polarization time on rotating  $^{13}\text{C}$  field strength in solid adamantane.*

# Monsanto

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Phone: (314) 694-1000

December 4, 1973

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

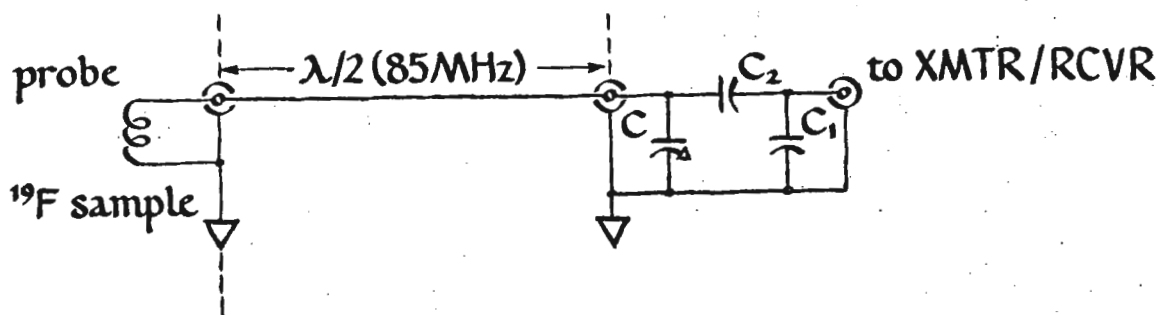
Title: An External  $^{19}\text{F}$  Lock for a  $^{13}\text{C}$ -NMR Probe

Dear Barry,

We have developed a simple, convenient external  $^{19}\text{F}$  lock for our  $^{13}\text{C}$  FT-NMR probe, capable of controlling the field to within 1 Hz (out of 22.6 MHz) for days.

We have located a 2 cm long piece of a 5mm spherical microcell filled with  $\text{C}_6\text{F}_6$  saturated with p-hydroxy di-tert-butyl nitroxide within about 2.5 cm of the  $^{13}\text{C}$  sample coil. This solution has  $T_1 \sim 13$  ms and  $T_2 \sim 11$  ms for  $^{19}\text{F}$  at 85 MHz. Three turns of two strands of #32 enameled copper wire are wound around this tube and heavily doped with polystyrene Q-dope.

We use the following circuit to couple this coil to the  $^{19}\text{F}$  receiver and transmitter, which operate on a time-share basis:



The half-wavelength of cable is self-resonant at the  $^{19}\text{F}$  frequency and can be ignored in analysing this circuit. However, the length of cable makes possible locating the tuning circuitry remote from the probe and eliminates concern over space and ferromagnetic circuit elements. The circuit is tuned to resonance by means of  $C_1$ .



but the ratio of  $C_1$  to  $C_2$  must first be chosen to match the impedance of the high-Q sample circuit to the impedance of the transmission line leading to the transmitter/receiver.<sup>1</sup> In our case, we use 50 ohm line and  $C = 3-25$  pf,  $C_1 = 43$  pf, and  $C_2 = 15$  pf. The ratio  $C_1$  to  $C_2$  was adjusted until a reflected power meter indicated that less than 1% of the power incident on this circuit was being reflected.

The  $^{19}\text{F}$  resonance is observed to have a half-width of about 50 mG. Because of the doping of the sample, considerable signal strength can be obtained without saturation. A strong signal is necessary to obtain control to within 1 mG as we have done.

Sincerely,

*Ed.*

E. O. Stejskal

*John*

J. Schaefer

1. F. E. Terman, Radio Engineers Handbook, (McGraw-Hill, 1943), p. 148.

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



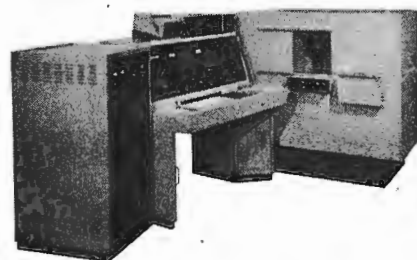
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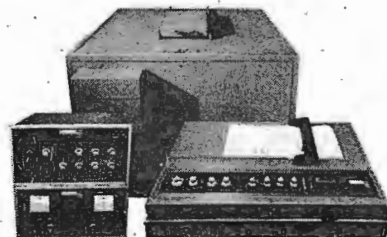
Instrument Division, Perkin-Elmer Corporation, Main Avenue, Norwalk, Conn. 06856.

\*Perkin-Elmer patent numbers 3,515,979 and 3,622,869.



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# B R O C K University

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St. Catharines, Ontario L2S 3A1

Glenridge Campus  
684-7201 Ext. 317

December 12, 1973.

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

Dear Prof. Shapiro:

$J_{11_{B-19_F}}$  Pairwise Additivity Parameters Related  
to the Sum of the Van der Waals Radii.

Steve Hartman (on leave this year in Bristol) and I have previously reported applications of  $19_F$  chemical shift pairwise interaction parameters to boron trihalide and mixed trihalide adducts (1), and have extended our correlations to  $^{11}B$  and  $J_{11_{B-19_F}}$  parameters (2). We have attempted to correlate the pairwise parameters with electronegativities, ionization potentials, other pairwise parameters etc. in an attempt to establish means of calculating as yet unmeasured parameters so as to be able to predict N M R spectra.

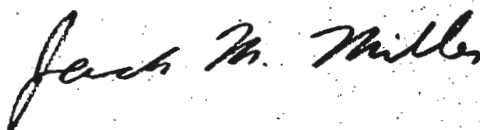
We were unable to find any smooth relationships to fit the chemical shift parameters, but when the  $J_{11_{B-19_F}}$  parameters were plotted against the sum of the electronegativities of the interacting atoms, we observed two smooth curves, one for halogen - halogen parameters and one for the donor - halogen data.

Perhaps a more significant relationship is shown in the figure, namely the correlation of the coupling constant pairwise additivity parameters with the sum of the Van der Waals radii (Pauling) of the two halogens or halogen and donor atom pair being considered. The existence of this

apparent throughspace or steric effect on the additivity parameters may reflect a geometric influence on the nature of the B-F bond, and hence on the B-F coupling constant. The deviation of the N-X and P-X parameters from the straight line are such as to indicate a greater steric effect of species such as  $\text{Me}_3\text{N}$  and  $\text{Me}_3\text{P}$  giving the donor atom an effectively larger Van der Waals radius, while  $\text{Me}_2\text{S}$  shows the opposite trend, i.e. there is no steric crowding about the sulphur.

We would appreciate any comment the Newsletter reader would care to make.

Yours sincerely,

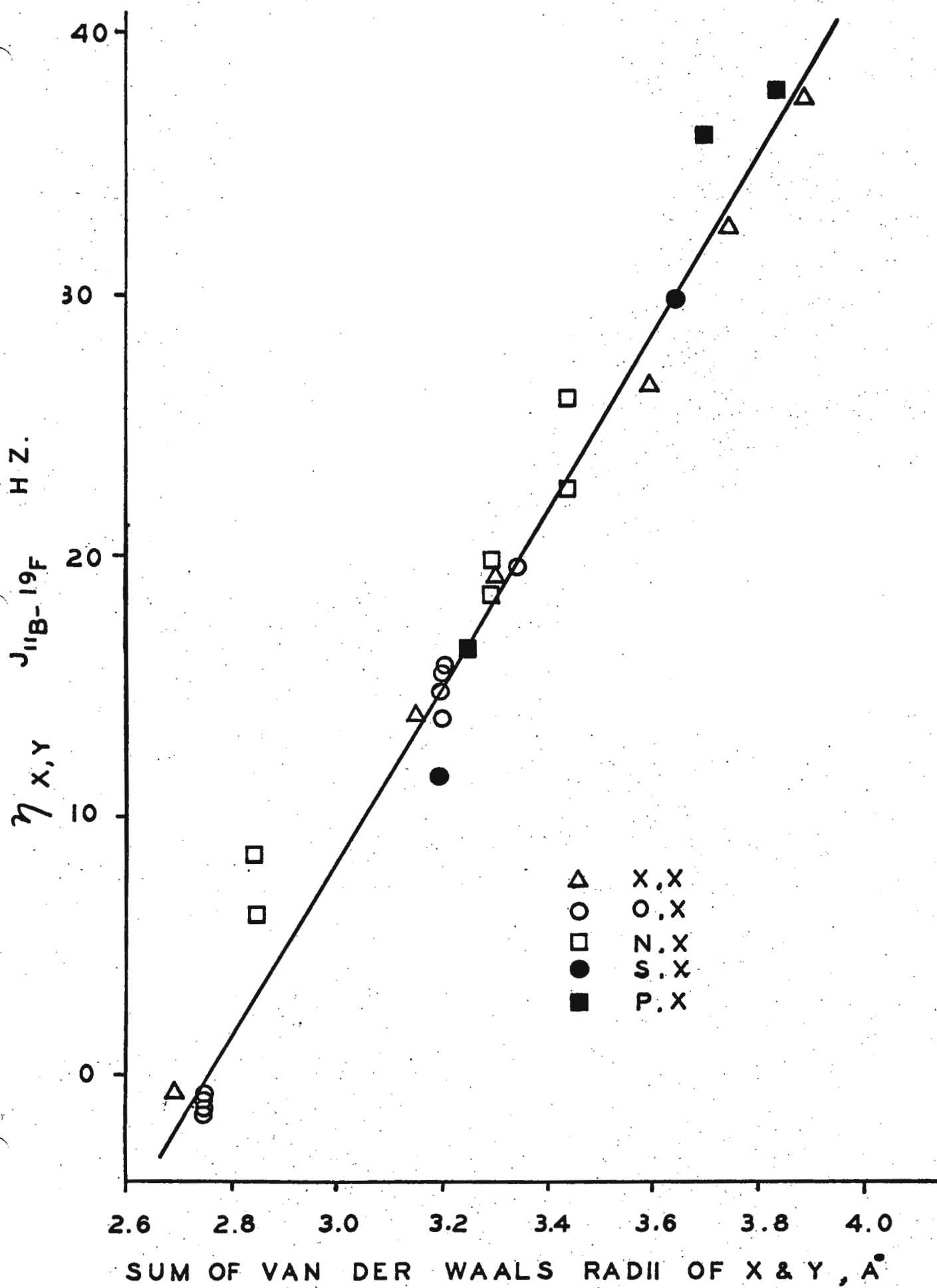


Jack M. Miller,  
Assoc. Prof.

JM/db

1. J. S. Hartman & J. M. Miller; TAMU NMR Newsletter, 174-4 (1973)
2. J. S. Hartman & J. M. Miller; paper presented at the 56th Canadian Chemical Conference, Montreal, June (1973)





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

3rd December, 1973

Dear Professor Shapiro,

The use of simple formulae for the estimation of rates of chemical exchange in NMR spectra has come into disrepute as a result of the large errors which are sometimes involved. For example, Allerhand and Gutowsky (1) have made a comparative study of the available formulae in their investigation of internal rotation in N,N-dimethyl-trichloroacetamide (DMTCA).

The utility of a single operational parameter (SOP) formula has interested me for some time and two such formulae are discussed in a paper entitled "Dynamic NMR: A Single Operational Parameter Approach for Evaluation of Lifetimes in an Uncoupled, Equally Populated AB System" which is to appear shortly in the Journal of Organic Magnetic Resonance.

More recently, I have investigated another simple formula which is concerned only with the intensity ratio in a two-site system in much the same way as that of Rogers and Woodbrey (2). The formula is

$$\tau = \frac{\sqrt{R}}{\pi \cdot \delta w}$$

where  $\tau$  is the mean lifetime before exchange and  $R$  is defined to be the ratio of the intensity at the point  $\nu = \frac{1}{2}\delta w$  ( $\delta w$  being the peak separation in the absence of exchange and may be either dependent or independent of temperature) and that at the centre of the spectrum ( $\nu = 0$ ). From this definition of  $R$  it follows that this formula is applicable above the coalescence point of the spectrum whereas that of Rogers and Woodbrey is not.

To demonstrate the superiority of this formula, I have used simulated spectra to show that the approximations inherent in its derivation lead to smaller errors than does that of Rogers and Woodbrey. I have also applied it to the case of DMTCA with the following results

	New formula	Rogers & Woodbrey formula own calc. (100 MHz)
$\Delta H^\ddagger$ kcal/mol	$11.34 \pm 0.08$	$11.54 \pm 0.13$
$\Delta S^\ddagger$ e.u.	$-12.7 \pm 0.3$	$-13.3 \pm 0.4$
$\Delta G^\ddagger_{298.2}$ kcal/mol	$15.12 \pm 0.08$	$15.51 \pm 0.04$
$E_a$ kcal.	$11.9 \pm 0.008$	$12.1 \pm 0.1$
$\log v_o$	$10.5 \pm 0.1$	$10.3 \pm 0.1$

A comparative study is now in progress using data obtained from both high resolution and spin-echo measurements on DMTCA. This work is being carried out in collaboration with Dr. J. A. Ladd at the University of Salford, while I am on leave from the Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria. I shall be grateful if you will therefore consider this to be a contribution to your Newsletter from Salford, and that you will add Dr. Ladd's name to your mailing list.

Yours sincerely,

*Valentin Dimitrov*

Valentin Dimitrov

#### References

1. A. Allerhand and H. S. Gutowsky, J. Chem. Phys. 41(1964)2115.
2. M. T. Rogers and J. C. Woodbrey, J. Phys. Chem., 66(1962)540.

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LEIDEN, dec. 7<sup>th</sup> 19.73

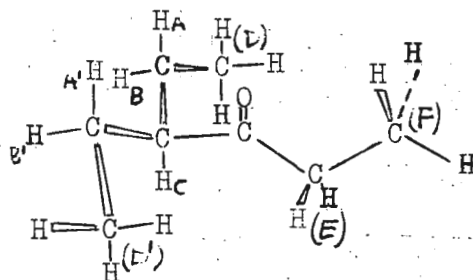
Professor B. L. Shapiro  
Department of Chemistry  
Texas A & M university  
College Station  
Texas 77843, U.S.A.

NMR analysis of a reaction product of the reaction of an organometallic with carbonmonoxide.

Dear Professor Shapiro,

One of the products of this type of reaction appeared to be a compound with the empirical formule  $C_8H_{16}O$ .

The NMR spectrum of this compound dissolved in  $CDCl_3$  was too complex to be analysed (Fig.1). As the presence of a carbonyl group was clear from the I.R. spectrum it was tried to simplify the spectrum with the aid of the shift reagent  $Eu(fod)_3$ . The resulting spectrum is shown in Fig.2. The L.I.S. spectrum could be analysed when the following structure was assumed:



The protons of the 3-pentyl group form a rather complex spin system i.e. an  $AA'BB'CD_3D'_3$  system, which is much too large to be handled by a computer program such as LAME. When the system is however approximated as  $AA'BB'CD_3$ , in which the methyl group is coupled with both A and A' and with B and B', the system just fits within the limits of LAME. However, only the  $AA'BB'C$  part can be simulated correctly, and not the methyl group signal, because in this approximation the methyl group is coupled to four instead of with two protons. This is not a serious objective, because the  $AA'BB'C$  part is the most important one for the identification of the compound. The  $AA'BB'C$  part of the simulated spectrum is shown in the insert of Fig.2. The following set of parameters is used:  $=300\text{Hz}$ ,  $=249\text{Hz}$ ,  $=395\text{Hz}$ ,  $=155\text{Hz}$   
 $J_{AB}=J_{A'B'}=-13.2\text{ Hz}$ ,  $J_{AC}=J_{A'C}=8.1\text{ Hz}$ ,  $J_{BC}=J_{B'C}=5.7\text{ Hz}$

$$J_{AD}=J_{A'D}=J_{BD}=J_{B'D}=7.3\text{ Hz}$$



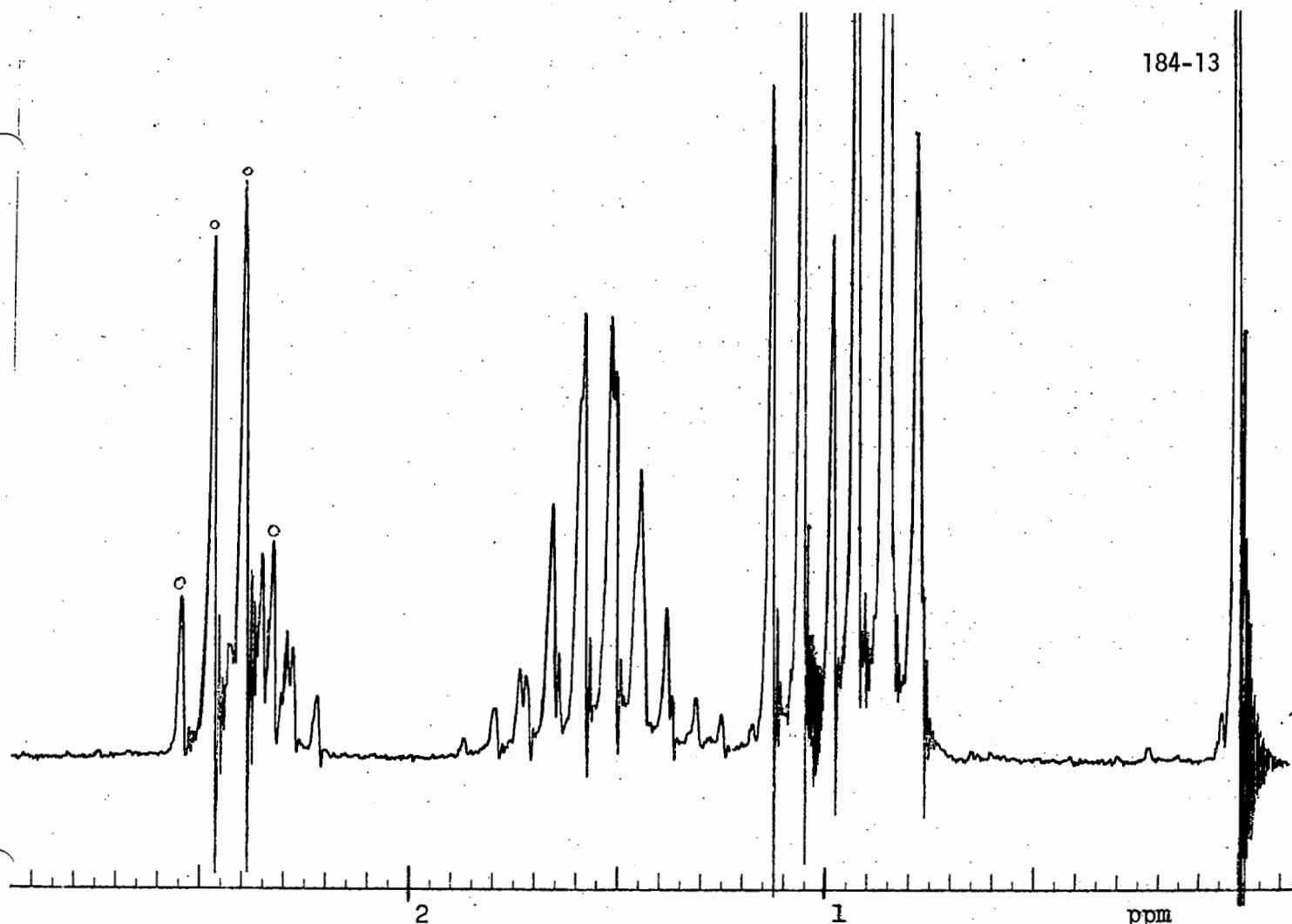


Fig.1 100Mc/s NMR spectrum of 4-ethylhexanon-3 in  $\text{CDCl}_3$

The signals of the ethyl-carbonylgroup were analysed "by hand";

$$\nu_E = 428.0 \text{ Hz} , \nu_F = 221.0 \text{ Hz} , J_{EF} = 7.0 \text{ Hz}$$

From the values used in the simulation an interesting feature of this system appears: the values of  $J_{AC}$  and  $J_{BC}$  are different in magnitude. This is an indication that there is a predominant conformer in which  $J_{AC} > J_{BC}$ . This conformer can be the one as shown above, because in this conformer the only gauche interactions are those between methyl and carbonyl. In all other conformations there exist gauche interactions between methyl and methylene groups, which are expected to be much larger. In the conformer shown protons A and C have an anti-relationship and B and C a gauche-relationship, giving rise to different coupling constants. By this analysis it has become clear that the NMR data are in full agreement with the proposed structure, making it quite sure that this structure is the correct one.

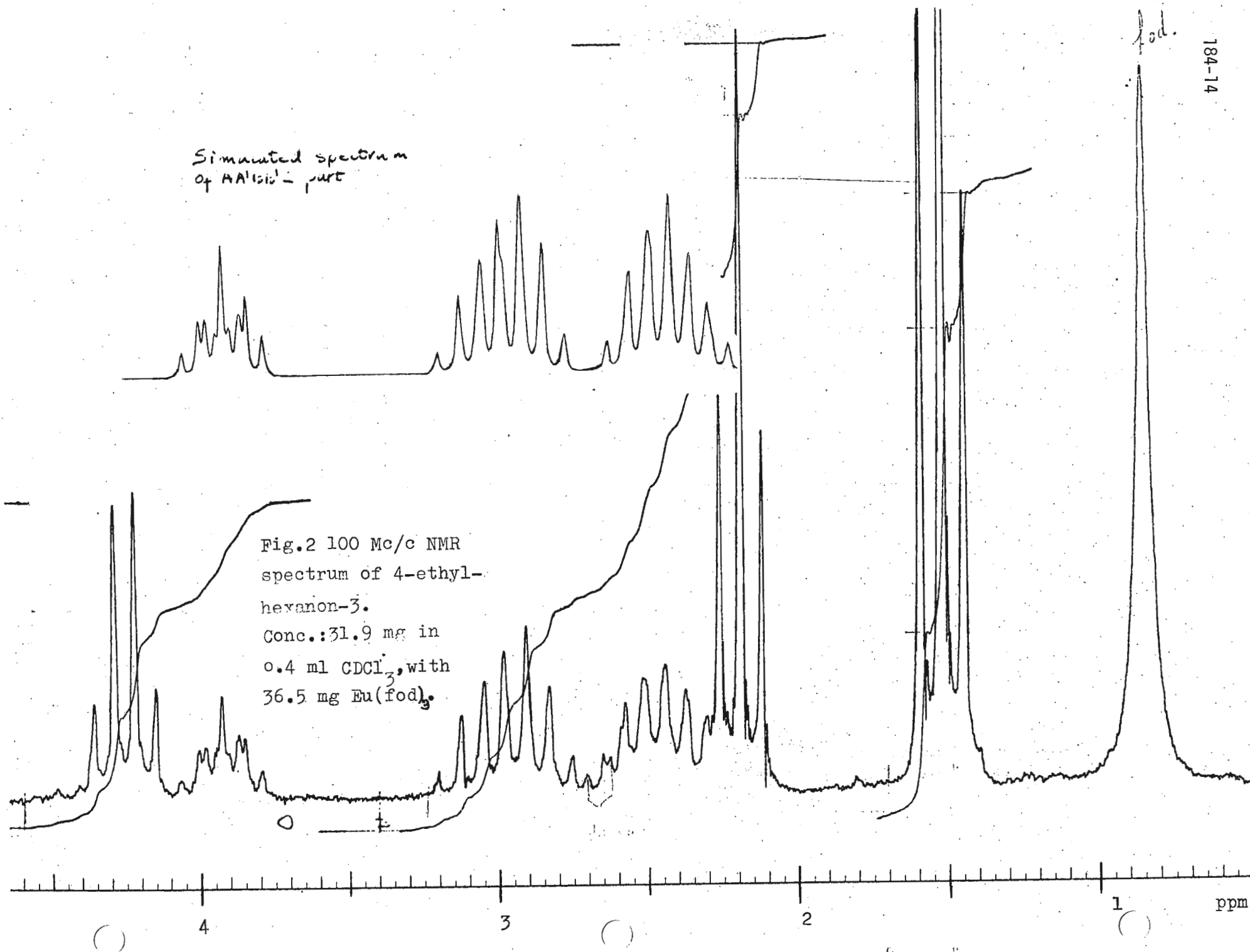
Sincerely Yours,

W.J.J.M. Sprangers

A.J. de Hoog

Simulated spectrum  
of AA'BB'-part

Fig.2 100 Mc/c NMR  
spectrum of 4-ethyl-  
hexanon-3.  
Conc.: 31.9 mg in  
0.4 ml  $\text{CDCl}_3$ , with  
36.5 mg  $\text{Eu}(\text{fod})_3$ .



Priv. Doz. Dr. H. Dreeskamp

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29 November 1973

Dr. B. L. Shapiro  
Department of Chemistry  
Texas A + M University

College Station, Texas 77843 / U.S.A.

"Bunsentagung", 23 to 26 May 1974,  
Request for Reprints and Preprints

Dear Barry,

the next meeting at Kassel from 23 to 26 May 1974 will be devoted to:

Neue Methoden in der Molekülspektroskopie.

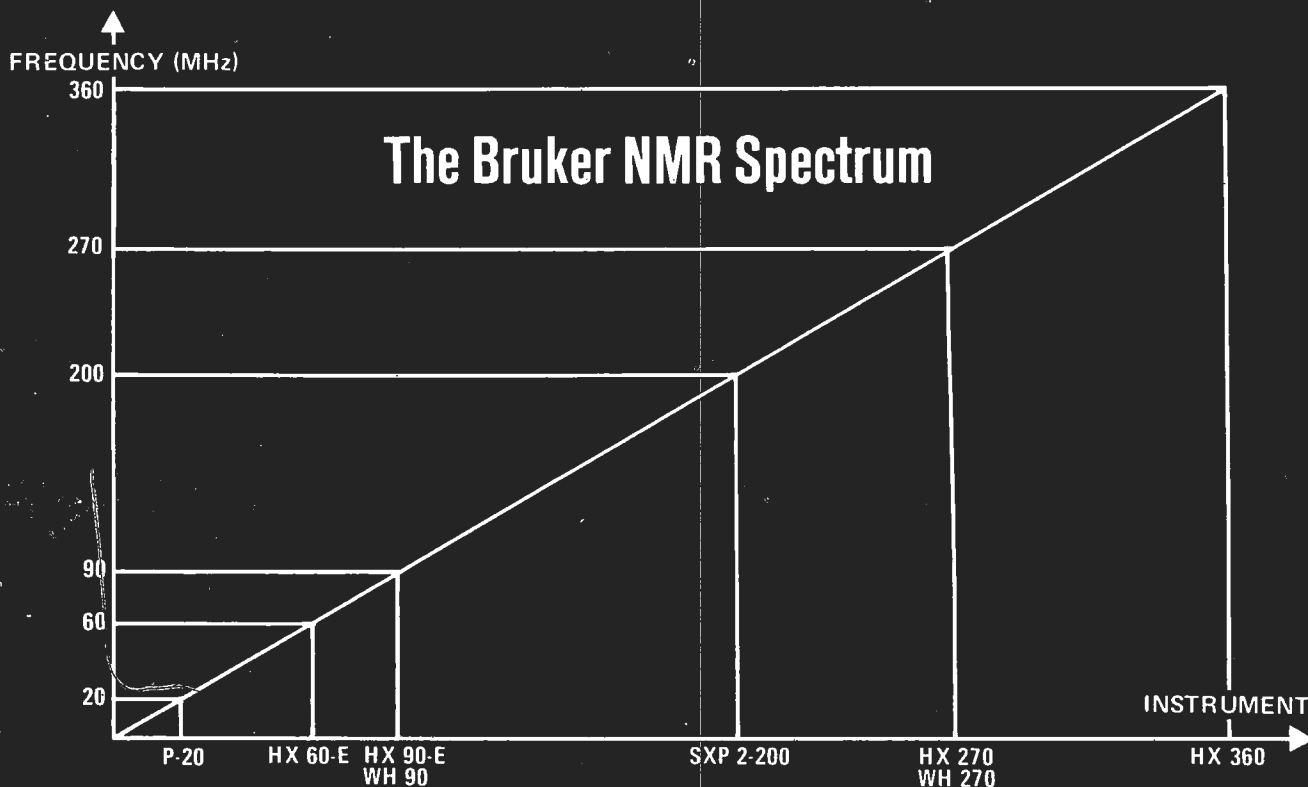
I am presently preparing a survey on "Fortschritte in der magnetischen Resonanzspektroskopie" (Advances in magnetic resonance spectroscopy).

I would appreciate reprints or preprints on this rather broad topic with special emphasis on such new topics like CIDNP, shift reagents, pulsed nmr, and relaxation.

Sincerely yours

*H. Dreeskamp*

# NMR



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| <b>WH 270</b>    | The specialized straight FT cryospectrometer            |
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## CANADA

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December 12, 1973

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

"NEW UNITS FOR CHEMICAL SHIFTS"

Dear Barry:

Recently one of my colleagues submitted a paper to a Journal which shall remain unnamed to protect the innocent. The paper was accepted with the requirement that the nmr chemical shift data be reported in micro grames/gram vice ppm since the journal in question did not permit the use of ppm. Lest you think I am "putting you on" a copy of the galley proofs is attached below.

Sincerely,



Michael L. Maddox, Ph.D.  
Institute of Organic Chemistry

MLM:lo

EG V-19

EG V-19

Plant(Feb) 11395 11-20-11B p.6 11-12 3758 (1) Gal.4X—  
NMR Spectra.  $^1\text{H}$  NMR ( $d_6$ -dimethylsulfoxide) 3.7 to 4.2  $\mu\text{g/g}$  (m, 4,  $\text{C}_3\text{H}$ ,  $\text{C}_1\text{H}$ , and  $\text{C}_3\text{H}_2$ ), 4.57 (dd, 1,  $J_{2',3'} \cong 5$  Hz,  $\text{C}_2\text{H}$ ), 5.90 (d, 1,  $\text{C}_1\text{H}$ ,  $J_{1',2'} = 5.5$  Hz), 7.24 (broad s, 2,  $\text{NH}_2$ ), 8.13, 8.36 (s, 1,  $\text{C}_2\text{H}$  and  $\text{C}_3\text{H}$ ). The  $^{31}\text{P}$  NMR spectra of both samples showed a chemical shift of 580  $\mu\text{g/g}$  upfield from phosphoric acid. The coupling constant  $J_{\text{PF}}$  was 934 Hz in both cases. This value is within the range observed for other fluorophosphate derivatives (8). The spectra were measured under conditions of noise modulated proton decoupling and no further attempt was made to measure the  $J_{\text{PH}}$  values.



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CENTRAL RESEARCH DEPARTMENT  
EXPERIMENTAL STATION

December 6, 1973

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

Phase Shift Compensation for the HA-100 (1)

The Varian Associates HA-100 was designed to measure proton NMR at 100 MHz. Audio field modulation is used to provide both the field-frequency internal lock and the analytical signal. Locking to a reference absorption via the 'manual oscillator' enables frequency sweep spectra up to 10 ppm wide to be obtained from 20 ppm to low field, up to 10 ppm to high field, of the lock.

This range must be extended for nuclei other than protons. The 'manual oscillator' and the 'sweep oscillator' are replaced by a wide range external oscillator and a voltage-controlled oscillator (WAVETEK Model 111), driven by a ramp from a CAT or from the recorder arm (2). Outside the normal range, frequency dependent phase shifts occur in the lock and analytical signals. To obtain upright absorption spectra, one must shift the phase of the lock signal independently of that of the analytical signal. A phase shifter can be installed (3), but rephasing is necessary whenever the oscillator frequencies are changed appreciably.

This problem has recently been tackled by P. N. Jenkins and L. Phillips (4) who found that the phase of the detected signals varies linearly with the audio-oscillator frequency. Thus, the phase shifts arise from the fact that the audio signals reach the phase detectors after the reference signals. By inserting the correct delay in the reference lines, the phase variations can be removed. One delay line is needed for each channel and a frequency independent phase shift of  $90^\circ$  must be provided in the lock channel.

Rather than copy the circuits given by Jenkins and Phillips, we have used a commercially available phase shifter and delay lines in applying this modification to our HA-100. Measurements indicated that about 50 microsecond delays were needed. The delay lines (5) have 100 microseconds total delay with 20 taps and 2000 ohms impedance. The frequency-independent phase shifter (6) is variable from  $0^\circ$  to  $370^\circ$ .

A 4-pole, 2-way switch mounted on the V4354A "lock box" switches the system in and out of circuit. For 'external phasing' the leads carrying the reference signals to the two phase detectors, pins R on cards J1319 and J1323, are broken and brought out to 4 BNC connectors. A 0.001 mfd capacitor on the control phase detector card (J1323) is removed. This provides a  $90^\circ$  phase shift for normal operation and is wired up to the switch so that it is restored in the 'internal phasing' position. Since the phase shifter output is a zero based, 3 volt square wave, a capacitor is used to make the output symmetrical to ground (Fig. 1). For correct operation, the delay lines must be matched. This is accomplished by  $A_1$  and  $A_2$  in Figure 2.  $A_2$  provides a gain of two so that the overall gain is unity. Once the tapings are chosen for minimum phase shift, no further adjustments are needed. In obtaining the spectrum of Figure 3, both the delay lines and phase shifter were out of circuit. Large phase shifts are observed. Figure 4 was obtained with the delay lines and phase shifter in circuit. In contrast to Figure 3, the phase shifts are quite small.

Since the phase correction circuitry operates in both channels, no phase changes are required if the lock is shifted from one peak to another. Furthermore, wide sweeps of 10 KHz or more can be made for quick spectral searches.

Please credit this contribution to the account of  
R. C. Ferguson.

*Derick W. Ovenall*

D. W. Ovenall

DWO/dew  
12/6/73

- 
1. Contribution No. 2100, Central Research Department.
  2. D. W. Ovenall, Rev. Sci. Inst. 40, 1506, (1969).
  3. A. W. Douglas, paper given at the 7th ENC, Mellon Institute, Pittsburgh, Pa., February, 1966.
  4. P. N. Jenkins and L. Phillips, J. Phys. E4, 530 (1971).
  5. Artronic Instrument Company, 11232 Triangle Lane, Silverspring, Md., Part No. NM-2000-100.
  6. Keithly Instruments, 28775 Aurora Road, Cleveland, Ohio, Model 811 Autotrack Phase Shifter.



FIGURE 1  
INTERCONNECTING DIAGRAM

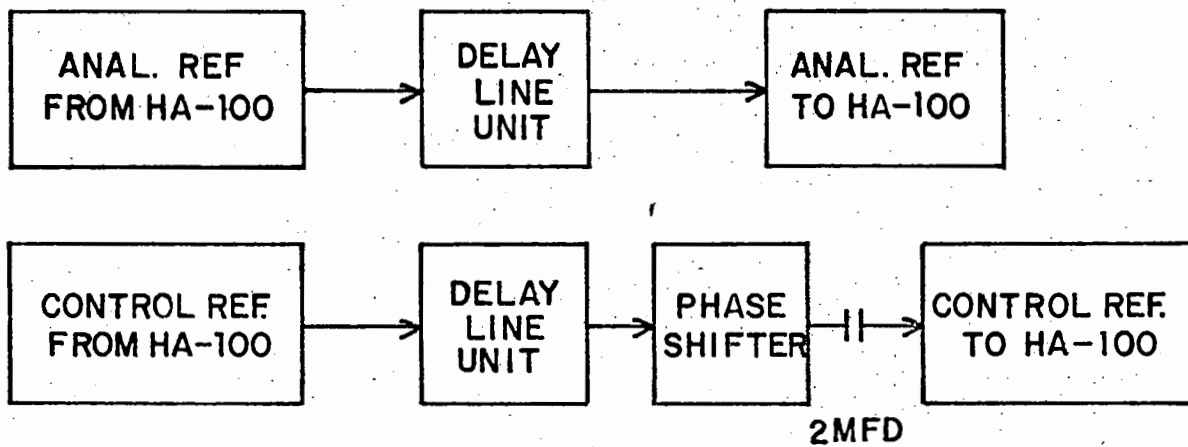
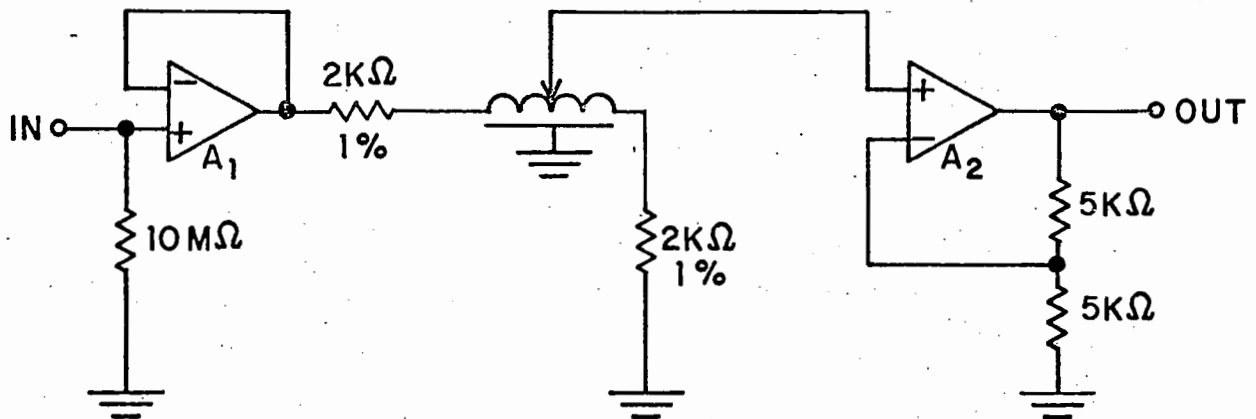
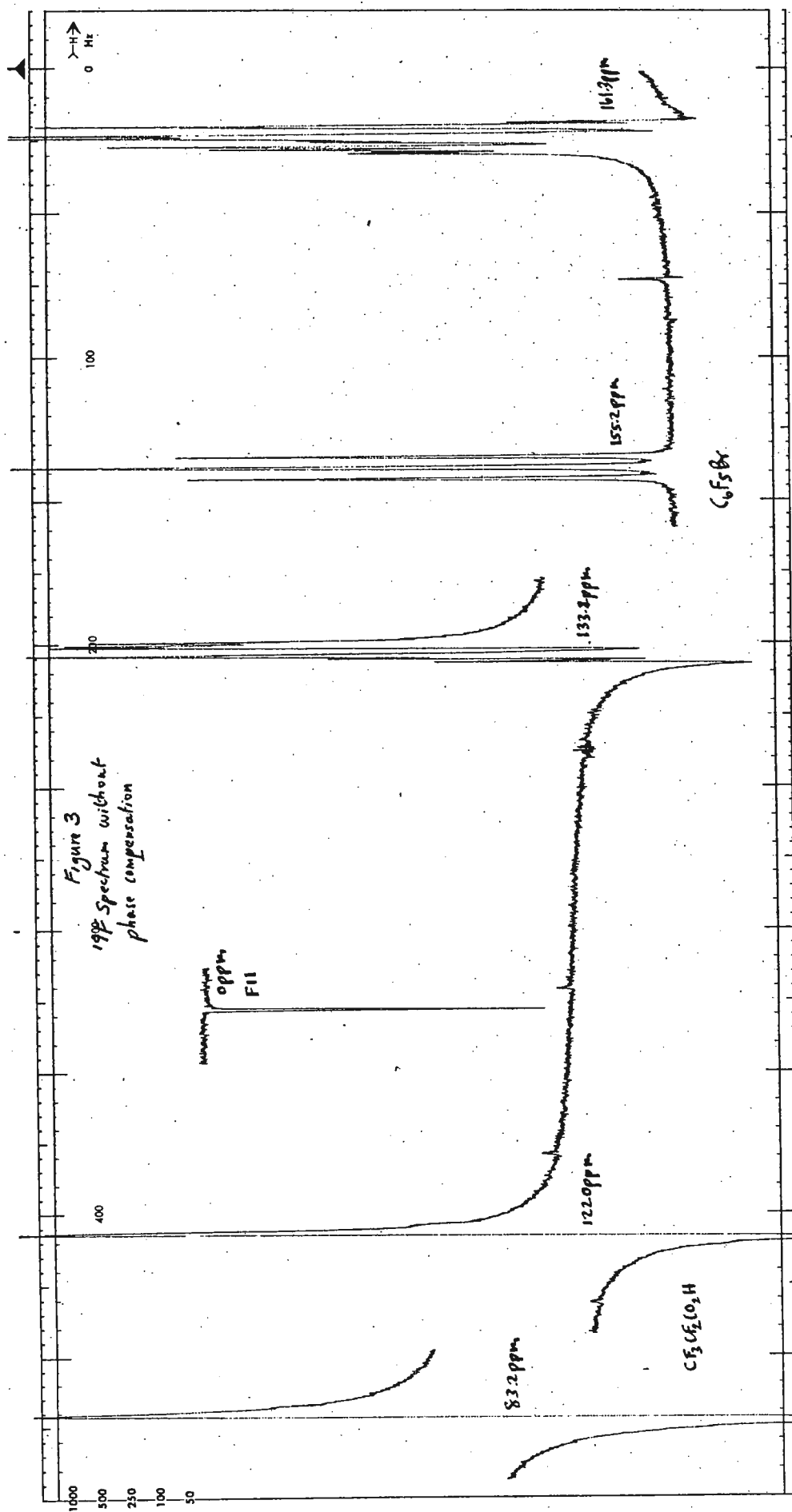
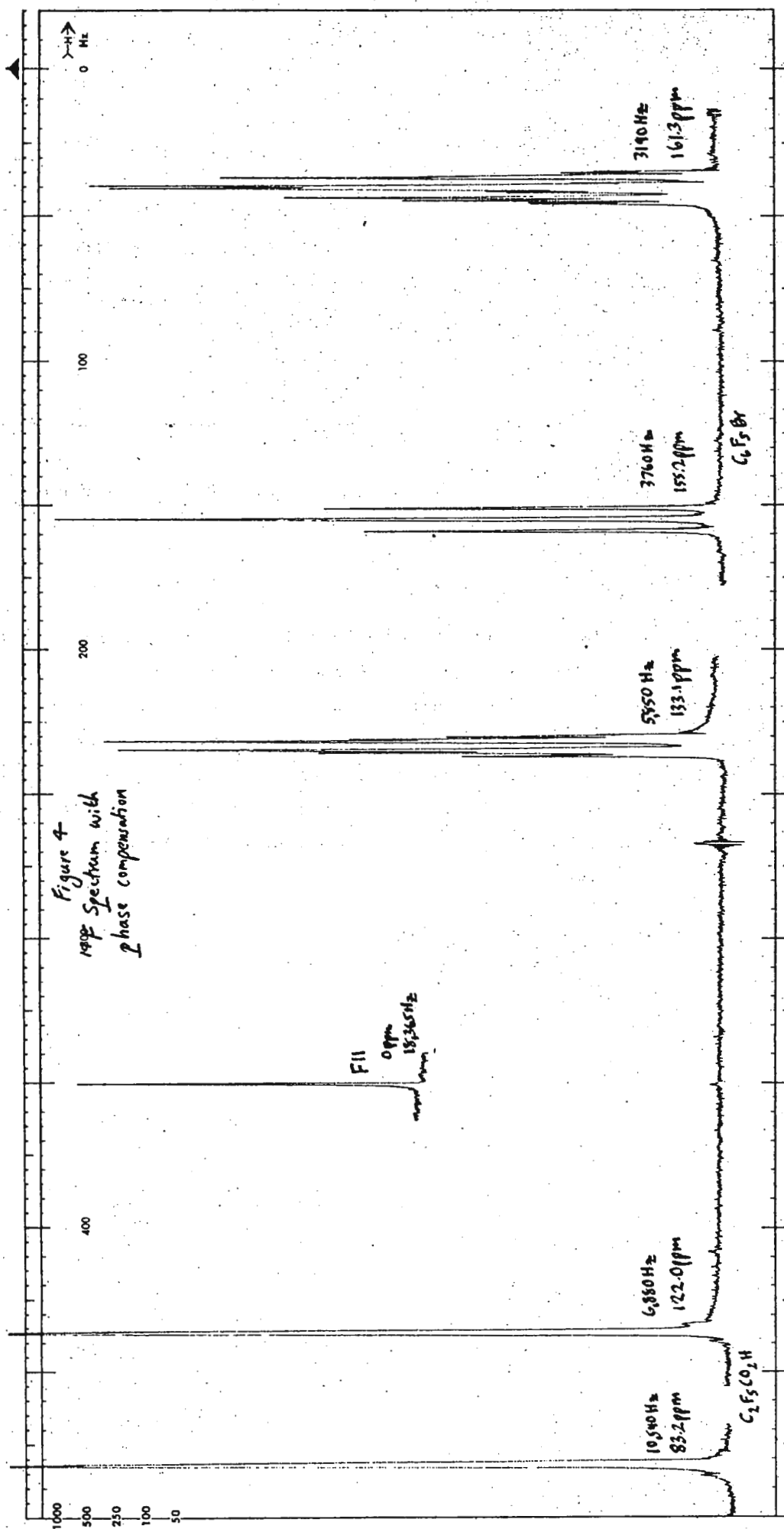


FIGURE 2  
DELAY LINE UNIT



AMPLIFIERS ARE PHILBRICK/NEXUS 1020





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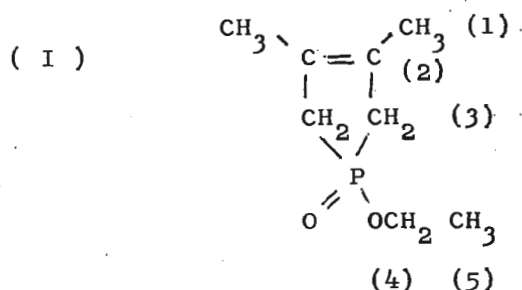
Pr. Bernard L. SHAPIRO

Department of Chemistry  
TEXAS A&M UNIVERSITY  
College of Science  
College Station,  
TEXAS 77843

Vert le Petit, le December 26, 1973

Dear Barry,

We long delayed this letter in spite of your (friendly) calls as we needed a much longer time than I expected to launch our new PFT-100. Our first  $^{13}\text{C}$  trials were on organic nitrates (we intend to study them by  $^{15}\text{N}$  resonance somewhat later on) and, of course, on organophosphorus compounds. ~~Thus~~ as an example of things we can get out of them, I give you the complete set of data for (I) obtained after proton-noise decoupling and off-resonance experiments. We have previously studied the  $\text{POCH}_3$  homolog.

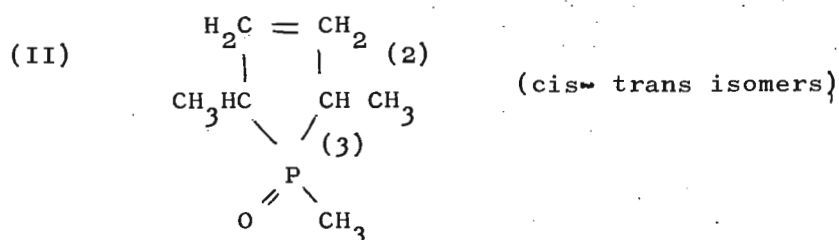


Chem. shifts    C (1) : 16.44 - C (2) 127.78 - C (3) 36.53  
                      C (4) : 60.40 - C (5) : 16.73 (all low field respect to TMS)

Couplings        C (1) .... P    16.6 Hz  
                      C (2) .... P    12.7        C (2) C (3)  $\text{H}_2$     6.3    C (2) C(1) $\text{H}_3$     6.3  
                      C (3) .... P    89.8        C (3) C (1)  $\text{H}_3$     3  
                      C (4) .... P    6.6        C (4) C (5)  $\text{H}_3$     4.2  
                      C (5) .... P    5.3        C (5) C (4)  $\text{H}_2$     3

Some conclusions can be drawn, first on the geometry of the  $\text{POCH}_2\text{CH}_3$  group. It has been shown in dioxaphosphorinane-2-ones (A.A. Borisenko, N.M. Sergeyev, E. Ye. Nifant'ev and Yu.A. Ustynyuk, Chem. Comm., 1972, p. 406) that  $^3\text{J}(\text{P}-\text{C})$  is ca. 5Hz for a cis-configuration (with a W arrangement of the  $\text{O}=\text{P}-\text{O}-\text{C}-\text{C}$  group), ca. 10 Hz for the trans-one. We would clearly be in the first case in our experimental conditions (neat compd. with about 5 % deuterated acetone for locking) as observed in similar phosphonates (G.A. Gray, J. Amer. Chem. Soc., 93, 2132, 1972).

Regarding the heterocycle, data available <sup>on</sup> five-member derivatives (T. Bundgaard and H.J. Jakobsen, Tetrah. Letters, 1972, p. 3353 ; J.J. Breen, S.I. Featherman, L.D. Quinn, R.C. Stocks, Chem. Comm., 1972, p. 657) mainly deal with P III compounds. We can nevertheless compare our couplings with that observed in two typical 3-phospholene oxides (G.A. Gray, S.E. Cremer, J. Org. Chem., 37, 3458, 1972). Thus, the effect of the phosphonate group (POEt) on the couplings is clearly seen : C (3) ...P is 89.8 Hz against 64.9 - 65.4 in (II)



when C(2)...P is slightly reduced 12.7 against 14.3 - 13.4. This agrees with an increased s-character of P-C(3) bonds in (I) compared to (II) (no such effect appears on chem. shifts : for C (3) in (I) 36.53, in (II) 36.89 - 39.06 for C (2), in (I) 127.78, in (II) 133.51 - 133.83). In addition, one notes the High C(1)...P coupling ; it may be associated with a W-type geometry.

Hoping to have more valuable things to communicate in a near future and with our Season's greetings.

R. MANKOWSKI - F. MATHEY - G. MAVEL

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Blackley Manchester  
M9 3DA

Telephone 061-740 1460  
Telex 667841/2/3  
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Professor B.L. Shapiro,  
Department of Chemistry,  
Texas A and M University,  
College Station,  
Texas 77843,  
U.S.A.

makers of dyestuffs,  
pigments, industrial  
and polyurethane  
chemicals

Your ref

Our ref

Date 14th Dec. 73

Dear Professor Shapiro,

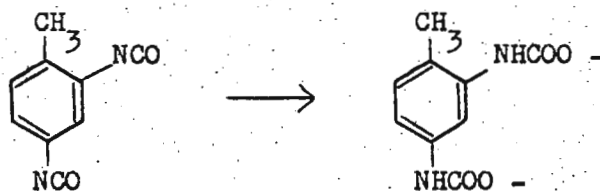
#### <sup>14</sup>N CHEMICAL SHIFTS IN URETHANES

Periodically over the past few years, we have reported the measurement of <sup>14</sup>N chemical shifts in a variety of compound types using the indirect method, whereby <sup>14</sup>N information is obtained by double resonance experiments, whilst observing the <sup>1</sup>H spectrum of the compound concerned. (1, 2, 3, 4 and references therein). The advent of Fourier Transform techniques has made the indirect method completely obsolete for <sup>13</sup>C work and the same will very shortly be true for <sup>14</sup>N work. However the indirect method for <sup>14</sup>N has given us good service over the years and it deserves an honorable retirement, despite its limitations (2).

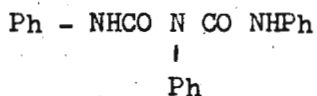
This Company is a major producer of polyurethane materials and a perennial problem in this field is the detection and estimation of urea (>NCON<), biuret (>N - CO - N - CON<) and allophanate (>N - CO - N - COO - ) groups which occur in the urethane materials (>N - COO - ). Proton NMR spectroscopy can give considerable information (5), but we have also tried to look at the system using <sup>14</sup>N NMR. Some values obtained for reference urethanes are given below together with those for the most equivalent ureas.

<u>Urethanes</u>	<u><sup>14</sup>N Shift ppm</u>	<u>Ureas</u>	<u><sup>14</sup>N Shift ppm</u>
H <sub>2</sub> NCCOCH <sub>3</sub>	304 ± 1	H <sub>2</sub> NCONHCH <sub>3</sub>	303 ± 2
H <sub>2</sub> NCOOC <sub>2</sub> H <sub>5</sub>	303 ± 1	H <sub>2</sub> NCONHC <sub>2</sub> H <sub>5</sub>	303 ± 1
CH <sub>3</sub> HNCOOCH <sub>3</sub>	307 ± 3	CH <sub>3</sub> HNCONHCH <sub>3</sub>	304 ± 4
PhHNCOOCH <sub>3</sub>	277 ± 3	PhHNCONH <sub>2</sub>	275 ± 3

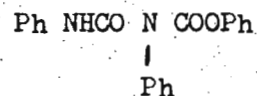
The shifts are quoted in ppm upfield from the nitrate nitrogen signal of a 4.5M solution of ammonium nitrate in aqueous 3N-hydrochloric acid. It can be seen that the values for a urethane and the equivalent urea are indistinguishable within the accuracy of our experiments. Also for the more complicated urethanes actually used in manufacture, e.g. those derived for toluene di-isocyanates:-



the sharpenings of the NH proton signals upon  $^{14}\text{N}$  irradiation were extremely small so that  $^{14}\text{N}$  chemical shift values could not be obtained with any accuracy. Unfortunately the same effect was found for the biurets and allophanates examined, for example:-



and



The particular compounds of interest therefore fall into the category where the double resonance method is limited by unfavourably fast NH proton exchange rates or nitrogen quadrupole relaxation rates. Thus our use of the indirect method for  $^{14}\text{N}$  appears to have finished not with a bang but with a whimper!

Yours sincerely,

*Alan Mathias*

A. Mathias

1. NMR Newsletters 111, 32, 1967; 120, 32, 1968; 129, 12, 1969; 144, 35, 1970
2. P. Hampson and A. Mathias, Molec. Phys. 11, 541, 1966
3. P. Hampson and A. Mathias, J. Chem. Soc. (B), 1968, 673
4. P. Hampson, A. Mathias and R. Westhead. J. Chem. Soc. (B), 1971, 397
5. M. Sumi et al. Makromolec. Chemie, 78, 146, 1964



# ANALYTISCHE MESSTECHNIK

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

Fällanden, 21st December 1973

## Frequency dependent line intensities in FT-Spectra

Dear Professor Shapiro,

I am very sorry for the delay of my contribution but this time of the year we usually are very busy giving courses and demos for our customers and there is not much time left for serious NMR work.

Giving demos we very often have to show the S/N-test for  $C^{13}$ . We as usual apply a  $90^\circ$  excitation pulse to a concentrated sample of aethylbenzene and measure the intensity of the higher peak of one aromatic carbon pair.

I was astonished recognizing that the most intense line is arbitrarily the signal of the pair at ortho or meta position and that the difference sometimes is almost 50 %.

The effect is dependent upon the peak frequency positions with respect to the digitization points of the fourier transformed result and occurs if the spectrometer resolution is better than that of the computer.

In order to have well defined conditions we simulated such NMR-lines using a frequency synthesizer. The attached figure shows that not only the appearance of the lines change drastically but also the values of the integral in both cases is different.

We are presently working out the theory of such effects in more detail.

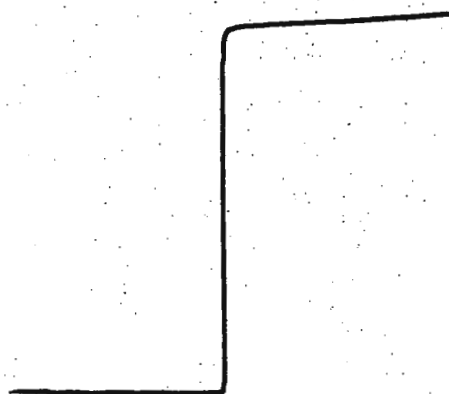
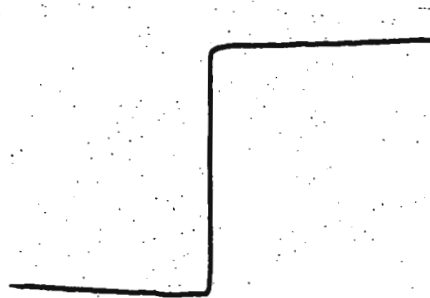
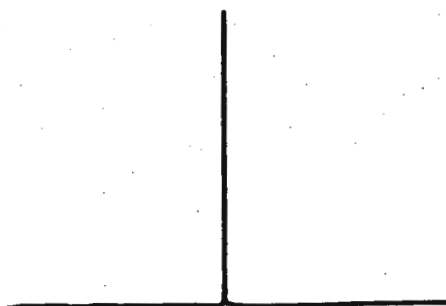
With best wishes for 1974

Yours Sincerely

SPECTROSPIN AG



(Dr. Hp. Kellerhals)

**A****B**

Fourier transform result of signals with  
equal time domain intensities

- A) Frequency corresponding to value of a sampling point
- B) Frequency corresponding to value in between two sampling points

3737 BELLAIRE BOULEVARD  
HOUSTON, TEXAS

December 6, 1973

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

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

Dear Barry:

SUBJECT:  $^{13}\text{C}$  NMR OF 1,4-POLY(BUTADIENE)

V. D. Mochel has concluded<sup>1)</sup> from the  $^{13}\text{C}$  spectra of n-BuLi-catalyzed poly(butadiene) that the polymer consists of "blocks" of cis-1,4 and trans-1,4 units separated by 1,2 units. The validity of this conclusion has been questioned<sup>3)</sup> primarily on the basis that the linewidths attainable in  $^{13}\text{C}$  spectra are too large to permit the detection of the cis-trans linkages expected for a polymer consisting of randomly placed cis-1,4 and trans-1,4 units. Two other studies<sup>2,4)</sup> have also failed to detect the presence of cis-trans linkages even though, in one case at least, they are known from X-ray analyses<sup>4)</sup> to be present.

As in the above studies, we have been unable to find any evidence for cis-trans linkages if we examine only the saturated C region of the  $^{13}\text{C}$  spectra. However, at least in one such polymer, Firestone Diene-55, the unsaturated C region does show evidence for such linkages (see enclosed Figure).

A tentative assignment of the four major olefinic C resonances based on intensity considerations, is as shown. The conclusion must be that this polymer is mainly a "random" one rather than a "blocky" one as concluded by Mochel.

CAR:bls

<sup>1</sup>V. D. Mochel, Journal Polymer Science, Part A-1, 10, 1009 (1972).

<sup>2</sup>J. M. Thomassin, E. Walchiers, R. Warin, Ph. Teyssie, Polymer Letter, 11, 229 (1973).

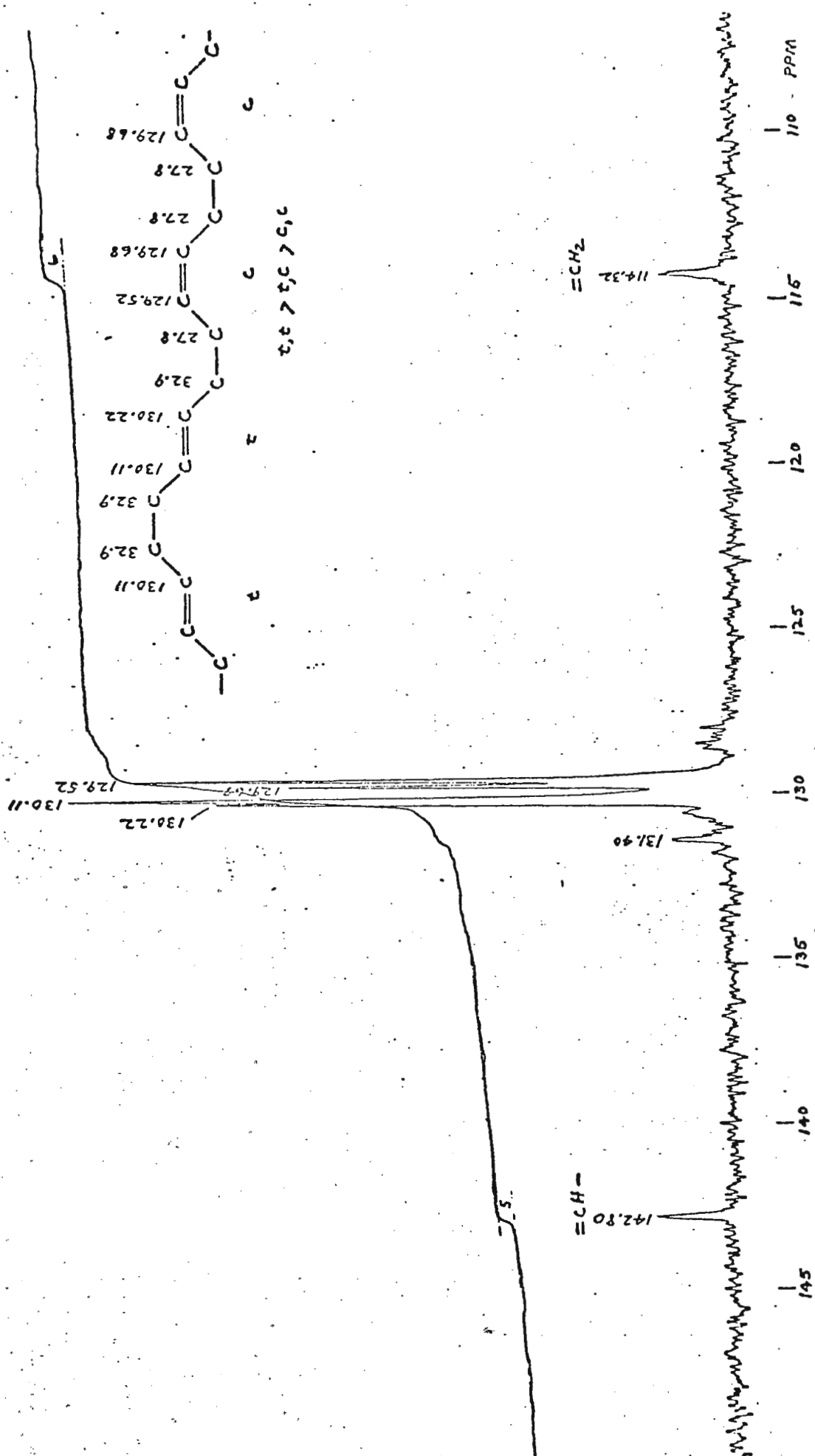
<sup>3</sup>A. D. H. Clague, J. A. M. van Broekhoven, and J. W. de Haan, Ibid., 11, 299 (1973).

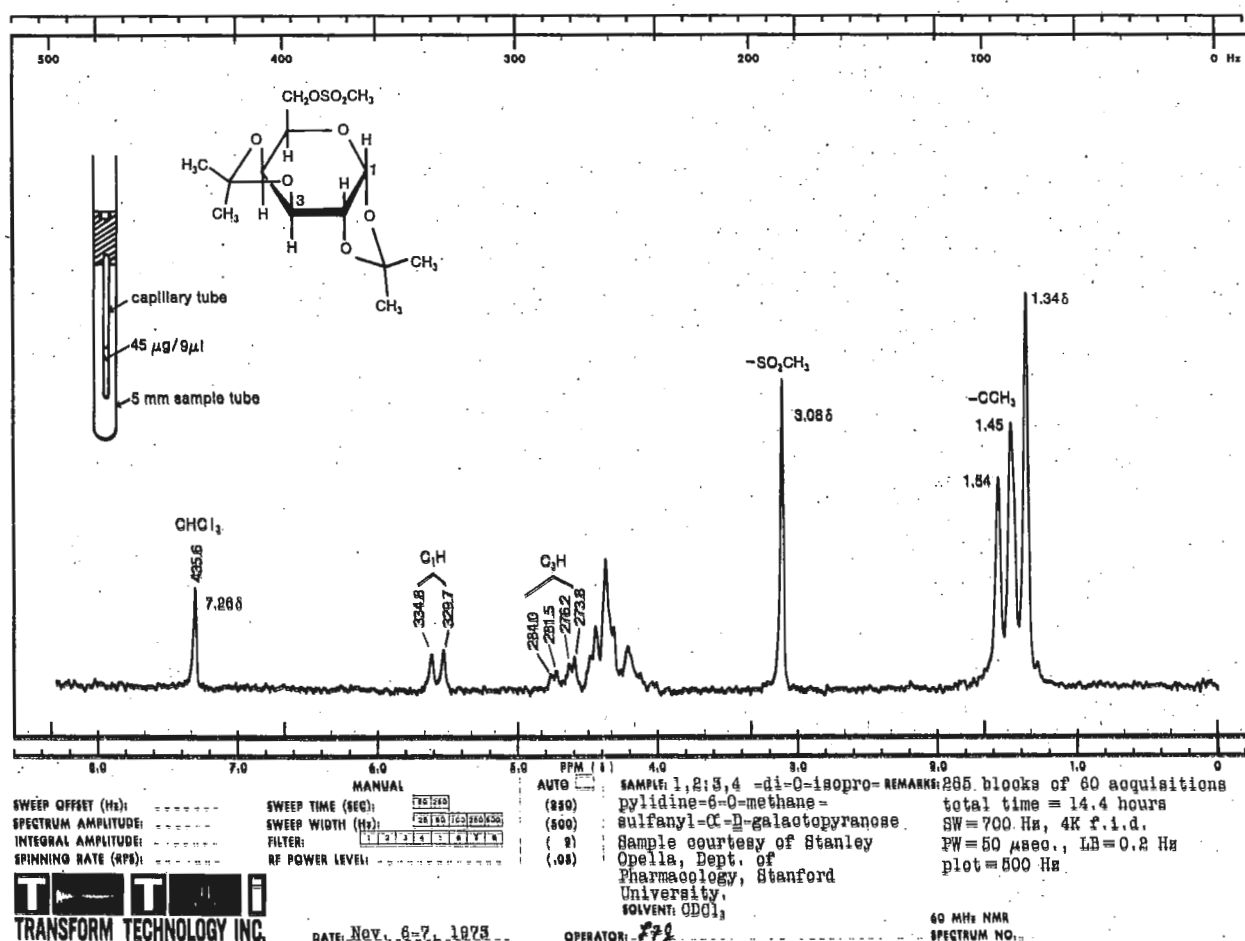
<sup>4</sup>Y. Tanaka and K. Hatada Ibid., 11, 569 (1973).

Sincerely,  
Charlie (Kelly)

8/31/73

Firstene Diene, 55

CDCl<sub>3</sub> 42°C



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 3.086, 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

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surements are available using the inversion-recovery technique as well as other multi-pulse experiments. In addition to sensitivity improvement and T<sub>1</sub> 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).

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OTTAWA, CANADA  
K1A 0R9

December 20, 1973

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

Spectral Simulation and Fluoride Complexes

Dear Barry,

Our group has been continuing its studies of exchange reactions with adducts of binary fluorides and Lewis bases. In order to do this we have had to do some development work on computer programs for calculation of theoretical spectra in exchanging systems. The program DNMR3 (Listed by the Quantum Chemistry Program Exchange) has been slightly modified by Dr. A. Steigel so that it now also handles the  $A_2B_2$  case. The modifications are available on request. If the system is considered as AABB, in order to check details of intramolecular exchange, problems may arise in matrix diagonalization. Dr. Steigel has altered the program to do the diagonalization in double precision and this seems to remove such difficulties.

Systems which have now been studied include  $MF_3 \cdot B$  (Old work),  $MF_4 \cdot 2B$  (by Dr. Steigel),  $MF_5 \cdot B$  (by Mrs. Farrall) and  $MF_6 \cdot B$  and  $MF_6 \cdot 2B$  by myself. In the latter case, under special circumstances, it is possible to obtain a triplet and a quintet when M is tungsten. In this case the triplet has a chemical shift of -118.3 p.p.m. and the quintet -36.8 p.p.m. (i.e. to low field of  $CFCl_3$ ) at 94.1 MHz. With a spin coupling constant of 92 Hz the spectrum is clearly first order, unlike that of Jeremy Musher (TAMUNMR 180-31), appropriately criticized by Rolf Johannesen (TAMUNMR 182-14). The tentative assignment for this spectrum is an octa-co-ordinated tungsten in which there is rapid partial averaging between the fluorine atoms to give two and four non-equivalent fluorines. At present we are trying to distinguish among the more plausible octa-co-ordinate species.

Yours truly,

S. Brownstein.

SB/dn

Mereside Alderley Park  
Macclesfield Cheshire  
SK10 4TG

Telephone Alderley Edge (0996 6) 2828  
Telex 669095/669388 (ICIPharm Aldley)  
Telegrams Avlontex Macclesfield



Imperial  
Chemical  
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Pharmaceuticals  
Division

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

Your ref

Our ref  
DG/LC

Tel ext  
7.462

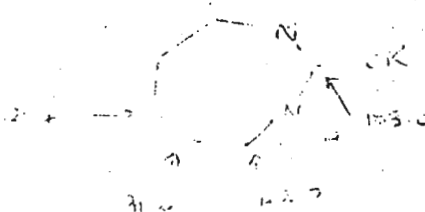
Date  
20th December 1973

The Case of the Disappearing NH

Dear Professor Shapiro,

In examining a series of compounds of general structure (I) in  $\text{CDCl}_3$  solution, the expected NH signal at 4-5 $\delta$  as previously observed in  $\text{CCl}_4$  (1), was not found. Instead we were able to show that a signal at 7.45 $\delta$  was due to chloroform. Thus a proton exchange was taking place with the solvent. We found that the seven and eight membered ring compounds had faster exchange rates than the six membered ring, although the pKa values in 50% acetone/water are all around 10.5. It would seem therefore that some factor other than basic strength is involved.  $^{13}\text{C}$  n.m.r., was used to confirm a symmetrical structure for the eight membered ring compound (with fast proton exchange between the two nitrogens) rather than any other unsymmetrical structure. The  $^{13}\text{C}$  chemical shifts relative to TMS, recorded on our new Bruker HX90E spectrometer, are shown on the structure (II).

Please credit this to Dr. G. R. Bedford's name.



Yours sincerely,

*D. Greatbanks*

D. Greatbanks.

*F. R. Foden*

F. R. Foden.

1) Le Barre, Renault and Giradean (Bull. Soc. Chim. France, 3245, 1971)



# Hunter College

OF THE CITY UNIVERSITY OF NEW YORK | 695 PARK AVENUE, NEW YORK, N.Y. 10021 | DEPARTMENT OF CHEMISTRY

Telephone  
360-2351

November 27, 1973

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

Title: Academic Opening for Electronics Engineer

Dear Barry,

The Chemistry Department of Hunter College of the City University of New York currently has an opening for a fulltime electronics engineer. Prospective applicants should be able to repair, maintain, and appropriately modify laboratory research and instructional instrumentation of a widely varying nature. They should also have thorough familiarity with and extensive experience in digital electronics and mini-computer technology, and should be able to design and construct accessories for computer-interfaced instrumentation. The latter include Fourier-transform ir and mmr spectrometers and laser raman spectrometers. The Department also has its own remote access terminal to CDC 6600 and IBM 370/165 computers via a Honeywell H316 minicomputer, high speed reader and line printer, CRT I/O device, and 1.1 M word disc, for which maintenance, development, and modification will be required.

Hunter College is located in the upper east side of Manhattan and is accessible to all parts of New York City. Salary scales are commensurate with the cost of living, and extensive fringe benefits are provided. Interested applicants should submit a detailed curriculum vita and names of personal references to

Professor B.J. Bulkin  
Chairman, Department of Chemistry  
Hunter College  
695 Park Avenue  
New York, New York 10021

Cordially,



Robert L. Lichter  
Assistant Professor

RLL:vg

varian /instrument division  
25 route 22/springfield/new jersey 07081  
tel. (201) 379-7610



December 27, 1973

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

Re: Career Opportunities - Field Service Engineers

Dear Dr. Shapiro:

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Sincerely,  
VARIAN Instrument Division

Frank R. Zamaroni, Manager  
Eastern Region Service

FRZ:fm



CARLETON UNIVERSITY  
OTTAWA CANADA  
JUNE 24-28 JUIN, 1974

Organizing Committee / Comité d'organisation

J. ApSimon (Chairman)  
H. H. Baer  
C. T. Bishop  
G. W. Buchanan  
O. E. Edwards  
D. W. Hughes  
R. E. Jones  
D. C. Wigfield  
R. H. Wightman  
M. K. Ward (Executive Secretary)

December 28, 1973

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

Dear Barry:

The attached information concerning the 9th IUPAC Natural Products meeting maybe of interest to some of your readers.

In particular, section 2 will feature one hour talks by Allerhand and Hirata and half hour presentations by Crabbé, Chan (Jamaica) Santavy, Mechoulam, Fales, I.C.P. Smith (Canada) and Nakanishi.

Yours sincerely,

J. W. ApSimon  
Chairman  
Organizing Committee

/mak  
Attach.



CARLETON UNIVERSITY  
OTTAWA CANADA  
JUNE 24-28 JUIN, 1974

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D. C. Wigfield  
R. H. Wightman  
M. K. Ward (Executive Secretary)

Please address communications to:  
Veuillez adresser communications à:  
M. K. Ward,  
Executive Secretary,  
9th International Symposium on the  
Chemistry of Natural Products,  
c/o National Research Council of Canada,  
Ottawa, Ontario K1A 0R6

9th International Symposium on the Chemistry of Natural Products

Carleton University, Ottawa, Canada

June 24-28, 1974

The 9th IUPAC International Symposium on the Chemistry of Natural Products will take place at Carleton University from June 24-28, 1974.

Six parallel subject sessions will be organized in the following areas:

1. Total synthesis of natural products
2. Structures and properties of natural products
3. Natural products of medicinal interest
4. Transformations of natural products
5. Marine and insect chemistry
6. Bio-organic chemistry

In each of these areas there will be two main invited speakers selected from amongst acknowledged leaders in their respective fields. There will also be a number of half hour talks presented by younger scientists invited by the programme committee. Besides this there will be an opportunity for the presentation of 15 minute contributed papers. These are invited in the above areas.

Accommodation will be available in University residence as well as in local hotels. Registration material and special forms for the preparation of abstracts for contributed papers are available from:

M. K. Ward, Executive Secretary,  
9th International Symposium on the  
Chemistry of Natural Products,  
c/o National Research Council of  
Canada,  
Ottawa, Canada K1A 0R6.



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