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Newsletter

*Bruce L. Sykes*

No. 143

AUGUST, 1970

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OVER



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All Newsletter correspondence, etc., should be addressed to:

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

ИНСТИТУТ ХИМИИ  
ПРИРОДНЫХ СОЕДИНЕНИЙ  
АН СССР

INSTITUTE FOR CHEMISTRY  
OF NATURAL PRODUCTS

ACADEMY OF SCIENCES OF USSR

Ul. Vavilova, 32. Moscow, USSR

2 July 1970

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

Title: "At last the shape  
of the combination  
signal".

Dear Barry:

Up to now we had succeeded only in noting that  
a frequency of a combination signal is evoked under certain con-  
ditions of multifrequency resonance (1, 2).

For direct recording of the combination signal a "synthesizer"  
of the frequencies of three audio oscillators has been developed.  
Two of these oscillators operate on fixed frequencies  $\nu_2$  and  
 $\nu_3$  while the third is the frequency sweep oscillator  $\nu_1$  of the  
spectrometer. The voltages of these three oscillator are used for  
modulating the magnetic field to generate the irradiating rf fi-  
elds in the triple resonance experiments. The phase detector of  
the spectrometer's recording channel is controlled by the referen-  
ce voltage of the combination frequency formed by the "synthesi-  
zer". The schematic block diagram of the equipment showing the  
interconnections of the main units is represented on Fig.I.

- 2 -

The experiments were carried out on the sample whose AMX spectrum was described in detail previously (I). Irradiation of the X2 and X4 transitions see Fig.I of (I) for notations by the weak  $\nu_2$  and  $\nu_3$  rf fields with equal amplitudes  $H_2 = H_3$  splits the M4 and M2 components of the M - proton signal into triplets (Fig.2b). This corresponds to the I2I-I case (Fig.2a) of the energy diagram fragment of the triple tickling experiment (I,2). When the sweep frequency ( $\nu_I$ ) passes through the M4 and M2 lines combination signals at frequencies  $\nu_{\text{comb.}} = \nu_I + \nu_2 - \nu_3$  and  $\nu_{\text{comb.}} = \nu_I - \nu_2 + \nu_3$ , respectively, are evoked in the spin system. Now if the phase detector of the recording channel is also controlled by the combination frequency voltage then the recorder will trace out the shape of the combination signal. The results of the experiment are shown on Fig.2c,d. The shape of the recorded I2I-I combination signals on exact tuning of the irradiating fields is in complete accord with that following from theory (3).

In order to visualize one of the possible areas for the practical application of the combination signal method it is sufficient to imagine the M-proton signal buried within a broad band ("finger-print") of other proton signals. In that case two triple resonance experiments  $\{X1, X3\}$  and  $\{X2, X4\}$  are sufficient for completely recording the M-proton spectrum, determining its resonance frequencies and evaluating its relative line intensities.

Sincerely yours

Vladimir Bystrov

*V Bystrov*

V.A.Afanas'ev

(Institute of Chemical Physics,  
USSR Academy of Sciences, Moscow).

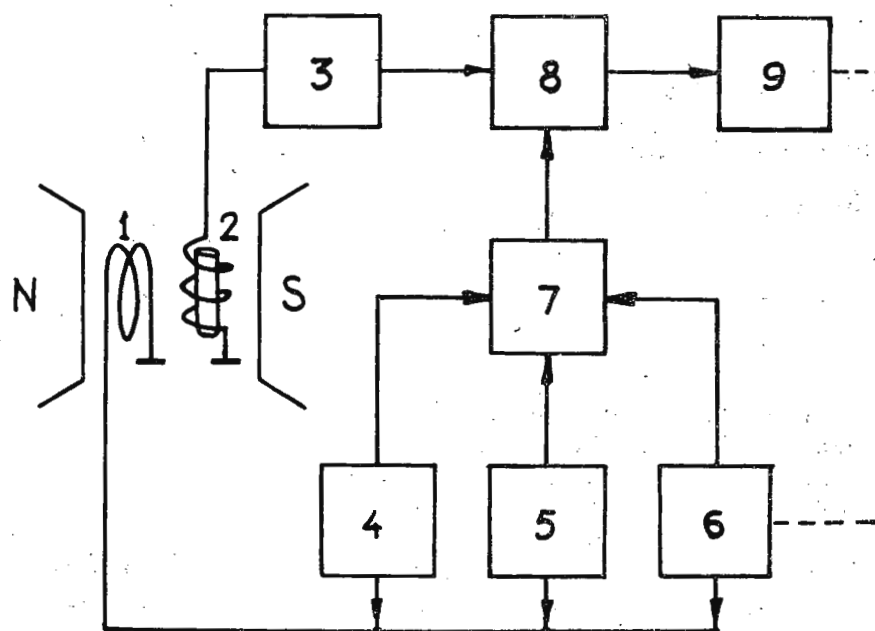


Fig. I

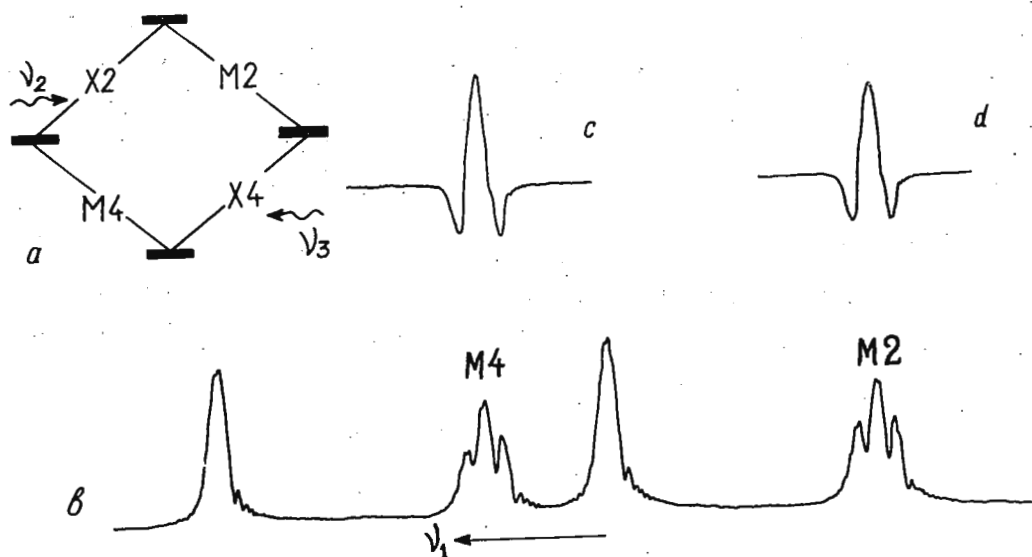


Fig. 2

### References.

1. V.F.Bystrov, J.Molec.Spectr. 28, 81 (1968); IIT NMR II8-10 (1968).
2. V.F.Bystrov, TAMU NMR I34-28 (1969), 138-2 (1970).
3. V.Sinivee, Bull.Acad.Sci.Estonian SSR, Phys.Math.Sci.Ser. I6, 444 (1967); V.Sinivee and V.Salum, *ibid*, I7, 64 (1968).

*Universidad de Buenos Aires*  
*Facultad de Ciencias Exactas*  
*y Naturales*

BUENOS AIRES, June 25, 1970.-

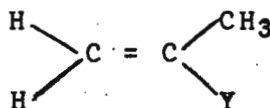
Physics Department

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

Subject: Correlations of Four-Bond Couplings with  
 Substituent Electronegativity in 2-Substituted  
 Propenes

Dear Professor Shapiro:

I am sending you the plot of  $J_{CH_3-H1}$  and  $J_{CH_3-H2}$  versus the electronegativity of the substituent in compounds of the type

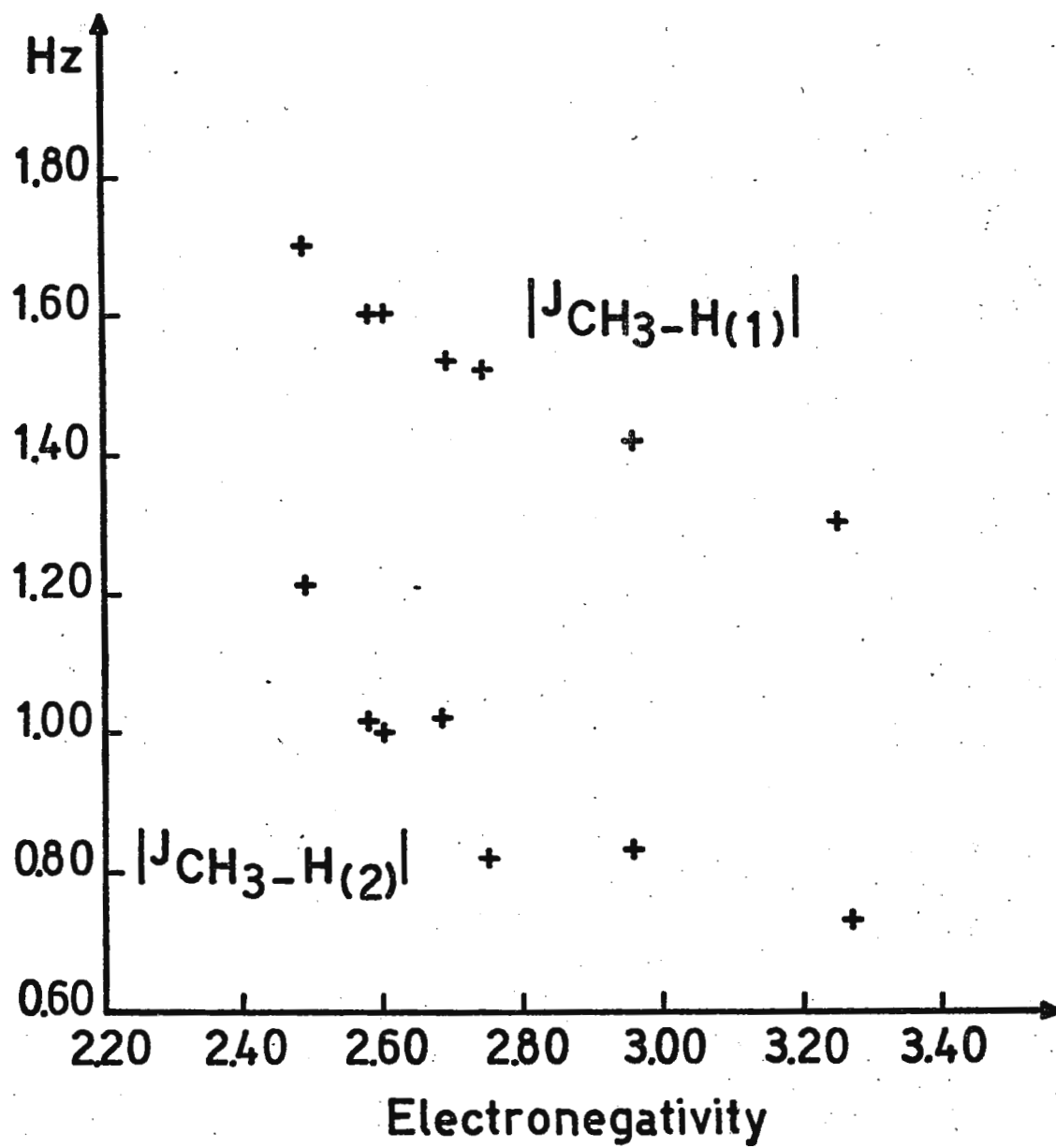


I must confess that the preliminary results communicated on 139-1 were based on my having tabulated the J's according to the position of the protons in the spectrum.

Sincerely yours,



Dora G. de Kowalewski  
 Associate Professor



varian associates limited  
Russell House / Molesey Road / Walton-on-Thames / Surrey / England  
Telephone Walton-on-Thames 28766 / Cables Varian Walton / Telex 261351



Your Reference:

Our Reference: DS/MSJ

8th July, 1970

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

An Unusual Coupling,  $J(^{13}\text{C} - ^{14}\text{N})$ ;  
Unreliable Reference,  $\text{CFCl}_3$ .

Dear Professor Shapiro,

My time for payment is due you inform me, can I settle my debt with an unusual coupling constant and an unreliable reference.

The unusual coupling constant is  $J(^{13}\text{C} - ^{14}\text{N})$  being 3.3.Hz in  $(\text{CH}_3)_4\text{N Br}$  and  $(\text{CH}_3 - \text{CH}_2)_4\text{N Br}$  as solutions in  $\text{D}_2\text{O}$ .  $J(^{13}\text{C} - \text{C} - \text{N})$  is less than 0.5 Hz in the second compound. This coupling has already been measured by Dr. Dreeskamp using double resonance techniques I believe, but in figure 1, you can actually see it. The spectrum is one minutes worth of pulsing on an XL-100-15 plus a little calculation!

The unreliable reference is  $\text{CFCl}_3$ . The spectrum in figure 2 and the data in the table represent the start of an evaluation of "other nuclei" references using T.M.S. as an absolute reference. Something has to be N.M.R.'s absolute deity so why not T.M.S? Preliminary work on  $\text{C}_6\text{F}_6$  reads like a horror story, its chemical shift is sensitive to everything.

Continued.....



Best wishes.

Yours sincerely,

*Derek Shaw*

Dr. D. Shaw.

An unusual coupling,  $J(^{13}\text{C} - ^{14}\text{N})$  and an unreliable reference  $\text{CFCl}_3$ .

TABLE

Chemical Shift of  $\text{CFCl}_3$  as a Function of Solvent  
Concentration and Temperature

| <u>% <math>\text{CFCl}_3</math></u> | <u>Temp. °C</u> | <u>Shift Hz</u> |
|-------------------------------------|-----------------|-----------------|
| 95% in $\text{CCl}_4$ (+ 1% TMS)    | +30             | + 5.0           |
| 50 " " "                            | "               | + 42.8          |
| 5 " " "                             | "               | + 81.7          |
| 95% in $\text{C}_6\text{F}_6$ "     | "               | - 13.2          |
| 50 " " "                            | "               | - 53.7          |
| 5 " " "                             | "               | -208.2          |
| 95% in $\text{C}_6\text{H}_6$ "     | "               | + 1.4           |
| 50 " " "                            | "               | + 11.0          |
| 5 " " "                             | "               | + 18.4          |
| 5% in $(\text{CH}_3)_2\text{CO}$ "  | +30             | + 97.4          |
| " " " "                             | +10             | + 98.3          |
| " " " "                             | 0               | + 98.5          |
| " " " "                             | -10             | + 99.7          |
| " " " "                             | -20             | + 99.6          |
| " " " "                             | -40             | +100.6          |

XL-100 locked to T.M.S. at 100, 099, 263.5Hz

Zero taken as neat  $\text{CFCl}_3$  + 1% T.M.S. at 94, 189, 837.3Hz.

P.S. Sorry for the strange lay-out, but I know how you hate to waste space.

Figure 1.

$C^{13}$  Spectrum

XL-100-15/FT 100

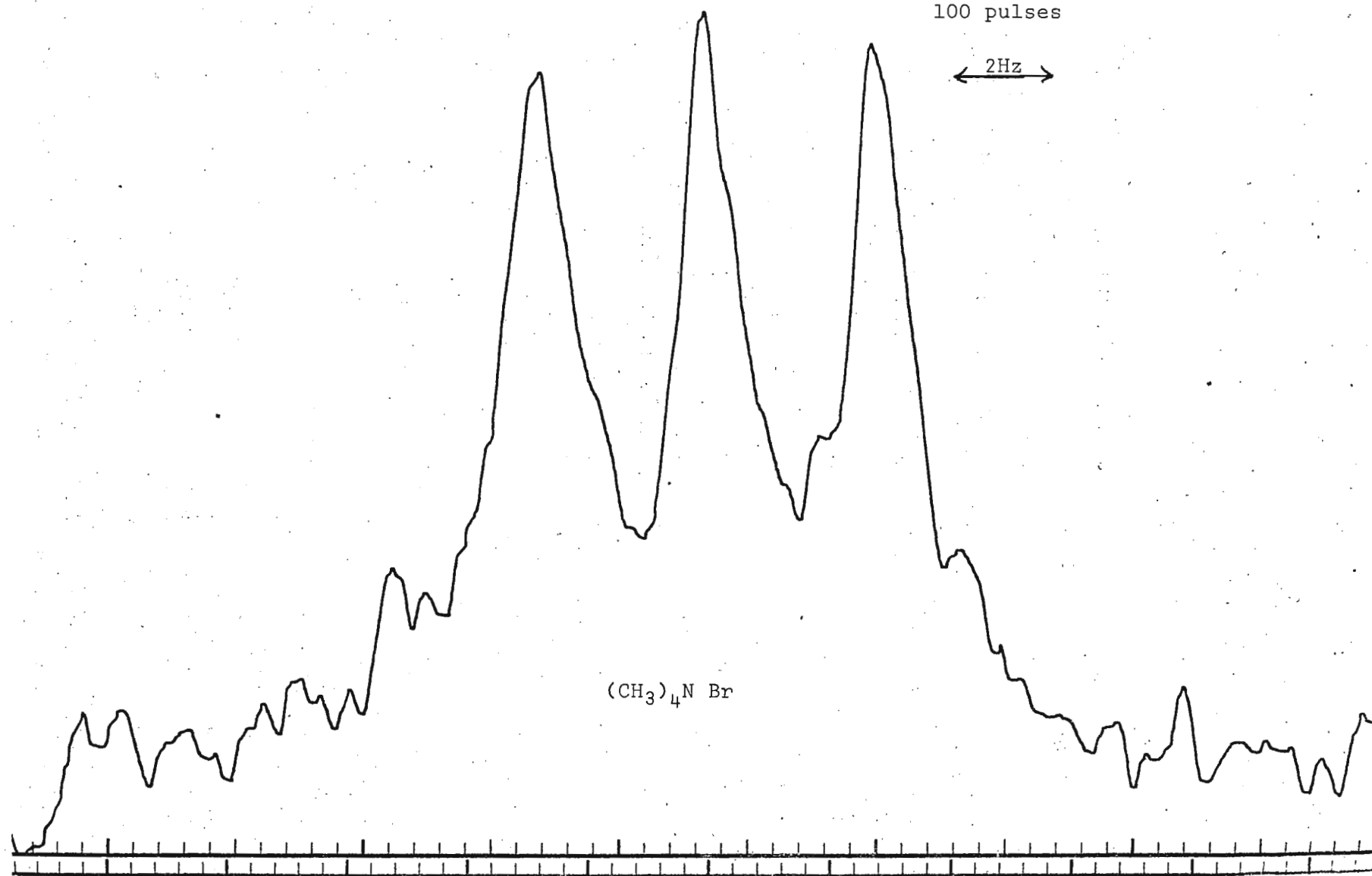
12 mm tube

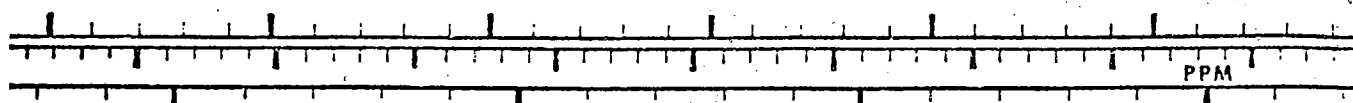
$^2H$  lock

$^1H$  noise decoupled

100 pulses

143-8





143-9

Figure 2.

88,538.17

88,537.60 Hz

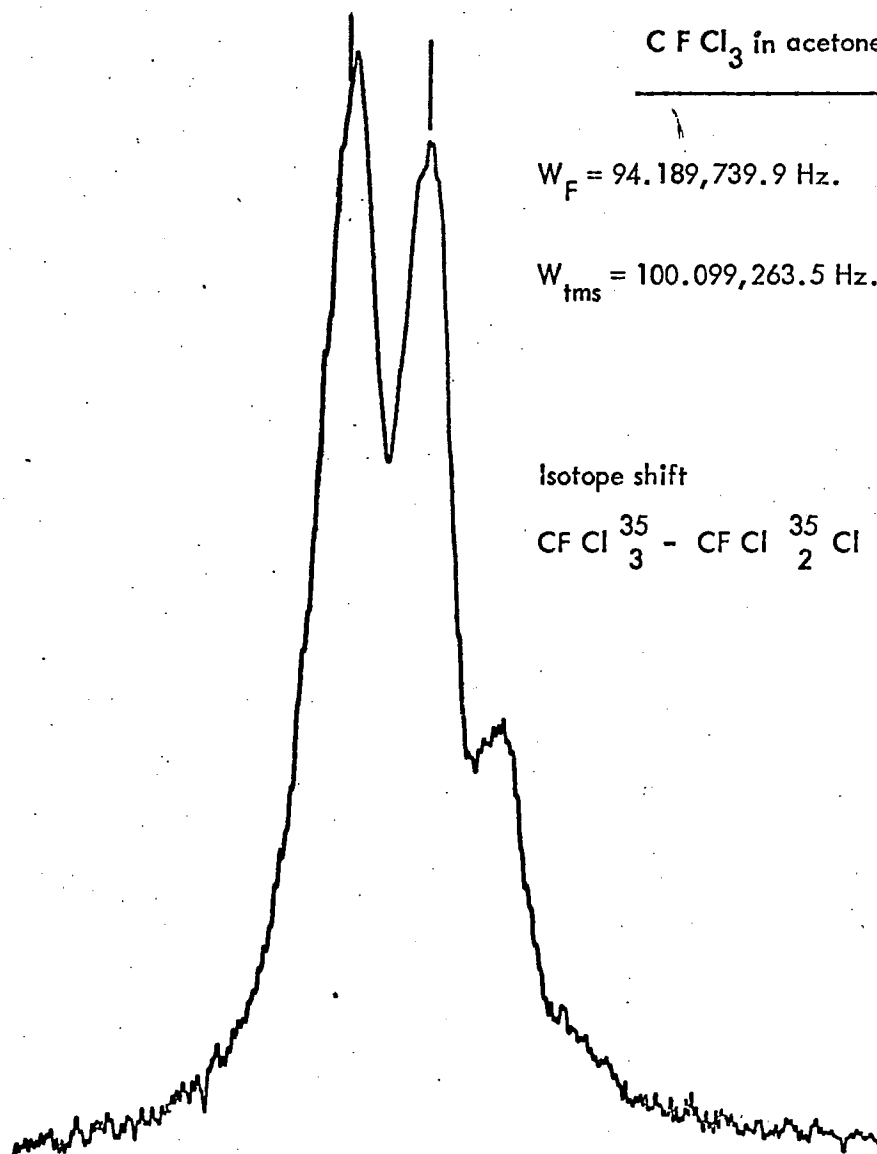
CFCl<sub>3</sub> in acetone

$W_F = 94.189,739.9 \text{ Hz.}$

$W_{\text{tms}} = 100.099,263.5 \text{ Hz.}$

Isotope shift

$\text{CF Cl } \frac{35}{3} - \text{CF Cl } \frac{35}{2} \text{ Cl } \frac{37}{1} = 0.57 \text{ Hz.}$





July 13, 1970

**The University of Sydney**Department of Organic Chemistry  
SYDNEY, N.S.W. 2006

IN REPLY PLEASE QUOTE:

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

PERIODIC CORRELATION OF  $J_{\text{gem}}$  in  $\text{Me}_n\text{X}$ 

Dear Barry,

Mr. M. Lacey and Mr. A. Pross having completed the preparation and NMR work on a number of compounds of the general type  $\text{Me}_n\text{X}$  [c.f. IITNMRN 116, 24 (1968)], we have tried to look at the data, and those from the literature<sup>1</sup> in a number of ways. Perhaps most instructive, is the apparent periodic correlation of  $J_{\text{gem}}$  in  $\text{Me}_n\text{X}$  shown here. Clearly, if the correlation is meaningful we should find the values for  $\text{X} = \text{P, As, Sb, Se and Te}$  at least, falling on the dotted lines and the appropriate syntheses are being contemplated at present.

With best regards

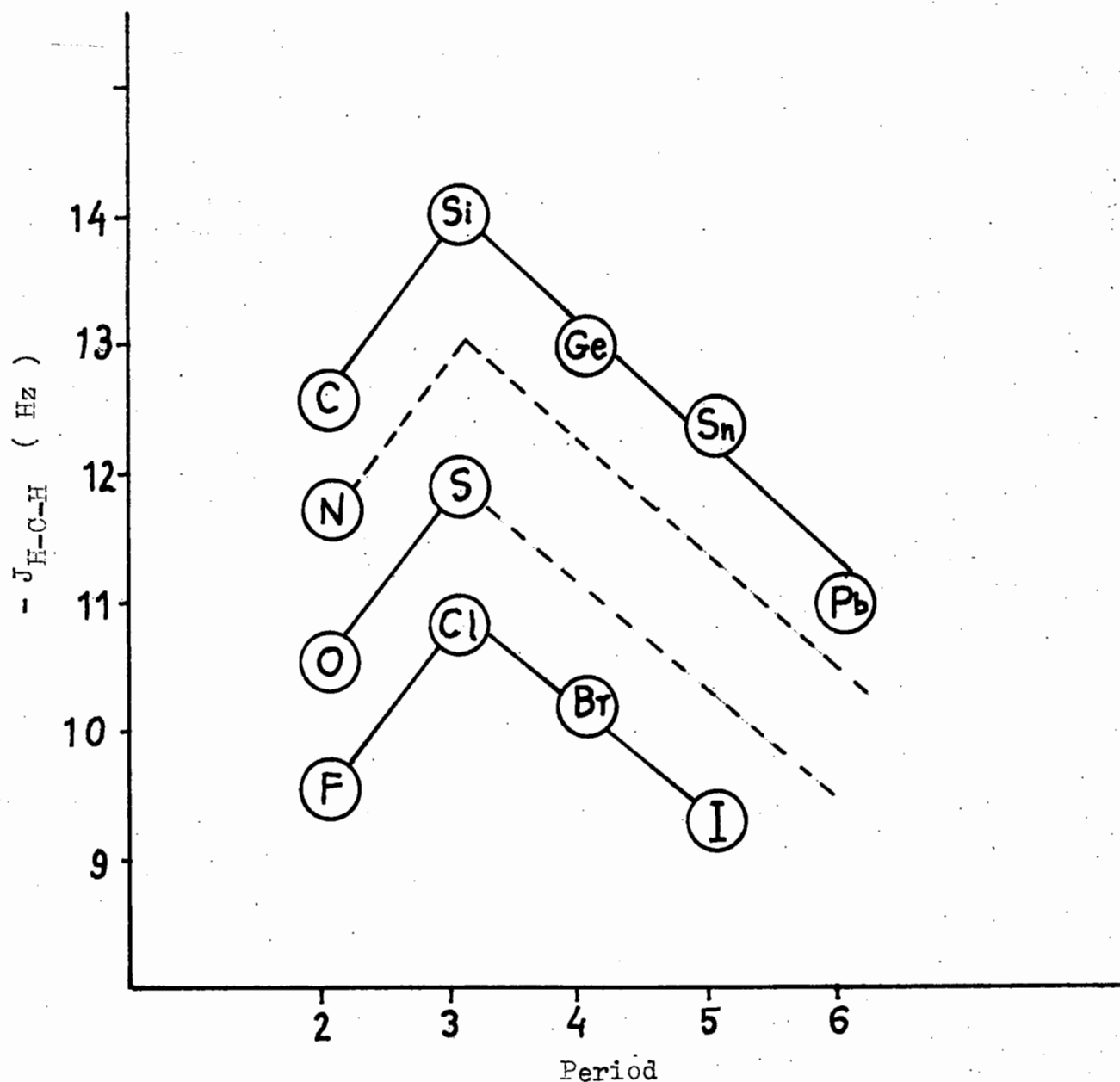
yours sincerely

Sev Sternhell

<sup>1</sup> Bernstein and Sheppard, J. Chem. Phys., 37, 3012 (1962);  
Bernheim and Lavery, ibid, 42, 1464 (1965).

-page 2 -

Plot of  $J_{\text{gem}}$  in the series  $\text{Me}_n\text{X}$  against the period of the element X. The value for  $\text{LiMe}$  ( $J_{\text{gem}} = (-?)12.89$  Hz for a solution in ether) does not fit, perhaps because  $\text{MeLi}$  is tetrameric in solution.





WESTERN  
RESEARCH CENTER



# Stauffer Chemical Company

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

July 14, 1970

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

Re: Diastereomers of Oxazolidines by NMR

Dear Barry:

We have observed an unusual doubling of the PMR signals of the methyl protons in 2-(O,S-dimethylthiophosphorylimino)-3-ethyl-5-methyl oxazolidine, I (Fig. 1). The methyl protons (B) at the 5-position gave a doublet of doublets with spacings of 6.14 and 1.10 Hz at 60 MHz and the spacings became 6.20 and 1.96 Hz at 100 MHz. In addition to the vicinal H-P coupling (13.50 Hz), an extra splitting (0.80 Hz) was observed for  $\text{CH}_3\text{S}$ . An extra splitting was observed only at 100 MHz for the methoxy protons. These extra splittings are solvent-dependent and are listed in the table.

Table

Chemical Shift Difference of Methyl Protons of I

| Methyl Protons               | <sup>a</sup><br>$\text{CDCl}_3$ | <sup>a</sup><br>$\text{C}_6\text{D}_6$ | <sup>b</sup><br>$\text{C}_6\text{D}_6$ | <sup>a</sup><br>$\text{Py-d}_5$ | <sup>a</sup><br>$\text{CD}_3\text{CN}$ |
|------------------------------|---------------------------------|--|--|---------------------------------|--|
| $\text{CH}_3\text{CH}_2$ (A) | 0                               | 0                                      | 0                                      | 0                               | 0                                      |
| $\text{CH}_3\text{CH}$ (B)   | 0.65                            | 1.10                                   | 1.96                                   | 1.60                            | 0.40                                   |
| $\text{CH}_3\text{S}$ (C)    | ~ 0                             | 0.80                                   | 1.40                                   | 0.26                            | ~ 0                                    |
| $\text{CH}_3\text{O}$ (F)    | ~ 0                             | ~ 0                                    | 0.38                                   | ~ 0                             | ~ 0                                    |

a, Taken at 60 MHz.

b, Taken at 100 MHz.

- 2 -

Since oxazolidine I contains a C=N bond, the extra splitting could possibly be attributed to the presence of syn and anti forms in I. If this were the case, one should be able to observe the same kind of doubling in the unrearranged 2-(0,0-dimethylthio-phosphorylimino)-3-ethyl-5-methyl oxazolidine, II. In deuterated benzene, oxazolidine II gave no extra doubling (Fig. 2).

By inspection of oxazolidine I, it is seen that I has two asymmetric atoms whereas oxazolidine II has only one asymmetric atom, thus it is possible that the extra doublings of B, C, and F methyl protons of I arise from diastereomers.

Sincerely,

*Tseng*

C. K. Tseng

*E. J. Gaughan*

E. J. Gaughan

*W. J. Smith*

W. J. Smith

CKT/EJG/WJS/1h

Attachment

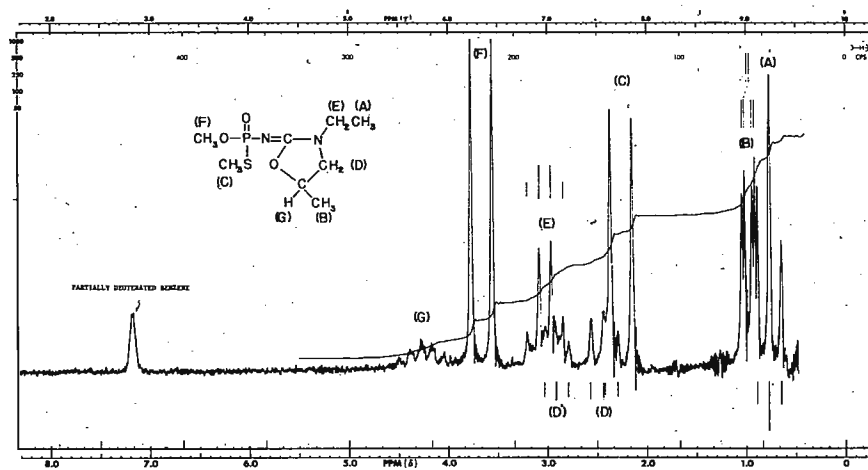


Fig. 1. PMR spectrum of oxazolidine I in  $C_6D_6$  solution.

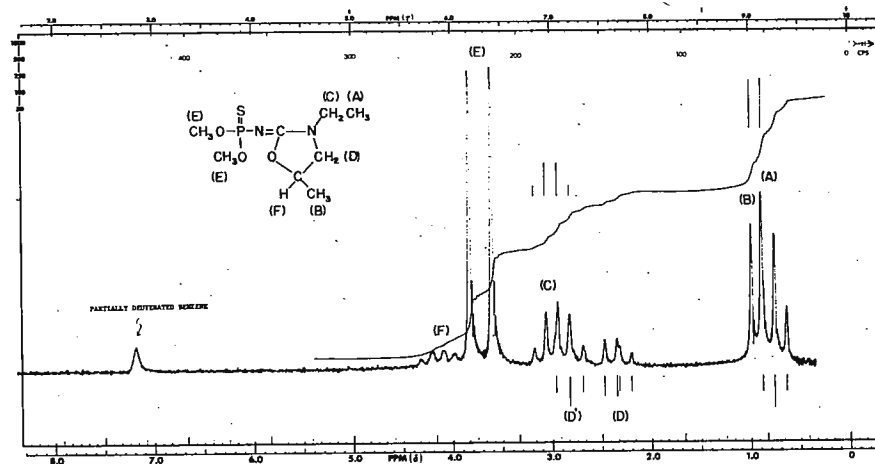


Fig. 2. PMR spectrum of oxazolidine II in  $C_6D_6$  solution.

## UNIVERSITY OF HOUSTON

CULLEN BOULEVARD  
HOUSTON, TEXAS 77004  
UNITED STATES OF AMERICA

DEPARTMENT OF CHEMISTRY

10 July 1970

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

Dear Barry:

UNUSUAL DIASTEREOTOPISM IN A SIMPLE COMPOUND

During a recent investigation of some camphor derivatives, Clint Boriack and I observed that the methylene hydrogens on the 9-position of 3,9-dibromocamphor exhibited a perturbed AB pattern at the appropriate chemical shift. Closer scrutiny revealed that each line of the down-field resonances of the AB pair appeared as a doublet, while the up-field resonances were very well defined 1:3:3:1 quartets. The coupling constants in both the doublet and quartet are approximately equal and are slightly less than 1 Hz. Double irradiation experiments revealed that coupling to the bridgehead hydrogen was responsible for the doublet. Moreover, irradiation of one of the two methyl groups (the one at 1.06  $\delta$  and not the one at 1.00  $\delta$ ) revealed the origin of the quartet.

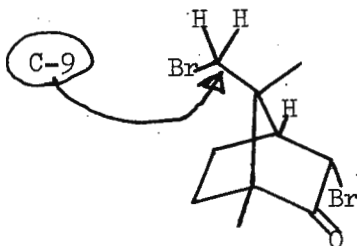
Dr. Shapiro, my quiz question is this: which methyl group is responsible for the quartet? What part of the theory of long-range coupling can be employed to explain the clear-cut distinction made by the diastereotopic methylene protons? Clint Boriack and I would be happy to receive any comments on this question that the News Letter readers may have.

The entire problem of interpretation was raised by John Grutzner.

Sincerely yours,

Bob

M. Robert Willcott





## SIR GEORGE WILLIAMS UNIVERSITY

MONTREAL 107, CANADA

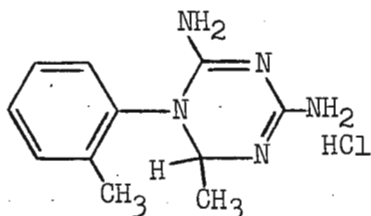
July 15, 1970.

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

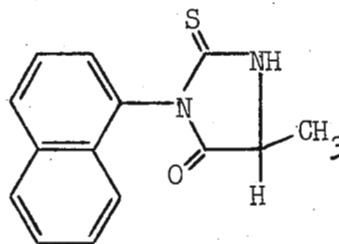
Dear Barry,

EQUILIBRATION OF DIASTEREOMERIC ROTATIONAL ISOMERS

In an earlier contribution to the newsletter (133 - 22.) I mentioned that we had been able to obtain one of the rotational isomers of the aryl substituted triazine (I) in substantial excess and that the rate of conversion to the equilibrium mixture could be followed in the n.m.r. spectrum. We have now succeeded in doing the same thing in the case of the  $\alpha$ -naphthyl substituted thiohydantoin (II).



(I)



(II)

The rotational isomers of these two compounds are diastereomers since, in addition to showing biphenyl-like isomerism, the molecules contain an asymmetric centre. Normal work-up procedures following synthesis were used. The rotational barriers are sufficiently high that little isomerization was likely to occur under these conditions. Recrystallization of (I) from ethanol yielded an isomeric mixture containing about 88% of the thermodynamically preferred isomer, whereas recrystallization of (II) from ethanol yielded a mixture containing about 87% of the thermodynamically less stable isomer.

The equilibration of the initially predominant isomer of (I) in trifluoroacetic acid was followed over the temperature range 22.5 - 52° C by measuring the rate of change in the relative intensities of the 2-methyl doublets of the predominant isomer (1.762  $\delta$ ,  $J$  = 6.1 Hz) and its rotamer (1.578  $\delta$ ,  $J$  = 6.1 Hz) by repeated integration of the 100 MHz n.m.r. spectrum. At equilibrium, the concentration ratio of these isomers was 1.64:1.00, respectively. The rate of conversion of the initially predominant isomer of (II) in pyridine to the equilibrium ratio (1.00:1.18) was measured over the range 24 - 78° by repeated integration of the overlapping 5-methyl doublets of the two forms, the initially predominant form absorbing at 1.505  $\delta$  ( $J$  = 7.0 Hz) and its rotamer at 1.575  $\delta$  ( $J$  = 7.0 Hz). Rate constants were obtained by non-linear regression analysis of the intensity ratio vs time curves.



- 2 -

TABLE

Activation Parameters at 298° K for Equilibration of Diastereomeric

| <u>Rotational Isomers</u> |   |                      |                  |                                    |                                    |                               |
|---------------------------|---|----------------------|------------------|------------------------------------|------------------------------------|-------------------------------|
|                           |   | $E_a$<br>(Kcal/mole) | Log A            | $\Delta H^\ddagger$<br>(Kcal/mole) | $\Delta G^\ddagger$<br>(Kcal/mole) | $\Delta S^\ddagger$<br>(e.u.) |
| (I)                       | A | $23.5 \pm 1.3$       | $12.13 \pm 0.90$ | 22.9                               | 24.4                               | - 5.0                         |
|                           | B | $23.5 \pm 1.3$       | $12.35 \pm 0.90$ | 22.9                               | 24.1                               | - 4.0                         |
| (II)                      | A | $21.1 \pm 0.4$       | $9.55 \pm 0.28$  | 20.5                               | 26.6                               | -16.8                         |
|                           | B | $21.1 \pm 0.4$       | $9.48 \pm 0.28$  | 20.5                               | 25.7                               | -17.2                         |

Activation parameters for the forward and reverse reactions are listed in the Table. The rotational barriers are comparable to those reported for many of the highly hindered 2,2'-substituted biphenyls which have been investigated by the classical method of resolution and racemization of enantiomers.<sup>1</sup> In a concurrent study by line shape methods of compounds related to the thiohydantoin(II) we have found that the hydantoin corresponding to (II) shows considerably less restriction to rotation, reflecting the difference in effective sizes of oxygen and sulfur. For this compound, the  $\Delta G^\ddagger_{298}$  (pyridine solution) is 18.3 - 18.4 Kcal/mole.

As expected, the deviation of the equilibrium constants from unity is influenced by the distance of the asymmetric centre from the torsional centre of the molecule, and is greater in (I) than in (II). The significance of the difference between the values of  $\Delta S^\ddagger$  for (I) and (II) is not clear at present, but the more negative value for (II) is consistent with values we have obtained by line shape methods for other hydantoins.

Collaborating on this project were Wes Bentz, Jim Fehlner, and Andre Rosowsky,

Best regards,

Yours sincerely,

*Laurie*

L.D. Colebrook,  
Associate Professor,  
Department of Chemistry.

LDC/mp

<sup>1</sup> D.M. Hall and M.M. Harris, J. Chem. Soc., 490 (1960).

БЪЛГАРСКА  
АКАДЕМИЯ НА НАУКИТЕ  
ИНСТИТУТ ПО ОРГАНИЧНА ХИМИЯ

BULGARIAN  
ACADEMY OF SCIENCES  
INSTITUTE OF ORGANIC CHEMISTRY  
Sofia 13, Bulgaria

Sofia, the 16.7. 1970

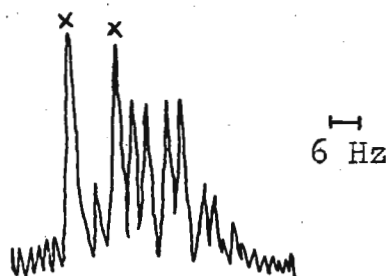
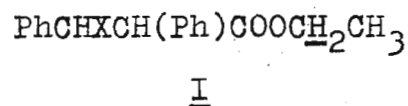
Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

Magnetic nonequivalence induced by two asymmetric centers

Dear Professor Shapiro,

Although the problem of nonequivalent methylene protons has experienced much attention, relatively few examples are known in which the effect is demonstrated for the  $-OCH_2-$  group of acyclic ethyl esters<sup>1,2/</sup>.

Looking at the proton spectra of the diastereomeric esters I ( $X = OH, NH_2, NHPh, NHCONH_2$ ), we found that in some solvents a higher multiplicity is observed for the  $-OCH_2-$  signal (figure



shows erythro-I,  $X = NH_2$  in benzene; peaks marked by x are due to the C-2 proton). The spectra are similar to those measured by Meyer et al.<sup>2/</sup> for some esters of trans-decalin derivatives, in which case the effect was attributed to the rigidity of the system.

The  $CH_2$  chemical-shift differences for I are relatively small (5-6 Hz at 60 MHz in benzene, somewhat smaller in pyridine, hardly observable in  $CDCl_3$ ). They are about the same for the

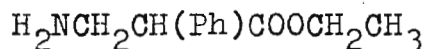
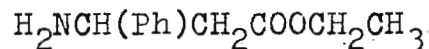
Professor B.L.Shapiro

Page 2

erythro and threo-forms, although it was shown<sup>3/</sup> that they exist predominantly in the conformations shown below, in which the Ph and X substituents are differently oriented with respect to the ester group:



We were interested to study the effect of "elimination" of the 2- and 3-asymmetric centers (through replacement of Ph and X by H) on the degree of nonequivalence. It turned out, however, that neither of the compounds I (X = H), II and III showed anything more than a simple CH<sub>2</sub> quartet in CDCl<sub>3</sub>, benzene, etc. Thus it

IIIII

seems that the CH<sub>2</sub> nonequivalence of the esters I might be attributed to the dissymmetry of the molecule as a whole.

Sincerely yours, *Stefan*

S.L.Spassov

1/ M.J.Martin and G.J.Martin, Bull.Soc.Chim.France 2117 (1966).

2/ W.L.Meyer, D.L.Davis, L.Foster, A.S.Levinson, V.L.Savin,  
D.C.Shew and R.F.Wedderton, J.Amer.Chem.Soc. 87, 1573 (1965).

3/ S.L.Spassov, Tetrahedron 25, 3631 (1969) and unpublished results.



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

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Tel ext

Date

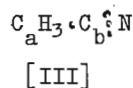
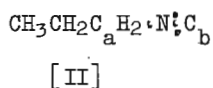
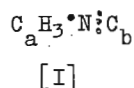
21st July, 1970.

Dear Professor Shapiro,

$^{13}\text{C}$  N.M.R. of Propylisocyanide

We recently observed the proton n.m.r. spectrum of propylisocyanide and noted a coupling of  $1.1 \pm 0.1$  Hz between the  $^{14}\text{N}$  nucleus and the protons of the methylene group adjacent to the nitrogen atom. The near zero electric-field gradient in isocyanides has been used by a number of workers (1-3) to obtain n.m.r. parameters involving  $^{14}\text{N}$  in these compounds.

We were interested to measure the  $^{13}\text{C}$  n.m.r. spectrum of propylisocyanide since it appears that the only reported  $^{13}\text{C}$  data of isocyanides was obtained on methyl isocyanide using an indirect method (4) and the nitrogen to carbon spin-spin coupling ( $J_{^{14}\text{N}-^{13}\text{C}_b}$  in [I]) could not be measured.



We have observed the  $^{13}\text{C}$  spectra of neat propylisocyanide [II] in a sealed 5 mm tube mounted concentrically in an 8 mm tube with dioxan as an external lock and obtained the following couplings.

$$\begin{aligned} J_{^{14}\text{N}-^{13}\text{C}_a} &= 6.1 \pm 0.2 \text{ Hz} \quad (\text{cf in [I]} \quad J_{^{14}\text{N}-^{13}\text{C}_a} = \pm 7.6 \pm 0.5 \text{ Hz}^4) \\ \text{and } J_{^{14}\text{N}-^{13}\text{C}_b} &= 5.3 \pm 0.2 \text{ Hz} \quad (\text{cf in [III]} \quad J_{^{14}\text{N}-^{13}\text{C}_b} = 17.5 \pm 0.5 \text{ Hz}^5) \end{aligned}$$

The relative signs of the coupling constants have not been determined but by analogy with the signs of the coupling constant for [I] and [II] it is probable that they are of opposite sign. The change in value of the nitrogen-carbon coupling in the formal triple bond from a



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cont'd .. ...

cyanide to isocyanide may reflect the relative degree of bond order and electron distribution in the two bonds. The chemical shifts of the carbon atom also tends to support this hypothesis since we found that in [II] the  $C_b$  shift was  $\delta_{CS_2} = 34.9$  p.p.m. which can be compared with a value of  $\delta_{CS_2}$  approximately 70 p.p.m. for a cyanide carbon.

Yours sincerely,

*G. R. Bedford D. Greatbanks*

G. R. BEDFORD D. GREATBANKS

Biological Chemistry Department

1. J.D. Ray, L.H. Piette and D.P. Hollis, J. Chem. Phys., 1958, 29, 1022.
2. I.D. Kuntz, P.R. Schleyer, and A. Allerhand, J. Chem. Phys., 1961, 35, 1553.
3. A. Lowenstein and Y. Margalit, J. Phys. Chem., 1956, 69, 4152.
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TEXAS CHRISTIAN UNIVERSITY

Fort Worth, Texas 76129

Department of Chemistry

July 22, 1970

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

Dear Barry: Solvent Effects on Fluoroform Shifts and Coupling

At long last we are moving into our new building. Our NMRs are all down, and one wonders if they will ever work again. It remains to be seen if the joys of all new quarters counterbalance the travails of building and moving into them.

Recently Art Ihrig has made a rather logical extension of the solvent effect work done by Lichter and Roberts (J. Phys. Chem., 74, 912 (1970)) on the proton and  $^{13}\text{C}$  chemical shifts of chloroform. The proton and fluorine chemical shifts of fluoroform in a variety of solvents have been determined using TMS and 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as internal references. The results are given below.

Lichter and Roberts chose to interpret their data as indicating a hydrogen bonding type interaction of the chloroform to the various solvents with a very specific complexation to benzene with the C-H bond along the six-fold axis of the solvent. However, fluoroform is a more polar entity (1.6D to 1.1D), and field effects of the solvent would be expected to be more important. There is a rough correlation of our data with  $(\epsilon - 1)/(\epsilon + 1)$ . Moreover, while the proton chemical shifts in all solvents except benzene are downfield from the value in cyclohexane, the fluorine chemical shifts move upfield with increasing solvent polarity.

Finally, using Johnson-Bovey type calculations leads to a value of 3.6-3.8 Å for the separation of the fluoroform proton and the center of the benzene ring if one assumes the sort of complex mentioned above. This view is supported by the fact that one then calculates that the fluorine chemical shift in benzene should be 0.23 ppm upfield from that in cyclohexane; a value in good agreement with the experimental value of 0.33 ppm.

Best regards,

*Bill*  
W. B. Smith  
Chairman  
Department of Chemistry

WBS/dc

## NMR Data for Fluoroform in Various Solvents

| Solvent                 | $\delta_{\text{H}}$ ppm | $\delta_{\text{F}}$ ppm | $J_{\text{HF}}$ Hz |
|-------------------------|-------------------------|-------------------------|--------------------|
| 1. Cyclohexane          | 6.25                    | 35.96                   | 79.31              |
| 2. Carbon tetrachloride | 6.46                    | 35.69                   | 79.23              |
| 3. Benzene              | 5.31                    | 35.73                   | 79.27              |
| 4. Anisole              | 5.89                    | 35.78                   | 79.26              |
| 5. Chloroform           | 6.47                    | 35.45                   | 79.25              |
| 6. Methylene chloride   | 6.54                    | 35.25                   | 79.35              |
| 7. Acetone              | 7.04                    | 34.70                   | 79.40              |
| 8. Nitrobenzene         | 6.83                    | 35.35                   | 79.32              |
| 9. Dimethylformamide    | 7.32                    | 34.63                   | 79.37              |
| 10. Acetonitrile        | 6.75                    | 34.39                   | 79.38              |
| 11. Nitromethane        | 6.74                    | 34.83                   | 79.38              |

## UNIVERSITY OF CALIFORNIA

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July 14, 1970

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

Dear Prof. Shapiro:

Metal Ion-Protein Interactions

1.  $^{35}\text{Cl}$  NMR of Zinc Proteins.

Larry Cottam (University of Texas SouthWestern Medical School) and I have been using  $^{35}\text{Cl}$  NMR and kinetics to study the zinc metalloenzyme, alkaline phosphatase from *E. coli*. The results, although disappointing in some respects, are interesting when compared to carbonic anhydrase a zinc enzyme recently reported on in the literature.<sup>1</sup>

The apo enzyme was prepared by dialysis against either EDTA or 8-hydroxy-quinoline-5-sulfonic acid. Titration of the apoenzyme at pH 8.0 with Zn, monitored by  $^{35}\text{Cl}$  NMR, open circles, revealed no chloride line broadening until the  $\text{Zn}^{2+}$ /protein ratio exceeded four. Corresponding titrations, monitored by hydrolysis of p-nitrophenylphosphate, closed circles, indicated that the enzyme was completely reactivated when the  $\text{Zn}^{2+}$ /protein ratio reached four, figure 1. The observed increase in chloride line width as the  $\text{Zn}^{2+}$ /protein ratio exceeds four is attributed to non-specific zinc binding by the protein.

The lack of a zinc-chloride interaction in the haloenzyme can be interpreted in terms of an inexcessable  $\text{Zn}^{2+}$  or a decrease in the chloride exchange rate such that the fast exchange criteria is no longer met.

2. NMR of Alkali Metal Ions.

Recent interest in alkali metal ion binding to proteins and nuclei acids has led us to examine the NMR of  $^{23}\text{Na}^+$ ,  $^{39}\text{K}^+$ , and  $^{205}\text{Tl}^+$ . A report in the literature that  $\text{Tl}^+$  can serve as a monovalent cation for the activation of pyruvate kinase and that there is close proximity of the  $\text{Tl}^+$  and  $\text{Mn}^{++}$  binding sites<sup>2</sup> has led us to study this system. We have been able to repeat the  $\text{Tl}^+$  experiment, but have been completely unsuccessful in observing an affect on the  $^{23}\text{Na}$  or  $^{39}\text{K}$  resonance upon the addition of  $\text{Mn}^{2+}$  to a solution of either NaCl or KCl and pyruvate kinase.


Prof. B. L. Shapiro

- 2 -

July 14, 1970

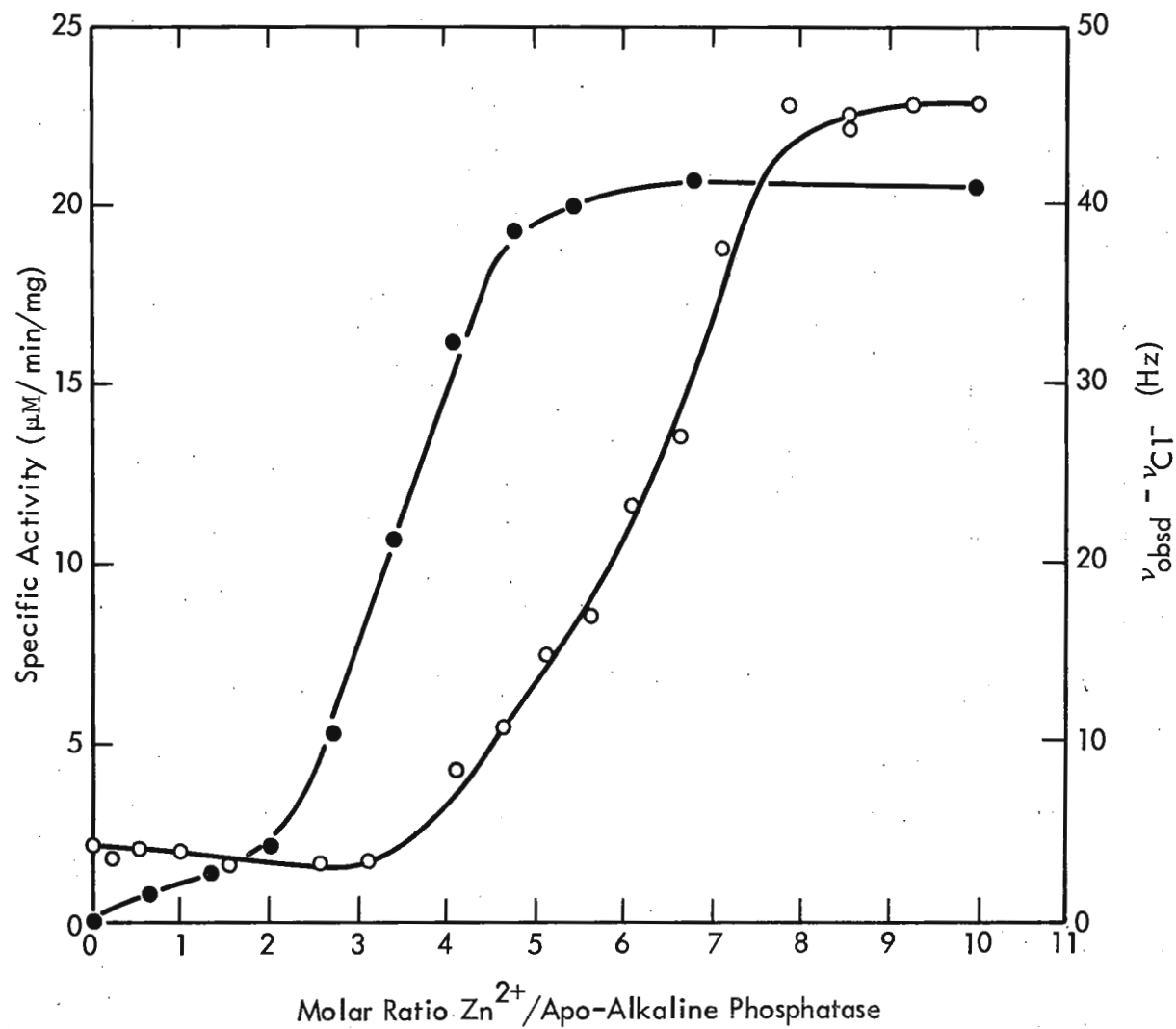
If the mechanism for the  $Tl^+$  broadening is a dipolar interaction with  $Mn^{2+}$ , as suggested by Kayne and Reuben, then one would expect the effect on the  $K^+$  and  $Na^+$  linewidths to be reduced by a factor  $\gamma_I^2$  or  $6.5 \times 10^{-3}$  and  $0.21$  respectively compared with  $Tl^+$ . The effect would be too small to observe in the case of  $K^+$ . The fact that no  $Na^+$  effect is observed might be related to the fact that  $K^+$  is an activator of the enzyme while  $Na^+$  is not.

Sincerely yours,



Bert Holder  
Raymond Ward (subscription credit)  
James Happe  
Al Maddux

- 
- (1) R. L. Ward; Biochemistry 9, 2447 (1970)  
(2) F. J. Kayne and J. Reuben; JACS 92, 220 (1970)



Titration of apoalkaline phosphatase with zinc ion. The reaction mixtures contained 3.13 mg per ml apoalkaline phosphatase, 0.57 M NaCl, 0.01 M Tris-HCl, pH 8.0, and the noted ratio of zinc/protein in a total volume of 0.70 ml.





July 13, 1970

Professor E. L. Shapiro  
Dept. of Chemistry  
Texas A and M University  
College Station, Texas 77843

<sup>35</sup>Cl and <sup>19</sup>F NMR Spin-Lattice Relaxation Time Measurements  
and Rotational Diffusion in Liquid ClO<sub>3</sub>F

Dear Barry,

Arthur Maryott and I at NBS and Dr. M. S. Malmberg from the University of Maryland have just finished a NMR relaxation time study of ClO<sub>3</sub>F over its entire liquid range (130 to 368 K). The chlorine relaxation which is due solely to the nuclear quadrupole interaction can be used together with the known quadrupole coupling constant to determine the correlation time for molecular orientation,  $\tau_{0,2}$ . The fluorine relaxation is dominated by the spin-rotation interaction with only a small intermolecular dipole contribution at the lowest temperatures. In order to obtain the angular momentum correlation time,  $\tau_j$ , an independent estimate of the spin-rotation tensor was made by combining gas phase measurements of  $T_1$  (<sup>19</sup>F) with previous data on the chemical shift and gas phase dielectric relaxation. The results for this quasi-spherical molecule are in accord with rotational diffusion theory and Hubbard's<sup>1</sup> relation,  $\tau_{0,2}\tau_j = 1/4\kappa T$ , at the lowest temperatures and agree over the entire range with the extended treatment of McClung.<sup>2</sup>

<sup>1</sup>P. S. Hubbard, Phys. Rev. 131, 1155 (1963).

<sup>2</sup>R. E. D. McClung, J. Chem. Phys. 51, 3842 (1969).

Best regards,

*T. C. Farrar*

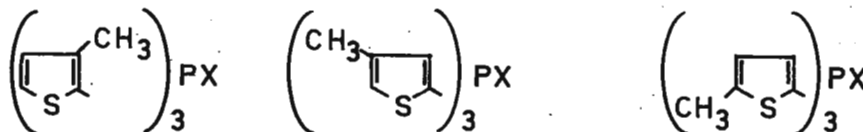
T. C. Farrar  
Crystallography Section  
Inorganic Materials Division, IMR

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

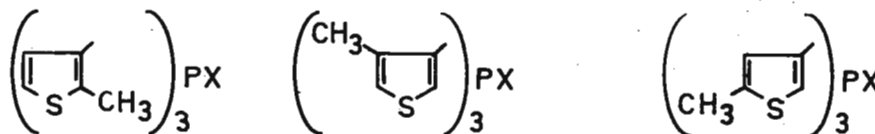
SIGNS AND MAGNITUDES OF LONG-RANGE  $\text{CH}_3$ - $^{31}\text{P}$  COUPLING CONSTANTS  
IN TRI-(METHYLTHIENYL)-PHOSPHINE DERIVATIVES

Dear Professor Shapiro,

In our studies on  $^1\text{H}$ - $^{31}\text{P}$  coupling constants in hetero-aromatic phosphine derivatives it was recently stated<sup>1</sup> that the signs of the couplings determined so far between ring protons and phosphorus are the same as the corresponding  $^1\text{H}$ - $^1\text{H}$  couplings. As an extension of this work it was of interest to see if this also holds for the long-range  $\text{CH}_3$ - $^{31}\text{P}$  couplings in the analogous methyl-substituted compounds. Up to now we have succeeded in the synthesis and PMR analysis of the derivatives listed below. The signs of the coupling constants were obtained from homonuclear selective decoupling and tickling experiments; an example is shown in the figure.



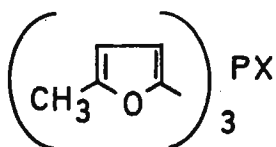
$$\begin{array}{lll} \text{a: } ^4J_{\text{CH}_3-\text{P}} = +0.44 \text{ Hz} & ^5J_{\text{CH}_3-\text{P}} = +0.25 \text{ Hz} & J_{\text{CH}_3-\text{P}} = +0.52 \text{ Hz} \\ \text{b: } ^4J_{\text{CH}_3-\text{P}} = -1.57 \text{ Hz} & ^5J_{\text{CH}_3-\text{P}} = +0.78 \text{ Hz} & |J_{\text{CH}_3-\text{P}}| < 0.15 \text{ Hz} \end{array}$$



$$\begin{array}{lll} \text{a: } ^4J_{\text{CH}_3-\text{P}} = +0.35 \text{ Hz} & ^4J_{\text{CH}_3-\text{P}} = +0.62 \text{ Hz} & |^5J_{\text{CH}_3-\text{P}}| < 0.15 \text{ Hz} \\ \text{b: } ^4J_{\text{CH}_3-\text{P}} = -1.72 \text{ Hz} & ^4J_{\text{CH}_3-\text{P}} = -0.65 \text{ Hz} & ^5J_{\text{CH}_3-\text{P}} = +0.68 \text{ Hz} \end{array}$$

a: X = Lone pair; b: X = Sulphur

-2-



X = Lone pair :  $J_{\text{CH}_3-\text{P}} = +0.19 \text{ Hz}$

X = Sulphur :  $J_{\text{CH}_3-\text{P}} = -0.46 \text{ Hz}$

X =  $\text{CH}_3\text{I}$  :  $J_{\text{CH}_3-\text{P}} = -0.38 \text{ Hz}$

A change in the sign for the long-range  $\text{CH}_3-^{31}\text{P}$  coupling is generally observed upon tetracoordination of phosphorus. The signs of the couplings in the phosphine sulphides are similar to those obtained for the analogous  $\text{CH}_3-\text{H}$  couplings in methylthiophenes<sup>2</sup>, the magnitudes being somewhat larger probably caused by larger  $\sigma$ -contributions to the couplings in tetracoordinated phosphorus derivatives.<sup>1</sup>

The opposite sign sequence generally observed for the  $\text{CH}_3-^{31}\text{P}$  couplings in the phosphines (X = lone pair) is probably related to a difference in the sign for the  $\pi$ -contributions to the couplings in the two series of compounds. Thus from the above results evidence is obtained for a positive hyperfine interaction ( $Q_{\text{C-P}} > 0$ ) in  $\text{P}^{\text{III}}$  compounds and a negative term ( $Q_{\text{C-P}} < 0$ ) in  $\text{P}^{\text{IV}}$  and  $\text{P}^{\text{V}}$  compounds. The details of this study will be published in J. Mol. Spectrosc.

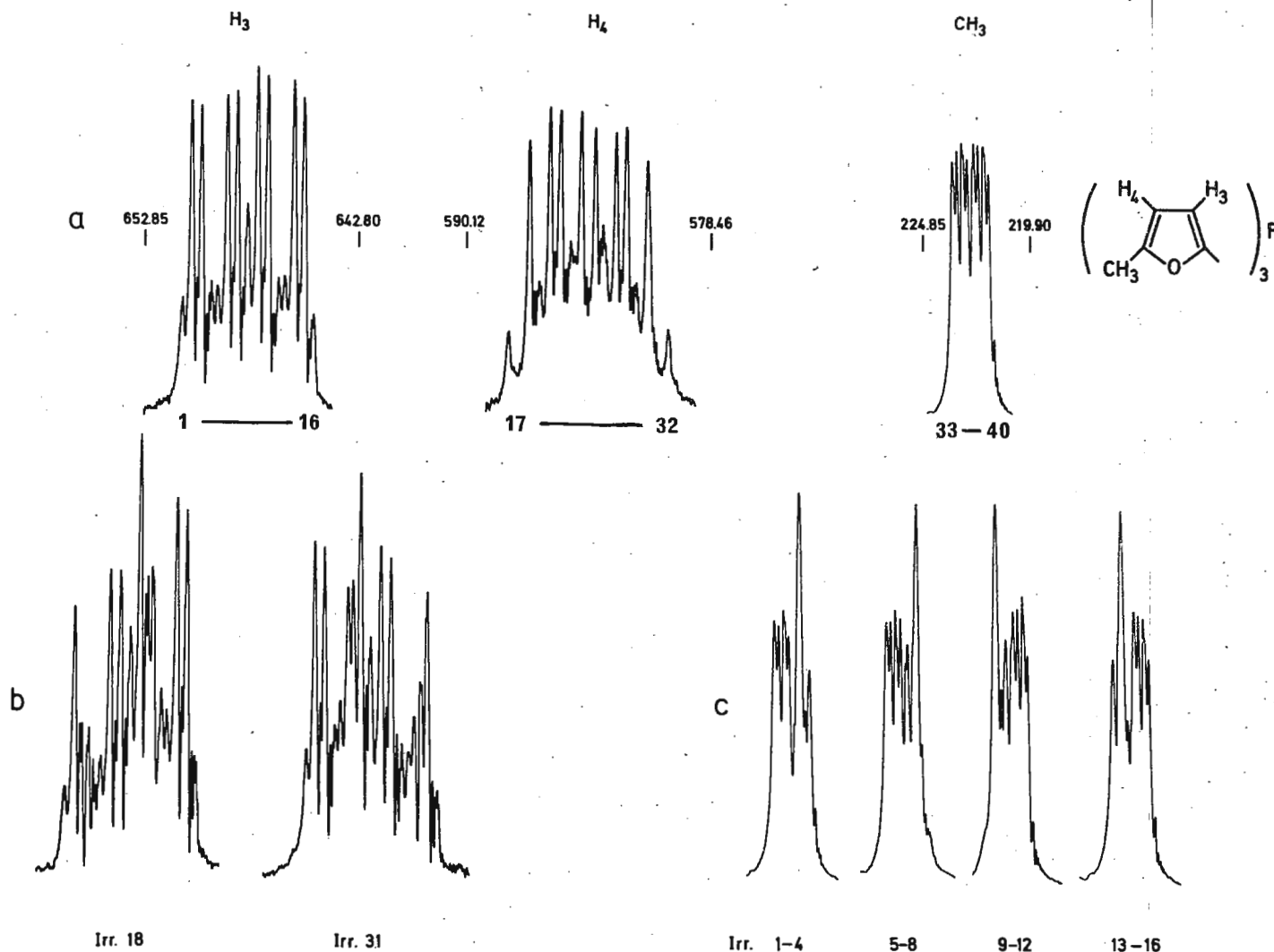
Sincerely yours,

*Hans Jørgen Jakobsen*  
Hans Jørgen Jakobsen

Please credit this contribution to the subscription of this institute (Dr. Henning Lund).

1. H.J.Jakobsen, J.Mol.Spectrosc. 34, 245 (1970) and refs. cited.

2. B.Gestblom et al., Arkiv Kemi 23, 517 (1965) and refs. cited.



**Figure.** 100 MHz single and double resonance proton spectra of tri-(5-methyl-2-furyl)-phosphine, 15% w/w in CS<sub>2</sub>. In (a) the single resonance spectrum is displayed. In (b) H(3) proton spectra are recorded while the H(4) transitions 18 and 31 are in turn being weakly irradiated (tickled). In (c) the methyl resonance spectra, obtained by in turn selective decoupling of <sup>5</sup>J<sub>CH<sub>3</sub>-H(3)</sub> in the four H(3) quartets, are shown. From these experiments it is concluded that <sup>3</sup>J<sub>P-H(3)</sub>, <sup>4</sup>J<sub>P-H(4)</sub>, and J<sub>CH<sub>3</sub>-P all have the same sign (positive), that <sup>4</sup>J<sub>CH<sub>3</sub>-H(4)</sub> and <sup>5</sup>J<sub>CH<sub>3</sub>-H(3)</sub> are of opposite sign (negative and positive, respectively), and that <sup>3</sup>J<sub>H(3)-H(4)</sub> and <sup>4</sup>J<sub>CH<sub>3</sub>-H(4)</sub> are of opposite sign (positive and negative, respectively).</sub>

THE UNIVERSITY OF NORTH CAROLINA  
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DEPARTMENT OF CHEMISTRY

July 22, 1970

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

Van Vleck's Moment Equations Revisited

Dear Barry:

In connection with recent experiments on magnetically dilute solids (1) we became interested in the resonance line shapes for such samples. Information about this point can be obtained from the ratios of the 4th moments to the squares of the 2nd moments of the lines. Limited calculations based on Van Vleck's equations (2) have indicated that the line shapes are probably Gaussian for high concentrations of magnetic particles and Lorentzian at low concentrations. (3) We thought it would be worthwhile to perform more extensive calculations for crystals, powders, and glasses with the help of a digital computer.

With a simple cubic lattice the lattice sums required for the 2nd and 4th moments and probably for the 2nth moment can be fit to power series of the

type  $\sum_{m=1}^{2n} c_m L_{2m}$  where  $L_p \equiv \sum_{i=1}^3 \lambda_i^p$  and the  $c_m$  are constants. We have calculated these constants for the 2nd and 4th moments and for example have obtained the following expression for the 2nd moment:

$$\langle \Delta v^2 \rangle = 37.326 g^4 \beta^4 h^{-2} d^{-6} \frac{S(S+1)}{3} (\lambda_1^4 + \lambda_2^4 + \lambda_3^4) - 7.2722$$

Van Vleck obtained 36.8 and -6.88 for the constants in a similar equation. Our calculations lead us to believe that he used between 200 and 500 lattice points while we have summed over  $10^5 - 10^6$  lattice points. The 2nd moments are shown in the figure for different directions of the magnetic field in planes passing through the crystallographic z-axis and for different angles  $\phi$  between these planes and the x-axis. The magnitude of the 2nd moment in a given direction is represented by the length of a vector from the origin in that direction. As indicated the 2nd moment reaches its minimum in the [1,1,1] direction and its maximum along the axes. Similar plots are being prepared for the 4th moment  $\langle \Delta v^4 \rangle$  and for the ratio  $\langle \Delta v^4 \rangle / \langle \Delta v^2 \rangle^2$ .

Professor Bernard L. Shapiro  
Page 2  
July 22, 1970

For a glass the lattice sums must be replaced by integrals involving the appropriate distribution functions for the magnetic particles. When the distribution is isotropic, the integration can be performed analytically for the 2nd moment, but for the 4th moment must be done numerically. Various types of numerical calculations are presently underway.

Exchange terms have not been taken into account in our calculations. This can, of course, be done if a definite functional dependence of the exchange interaction upon interparticle distance is assumed. Also, the programs can easily be modified to permit calculations for lattices with lower than cubic symmetry. Details of the calculations will be presented elsewhere.

Sincerely yours,

  
G. W. Canters

  
C. S. Johnson, Jr.

GWC:CSJ:bs

1. H. M. McIntyre, T. B. Cobb, and C. S. Johnson, Chem. Phys. Lett. 4, 585 (1970).
2. J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).
3. C. Kittel and E. Abrahams, Phys. Rev. 90, 238 (1953).

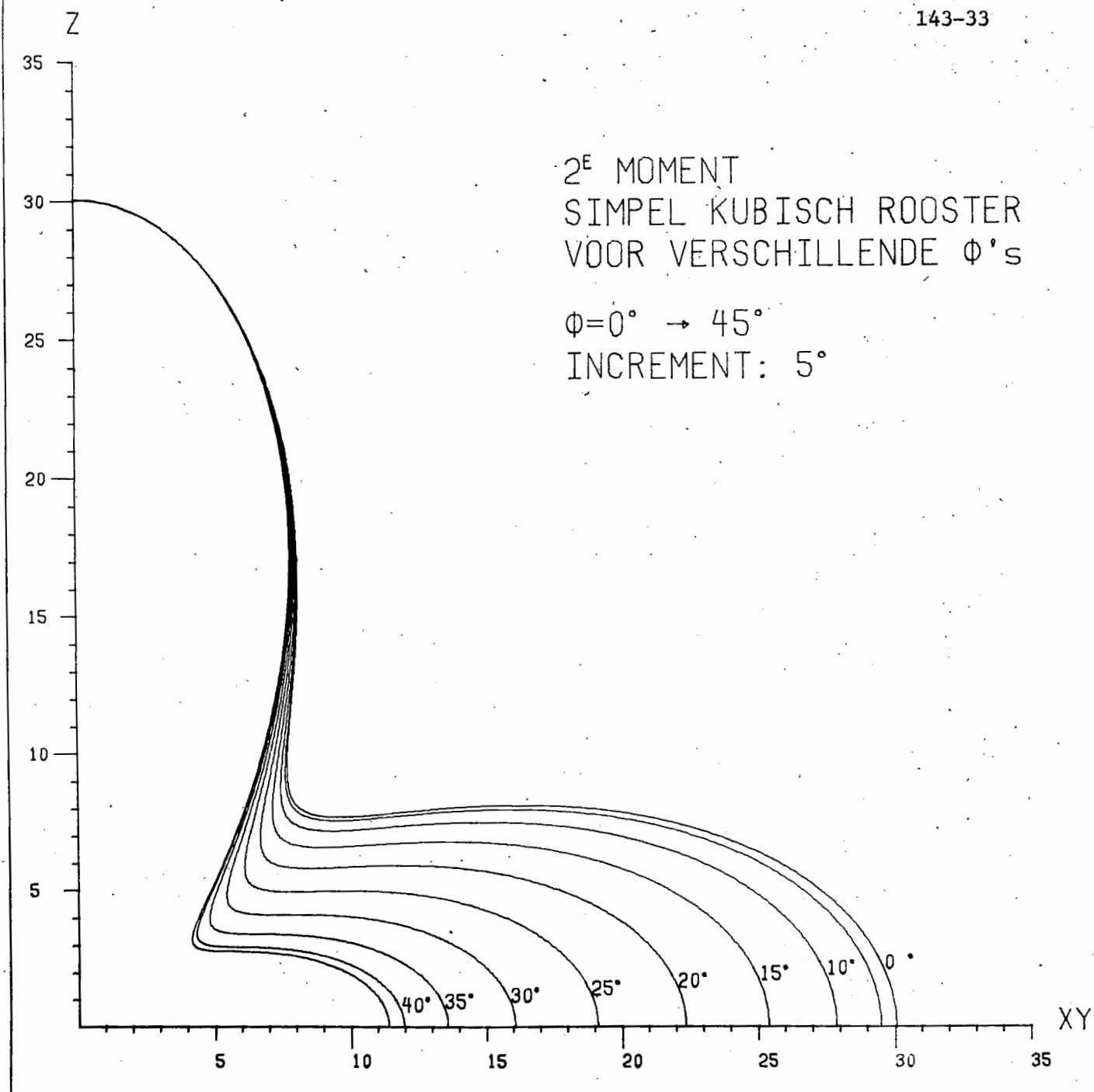


FIGURE 1

(Second moment)/A of simple cubic lattice for different directions of external field.

$$[A = \frac{1}{3} S(S + 1) g_N^4 \beta_N^4 h^{-2} d^{-6}].$$

DEPARTMENT OF ORGANIC CHEMISTRY  
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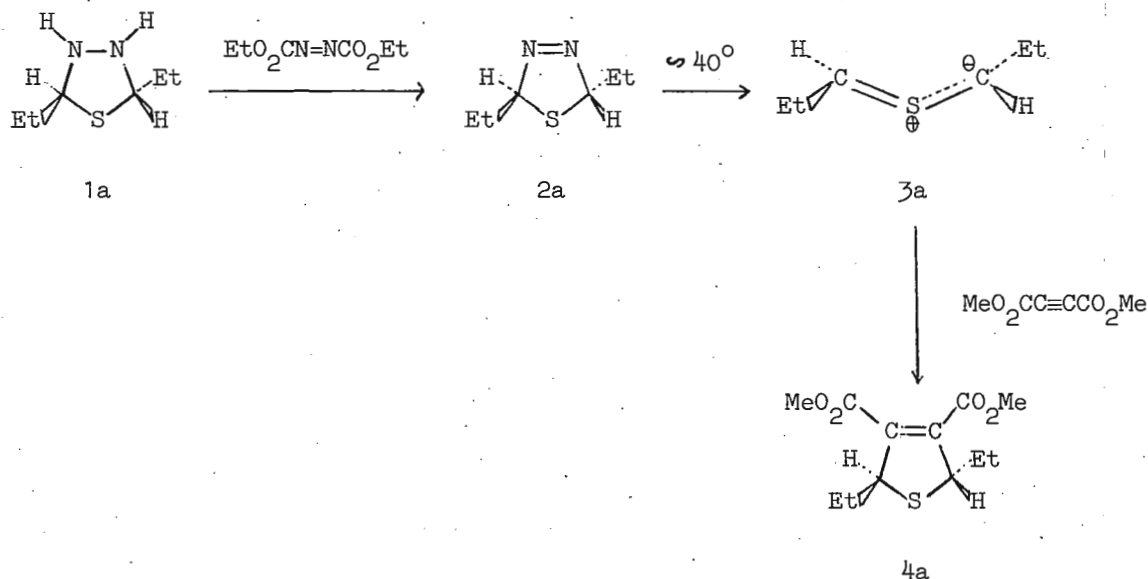
Groningen, July 23, 1970.

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

The stereochemistry of symmetrically substituted 2,5-dihydrothiophenes and  
2,5-dihydro-1,3,4-thiadiazolines.

Dear Professor Shapiro,

We recently have had occasion to use nmr in defining the stereochemistry of a cycloaddition reaction. Normal chemical techniques allowed isolation of 1a, presumed but not proven to be trans. Oxidation of 1a to 2a was accomplished as

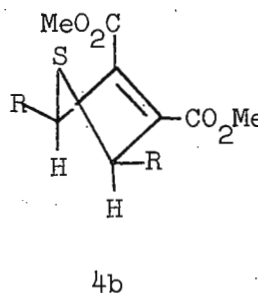
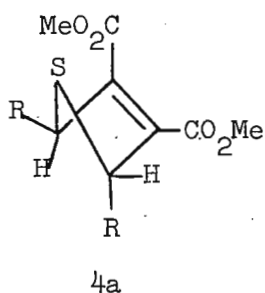


shown and 2a decomposes smoothly ( $\Delta G^* = 28$  kcal/mol, as determined by nmr) to give the highly reactive thiocarbonyl ylide 3a, which in turn undergoes cycloaddition with dimethyl acetylenedicarboxylate to yield the 2,5-dihydrothiophene 4a. Although the stereochemical assignments shown were expected, confirmation was required and this was obtained from nmr spectra. Compound 4a showed the 2 and 5-protons



(tertiary) as a symmetrical 12 line (at least) multiplet. The adjacent methylene protons were decoupled leaving a nearly degenerate AB system,  $J = 6.0$  cps. When the reaction sequence was repeated starting with a mixture of 1a and the corresponding compound 1b, presumed to be cis (1b is so unstable as to preclude independent isolation), a mixture of 4a and 4b was ultimately obtained. The tertiary protons were well separated in 4a and 4b with those of 4b lying at 0.2 ppm higher field. The absorptions of the tertiary protons of 4b consisted of a triplet,  $J = 6.0$  cps, with an imposed splitting of 1.5 cps. Decoupling of the methylene protons gave a singlet for the tertiary protons.

These data require that 4a be trans and 4b cis; this follows since models



show 4a to be puckered and the tertiary hydrogens to be nonequivalent so long as the average conformation remains puckered. The AB system remaining after decoupling of the methylene protons arises from long-range 2,5-coupling. In 4b a plane of symmetry is always maintained during ring-flip and the tertiary protons are necessarily equivalent.

Similar phenomena are observed with both 2a and 2b allowing unambiguous assignments of the stereochemistry of 2a and 2b (and by deduction of 1a and 1b also). The stereochemical course must then be as depicted in the scheme.

Sincerely yours,

*Richard M. Kellogg*

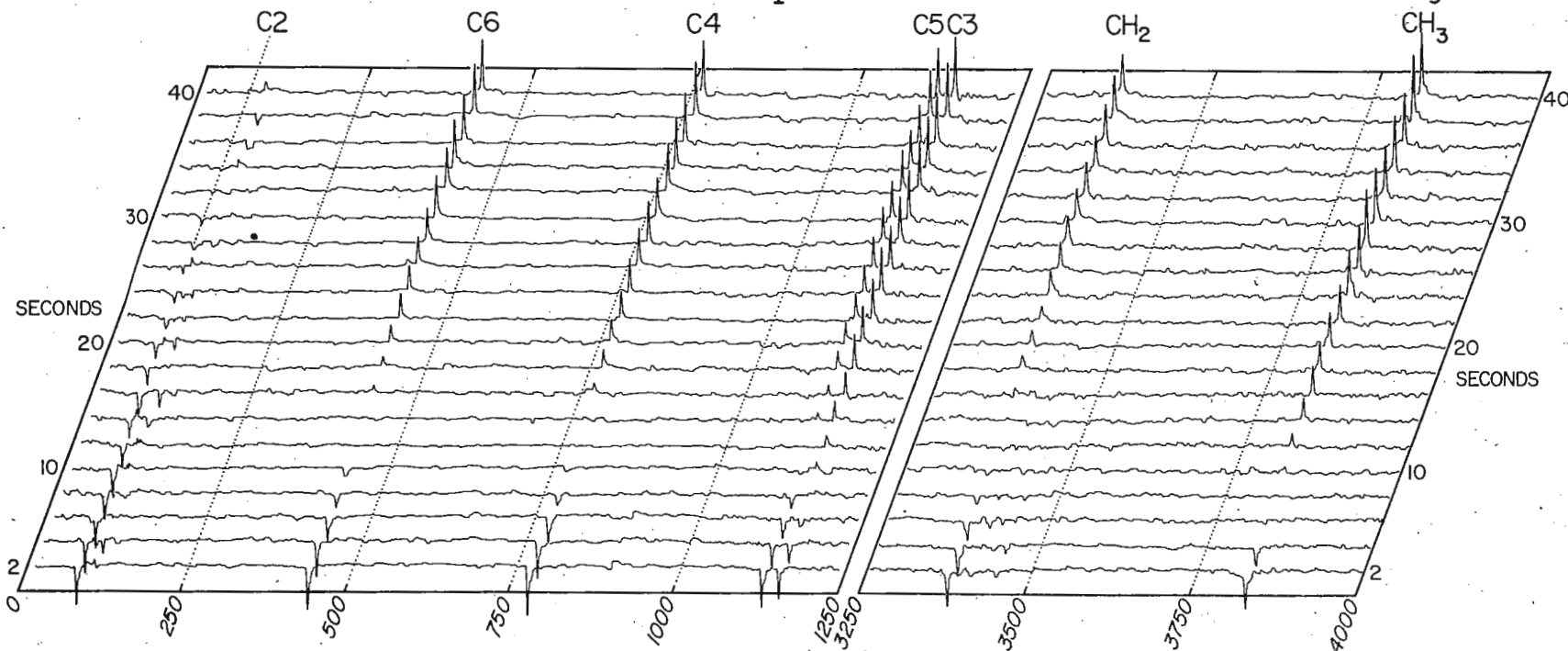
Dr. R.M. Kellogg.

Dear Barry,

A new dimension in Carbon-13 spectroscopy ?

July 27th 1970

Stung by criticism that we can only handle two- and three-spin systems<sup>1</sup> we have recently turned to the ideal single-spin system -- carbon-13 with proton noise decoupling. A Fourier transform machine (VFT-100) and an XL-100 have been automated to measure individual spin-lattice relaxation times by an adaptation of the technique first described by Vold et al.<sup>2</sup> The pulse sequence can be written  $(T - 180^\circ - t - 90^\circ)_n$ , where the waiting time  $T$  is long compared with the longest  $T_1$ , the interval  $t$  is varied over a range of  $m$  values, and the accumulation number  $n$  is determined by the required signal-to-noise ratio. The total experimental time (very roughly mnT sec) is normally arranged to be overnight or over the weekend, and the program automatically stacks the spectra on the recorder to give a 3D plot of the spin-lattice recovery after population inversion, carefully shaking the pen before starting each record. (Note the analogy with a graduate student.) The resulting  $T_1$  values can be used for diagnostic purposes or as collector's items. The attached diagram is for 2-ethylpyridine, and gives for C2, (no directly attached protons) 68 sec; for CH<sub>2</sub>, C4, C5, C6,  $22 \pm 1$  sec; for C3, 15 sec and for CH<sub>3</sub>, 14.4 sec. Note that C3 and C5, which are very difficult to assign on the basis of carbon or proton shifts, can be differentiated if the shorter  $T_1$  is assumed to be due to proximity to the CH<sub>3</sub> protons.



<sup>1</sup>Shapiro, "Son of Epexegesis" I.I.T.N.M.R. 107, 67 (1967).

<sup>2</sup>Vold, Waugh, Klein and Phelps, J. Chem. Phys. 48, 3831 (1968).

Best wishes, *Ray*

Ray Freeman, Howard Hill.





## NORTHERN ILLINOIS UNIVERSITY

DEKALB, ILLINOIS 60115

THE MICHAEL FARADAY LABORATORIES

Area Code 815

DEPARTMENT OF CHEMISTRY

Telephone 753-1181

July 31, 1970

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

## Tone Bursting and Heteronuclear Spin Decoupling

Dear Barry:

During the course of our experiments concerning hydrogen bonding in amides we have employed  $1_{\text{H}} - \{14_{\text{N}}\}$  spin decoupling in order to obtain more accurate chemical shifts of the NH proton. A problem which arises is that the relatively high radiofrequency levels used cause sample heating which makes temperature control difficult. A simple and inexpensive technique which relieves this difficulty is described herein.

In our experiments an NMR Specialties HD - 60B heteronuclear spin - decoupler was used with a Varian A60-A nmr spectrometer and a General Radio 1396-B Tone - Burst Generator (TBG). The duration of a burst and the interval between bursts, in cycles or seconds, can be individually adjusted. The TBG cannot be connected directly between the decoupler, which has an output of approximately 4.33Mhz, and the irradiation coil in the probe because of the 2Mhz upper frequency limit of the TBG. However, the sinusoidal audiofrequency input to the decoupler can be tone - burst giving the desired pulse effect at the sample provided the decoupler carrier signal is properly nulled. In typical experiments the on and off times were of the order of 10-20 microseconds.

Sincerely,

*John*  
John D. Graham

*Lori*  
Laurine L. Graham



dr. L. Lunazzi

Istituto di Chimica Organica e di Chimica Industriale  
dell'Università di Bologna

li 26.5.1970

Viale Risorgimento, 4 - Tel. 42.18.80  
c.a.p. 40136

Prof. B.L. SHAPIRO  
Texas A and M University  
Chemistry department  
College Station

TEXAS 77843 - U.S.A.

Title: Proton-carbon couplings of the halogeno acetylenes.

Dear Professor Shapiro,

following our previous investigations [L. Lunazzi and F. Taddei, Spectrochim. Acta 23A, 841 (1967) and ibid. 25A, 553 (1969)] on the  $J_{C^{13}H}$  in aliphatic and ethylenic derivatives, we begun the task to determine the proton-carbon couplings of  $X-C \equiv C-H$  where  $X = F, Cl, Br, I$ .

While many values are reported on carbon-proton coupling in acetylenic derivatives [Bull. Soc. Chim. France 1966, p. 1774 and Recueil 87, 1387 (1968)] no such data are available for the halogeno acetylenes.

They are actually very dangerous compounds, since easily explode at the contact with air, nonetheless we managed to collect them as neat liquids in NMR tubes by using a vacuum line; the spectra of  $F-C \equiv C-H$  and  $Cl-C \equiv C-H$  had to be recorded, however, at low temperature because of their boiling points ( $-104^\circ$  and  $-29^\circ$ ).

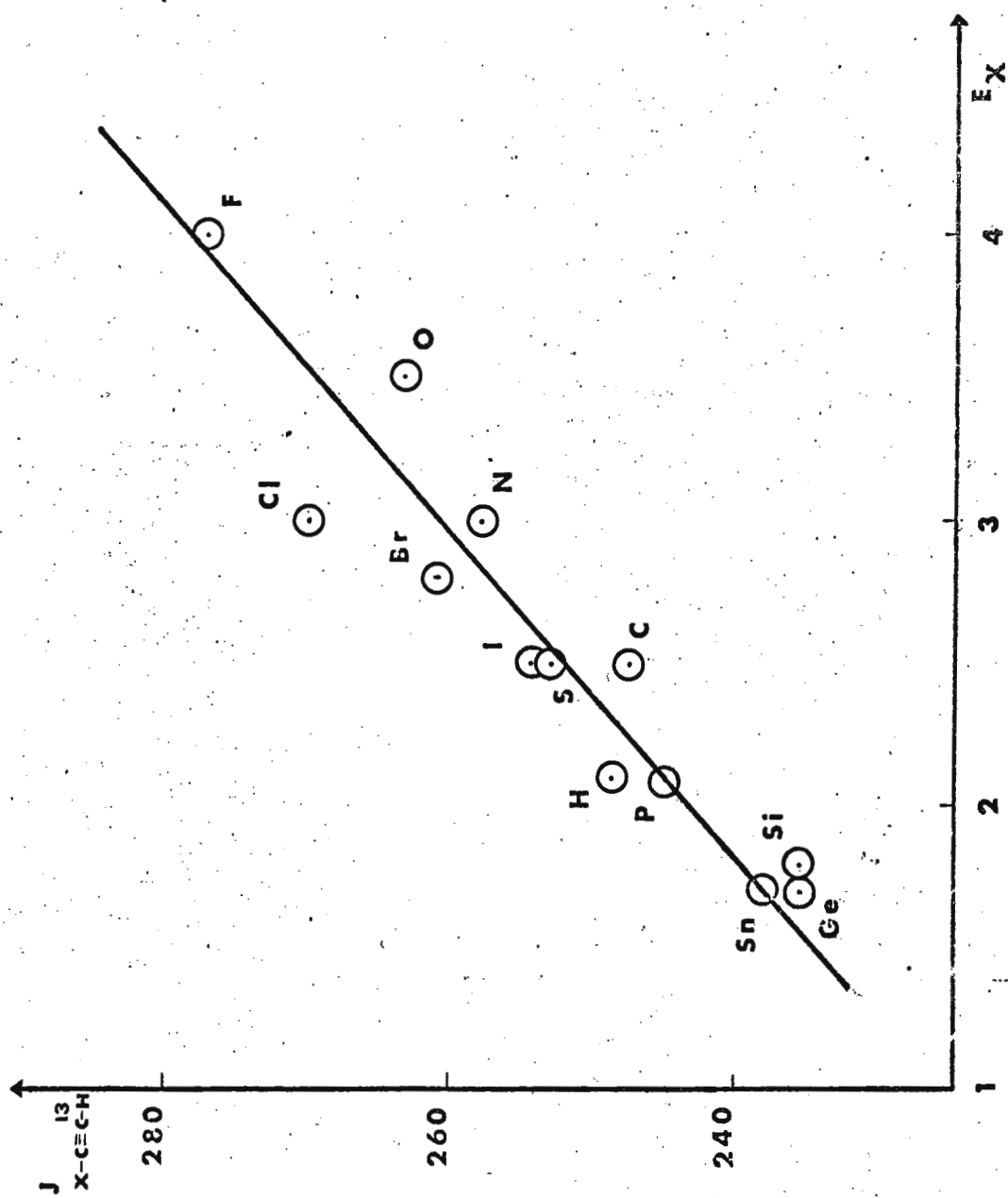
The  $C^{13}$  satellites were detected from both the isotopic species  $X-C^{13} \equiv C^{12}-H$  and  $X-C^{12} \equiv C^{13}-H$  in natural abundance: the corresponding values are as following:

|                   | $J_{C^{13}CH}$ | $J_{CC^{13}H}$ |
|-------------------|----------------|----------------|
| $F-C \equiv C-H$  | 65.5           | 277.5          |
| $Cl-C \equiv C-H$ | 60.5           | 270.0          |
| $Br-C \equiv C-H$ | 56.0           | 261.0          |
| $I-C \equiv C-H$  | 51.5           | 255.0          |

These values are depending on the electron withdrawing power of the substituent and a linear relationship, including all the known  $J_{CC^{13}H}$  couplings, is thus proposed with the Pauling's electronegativity (see Figure).

The complete communication is scheduled to appear soon on Molecular Physics. Yours sincerely

(Ludovico Lunazzi)  
Ludovico Lunazzi





dr. L. Lunazzi

Istituto di Chimica Organica e di Chimica Industriale  
dell'Università di Bologna

li 26.5.1970

Viale Risorgimento, 4 - Tel. 42.18.80  
c.a.p. 40136

Prof. B.L. SHAPIRO  
Texas A and M University  
Department of Chemistry  
College Station  
T E X A S 77843 - USA

Title: What about E.S.R.?

Dear Professor Shapiro,

with the shameful purpose to take the greatest advantage from the small amount of money invested on the TAMU Newsletters I wish to advance a proposal concerning the feasibility to host in these pages accounts of researches in the field of the Electron Spin Resonance spectroscopy (E.S.R.).

The number of NMR workers interested, and in many cases actually working, on this field is steadily growing and the applications of ESR to chemical and physical problems are probably now as large as were those of NMR when the "Founding Fathers" first edited the MELLON Newsletters.

Proofs of the strong ties between the two sister disciplines are, among the others, the statements of the two more recent Journals devoted to NMR studies (the american J. Magnetic Resonance and the british Organic Magnetic Resonance) which welcome papers dealing with ESR spectroscopy.

I would like therefore to know the opinions of the readers of TAMU Newsletters about the usefulness and the opportunity of opening the pages of our report to accounts on ESR researchs.

I also request the opinion of our "magister et dominus" (better known as professor B.L. Shapiro) about the financial implications of such a proposal.

Does he forecast that such an event will make the editing work by far too cumbersome to be handled in the satisfactory way we are used to?, or does he think that the greater number of contributors would help to relative the financial strain always ominously pending upon the TAMU Newsletters?.

On a purely scientific ground I am convinced that such a generous step would lead to a wider and deeper knowledge of the problems debated in the Laboratories of magnetic resonance, for, even though in the beginning the flow of ESR accounts cannot be expected to be too large, I have no doubt that the "advertising work" made by NMR scientists to the colleagues operating in ESR will make it grow very quickly.

I apologize for daring to make such an unorthodox (and perhaps even heretic) proposal and, in order to avoid the obvious suspicion of using the present letter as a tricky device for delaying the arrival of the coloured cards I include a report on the most recent results (obviously on NMR!) obtained in our lab.

Best wishes  
(Lodovico Lunazzi)

*Lodovico Lunazzi*

## TEXAS A&amp;M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

Department of  
CHEMISTRY

3 August 1970

Professor L. Lunazzi  
Istituto de Chimica Organica  
e di Chimica Industriale  
Viale Risorgimento, 4  
40136 Bologna, Italy

Reply to "What About E.S.R.?"

Dear Professor Lunazzi:

Let me reply to your thoughtful letter entitled "What about E.S.R.". First of all, let me assure you that I am delighted at any suggestions--unorthodox or even heretical--about the NMR Newsletter. You, and indeed all Newsletter recipients, have an open, permanent invitation to continue to write on any and all matters of interest to you.

I regret that my initial reaction to your proposal to include E.S.R. matters in the TAMU NMR Newsletter is somewhat negative. Over the years I have resisted such a move, for a variety of reasons, including some rather strong practical ones. However, I do not have a closed mind on the subject, and I will look forward to hearing from other Newsletter recipients about your idea of opening up the scope of the Newsletter to include E.S.R. In the absence of substantial feedback from the recipients of the Newsletter, however, I will probably take the easy way out (hardly the attitude of a real "magister et dominus") and limit the Newsletter to matters involving at least some NMR component.

As with other forms of spectroscopy, it is quite possible that E.S.R. could benefit from a newsletter. Indeed, one or two other spectroscopic areas already have newsletters patterned to some extent on the now almost twelve-year old NMR Newsletter. Perhaps it would be more effective, as well as better for the NMR Newsletter, if a separate NMR Newsletter were operated by someone with interest and competence in this field. (Perhaps not. Maybe you yourself would like to undertake such a venture. If so, I will be happy to provide whatever help and/or warnings you or anyone else might find useful.

I will keep you posted about any feedback from the Newsletter recipients which I receive concerning your suggestion.

Sincerely,



Bernard L. Shapiro

BLS:ic

## THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

July 31, 1970.

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

RE:  $^1\text{H}-\{^1\text{H}\}$  INDOR Studies

Dear Barry,

Some time ago, Roland Burton, Paul Steiner and I developed a very convenient method for measuring  $^1\text{H}-\{^1\text{H}\}$  INDOR spectra on our Varian HA-100. Details of our early development studies on carbohydrate derivatives are contained in a paper which should appear shortly in the Canadian Journal of Chemistry.

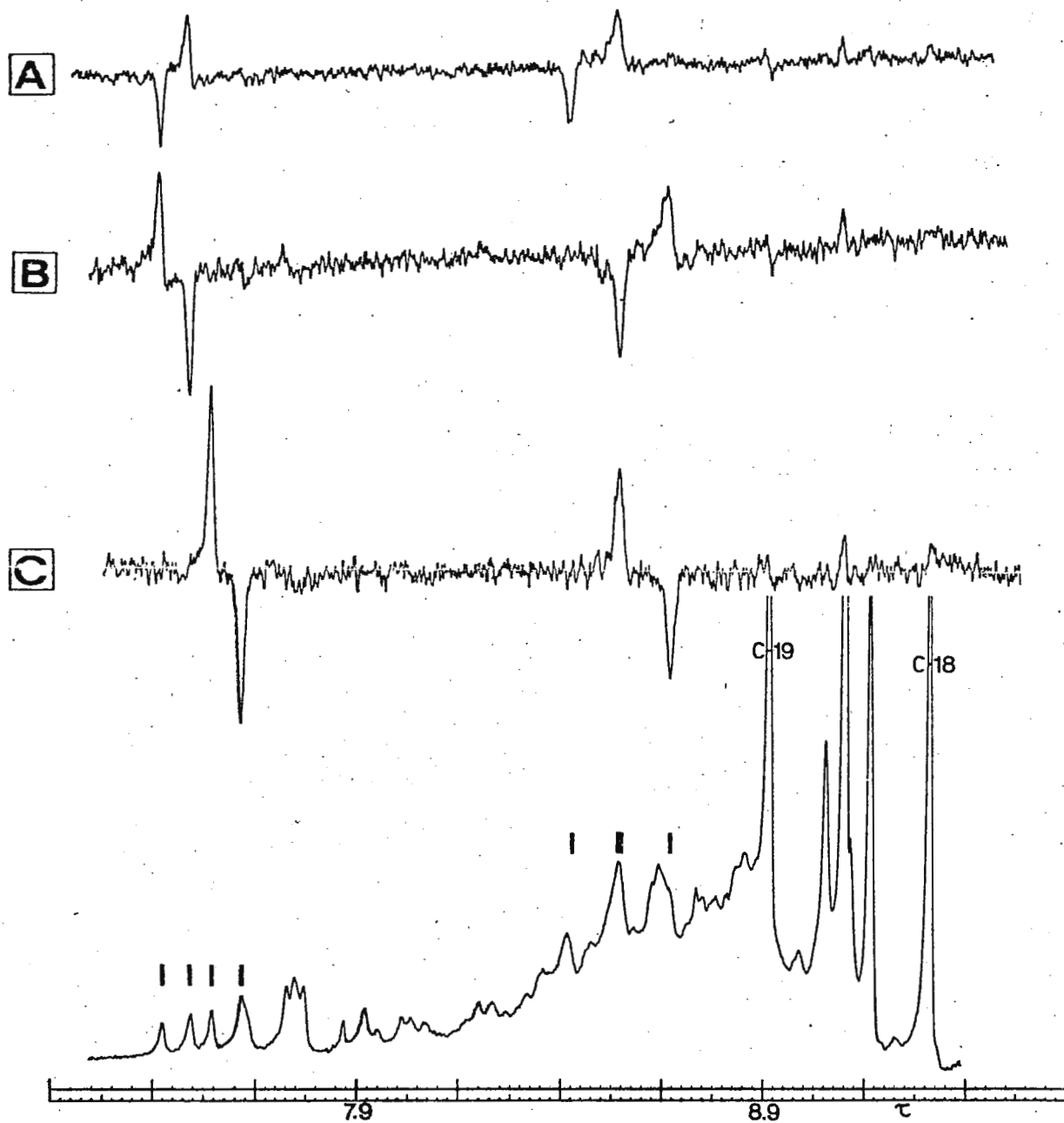
Chris Grant has now extended that work to more complex systems, with some success. The attached spectrum shows the responses obtained from a steroid derivative. Three transitions of a low field proton were monitored in turn, giving the traces shown in A, B and C. The relationship between these three sets of responses and the original spectrum is quite obvious. Clearly this is an incisive method for solving the "hidden resonance" problem which appears to plague p.m.r. studies of so many natural products.

With best wishes,

*L.D. Hall*

L.D. Hall





Universidad de Buenos Aires  
Facultad de Ciencias Exactas  
y Naturales

BUENOS AIRES, July 24, 1970.-

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

Position Available

Dear Dr. Shapiro:

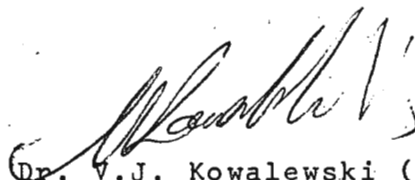
We are interested in graduates in Physics or Chemistry for a full-time position in the field of N.M.R. beginning September 1st. (or later)

Any person interested should write to either of the undersigned as soon as possible.

Sincerely yours,



Dra. D.G. de Kowalewski (2)  
Associate Professor



Dr. V.J. Kowalewski (1)  
Professor

Field of research:

(1) Development of new NMR techniques <sup>and</sup> experiments.

(2) Properties of J's, Determination of small equilibrium constants

Address

Department of Physics  
Faculty of Exact Sciences  
Perú 222 - Buenos Aires  
ARGENTINA



## BELFER GRADUATE SCHOOL OF SCIENCE

Amsterdam Avenue and 186th Street / New York, N.Y. 10033 / (212) Lorraine 8-8400

July 29, 1970

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

Dear Professor Shapiro:

I would very much appreciate your including the following information in your next News Letter.

Postdoctoral position available with primary responsibility for work in the following area:  
Pulsed and c.w. wide-line nmr spectroscopy. "On-line" interfacing PDP 12 computer with pulsed and c.w. wide line nmr spectrometers. Pulsed nmr experiments on adulterated hydrocarbons in the gas phase.

Many thanks for your kind assistance.

Sincerely yours,

A handwritten signature in cursive script, appearing to read "Max Lipsicas".

Professor Max Lipsicas

ML:hm

## TEXAS A&amp;M UNIVERSITY

## COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

Department of  
CHEMISTRY

3 August 1970

TAMU NMR NEWSLETTER SUBSCRIPTIONS

It is once again getting close to the annual "renew the subscription" time. I would appreciate very much any comments from the Newsletter readers about possible realistic improvement in the (financial) subscription handling of the NMR Newsletter. If our Sponsors and Contributors come through again this year like last, we will be able to maintain the same subscription rate for the 1970-71 year as for the present year. Much as I would like to, a reduction in this rate seems unlikely in the absence of a few rather sizable contributions from our industrial benefactors. In any event, we will soon have to send out some kind of a form and start the annual collection of money to keep the Newsletter coming off the presses. The current (financial) subscription year ends with the September 1970 issue. The necessary, periodic technical contributions will continue as ever.

*PL Shapiro*



*the University of Alabama in Birmingham* / 1919 SEVENTH AVENUE SOUTH / BIRMINGHAM, ALABAMA 35233  
*the Medical Center*

August 5, 1970

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

Dear Barry:

Due to the closing of the Institute for Biomedical Research, we have relocated our research program at the University of Alabama School of Medicine in Birmingham. We are pleased to have obtained all of our equipment and supplies as part of my settlement with the American Medical Association. This includes our HR 220 with SS 100.

The research group has moved substantially intact with an important exception. Our very able research engineer, Dennis Wisnosky, was induced to accept a position at Wright-Patterson Air Force Base in Dayton, Ohio. While we are fortunate that Dennis will be available on a consulting basis; we are presently looking for a head research engineer for the laboratory of Molecular Biology. His general area of expertise should be in spectroscopic instrumentation with special emphasis on nuclear magnetic resonance. Duties are to design and develop new instrumental capacities and accessories and to service present instrumentation. Depending on qualifications, salary in excess of \$15,000.00/year is possible.

Sincerely yours,

*Dan*

Dr. D.W. Urry, Director  
 Section of Molecular Biophysics  
 Laboratory of Molecular Biology  
 School of Medicine  
 University of Alabama  
 Birmingham, Ala.

Phone: (205) 934-3543



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