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Newsletter

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JUN 23 1972

BRUKER SCIENTIFIC INC.

No. 165

June, 1972

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IN REPLY PLEASE QUOTE
REF.



THE UNIVERSITY OF NEW ENGLAND
ARMIDALE, N.S.W.

18th April, 1972.

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

Title: Study of Long-Range Heteroatom-Carbon-13 Scalar Coupling

Dear Professor Shapiro:

As an initial contribution to the TAMU-NMR Newsletters we would like to describe some of our results on long-range heteroatom-carbon-13 scalar coupling. This work originated from a study on carbon-metal hyperconjugation by carbon-13 NMR and an interest in long-range ^{13}C - ^{19}F coupling.


Proton-decoupled carbon-13 spectra were determined using audio side-band sweeping on a HA60IL spectrometer controlled by a VDM 8K 620i computer. Substantial modification (both hardware and software) had to be made to the system before reasonable spectra could be obtained. (If any of your other readers have a similar system and require further information we would be pleased to provide greater details).


For the benzyl derivatives the metal-carbon-13 coupling constants alternate in magnitude about the ring with quite large coupling constants to the para carbon C4. However, if the metal is directly attached to the ring long-range coupling is largest to the meta carbon C3. A similar state of affairs was reported by Roberts and Weigert for diphenyl mercury.¹ We have proven the spectral assignments in this case by recording the spectrum of m,m'-dideuterodiphenyl mercury. The assignments for the benzyl derivatives are only tentative at present (based on the chemical shifts in the series $\text{X} = \text{Si}(\text{CH}_3)_3$, $\text{Ge}(\text{CH}_3)_3$, $\text{Sn}(\text{CH}_3)_3$, and $\text{Pb}(\text{CH}_3)_3$), but we are making some deuterated derivatives to clear up this point. We have re-examined the carbon-13


spectrum of trifluoromethyl benzene (original reported by Weigert and Roberts²) and some derivatives. In this case as well long-range ^{13}C - ^{19}F coupling alternates in magnitude about the ring whereas in fluorobenzene the magnitude of the coupling falls off as the number of intervening bonds increase.² As in p-fluorostyrene we have observed a substantial coupling (1.9Hz) to the α -carbon (C8) of the vinyl side-chain, it does not appear to be generally true that in fluorinated aromatics ^{13}C - ^{19}F coupling constants decrease in magnitude with the number of intervening bonds. We hope these results will be of interest to your readers.

Yours sincerely,


D. Doddrell

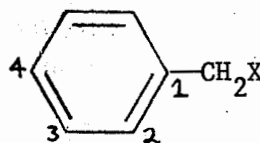

N.V. Riggs


W. Kitching
(University of
Queensland)


W. Adcock
(Flinders University)

Footnotes

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M-¹³C Long-Range Coupling^a for Some Benzyl Derivatives

X	M	$J_{M-^{13}C_1}$	$J_{M-^{13}C_2}$	$J_{M-^{13}C_3}$	$J_{M-^{13}C_4}$
Sn(CH ₃) ₃	^{117,119} Sn	36.6	22.6	12.0	14.8
Pb(CH ₃) ₃	²⁰⁷ Pb	64.4	44.2	26.4	32.2
HgCl	¹⁹⁹ Hg	151.2	110.0	50.6	62.4

M-¹³C Long-Range Coupling^a for Directly Attached Phenyl Rings

M	$J_{M-^{13}C_1}$	$J_{M-^{13}C_2}$	$J_{M-^{13}C_3}$	$J_{M-^{13}C_4}$
 <chem>C[C@H](C)(c1ccccc1)c2ccccc2</chem> $^{117,119}\text{Sn}$	486.0(464.0)	36.8	47.2	10.8
 <chem>C[C@H](C)(c1ccccc1)[Pb](C2=CC=CC=C2)C3=CC=CC=C3</chem> ^{207}Pb	488.4	69.4	83.2	18.8
 <chem>c1ccccc1[Hg]c2ccccc2</chem> ^{199}Hg	1218 ^b	86.3 ^b	100.2 ^b	18.0 ^b
 <chem>C=Cc1ccc(F)cc1</chem> $^{19}\text{F}^c$	249.7	21.1	8.1	3.3

^a Coupling Constants are in Hz.^b Slightly different values than those reported by Weigert and Roberts.^c $J_{^{19}F-C_7}^{^{13}C} = 0.0$; $J_{^{19}F-C_8}^{^{13}C} = 1.9$ Hz.

EMORY UNIVERSITY
ATLANTA, GEORGIA 30322

DEPARTMENT OF CHEMISTRY

April 26, 1972

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

Title: Update on High-Resolution Carbon-13 Studies

Dear Barry:

Since our presentation at the 12th ENC and our TAMU NMR Newsletter contribution¹ of last year, we have further extended our high-resolution carbon-13 studies of substituted benzenes. The remarkable stability of our Bruker HFX-90 for long-term time averaging has, of course, been tremendously valuable. This is particularly evident in cases of relatively dilute samples where, in addition, relatively small second-order lines are quite important in the determination of a spectral analysis fit.

The high-resolution ^{13}C spectrum of the carbon bonded to the substituent in para-dibromobenzene (saturated solution in acetone) will serve to illustrate this point. As shown in Figure 1, the most intense portion of the spectrum consists of a reasonably symmetrical pentet and would perhaps be the only portion observed during a short-term accumulation. However, since substituent effects on the ^{13}C -H coupling constants in bromobenzene are available and additivity of these effects has been demonstrated², we are able to predict at least twelve additional lines which as shown by the fits in Figures 1 and 2 are actually observed after long-term time averaging. Figure 2 demonstrates a more accurate determination of the four lowest field resonances appearing in Figure 1.

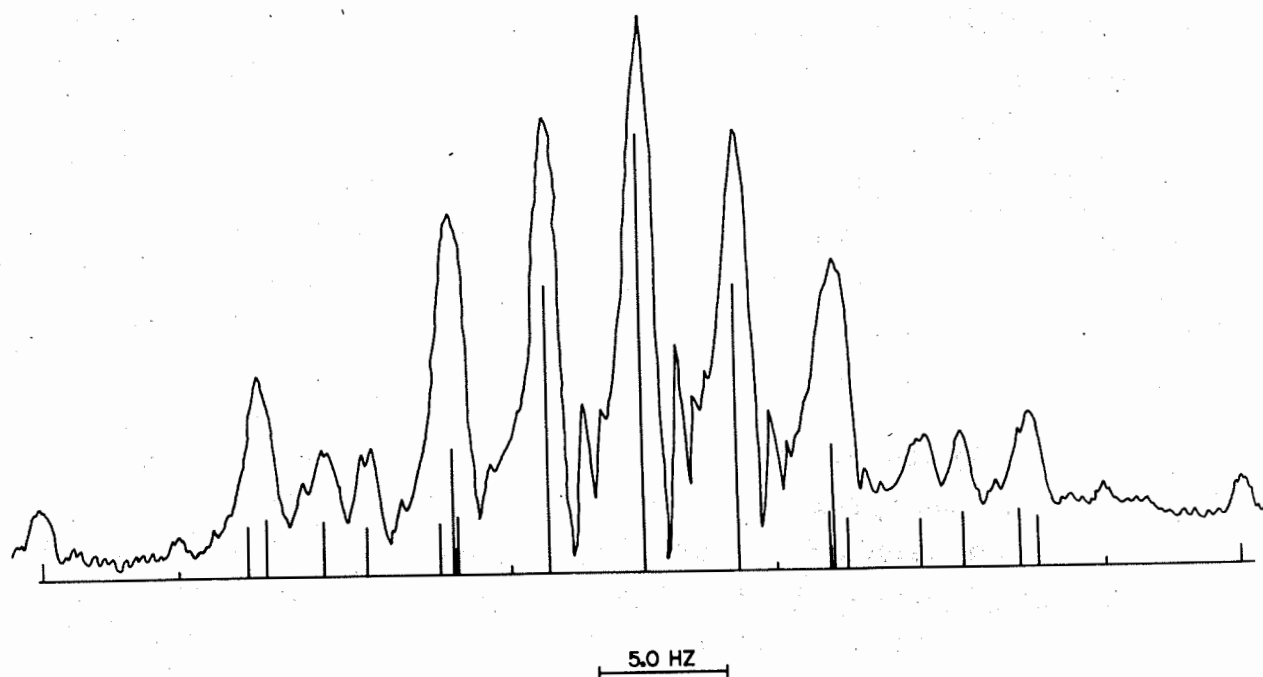
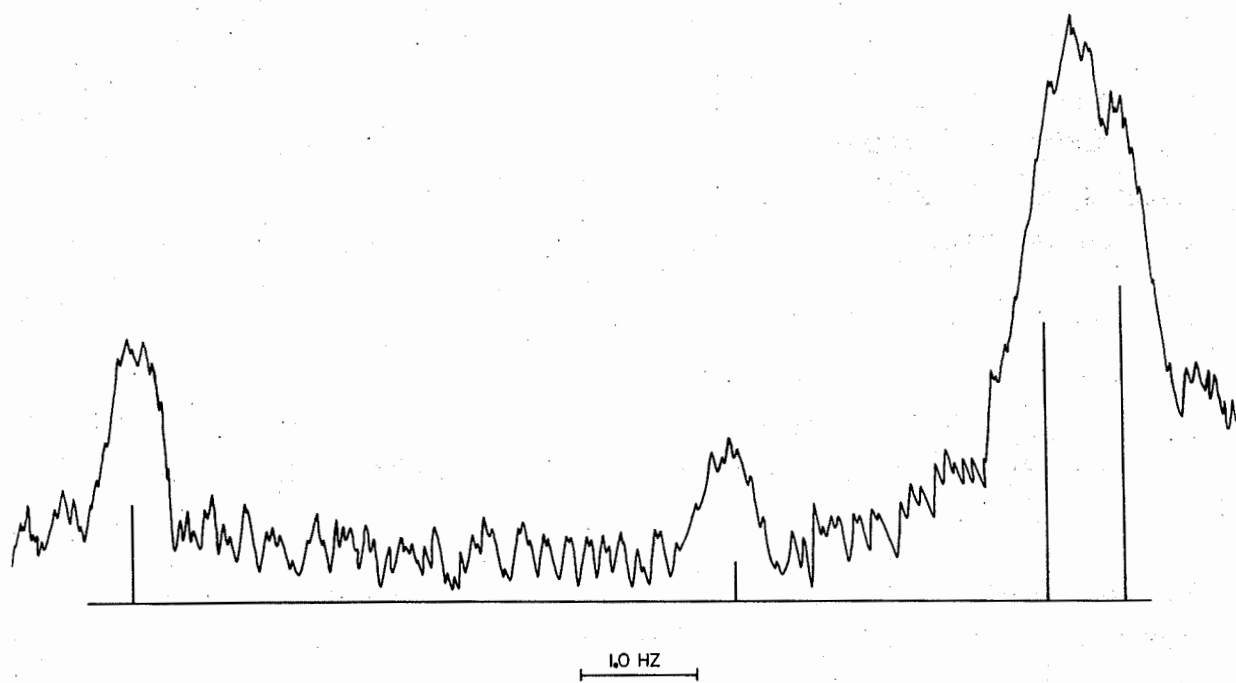
In addition to high-resolution ^{13}C work in relatively dilute solution, we have been able to extend our studies to the much more complex cases of seven-spin fluorobenzenes. In these cases, long-term time averaging, prediction by analogy from other substituted benzenes, and prediction assuming additive substituent effects have all proven to be invaluable.

Sincerely,

A. R. Tarpley, Jr.
A. R. Tarpley, Jr.

J. H. Goldstein
J. H. Goldstein

- (1) TAMU NMR Newsletter No. 154, p. 20.
- (2) J. Phys. Chem., 76, 515 (1972).



April 27, 1972

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L. dz. _____

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

Dear Professor Shapiro,

Computer Evaluation of Errors in the Calculation of Lanthanide -
Induced NMR Shifts as a Function of Substrate - Paramagnetic Ion
Distance

The lanthanide induced shifts in nuclear magnetic resonance spectroscopy are considered to be largely of pseudocontact nature /1/, described by the equation 1 /2/,

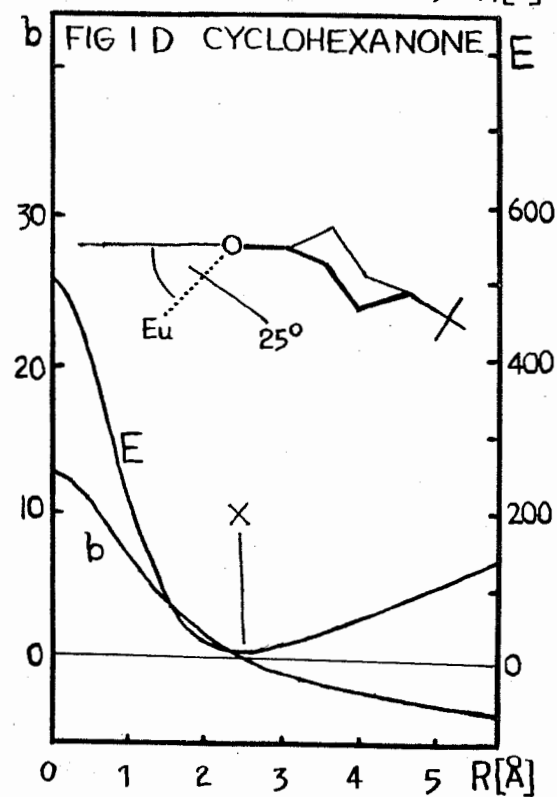
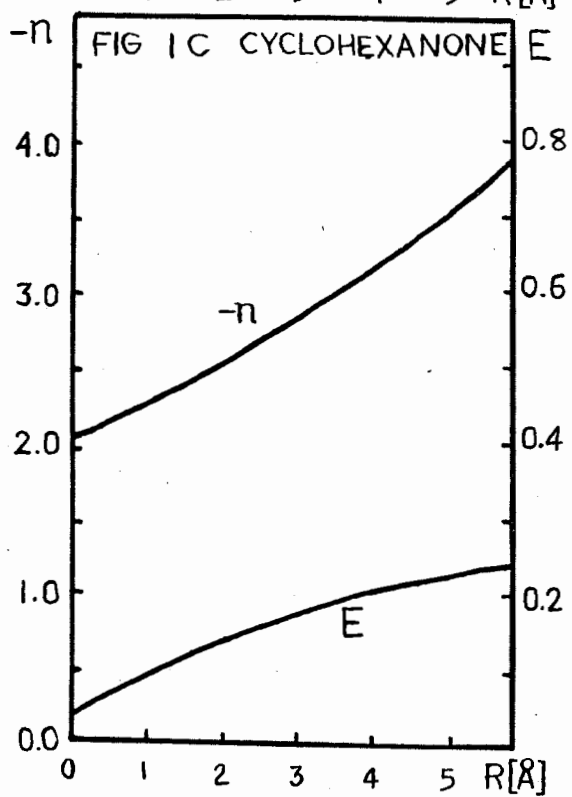
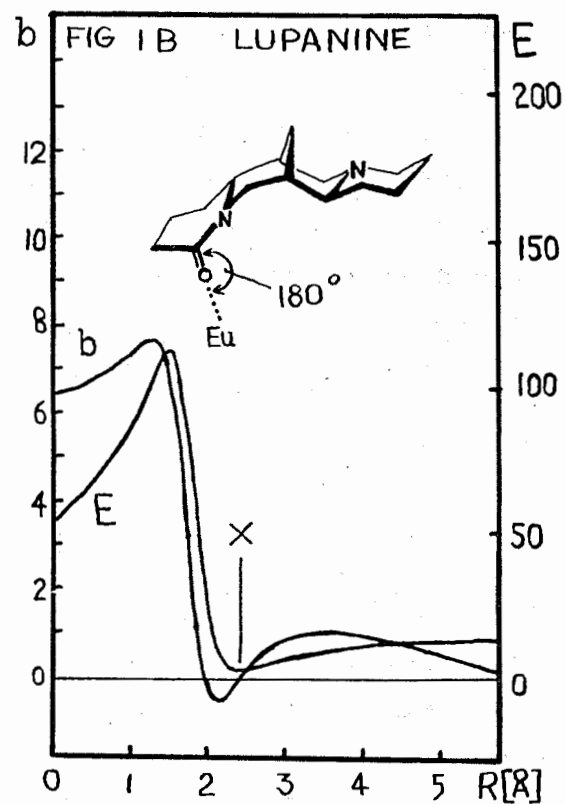
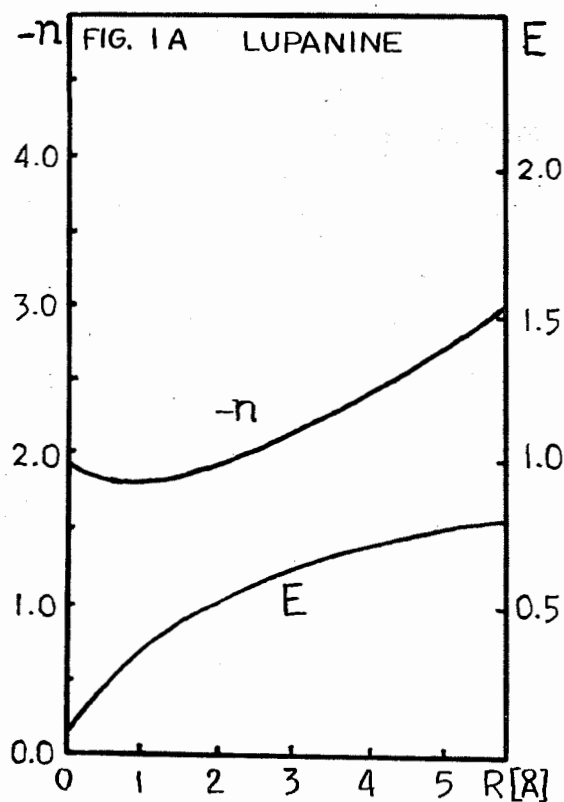
$$S_i = K/3\cos^2\Theta_i - 1/r_i^{-3} \quad 1$$

where S_i is the pseudocontact shift of the i -th proton at relative molar concentration of shift reagent equal to 1, K - constant for a given substrate, shift reagent, solvent and absolute concentration of substrate /3/, r_i is the distance between paramagnetic ion and the i -th proton, and Θ_i is the angle between vectors: lanthanide ion - complexation centre \vec{R} , and lanthanide ion - the above proton \vec{r} . In practice a simplified equation 2 was used for the quantitation of experimental data, apparently with good results /4/.

$$S_i = K_1 r_i^{-n} \quad 2$$

Various authors used $n = 2$ or $n = 3$. Direct analysis showed some errors in these assumptions /5/. It was proved recently that the angular factor $3\cos^2\Theta - 1$ is very significant and cannot be omitted /6/. Another cause of errors lies in the rather arbitrary selection of lanthanide position in all calculations.

For the analysis of these problems we have devised a computer program, which analyses induced shifts for a given molecule by exponential /equation 2/ and angular /equation 1/ methods in function of distance between lanthanide ion and the heteroatom of the functional group active in complexation.



The program, written in ALGOL 60, for ODRA 1204 computer is available from the authors on request. Input data consist of the shift S values for assigned signals in the spectrum, cartesian coordinates of corresponding protons and coordinates of two points describing the expected axis of complexation, i.e. line connecting lanthanide ion with the heteroatom complexing to it. Separation of these two points by 5 Å is adequate, because larger distances lanthanide - heteroatom $/R/$ are rather unprobable. Several possible axes of complexation are frequently tried. Coordinates of hydrogen atoms are calculated from the geometry of the investigated molecule. It can be done by means of a separate computer program $/8/$. From these data r and \odot are calculated as the lanthanide ion $/M^{III}/$ moves along the axis. Approximation by the method of least squares gives K_1 and n $/equation 2/$ for different distances R , printed out together with the value of approximation error E . The results are presented as graphs of n and E dependence on lanthanide - coordination centre distance R $/Fig. 1 A,C/$. We have found that n depends strongly on lanthanide position and frequently it is possible to select one M^{III} position corresponding to $n = 2$ and another corresponding to $n = 3$. This clarifies the misunderstanding concerning correct value of n $/5/$. For most of the compounds studied $n = 2$ appears at more reasonable distances $/2 - 3 \text{ Å}/$ and at lower error values. Basically the position of M^{III} , which gives the lowest error E , should be correct. This limitation leads however to unprobable distances, e.g. 1 Å for pyridine or 0.0 Å for 4 - t butylcyclohexanone. The above observations prove the inadequacy of simple exponential approximation in more exact calculations, regardless of its utility in selected cases.

Figure 1 Distance dependence of n and approximation error E for lupanine $/A/$, 4 - t butylcyclohexanone $/C/$ calculated from equation 2. Distance dependence of b and approximation error E for lupanine $/B/$, 4 - t butylcyclohexanone $/D/$ calculated from equation 3. Shift data for lupanine we have reported previously $/11/$, for 4 - t butylcyclohexanone - as in $/12/$.

In the second part of the program equation 3 is applied.

$$S_i = K/3\cos^2 \Theta_i - 1/r_i^3 + b \quad 3$$

In theory b should be zero, because for $r = \infty$, $S = \text{zero}$, so values of b different from zero obtained in practice constitute an independent measure of error in positioning M^{III} , besides approximation error E , in this part of the program. The results again are presented as graphs of dependence of b and E on R /Fig. 1 B, D/. Actual position of lanthanide in relation to the substrate is defined by the point, where b and E simultaneously reach minimum /point X on figure 1/. This point is selected by the computer and here r, Θ for all protons are displayed besides K, b, E . It allows to calculate distances from M^{III} for all protons of known shifts S , and vice versa with high accuracy, for use in interpretation of spectra and in stereochemical analysis. A program for automatic interpretation of shifted spectra is now in preparation /7/. For the compounds investigated europium ion lies between 2 and 3 Å from the atom active in complexation. In the examples given in Fig.1 R is 2.3 Å and 2.4 Å for 4 - t butyl-cyclohexanone and lupanine, respectively. It is in excellent agreement with X - ray determined Yb....O /oxygen/ distance equal to 2.34 Å /9/. The above described program is generally useful for shift and distance calculations as well as lanthanide positioning if observed effects are of pseudocontact nature only. For some hetero-aromatic compounds, e.g. pyridine, quinoline our calculations have shown for all distances poor agreement with equation 1, caused probably by significant contribution of contact interactions. This problem we will discuss separately. A different method for calculation of lanthanide position was described by Farid et al. /10/.

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Sincerely yours,

Jan Barciszewski

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1 May 1972

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

MULTIPLE ECHOES IN FOURIER SPECTROSCOPY

Dear Barry,

It is well-known that an inhomogeneous magnetic field in pulse Fourier spectroscopy leads to echo-like effects.¹⁻³ The magnetization which decays after the exciting rf pulse almost to zero due to field inhomogeneity is partially refocussed immediately before the next pulse and gives rise to a half echo.

If one purposely stops an infinitely long, repetitive pulse sequence, the following half echo develops into a full echo and is followed by an infinite sequence of further echoes. Three examples are shown in the following figure. The maxima of the equidistant echoes occur at the positions of the suppressed rf pulses. The decay constant of the echo sequence obviously depends on the flip angle.

It is not difficult to compute the echo amplitudes assuming a sufficiently inhomogeneous magnetic field such that the echoes are well separated from each other. One obtains the following expressions:

$$M_y(0) = M_0(1-E_1) \frac{\sin \alpha}{\sqrt{a^2-b^2}} \left[1 - E_2(\sqrt{a^2-b^2} - a)/b \right]$$

$$M_y(nT) = M_0(1-E_1) \frac{\sin \alpha}{\sqrt{a^2-b^2}} \left[1 - E_2b/(\sqrt{a^2-b^2} - a) \right] \cdot \left[(\sqrt{a^2-b^2} - a) \frac{E_2}{b} \right]^n$$

with

$$a = 1 - E_1 \cos \alpha - E_2^2(E_1 - \cos \alpha)$$

$$b = -E_2(1 - E_1)(1 + \cos \alpha)$$

$$E_1 = \exp(-T/T_1), \quad E_2 = \exp(-T/T_2) \quad .$$

$$n = 1, 2, 3, \dots$$

Here, T is the pulse spacing and α the flip angle.

The expression for $M_y(nT)$ shows that there is a constant amplitude ratio of successive echoe maxima:

$$R = (\sqrt{a^2 - b^2} - a)E_2/b .$$

This implies that the echoe decay is exponential with a time constant which depends on α , T/T_1 and T/T_2 . However, the initial signal amplitude $M_y(0)$ does not lie on the exponential envelope, in general. But, there is a particular flip angle, $\cos \alpha = E_1$, for which even $M_y(0)$ fits the exponential decay (compare second curve). In this case, the amplitude ratio of successive maxima is given by $R = 1 - \sqrt{1 - E_2^2}$ and is independent of T_1 and of field inhomogeneity.

The figure shows that the smaller the flip angle the slower is the echoe decay. For small flip angle, $\alpha \rightarrow 0$, the time constant of the decay of the envelope approaches $T_2/2$. An evaluation of the given formulas shows that the amplitudes of all echoes have signs opposite to the sign of the initial decaying signal.

It may appear that the observation of the echoe decay provides a convenient and simple measurement of T_2 . But it must be emphasized that there is no compensation, what so ever, for diffusion effects, in contrast to the well-known spin-echoe experiments. On the other hand, a comparison of the echoe decays in a homogenous and in an inhomogenous magnetic field will provide at least qualitative information about the diffusion rates. Details will be presented at another occasion.

Sincerely yours,

Richard

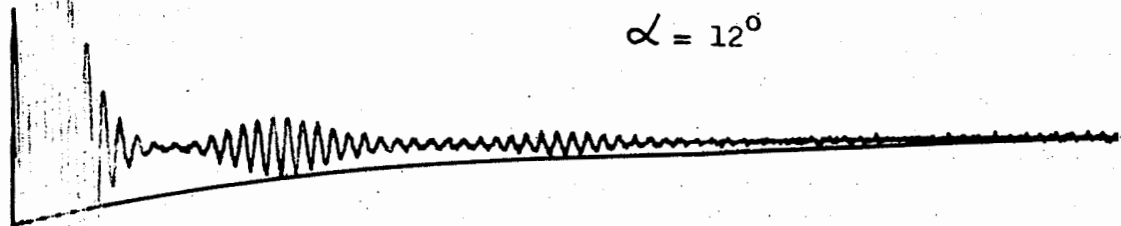
Richard R. Ernst

Enrico Bartholdi

Enrico Bartholdi

- 1) R. Freeman and H.D.W.Hill, J.Magn.Resonance 4, 366 (1971)
- 2) P. Waldstein and W.E.Wallace, Rev.Sci.Instr. 42, 437 (1971)
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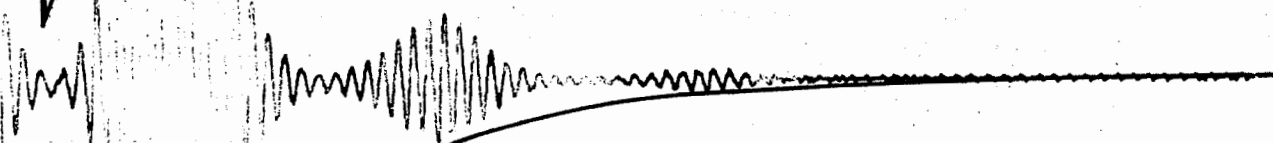
$$\alpha = 12^\circ$$



$$\alpha = 24^\circ$$



$$\alpha = 66^\circ$$



Echoe train in an interrupted pulse experiment
for a single resonance line for three different
flip angles α

University of Waterloo



Waterloo, Ontario, Canada

Faculty of Science
Department of Chemistry

May 1, 1972

Dr. B.L. Shapiro
Dept. of Chemistry
Texas A & M University
COLLEGE STATION, Texas 77843

Dear Barry:

We have measured some gas to infinite dilution shifts for hexafluorobenzene that might interest readers. The shifts were obtained by extrapolation to infinite dilution in respective solvents and measured with an external pure C_6F_6 capillary at $33^\circ C$ and 94.1 MHz. We operated in a locked mode to this capillary sample and obtained the gas to infinite dilution shifts by adding the gas to pure liquid shift measured by Raynes and Raza. (Mol. Phys., 20, 555 (1971)). " δ_{obs} " is the uncorrected data in the table and $\Delta\sigma(F)$ is corrected for the bulk susceptibility effect in cylindrical samples. There is no doubt that Van der Waals forces dominate the large shift effect and that molecular diamagnetic anisotropies are negligible. There is correlation within the separated groups of solvents with the molecular polarisability.

This work is associated with Dr. M.A. Raza and Dr. N. Cyr now at McGill University.

Kind regards.

Yours sincerely

L.W. Reeves

LWRcs

Table

Downfield ^{19}F chemical shifts (in p.p.m.) of hexafluorobenzene at infinite dilution in a series of solvents with respect to the solute gas phase chemical shift at 33°C and molar susceptibilities, densities at 33°C and bulk susceptibility shifts for the solvents used in the present work.

Solvent	$-\chi_m \times 10^{-6}$ (c.g.s.units)	Density at 33°C (gm/ml)	$-\sigma_b^\dagger$ (p.p.m.)	δ_{obs} (p.p.m.)	$\Delta\sigma(\text{F})$ (p.p.m.)
CCl_4	66.8	1.5691	1.43	10.52	9.09
CHCl_3	59.3	1.4650	1.52	10.19	8.67
CH_2Cl_2	46.6	1.3025	1.50	9.25	7.75
Cyclohexane	68.1	0.7662	1.30	8.70	7.40
Benzene	54.9	0.8651	1.27	8.48	7.21
Pyridine	48.5	0.9699	1.25	8.41	7.16
Thiophene	57.4	1.0490	1.50	9.86	8.36
Furan	44.8	0.9206	1.27	7.85	6.58

$^\dagger \sigma_b$ correction for bulk diamagnetic susceptibility in a cylindrical sample.

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Basel, May 4, 1972/ho

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

" A classical model for hindered CH₃-rotation"

Dear Barry,

In our studies of intramolecular motions by NMR of oriented molecules one of the most embarrassing and time consuming steps has always been the solution of the Mathieu equation arising from the quantummechanical treatment of the problem. We consequently asked ourselves how far a simple classical model could serve as an approximation, knowing that for the extremes, i.e. with stable rotamers and free rotation, the results of the two models would be identical.

The probability distribution of the CH₃-rotational angle (for a three fold potential) based on classical Boltzmann statistics is:

$$W(\varphi)d\varphi \propto \exp \left[- \frac{V_3}{2} (1 - \cos 3\varphi) / kT \right] d\varphi$$

Obviously this could not be a good function for the whole range of possible V_3 since, contrary to the quantummechanical solution, $W(\varphi)$ does not depend upon the moment of inertia of the methyl group.

However, for a determination of the height of the hindering potential V_3 from the observed average of the direct couplings, it turned out that the classical model did not deviate by more than 10% from the quantummechanical

model for the range of V_3 between 0 and 5kcal/mole.
The exact figures are summarized in the table.

Table: Comparison of quantummechanical and classical models for hindered CH_3 -rotation in o-iodo-toluene.

quantummechanical model:

classical model:

V_3 (cal/mole)	rel.error of $W(\varphi)$ at $\varphi=0$ %	abs. error of V_3 (cal/mole)
500	0.7	10
1000	1.9	30
2000	3.8	100
3000	5.5	150
5000	8.6	400
10000	15.3	1500
15000	21.3	> 3000

As the errors arising from the inaccuracy of direct couplings by far exceed the errors from the classical approximation for the stated range of energies, it seems safe to use the much simpler classical formula for hindered CH_3 -rotation.

It is difficult to judge how far such approximations may also be used in the determination of the hindering potential to methyl rotation from observed indirect couplings. However, we would like to suggest that similar comparisons be made by people who are working in this field.

Sincerely yours,

Peter
P. Diehl

S. Niederberger
W. Niederberger

J. Vogt
J. Vogt

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May 4, 1972

Professor B. L. Shapiro
Department of Chemistry
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Subject: Low Noise Broadband Preamplifier for NMR Probes

Dear Professor Shapiro,

The amplifier shown in the accompanying diagram is designed for use in (or at) an NMR probe to provide the first stages in amplification of the signal picked up by the receiver coil. It operates with low noise over a wide range of frequencies. The first two transistors form a cascode section with especially low dissipative feedback to the input. The third transistor drives the 50 ohm line and has R_2 and C_5 in the emitter circuit to compensate for losses in gain at high frequencies. If one is interested in extending the bandwidth at the high end, one could try lowering R_1 and experimenting with C_5 (and R_2 ?). The only unavoidable magnetic parts are the short transistor leads, which cause no apparent homogeneity problem.

The following measurements were made on the bench:

Bandwidth, 3dB: <3MHz to 100 MHz

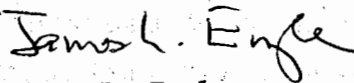
Power Gain: >20dB at 60 MHz

Equivalent input noise voltage generator: $1.9 \times 10^{-9} \sqrt{BW}$ (i.e. almost as low as for the TIS88 alone).

Equivalent input noise current generator: Not measured.

I hope that this will be useful to others. We use it in our multi-frequency pulsed instrument.

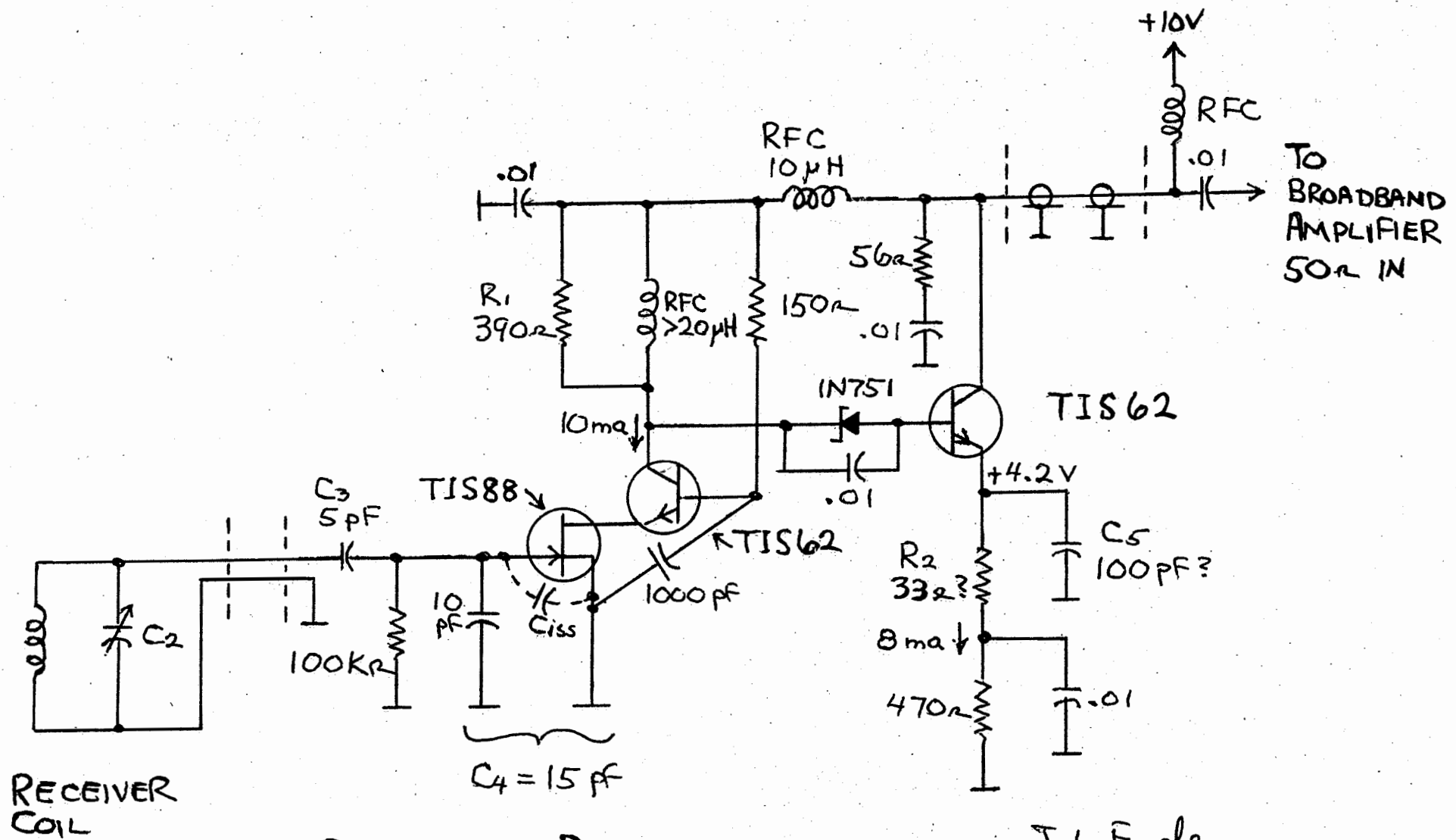
Sincerely,



James L. Engle

JLE/lvm

Enc.



BROADBAND PREAMPLIFIER

J.L. Engle
MAY 4 1972

NORTH TEXAS STATE UNIVERSITY
DENTON, TEXAS

DEPARTMENT OF CHEMISTRY

May 9, 1972

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

Dear Barry:

The major part of our research effort for the past two years has been the study of carbon-13 labeled compounds to get the long-range carbon-carbon and carbon-hydrogen coupling constants. The beginning of this study was described in an earlier contribution to your Newsletter (Number 155, p 16). Since then, our studies have been extended to 1-labeled monosubstituted benzene derivatives, 7-labeled disubstituted (ortho and para) benzene derivatives, 9-labeled anthracene derivatives, 1-labeled cyclohexane derivatives, and 1-labeled aliphatic carboxylic acids. Our biggest surprise so far has been the relative magnitude of the three-bonded and the two-bonded carbon-carbon coupling constants: in every instance the three-bonded value has been the larger. This observation is becoming so general that we have been tempted to make chemical shift assignments on the basis of carbon-carbon coupling constants. An example might bear this out: We expected the chemical shift for the 2-carbon of 1,4-dihydrobenzoic acid to be downfield from that for the 3-carbon; however, the splitting in the downfield signal of the two olefinic carbon atoms (C-2 and C-3) for carboxyl-labeled 1,4-dihydrobenzoic



acid was larger than that of the upfield signal. If the three-bonded coupling constant was to be larger than the two-bonded value, then the chemical shift assignments had to be reversed. We then synthesized 3-deuterio-1,4-dihydrobenzoic acid to identify the 3-carbon, which indeed turned out to be the downfield signal. Thus, again the three-bonded coupling was larger than the two-bonded coupling.


We are now extending these studies into the area of labeled alicyclic compounds -- compounds with rigid skeletons to help establish the dependence of the three-bonded coupling constants upon geometry.

The success of these studies has depended critically upon the high sensitivity of our JEOL PS-100. To illustrate the high quality spectra we have been able to get from this instrument, we include CMR spectra of natural and 7-labeled benzoyl chloride. Both spectra are *single scans* of *natural abundance* carbons in the aromatic region. Thus, although we were too poor to buy Fourier Transform, the high sensitivity of the JEOL PS-100 has allowed satisfactory work nevertheless.

Unfortunately, Dr. Arthur Ihrig, who has been doing such a splendid job with these studies, is now leaving us to make employment elsewhere. Part of his duties has been to maintain the departmental nmr and ir instruments, and we are looking for a replacement. This new opening is for a person whose duties will be half-time maintaining the nmr (JEOL MiNiMaR and PS-100) and ir instruments. The other half of the responsibilities will be research and/or teaching; or if the applicant is familiar with the mass spectrometer, the other half of his responsibilities may be with this instrument (Hitachi Perkin-Elmer RMU-6E). Interested parties may contact me by writing to the above address or by calling me at 817-788-2031.

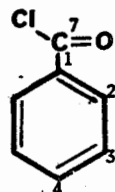
Best personal regards.

Sincerely,



James L. Marshall
Associate Professor

- TITLES: 1. CONTINUING STUDIES ON LONG-RANGE CARBON-CARBON COUPLING
CONSTANTS
2. AN OPENING FOR A PERSON WITH NMR EXPERIENCE

CMR**natural****C₄****C₁****C₂****C₃****¹³C-7****labeled**

Milano, April 30, 1972

Title: -Sign determination of long-range couplings in
 1-methyl- Δ^3 - and 1-methyl- Δ^4 -pyrrolin-2-one.

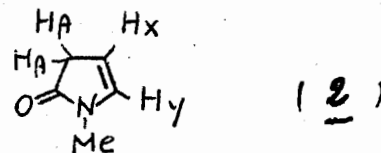
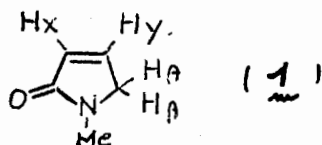
-NMR analysis of Roxburghine E: structure and
 stereochemistry determination.

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

Dear Professor Shapiro,

I apologise for mine being so
 late, with many thanks for your blue and pink remainders !

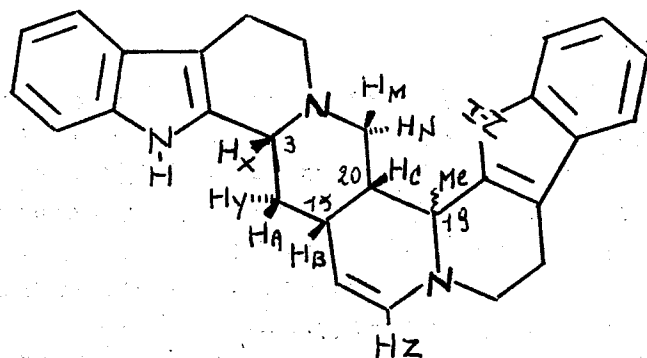
Going on with our study of Δ^3 - and Δ^4 -pyrrolin-2-one
 isomers (1), we have completed the analysis and sign de-
 termination of all the ^1H - ^1H coupling constants in the
 corresponding 1-methyl derivatives. The measurements, toge-
 ther with double resonance experiments, were performed
 on a mixture of 1 (90%) and 2 (10%) isomers, obtai-
 ned by oxidation of N-methylpyrrole. The parameters ob-
 tained are the following:



J_{XY}	+6.05
J_{AY}	+1.75
J_{AX}	-1.90
$J_{Me,A}$	-0.60
$J_{Me,X}$	+0.22
$J_{Me,Y}$	≤ 0.05

J_{XY}	+4.95
J_{AY}	-2.25
J_{AX}	+2.45
$J_{Me,A}$	≤ 0.05
$J_{Me,X}$	≤ 0.10
$J_{Me,Y}$	≤ 0.15

The complete NMR analysis of the 2° ord. seven-spin system corresponding to the protons ABCMNXY of Roxburghine E, **3**, led to the structure and stereochemistry determination of this new alkaloid of the Roxburghines series(2), isolated from a variety of *Uncaria* (Rubiaceae). The parameters, listed below, together with the long-range coupling J_{BZ} , have been obtained by double and triple resonance experiments, and were confirmed by iterative analysis. From coupling constants values, the sequence of protons on the inner rings has been deduced, together with the ring junctions. Consequently, also the relative configuration at the asymmetric centers can be established as C-3 β , C-15 α , C-20 β (or their antipodes). Nothing can be said about the configuration at C-19 in respect to the other centers.



J_{AB}	12.02	δ_A	1.612	(CDCl ₃)
J_{AY}	-13.68	δ_B	2.001	
J_{AX}	4.60	δ_C	2.188	
J_{BC}	11.35	δ_M	3.119	
J_{BY}	3.40	δ_N	3.259	
J_{CM}	3.21	δ_X	4.470	
J_{CN}	11.82	δ_Y	3.350	
J_{XY}	2.50	δ_Z	7.32	
J_{BZ}	± 0.9			

write R.T
rep axls
R.M. Mondelli

- (1) R. Mondelli, V. Bocchi, G.P. Gardini, L. Chierici
Org. Magn. Res. 3, 7 (1971).
(2) L. Merlini, R. Mondelli, G. Masini, M. Hesse
Tetrahedron 26, 2259 (1970).

The University of Manitoba

Department of Chemistry
Winnipeg, Manitoba
Canada R3T 2N2



May 4, 1972.

REGISTERED MAIL

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

Dear Barry:

Short title: Worked problems or micturated matrices.

In the May issue of the Newsletter I offered a planned compilation of worked problems from the book by Carrington and McLachlan. The reader response was encouraging and forced me to work (curses) in the marvellous autumn weather in Oxford. The final, informal collection consists of 250 typewritten pages of 108 of the problems in the monograph. Some copies for lazy learners or busy bodies are still available at \$15.00 a copy.

Best wishes from,

T. Schaefer

Ted Schaefer,
Professor.

TS/jf

DIVISION OF PHYSICAL CHEMISTRY
THE ROYAL INSTITUTE OF TECHNOLOGY

STOCKHOLM 70

SWEDEN

Cable address: Technology

Stockholm, June 1, 1972

Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station
Texas 77843
U.S.A.Pulsed NMR for biophysics

Dear Barry:

The installation of a new Bruker pulsed NMR Spectrometer B-KR 323 S, together with the planning of a more or less new research program has taken a considerable part of the time usually allotted to the normal activities of the NMR group. I have consequently very little to report regarding new experimental data.

The reason for the new spectrometer derives from our long standing interest in water and hydrogels, which to a rapidly increasing extent, is turning over to biophysical applications. The new instrument will give us the opportunity to observe some hitherto inaccessible transport processes in cell membranes and to attack such problems as frost and heat resistance of plants, the lipid-water-protein balance during ion transfer and similar interface phenomena. Just now we are familiarizing ourselves with the instrument by looking at some fairly simple systems like



in H_2O and D_2O to see whether water monomer bridges can link the carbon chains in the micelle. (cf. N.Muller R.H.Birkhahn J.P.C. 71, 957, 1967). The corresponding deuterated surfactants will permit us to separate the intra- and inter-molecular contributions to the micellar relaxation rate. There are also a number of solubilization problems which we shall report in due course of time. The critical micelle concentrations are well defined and the observations made so far give us the promise of accurate micellar relaxation time data. These investigations are initiated and carried out by Lars Ödberg and Ulf Henriksson.

In conjunction with photochemical investigations on nitroso-compounds, Per Forslind has undertaken an NMR-study aiming at a clarification of the kinetics of processes, like the monomer-dimer formation and dimeric isomerisation.

In one particular instance, the o-nitrosotoluene, we have been able to follow these processes in the PMR spectra as well as additional molecular motions of one of the dimeric forms. Preliminary results indicate that the cis-trans isomerisation goes via the monomeric form in solution.

The temperature range covered in which line shape effects are observed amounts to some 150°C. Since the monomer is strongly coloured whereas the dimer is colourless we hope to extend the kinetic study to temperatures outside the reach of the NMR-method by using spectrophotometric techniques. In this way one would also have the option of checking the kinetic parameters obtained from a line-shape analysis of the PMR spectrum.

Kind regards,

Yours,

A handwritten signature in cursive script, appearing to read 'Erik'.

Erik Forslind



Oklahoma State University

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

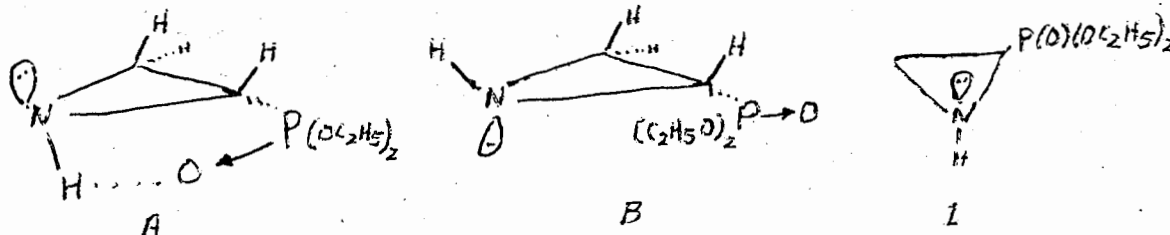
May 12, 1972

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

Re: PMR Studies of phosphorylated Aziridines using Shift Reagents—
Separation of Invertomer

Dear Dr. Shapiro:

In the aziridine system's, we expected slow nitrogen inversion due to the presence of intramolecular hydrogen bonding between the $P \rightarrow O$ group and the $N-H$ group. Such a hydrogen bonding should be favored in the invertomer A due to the cis relationship of $P \rightarrow O$ and $N-H$ hydrogen atom. But in the invertomer B the trans relationship of these groups and the repulsion between the nitrogen lone pair and the $P \rightarrow O$ group will destabilize this invertomer.

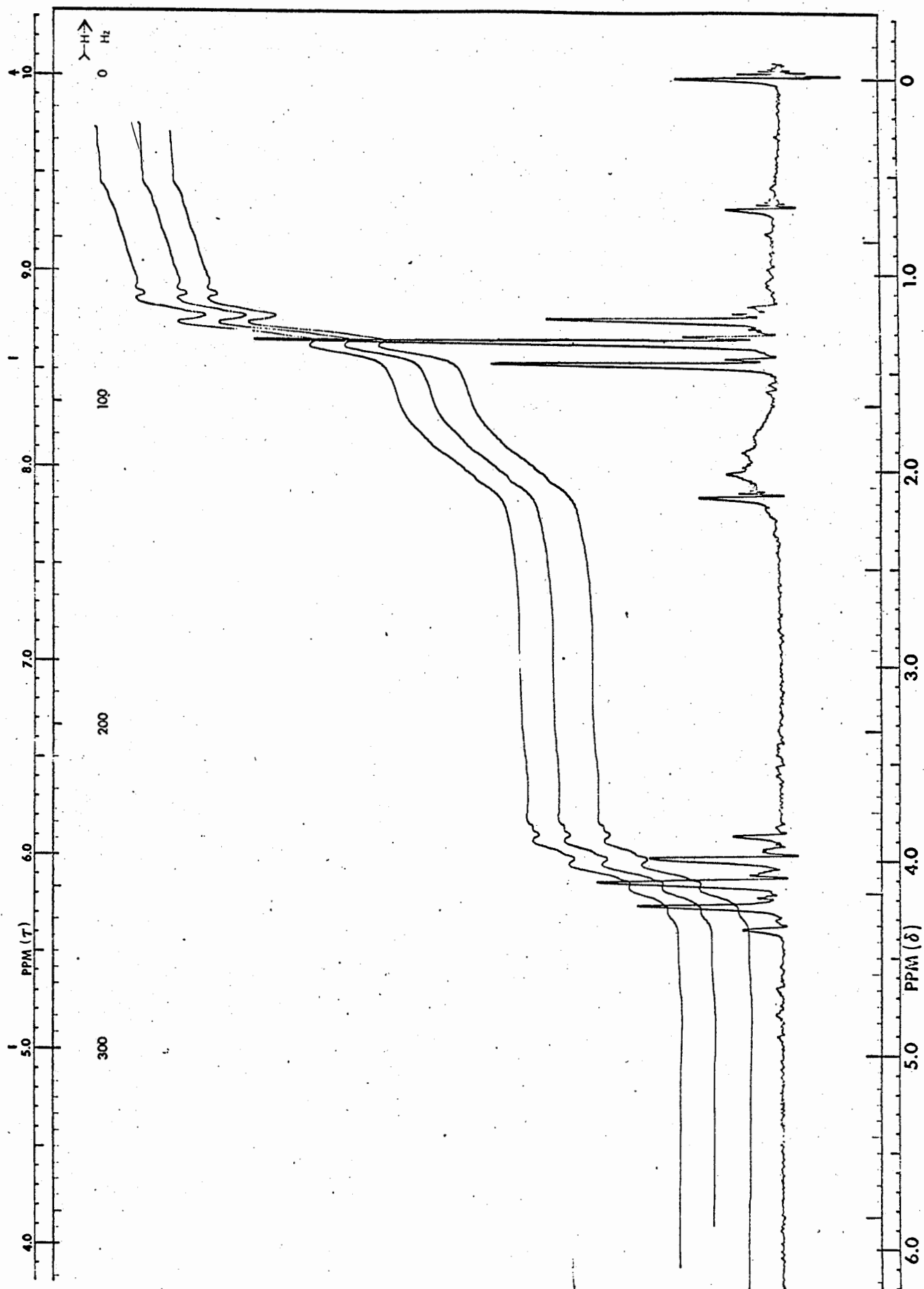


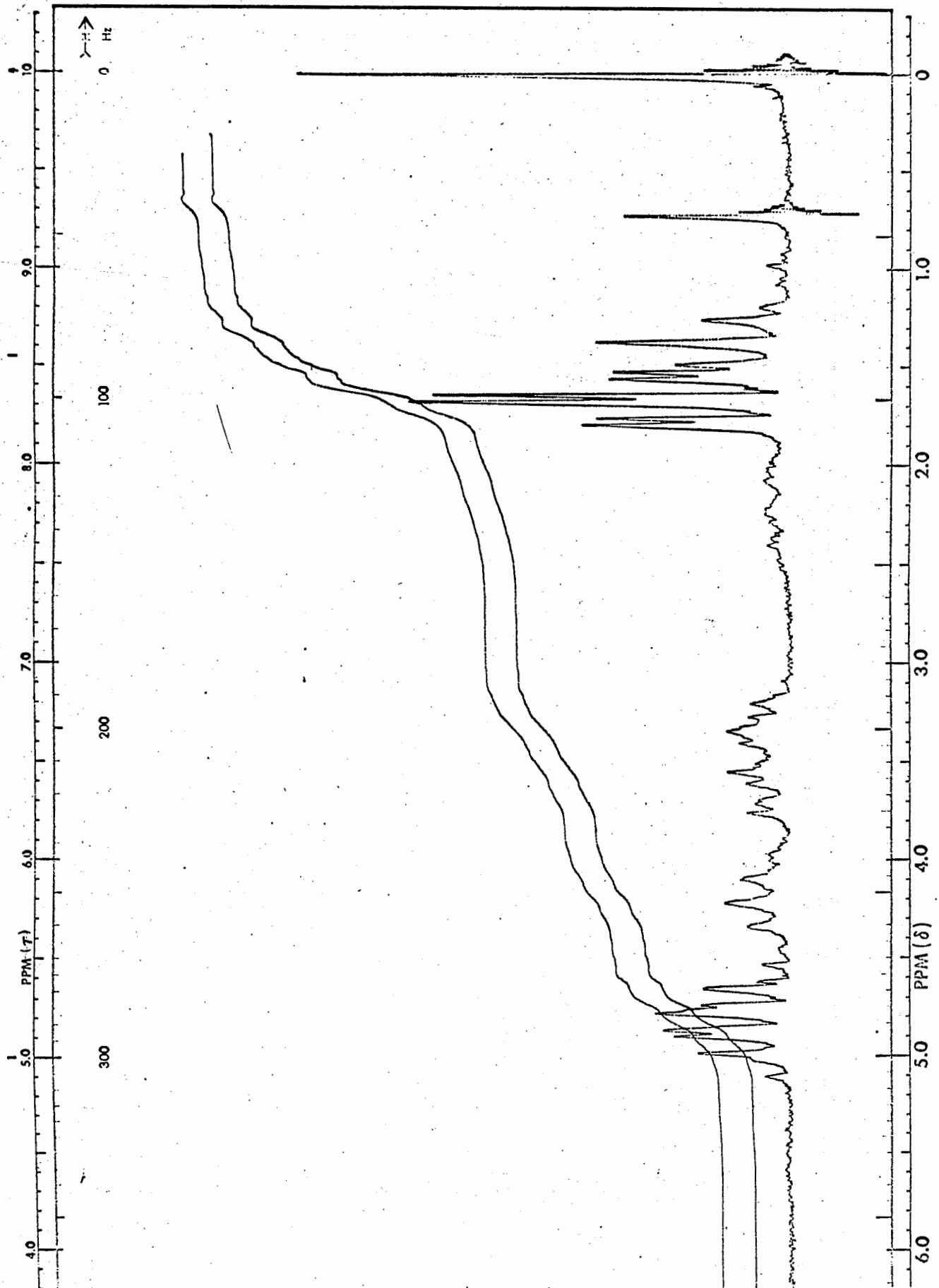
Paramagnetic shift reagent $Eu(DPM)_3$ was used to study this system. Figure 1 shows the 60 MHz spectrum in $DCCl_3$. The presence of both the invertomers can be inferred from the presence of a big and small triplet at δ 1.35 and δ 1.33, respectively, for the methyl proton of OCH_2CH_3 group. Addition of $Eu(DPM)_3$ shifts the peaks of the invertomer A to the downfield without affecting the peaks of the invertomer B, (Fig. 2). The absence of shift for the peaks of invertomer B shows that there is no coordination of the shift reagent with this invertomer. This can be explained due to the steric hindrance of the nitrogen lone pair by the bulky $P(O)(OCH_2CH_3)_2$ group. Apart from the downfield shift of the peaks of the invertomer A, doubling of the CH_3 triplet and the CH_2 multiplet of the $P(O)(OCH_2CH_3)_2$ group was also observed. This can be explained due to the restricted rotation of the C-P bond in the invertomer A due to internal hydrogen bonding and also due to the presence of an asymmetric center. The ratio of A to B was found to be 3:1 from the nmr spectrum (Fig. 2).

Sincerely yours,

K. D. Berlin

K. D. Berlin
Regents Professor





POSTDOCTORAL POSITION AVAILABLE

POSTDOCTORAL POSITION - A research-teaching postdoctoral appointment at the Chemistry Department of Vanderbilt University, with an annual stipend of \$7,500 is open for a person well versed in nmr technique (particularly on the Varian XL-100-15 instrument). The teaching will consist of 9 contact hours per semester and the research activities will be carried out under the direction of Dr. John R. Van Wazer, with emphasis on nuclei other than ^{13}C and ^1H . Please send applications with resumé and references to Prof. John R. Van Wazer, Department of Chemistry, Vanderbilt University, Nashville, Tenn. 37235.

UNIVERSITY OF COLORADO

BOULDER, COLORADO 80302

DEPARTMENT OF CHEMISTRY

May 16, 1972

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

Measurement of $^1J_{(^{29}\text{Si}-^{31}\text{P})}$ in $(\text{SiH}_3)_3\text{P}$

Dear Professor Shapiro:

Several years ago E.A.V. Ebsworth and co-workers [Trans. Faraday Soc., 62, 3282 (1966)] tentatively reported the measurement of the one-bond silicon-phosphorus coupling constant, $^1J_{(^{29}\text{Si}-^{31}\text{P})}$, in $(\text{SiH}_3)_3\text{P}$. In connection with our studies of physical and structural properties of silicon-phosphorus hydrides we have re-examined the ^{31}P NMR spectrum of $(\text{SiH}_3)_3\text{P}$. We obtain a value of $^1J_{(^{29}\text{Si}-^{31}\text{P})}$ of $42.2 \pm 0.1 \text{ Hz}$, in agreement with and confirming Ebsworth's measurement. This appears to be the first $^1J_{(^{29}\text{Si}-^{31}\text{P})}$ value to have been measured.

Phosphorus-31 n.m.r. spectra were obtained on neat liquid samples at ambient temperature (32°) using a Varian Associates HA-100 spectrometer equipped with standard 40.5 MHz probe and r.f. unit accessories. All spectra were obtained in the HR mode and were calibrated using the audio-frequency integrator side bands. This calibration was verified by comparing the value of J_{HSiP} obtained from the ^{31}P spectrum with the corresponding value measured from the ^1H n.m.r. spectrum.

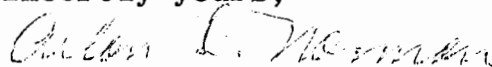
The ^{31}P n.m.r. spectrum of $(\text{SiH}_3)_3\text{P}$ obtained at a high spectrum amplitude is shown in the Figure. The spectrum consists of a large symmetrical ten-line multiplet ($\delta = 367 \pm 3 \text{ p.p.m.}$; $J_{\text{PSiH}} = 17.0 \pm 0.1 \text{ Hz}$) with binomial intensity distri-

bution. In addition, the sixteen symmetrically distributed satellite peaks, c_1-c_8 and $c'_1-c'_8$, which occur in a doublet of decets pattern can be assigned to the ^{29}Si satellite spectrum. Due to the low intensity of the outermost peaks of a binomial distribution decet pattern, these lines are not clearly visible in the satellite spectrum. However, the assignment of peaks c_1-c_8 and $c'_1-c'_8$ to the ^{29}Si satellite resonance appears unambiguous since the ratio of intensities of lines 5+6 to $c_4+c_5+c'_4+c'_5$ is 6.75:1.0 in good agreement with the theoretically expected value of 6.85:1.0. From the satellite spectrum the absolute value of $^1J(^{29}\text{Si}-^{31}\text{P}) = 42.2 \pm 0.1$ Hz is obtained.

Our studies of silicon-phosphorus coupling constants will be continued and expanded greatly with recent acquisition of a ^{29}Si probe for our JEOL PFT-100 spectrometer.

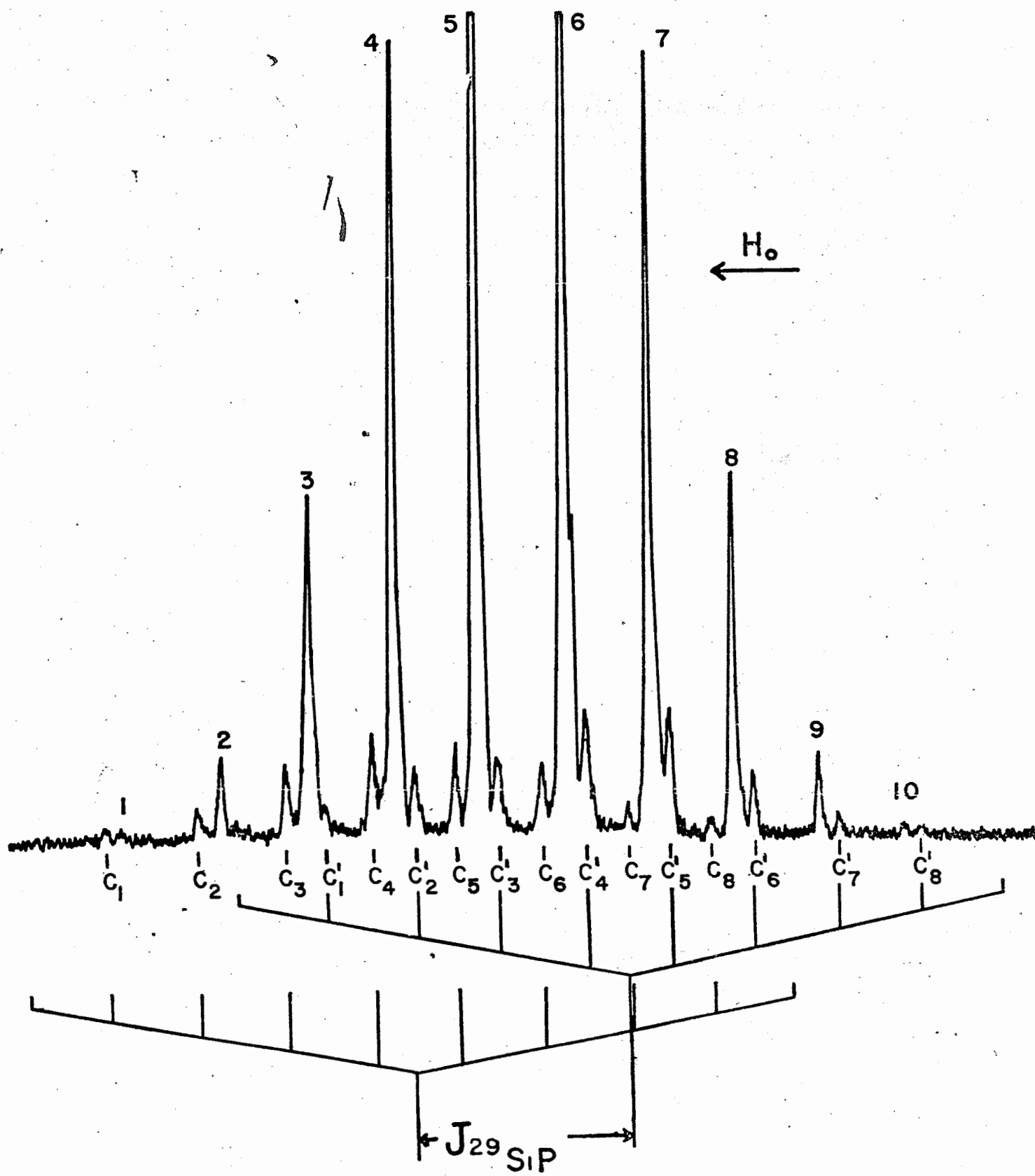
Please credit this to the University of Colorado subscription.

Sincerely yours,



Arlan D. Norman

Assoc. Professor of Chemistry



University of Toronto
FACULTY OF PHARMACY
19 Russell Street

TORONTO 181, ONTARIO

May 16, 1972.

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

Dear Barry:

Would you please enter the following announcement into the next issue of the TAMU NMR Newsletter:

Postdoctoral Position Available

A postdoctoral position for the academic year 1972-73 is available in my laboratory. The fellowship pays a stipend of approximately \$10,500 per year, and it is renewable.

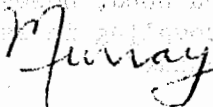
Our equipment consists of a Varian XL-100-15 spectrometer equipped with FFT for ^1H , ^{13}C , and ^{19}F . We have access to an HR-200 equipped for ^1H with time averaging.

The main current interest in my group is the study of ^{13}C chemical shifts and relaxation times of a number of biologically interesting macromolecules. Other biological NMR studies involved both ^1H and ^{19}F nuclei.

I am looking for a student with a good background in physical chemistry (especially in NMR) with interests and experience in ^{13}C -NMR and computer programming.

Further inquiries or applications should be made by the interested persons directly to me at their earliest convenience.

Sincerely yours,



Murray H. Freedman, Ph.D.,
Associate Professor of Biochemistry.

MHF:pm

Department of Chemistry



YORK
UNIVERSITY

FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW 463, ONTARIO

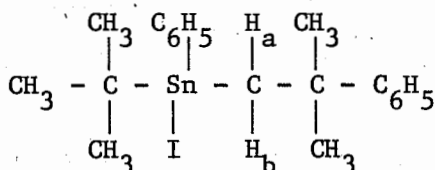
12 May 1972

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

Dear Dr. Shapiro,

NMR of Organo-Tin Enantiomers,
-nonequivalent coupling.

As indicated in our last letter (Dec. 1971) we are currently interested in dissymmetric tin compounds. Further probes into the nmr of these materials have indicated that correlations of $^2J_{\text{SnH}}$ and percent s-character are not reliable. This has been suggested previously¹ from other correlations but we have now found several cases in which two or three values for percent s-character of a single tin-carbon bond can be obtained. The most striking example so far is



Where the protons a & b give an AB spectrum plus an ABX spectrum when Sn(117) or Sn(119) is present. In the ABX system J_{AX} and J_{BX} differ by a large amount, i.e. 35 Hz and 55 Hz. Clearly, the orbital character of the relevant Sn-C bond through which Sn-H coupling is supposed to be transmitted must either have two "planes of existence" or the SnH coupling is also transmitted independently of this bond. One could argue that the difference lies in the C-H bond, however this is not consistent with previous reports of C-H coupling in assymmetric compounds² or C-13 data on some of the present compounds³.

Professor B.L. Shapiro
College Station, Texas

12 May 1972

In recent issues of Organomet. Chem. and earlier issues of Chem. Comms. and elsewhere, the nonequivalence of Sn-CH₃ coupling in systems where tin is next to an assymetric carbon centre has been reported. The differences are very small and not comparable to our systems. Elsewhere, scattered throughout the literature one finds other cases of non-equivalent geminal MX couplings of the type M-C-X where X is F, H, or C (for example the recent report in TAMU), and M is usually Phosphorus, but examples involving Rh and now Sn⁴ can also be found in the literature.

We are currently looking for a common feature in all the examples we can find. A pattern seems to be emerging, but perhaps the most challenging aspect remains the theoretical explanation of these effects.

Yours sincerely,

C.E. Holloway *S.A. Kandil*

C. E. Holloway & S. A. Kandil

CEH:pc

References

1. For example: W. McFarlane, J.Chem.Soc. A, 528 (1967)
2. L.S. Rattot, L. Mandel & J.H. Goldstein, J.Amer.Chem.Soc., 89, 2253 (1967).
3. Courtesy of Prof. J. Stothers, University of Western Ontario.
4. Forthcoming J.Amer.Chem.Soc.



SIR GEORGE WILLIAMS UNIVERSITY

MONTREAL 107, CANADA

April 4, 1972

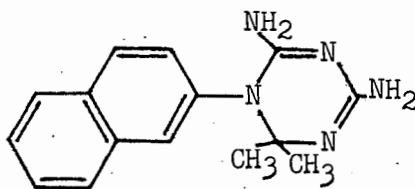
Professor B.L. Shapiro
 Department of Chemistry
 Texas A and M University
 College Station, Texas 77843
 U.S.A.

Dear Barry,

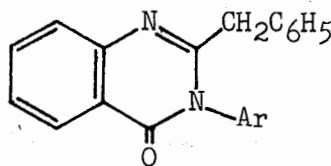
Hindered Rotation About Aryl C-N Bonds in Compounds Lacking Bulky Aryl

Substituents

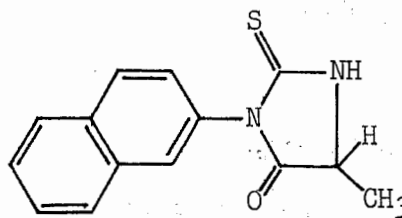
In the course of a study of hindered rotation about aryl C-N bonds we have recently investigated the behaviour of some aryl substituted heterocyclic compounds which lack bulky ortho substituents on the aryl group. We have now found some compounds which have substantial rotational barriers. The heterocyclic moiety is sufficiently bulky that rotation is slow on the n.m.r. time scale at normal temperatures even though the blocking substituents on the aryl groups are hydrogen atoms.



(I)



- (IIa) Ar = β-naphthyl
 (IIb) Ar = 3-bromophenyl
 (IIc) Ar = 3-acetylphenyl



(III)

At room temperature, the diastereotopic methyl groups of 1-(β-naphthyl)-1,2-dihydro-2,2-dimethyl-4,6-diamino-s-triazine, (I) give rise to two lines and the diastereotopic benzylic methylene protons of the 3-aryl-2-benzyl-4(3H)-quinazolones, (IIa), (IIb), and (IIc), give rise to AB quartets, indicating slow rotation of the aryl group on the n.m.r. time scale. When the samples are heated the spectra arising from these protons collapse to a singlet in each case, indicating fast rotation on the n.m.r. time scale. Similarly, the 5-methine protons of the two diastereomeric rotational isomers of 3-(β-naphthyl)-5-methyl-2-thiohydantoin, (III), give rise to two overlapping quartets at room temperature and a single, time averaged quartet at higher temperatures.

(CONTINUED)



SIR GEORGE WILLIAMS UNIVERSITY

MONTREAL 107, CANADA

Professor B.L. Shapiro
Department of Chemistry

Because of the rather small chemical shift differences involved in the temperature dependent regions of the spectra we have not attempted to obtain a complete set of activation parameters by line shape analysis over a range of temperatures. The rate constants for (I) and (II) were obtained by the usual coalescence point methods. The rate constant for (III) was obtained by computer simulation of the line shape at coalescence.

Activation parameters and other details are listed in the Table.

Best regards,

Yours sincerely,

Laurie Colebrook

L.D. Colebrook
H.G. Giles

LC/bb

TABLE

N.m.r. data, coalescence temperatures, and free energies of activation

Solvent	Chemical shift difference, p.p.m. ^a	J_{AB}	Coalescence ^b temperature	ΔG^\ddagger ^c
(I) Perfluorobutyric acid	0.032 ^d		141	22.9
(IIa) Nitrobenzene	0.132	15.1	116	20.1
(IIb) Nitrobenzene	0.088	15.1	94	18.9
(IIc) Nitrobenzene	0.105	15.0	102	19.3
(III) DMSO-d ₆	0.011		97.5	21.7

^a100 MHz spectra

^bDegrees C.

^cFree energy of activation (kcal. mole⁻¹) at coalescence temperature.

^dMeasured at 109°C.

KEMISK INSTITUT

AARHUS UNIVERSITET

LABORATORIET FOR ORGANISK KEMI

8000 Århus C, den May 26, 1972
Telefon (06) 12 46 33 HJJ/ATLProfessor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
COLLEGE STATION, Texas 77843
USA

Dear Professor Shapiro:

Effect of Lone-Pair Electrons on $^2J_{\text{CCP}}$ in Arylphosphines

Stereospecificity on $^2J_{\text{CCP}}$ in some cyclic phosphines has recently been the subject of some contributions to your newsletters (1,2). In connection with a ^{13}C NMR study of ^{13}C - ^{31}P coupling constants in some arylphosphines (3) we have observed that ortho-substituents have a profound influence on $^2J_{\text{CCP}}$ in these systems. The signs and magnitudes of some of the ^{13}C - ^{31}P couplings, obtained from noise and selective proton decoupled ^{13}C spectra (Figure) on a Varian XL-100-15 spectrometer, are given below the formulas

$^2J_{\text{C}(2)-\text{P}}:$	+33.88 Hz	+23.09 Hz	0.25 Hz	-1.66 Hz
$^2J_{\text{C}(4)-\text{P}}:$	+1.09 Hz	+17.50 Hz	+27.38 Hz	+35.10 Hz
$^2J_{\text{C}(2)-\text{P}}:$	+19.65 Hz	+26.44 Hz	+27.90 Hz	
$^2J_{\text{C}(6)-\text{P}}:$	+19.65 Hz	0.41 Hz	0.63 Hz	

The observed influence of ortho-substituents on $^2J_{\text{CCP}}$ may be explained as a geometrical dependence of this coupling on the orientation of the non-bonded electrons on phosphorus with respect to the ring planes. The experimental data indicate a preferred conformation for the ortho-substituted arylphosphines in which the ring planes are twisted so as to align the substituent towards the phosphorus lone-pair of electrons.

A communication of this work has been submitted to J.A.C.S. A few preprints are available.

Yours sincerely,

Hans J. Jakobsen *Stig Sørensen* *R. S. Hansen*
Hans J. Jakobsen Stig Sørensen R. S. Hansen

References

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G. A. Gray and S. E. Cremer, Chem. Commun. 1972, 367.
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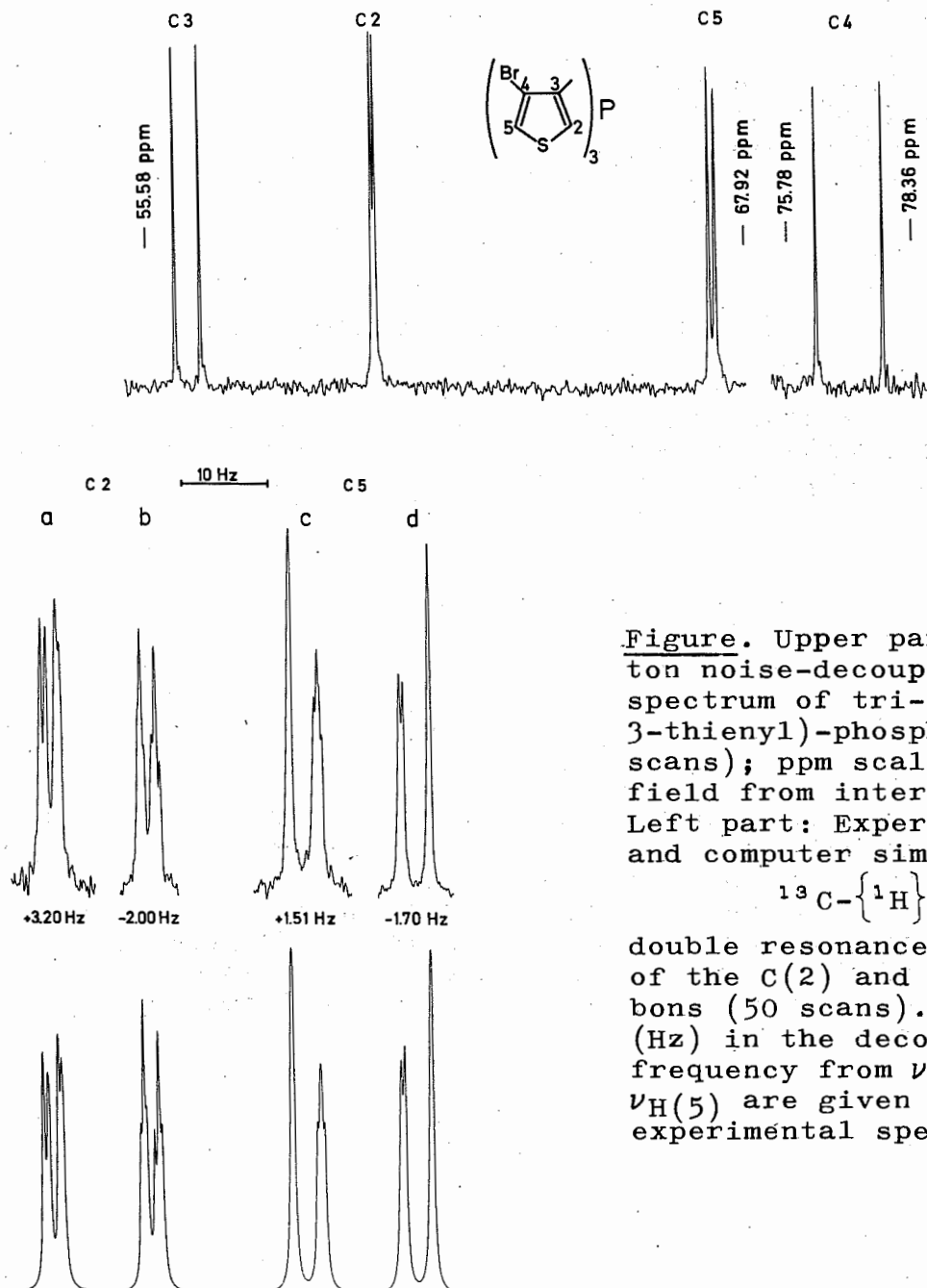
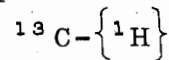


Figure. Upper part: Proton noise-decoupled ^{13}C spectrum of tri-(4-bromo-3-thienyl)-phosphine (50 scans); ppm scale is upfield from internal CS_2 . Left part: Experimental and computer simulated



double resonance spectra of the C(2) and C(5) carbons (50 scans). Offsets (Hz) in the decoupling frequency from $\nu_{\text{H}(2)}$ and $\nu_{\text{H}(5)}$ are given below the experimental spectra.

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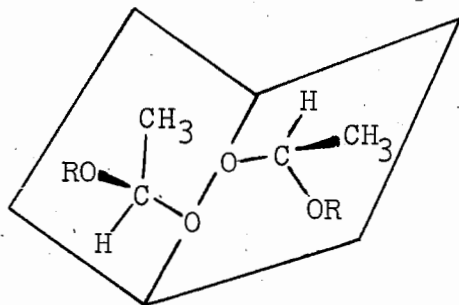
May 30, 1972

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

Dear Barry,

Title: Diastereomeric Peroxides

Although you have probably had enough letters on non-equivalent hydrogens in a methylene group here is one with a slightly different twist. The peroxide



shown in the diagram has two assymetric centers and is therefore capable of existing as d, l and meso isomers. When R is an ethyl group the methylene protons should be magnetically non-equivalent. If there is rapid inversion about the oxygen-oxygen bond (flapping of the pages in the diagram) that is the end of the story. If the inversion is hindered both conformations are equivalent for the meso isomer but not the d, l isomer.

The above peroxide with an ethyl group as R was provided by Dr. Howard of these laboratories. It was shown, both by gas chromatography and by its proton resonance spectrum, to be an equimolar mixture of the two stereoisomers whose spectral parameters, at room temperature, are given in the table. In methylene chloride as solvent all the lines from the protons of the peroxide, but not the solvent, had broadened somewhat by -90°C . In the hope that we were seeing the onset of hindered inversion spectra were obtained down to -130°C in CF_2Cl_2 as solvent. Also the lines remained sharp and another piece of negative information has been accumulated.

Yours truly,



SB/dn

S. Brownstein.

	Isomer I	Isomer II
$\delta \text{ CH}_3$ p.p.m.	1.244	1.273
$\delta \text{ CH}$	4.958	4.891
$J \text{ CH-CH}_3$ Hz*	5.5	5.6
<hr/>		
$\delta \text{ CH}_2\text{A}$	3.676	3.707
$\delta \text{ CH}_2\text{B}$	4.078	4.025
$J \text{ A-B}$	9.7	9.7
$\delta \text{ CH}_3$	1.171	1.171
$J \text{ CH}_2\text{-CH}_3$	7.2	7.2

* The assignments to isomers I and II only above and only below the line are unique. Those below the line may be interchanged relative to those above the line without significant change in the spectra.

Laboratorio dei composti del carbonio contenenti etero-atomi e loro applicazioni
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Dr.C.Andrea Boicelli

li. 29/5/1972

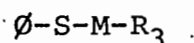
Professor Bernard L. SHAPIRO
Department of Chemistry
Texas A & M University
College Station - TEXAS 77843

Title: ^{13}C Shift in Aryl-Metal Alkyl-Sulphides.

Dear Professor Shapiro,

Recently we have successfully employed our JEOL PS 100 to record ^{13}C spectra in CW mode; we found this system very nice and easy to use, and this fact is encouraging in view of the conversion of our presents CW system to FT.

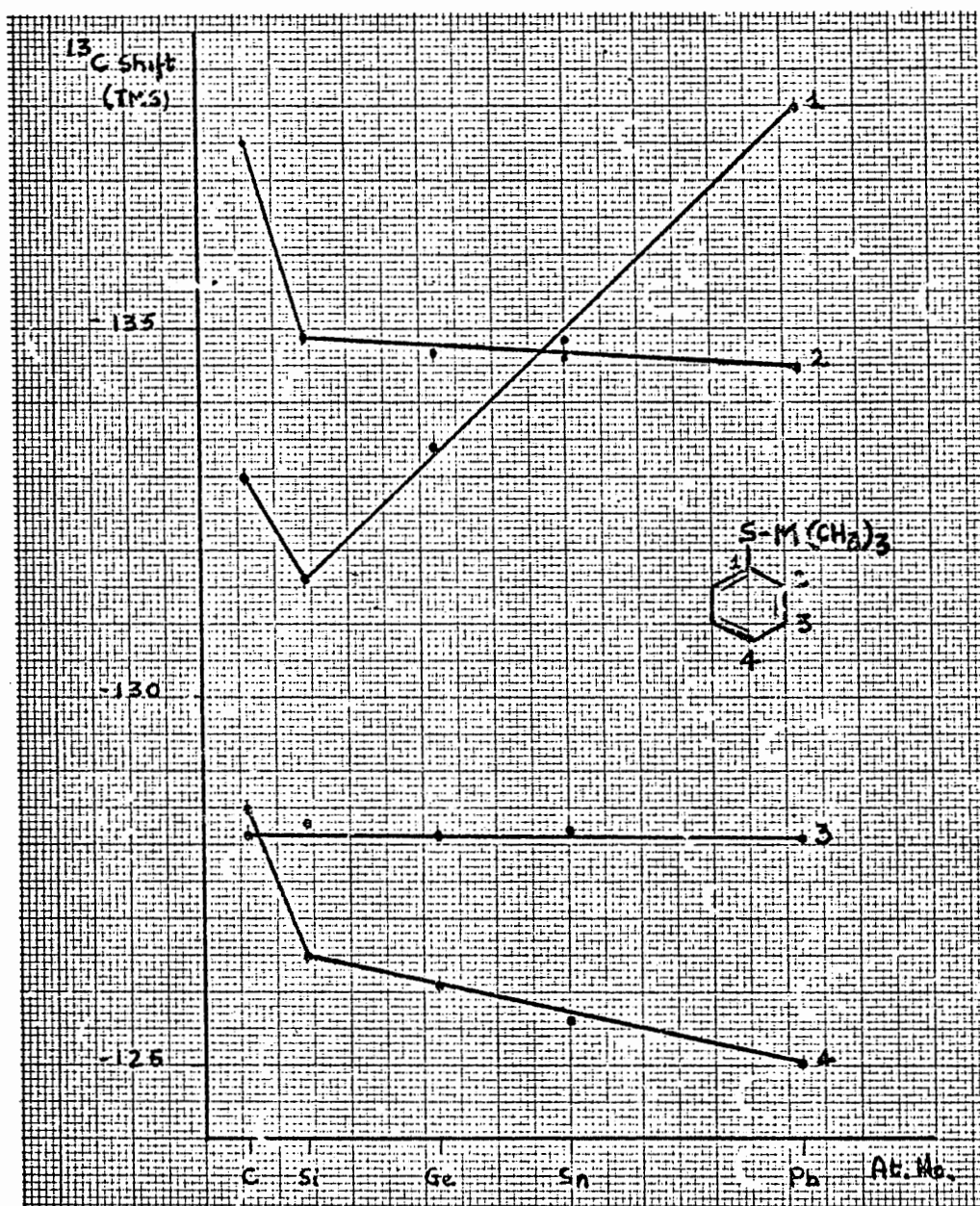
Among other things we studied this class of compounds:



where M = C, Si, Ge, Sn, Pb and R = CH_3 .

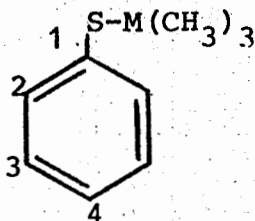
In the aromatic region the ^{13}C shift seems to be only dependent from the electronic structure of M; in fact the trend of 1 and 4 carbon shifts are simply related to the atomic number of M, whilst the 3 carbon shift is remarkably constant.

In view of the fact the meta shift reflects mainly the inductive effect of the substituents and the para shifts its resonance effect (G.E.Maciel, J.J.Natterstad - J.Chem.Phys., 42, 2427, 1965) we feel that the effect of the different -S-MR₃ groups is mainly mesomeric.



^{13}C Shift (ring) versus atomic number.

h.



Chemical Shifts (in p.p.m.) respect to
TMS at 25.2 MHz.

	1	2	3	4	CH ₃
C	-132.99	-137.52	-128.15	-128.46	-32.0
Si	-131.63	-134.87	-128.30	-126.49	-2.0
Ge	-133.44	-134.72	-128.15	-126.12	-1.5
Sn	-134.80	-134.57	-128.23	-125.59	+3.0
Pb	-138.04	-134.50	-128.08	-125.06	-10.5

The spectra were recorded in solution (60% v-v) in CCl₄, used as internal reference, and the shifts are converted on TMS scale (G.C.Levy, J.D.Cargioli - J.Magn.Resonance, 6, 143, 1971).

The accuracy of the measurement is ± 0.05 p.p.m.

This conclusion is also supported from the reactivity behaviour in the hydrolytic reactions.

To confirm this conclusion we will study also the class of compounds ϕ -X-MR₃ where X are the VIA groups elements.

The methyl shift, however, cannot be explained in the simple terms of atomic number and of electronegativity of M.

Sincerely Your
C.Andrea Boicelli

Andrea Boicelli



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION
WASHINGTON, D.C. 20204

23 May 1972

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

PMR ? Heteronuclei ?

Dear Barry,

You may want to consider the following as a negative contribution to the Newsletter, inasmuch as it contains suggestions to abandon something, for instance the use of some inconsistently used and misleading acronyms.

It has become quite common to abbreviate "proton magnetic resonance" by "PMR" or "carbon magnetic resonance" by "CMR". Admittedly, "CMR" makes some sense, whereas "PMR" does not: at first sight, at least I would think it means "phosphorus magnetic resonance", which it does not. In the same vein, "NMR" then would mean "nitrogen magnetic resonance"; but now, which isotope of nitrogen is meant?

My plea is to leave NMR intact and never replace its N by a letter denoting - in a correct, ambiguous or incorrect fashion - the nucleus whose resonance is observed. In positive terms, proton NMR could be abbreviated "¹H-NMR". I hope that current trends in the direction of PMR and CMR can still be reversed.

While I am in griping mood, as far as language is concerned, I'd like to voice my opinion on the use of "hetero" as a prefix. I believe it is alright to use it in connection with "nuclear", when multiple resonance is referred to, as long as the observed nuclei and the others ("heteros") additionally irradiated are both specified in a general or particular way. However, I think it is objectionable to use "heteronuclear NMR" to denote "NMR of nuclei other than protons", without saying explicitly that the 'non-heteronuclei' are protons. To my mind it is equally wrong to refer to such nuclei as "heteronuclei" without defining the 'non-heteronuclei'. After all, the tide is turning, and in a few years the nuclei may be ¹³C and all others "heteronuclei". Briefly, referring to heteronuclei as such is like asking in a store "Do you sell any counterparts?".

So there it is, rammed into the ground.

I trust that the above will not be counted against my period of grace for the Newsletter subscription.

Sincerely,
Ernest
Ernest Lustig

Princeton University DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08540

March 14, 1972

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

Title: Amide Rotation

Dear Barry:

Your reminder letter found me on sabbatical leave from UCR at Princeton. I am associated with Prof. Walter Kauzmann and trying to learn a little protein chemistry. This has particular relation to our continuing program involving studies of effects of pressure on chemical systems, not our nmr work.

In my absence, Dr. Violet Jonas has been continuing her nmr studies of rotational barriers in amides. She is particularly concerned with trying to get activation parameters for C-N rotation at very low concentrations of amide or thioamide in non-polar solvents. The goal, of course, is to attempt to get data for unassociated monomers. The studies require optimal performance of the spectrometer; something that is not consistent. The data have now been obtained and are being analyzed. I'll report the results when they are available.

Sincerely yours,



Robert C. Neuman, Jr.
Visiting Associate Professor

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