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Newsletter

No. 163

APRIL, 1972

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A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

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Deadline Dates:	No. 164: 1 May 1972
	No. 165: 5 June 1972

All Newsletter correspondence, etc. should be addressed to:

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

N° 15

March 13, 1972

Prof. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
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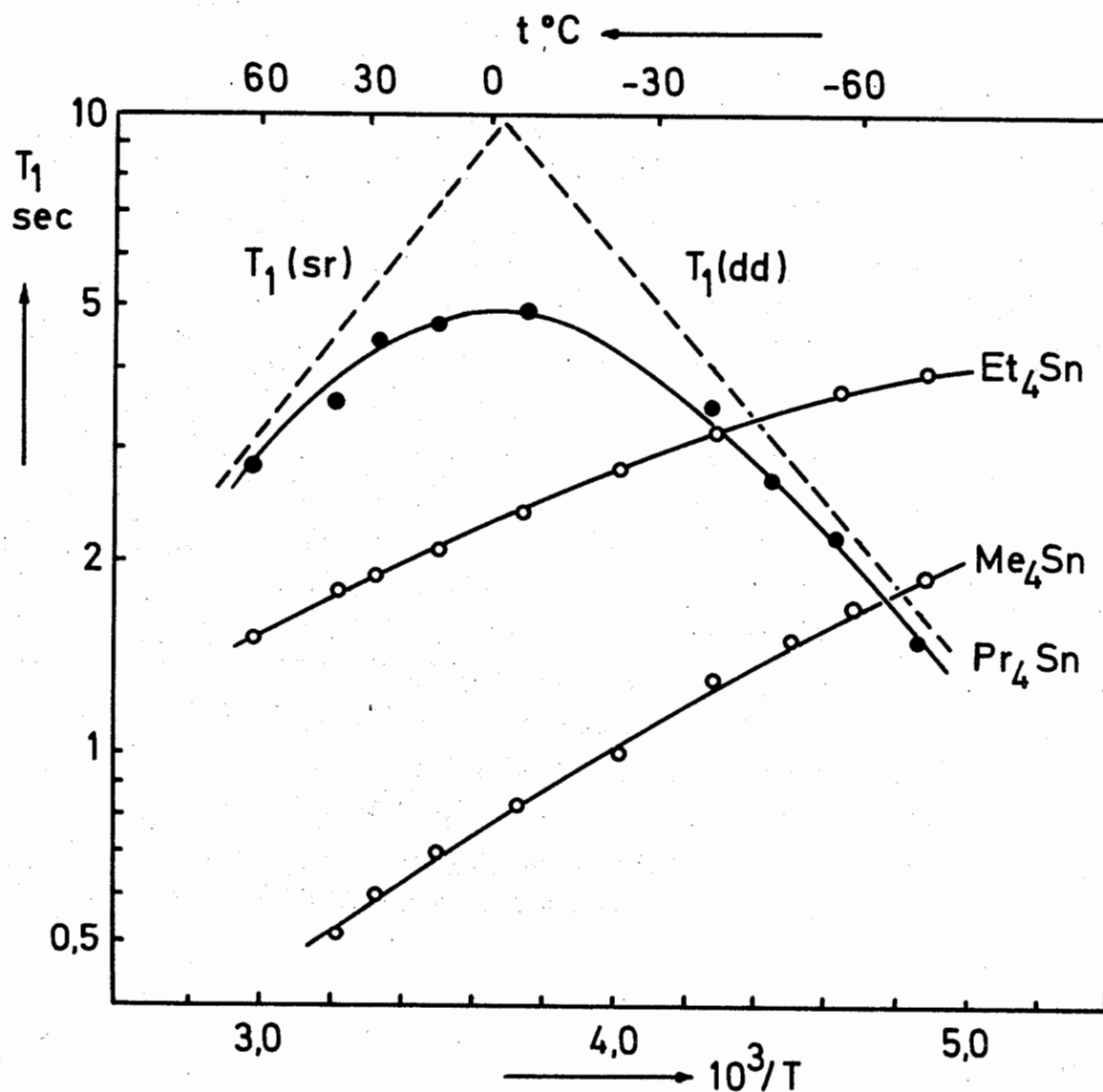
Spin-lattice relaxation of tin ^{117}Sn nuclei

Dear Professor Shapiro ,

Thank you for your nice blue letter. I was afraid of getting it for some time already.

We have recently studied the spin-lattice relaxation of tin ^{117}Sn nuclei in organic compounds. As is well known by now, ^{13}C relaxation provides much useful information about molecular structure, conformation and movement and we were interested, whether heavier nuclei can be used for similar purposes. Also, chemical polarization of heavier nuclei can give interesting information about homolytic reaction mechanisms, but some idea about the relaxation times is needed for successful experiments. It has been sometimes assumed that the relaxation times of heavy nuclei can be rather long. Such assumption is based on the predominance of dipole-dipole interactions and has already been shown to be only partly true for ^{13}C and ^{15}N . As can be seen from the Figure the relaxation times T_1 of tin ^{117}Sn nuclei, measured at 21.38 MHz frequency and room (23°C) temperature, are actually rather short, much shorter than those of carbon ^{13}C or protons in

similar molecules. At room temperature the spin-rotation interaction is clearly predominant as could be expected on the basis of increasing paramagnetic shielding and total shift range for the heavier nuclei. It is apparent that tin and other, still heavier nuclei, like mercury ^{119}Hg , thallium $^{203,205}\text{Tl}$ or lead ^{207}Pb can hardly give much useful information about the proximity of protons and are not very good objects for chemical polarization experiments. On the other hand, some rough mean values \bar{c} of the tin ^{117}Sn spin-rotation coupling tensor can be calculated from the room temperature relaxation data.



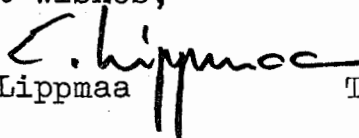
Compound	$I \cdot 10^{-38}$ gcm ²	ν cst	T_1 (sr) sec	$\tau_c \cdot 10^{-11}$ sec	$\tau_{sr} \cdot 10^{-14}$ sec	\bar{c} kHz	δ ppm*
Et ₄ Sn	9.5	0.62	1.9	0.73	5.3	10.5	1.3
Pr ₄ Sn	22	1.23	5.4	1.81	5.0	4.2	-16.3
Et ₃ SnCl	9.5	1.40	2.0	1.70	2.3	15.5	163.8
Pr ₃ SnCl	19	1.95	2.0	2.78	2.8	10.0	143.8

* downfield from Me₄Sn

The ¹¹⁷Sn spin-rotation coupling constants are large, but perhaps not too large for such a heavy nucleus.

At the present time we are planning some further work with tin, silicon and carbon relaxation and are experimenting with an analogue technique for a simple and fast Fourier Transform of these spectra. It seems to work rather nicely for relaxation studies, although naturally, no pure absorption spectra can be registered this way.

With best wishes,


 E. Lippmaa


 T. Saluvere

DOW CORNING

March 6, 1972

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

Dear Professor Shapiro:

Subject: LIS (Lanthanide-Induced NMR Shift) Reagents:
A Better Way to Use Them

I am particularly interested in the usefulness of LIS reagents (1) for the identification and quantitative analysis of components in otherwise intractable mixtures. For this purpose LIS bands must be assigned to particular components in the mixture. When one has the luxury of selecting the problem, the splitting patterns or gross magnitudes of LIS values may enable these assignments to be made. However, in "real life" mixtures, often neither splitting patterns nor LIS values are of great help. The LIS value becomes less diagnostic of a particular component due to preferential complexation of the LIS reagent. Hence the results of LIS studies of pure components are not presently of general utility when characterizing mixtures.

I recently developed a technique which remedies this difficulty (2,3). LIS values of components in mixtures can be predicted from LIS studies of "pure" components provided that a shift monitor is added in both instances. The shift monitor should form a 1:1 complex with LIS reagent and should display a simple NMR spectrum (e.g., methanol, dimethyl sulfoxide, acetone, or acetonitrile). The LIS band of the shift monitor may, of course, be assigned by "spiking" the sample. It is necessary that all experiments be done with the same LIS reagent and temperature although not necessarily with the same shift monitor. It may also be necessary to use the same, inert solvent.

My concern is that a large data base of LIS studies is building up in the literature whose general usefulness will be impaired unless the "shift monitor method" is rapidly adapted by those contributing to this field. A standard temperature and solvent and a limited number of LIS reagents should also be agreed upon as soon as possible, I feel.

Professor B. L. Shapiro
Page 2
March 6, 1972

This concern presumes, of course, that the "monitor shift" method is in fact valid and useful. I have proven this presumption to my satisfaction with carefully-designed experiments and with practical use of the method. I invite comments and criticisms of the method and will send preprints (2) to those who wish to use or test the method.

Sincerely,

Dwight E. Williams

Dwight E. Williams

- (1) C. C. Hinckley, J. Amer. Chem. Soc., 91, 5160, (1969).
- (2) D. E. Williams, Tetrahedron Lett., in press.
- (3) D. E. Williams, TAMU NMR 159-4.

gb

MCMMASTER UNIVERSITY

HAMILTON, ONTARIO, CANADA

DEPARTMENT OF CHEMISTRY

March 8, 1972

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

Dear Barry:

Re: Deuterium Isotope Effects on ^{13}C
Chemical Shifts

During the past year, among other things, we have been studying the effects of Deuterium substitution on the ^{13}C spectra of substituted benzenes. Despite our somewhat inadequate instrumentation by today's standards, this work has yielded some interesting results.^{1,2}

Our ^{13}C equipment consists of an 8 year old, second hand HA 100 to which we have added a multitude of modifications including an audio device to herald the arrival of a signal, a Wavetek model 114, a Varian Associates V 3512-1 noise decoupler and a C. 1024 time averaging device. Being blessed with only a 12 inch magnet, we are limited to using 5 mm o.d. sample tubes. Our sample size is again reduced by the inclusion of a 1.5 mm o.d. capillary tube containing $^{13}\text{CS}_2$ to provide a lock. We understand that many other workers with similar instrumentation have given up the battle, however we find our persistence has proved fruitful.

In the measurement of data, we have found it necessary to apply certain correction factors; for example, over long periods, the wavetek sweep time can drift up to 0.5%. Also we have found that the length of the spectrum when printed out from the CAT may vary by up to 1% due to variations in CAT print out time and recorder travel time. These factors are critical for our particular mode of operation. For greater accuracy and simplicity of operation of the Wavetek, the one turn potentiometers associated with the "sweep position", "sweep width" and "sweep rate" controls have been replaced with ten turn potentiometers.

March 8, 1972

It is surprising to note that very little work has been done on the effects of Deuterium substitution on ^{13}C chemical shifts. The spectrum of monodeuteriobenzene (fig. 1) at first glance appears quite unusual, however it is quite typical of the pattern observed for other substituted compounds. The carbon bearing the Deuterium is split into a triplet (not all shown here) $J^{13}\text{C}, ^2\text{H} = 25.00$ Hz and is shifted to higher field (0.289 ppm). The two ortho carbons ($J^{13}\text{C}, ^2\text{H} = 0$) are shifted upfield to a lesser extent (0.110 ppm). The meta carbons show a pronounced coupling of 1.14 Hz to the Deuterium and are moved upfield by 0.011 ppm. It is interesting to note that this long range coupling has been observed in all the substituted benzenes so far investigated and coupling constants vary from 0.7 to 1.3 Hz. The second order isotope shifts i.e. the carbon adjacent to the carbon bearing the deuterium, range from 0.09 to 0.12 ppm.

Our current work involves the measurement of directly bonded shifts for Deuterium in the ortho position of a number of substituted benzenes, which we are proposing as a measure of a Hammett σ .

1. G. L. Lebel, J. D. Laposa, B. G. Sayer, R. A. Bell, *Analyt. Chem.*, 1971, 43, 1500.
2. R. A. Bell, C. L. Chan, B. G. Sayer, *J. Chem. Soc.*, 67, (1972).

Yours sincerely,

Russell Bell, Brian Sayer
R. A. Bell, B. G. Sayer

P.S. Ron Gillespie has been hypnotised of late by the eye of the laser Raman — would you consider this contribution to Newsletters from McMaster to be in my name.

Figure 1

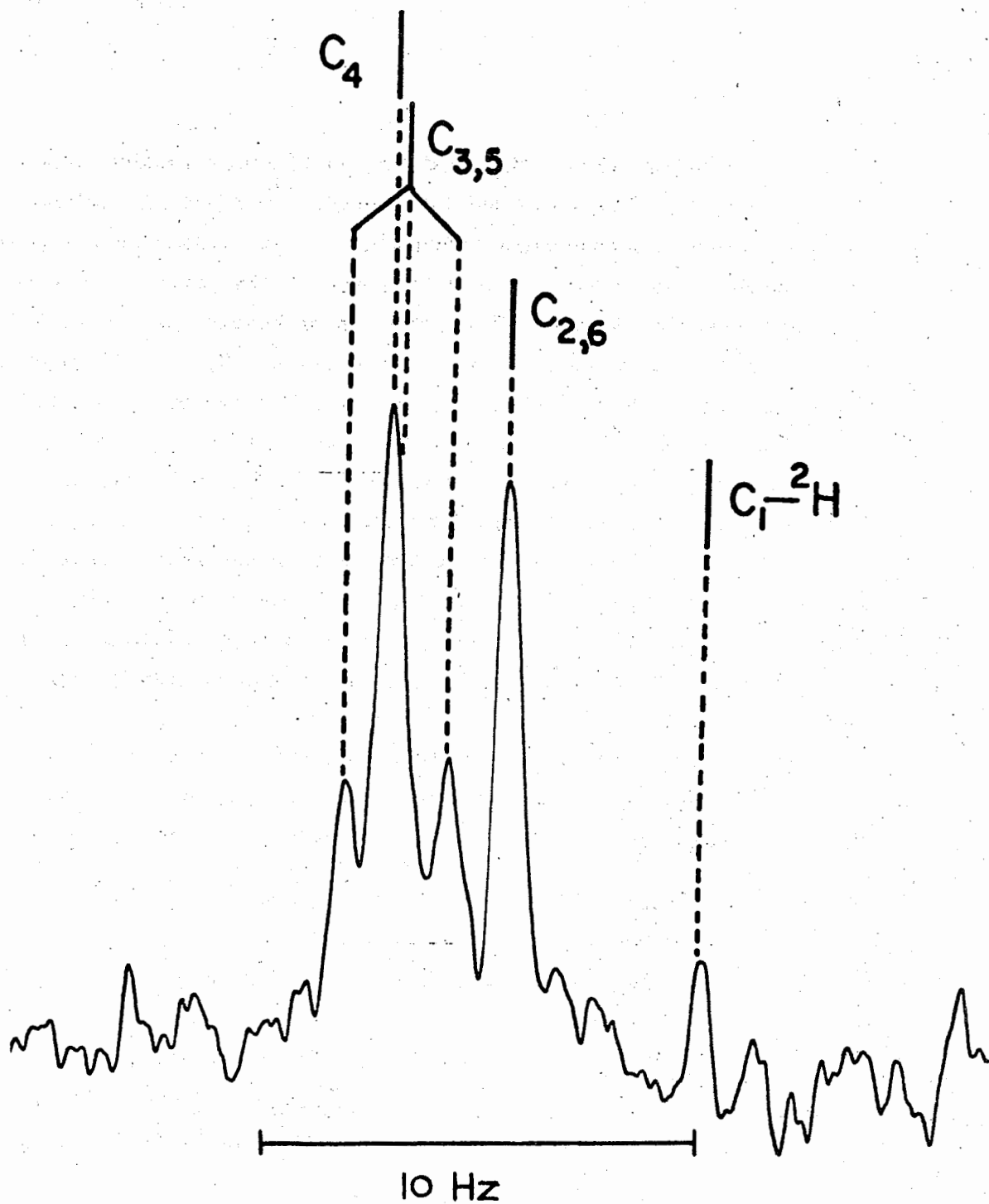


Figure 1. Part of ^{13}C spectrum of monodeuteriobenzene after a signal accumulation of 4 scans.



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ISOTOPE DEPARTMENT

מחלקת איזוטופים

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

March 12, 1972

Dear Professor Shapiro:

Recently Mordechai Shporer and myself have been experimenting with shift reagents (who doesn't?). We followed the proton resonances of the ligands of $\text{Eu}(\text{fod})_3$ and $\text{Pr}(\text{fod})_3$ and found that they are very sensitive to substrate concentration. Using Scatchard plots to analyse data we concluded that a 1:1 reagent-substrate complex is formed. A similar conclusion was reached by Karin Norlen, Jack Leigh (of Philadelphia) and myself by following the substrate resonances in the pyridine - $\text{Eu}(\text{dpm})_3$ system (submitted to JACS).

We also tried to use shift reagents to evaluate conformations of some ionophores. We observed stereospecific shifts with the free ionophores; however, when we tried to introduce monovalent-ion salts, the anion totally complexed the shift reagent.

I am writing now a review article on shift reagents and would appreciate receiving preprints on the subject.

Sincerely yours,

Jacques Reuben

Title: Shift reagents - stoichiometry of adducts; use with ionophores;
 request for preprints.

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

Your ref	Our ref	Tel ext	Date
	DG/RB	7-462	13 March 1972

Dear Professor Shapiro,

Time sharing F.T. NMR with mass spectrometry

We have, for the past three months, been developing a Fourier Transform NMR system for ^1H and ^{13}C nuclei using a Varian HA100D with an F.T.100 accessory, an interface system supplied by Instem Ltd. and a G.E.C. M.2140 32K computer which is also on line to one high and one low resolution mass spectrometer. The time sharing of the computer core has been arranged such that the NMR system is inhibited during its accumulation time, only when high resolution mass spectral data is being acquired. 8K of core is available for accumulated data and this allows up to 4K output points.

The physical separation of spectrometer and computer (i.e. ca 20 yds and 2 brick walls), extensive use of the computer typewriter by the mass spectrometer system, together with the cost of an additional typewriter necessitated the design of a control panel for F.T. operation located in the HA100D console. This control panel is built around two three-pole eight way switches which are wired to place binary coded information into six sense lines to the computer. One switch is designated as 'FUNCTION' and directs the computer to perform eight operations - (1) initialise (2) accumulate (3) stop accumulate (4) apodise, smooth and transform (5) output to oscilloscope (6) select Y expansion (7) integrated output to recorder (8) normal output to recorder. The second switch gives corresponding data for any of these eight operations, i.e. spectral width, accumulation time, scaling factors, phasing routines etc. The control panel also has eight indicator lights switched by the decoded output of three reed relays controlled by the computer, an alarm which sounds if the lock on the spectrometer fails during a data transfer, and an electromechanical counter to indicate the number of F.I.D.'s accumulated.

Although this idea of using a control panel instead of a teletype does not give us a flexible system where we can do pulse sequence work, we

Professor B. L. Shapiro

6 March 1972

have a simple working system capable of providing us with ^1H and ^{13}C NMR spectra. A future development will be to measure ^{13}C frequencies accurately and display these on a frequency counter. This again means that the computer console typewriter will not be needed.

Please credit this contribution to Dr. G. R. Bedford of these laboratories.

Yours sincerely,

D. Greatbanks *I. C. Wright*

D. Greatbanks, I. C. Wright,
Physical Methods Section.

UNIVERSITY OF CALIFORNIA, DAVIS

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SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

March 13, 1972

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

Proton Relaxation in High-Spin Ferric Porphyrins

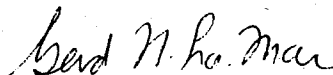
Dear Barry,

A recent review¹ has emphasized the developing utility of proton nmr spectra in investigating the solution structures of paramagnetic heme-iron complexes and proteins. Most investigations have been restricted to low-spin ferric systems for which inefficient proton relaxation leads to well-resolved proton nmr traces. In the high-spin forms, line broadening has prevented extensive applications. Since interesting systems may possess the heme-iron in the high spin state, we have investigated methods for decreasing the efficiency of the proton relaxation by selective perturbations on the electronic structure of the porphyrin complex.

It is observed for the series of high-spin complexes, TPPFeX, (where TPP is tetra-phenylporphyrin), with X = I, Cl, Br, N₃, and F, that the pyrrole proton peak linewidth is markedly dependent on X, with values of 110, 160, 250, 370, and > 800 Hz at 100 MHz, respectively, using CDCl₃ as a solvent. The paramagnetic shift is essentially independent of X, (~ -80 ppm from TMS). It has been shown² that the zero-field-splittings in such porphyrins can be very large, and vary with X in the order I > Br > Cl > N₃ > F. The observed linewidth trend is therefore consistent with a relaxation mechanism³ where the correlation time for the proton relaxation is the electron spin-lattice relaxation time, T_{1e}, which in turn is determined by modulation of the zero-field splitting by the tumbling of the complex in solution.

The observed reduction in linewidth by a factor of ~ 2.5 by substituting I for the more conventional Cl ligand suggests the possibility that a judicious choice of axial ligand may improve considerably the resolution of proton nmr spectra of high-spin iron porphyrins, thereby permitting the investigation of the solution structure of high-spin heme proteins.

Sincerely,



Gerd N. La Mar

1. K. Wütrich, Structure and Bonding, 8, 53 (1970).
2. G.C. Brackett, P.L. Richards and W.S. Caughey, J. Chem. Phys., 54, 4383 (1971).
3. M. Rubinstein, A. Baram, and Z. Luz, Mol. Phys., 20, 67 (1971).



UNIVERSITY OF SASKATCHEWAN REGINA CAMPUS

DEPARTMENT OF CHEMISTRY

REGINA SASKATCHEWAN

S4S 0A2

March 14, 1972

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

Dear Dr. Shapiro:

The rôle of the reference compound in ASIS

We have just completed a study of the influence the reference compound has on ASIS and its application. Using 5 α -androstane and its 3-one, 17-one and 3,17-dione derivatives as solutes and using TMS, C₆H₆, cyclohexane, acetone and chloroform as the internal references, we have found the following:

1. For any solute (proton signal) the ASIS depends very strongly on the choice of reference compound. The range is usually more than 1 ppm and covers both negative and positive ASIS's.
2. The additivity of ASIS also depends very strongly on the choice of internal reference. In some cases indeed good additivity is observed while with other references discrepancies of up to 1 ppm are observed.
3. A theoretical analysis, in which all shifts are referred to zero pressure gas-phase shows that the above results are to be expected. In spite of the double difference technique in ASIS the solvent effects of the reference compound do not cancel out at all.
4. It is also found that ASIS additivity can be achieved if the following two conditions are simultaneously met:
 - (i) that the differential (CHCl₃ - C₆H₆) medium effect ΔR_m for the reference is equal to that of the solute hydrocarbon analogon ΔX_{om} .
 - (ii) that the increments (due to substitution) of the differential (CHCl₃ - C₆H₆) medium effects of the solute are additive.

These conditions are quite different from any advanced so far {1}

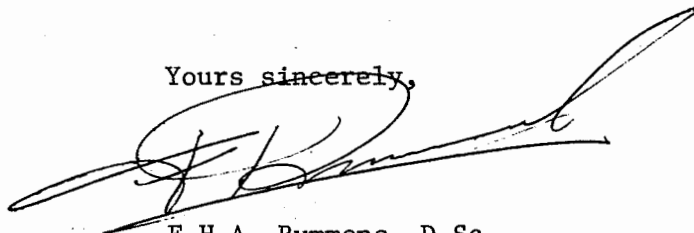
5. For solutes with two (or more) proton signals the difference of the ASIS's is free from internal reference problems, but the ratio {2} is not.
6. Engler and Laszlo's statement {2} that if two ASIS's of a solute relate linearly with variation of aromatic solvent, that then ASIS can be separated into a solute factor and a solvent factor is shown to be insuf-

ficient. There are three additional requirements for such a separation

- (i) The line must have unity slope
 - (ii) The intercept must be zero
 - (iii) The data must be independant of the reference.
7. A modified ASIS is proposed which takes into account the effect of the reference, and is therefore independent of the choice of reference. A modified additivity rule is also developed. Conventional ASIS can be converted to the new scale and conversion data have been obtained. The use of the modified ASIS would provide more certainty in structural applications and will certainly avoid large systematic errors in the thermo-dynamic parameters for aromatic solvent "complexes" that are inherent if the conventional ASIS is used.

A paper describing the above in detail has been submitted to J.A.C.S. A few pre-prints are still available.

Yours sincerely,



F.H.A. Rummens, D.Sc.
Assoc. Prof. of Chemistry

FHAR/tag

- {1} For a Review see P. Laszlo in "Progress in NMR Spectroscopy" (Emsley-Feency-Sutcliffe). Volume 3 1967 pp.231-402.
- {2} E.M. Engler, P. Laszlo, J.A.C.S. 93, 1317 (1971)

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INORGANIC CHEMISTRY: PROFESSOR B. O. WEST

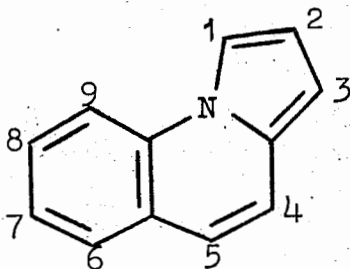
March 16, 1972

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

Cross-Ring Coupling in Pyrrolo [1,2-a] quinoline

Dear Barry,

For a while now we have been looking at the NMR Spectra of heterocyclic molecules containing bridgehead N atoms and one we have been sneaking up on is pyrrolo [1,2-a] quinoline.



There are nine protons, situated in three rings, forming ABC (protons 1-3), AB (protons 4,5) and ABCD (protons 6-9) systems, all of which are expected to interact, although fairly weakly. We have looked at the spectra in DMSO-d₆ and CDCl₃ (the spectrum in DMSO-d₆ is enclosed) and attempted a full analysis using LAOCOON III and various double resonance experiments. We were particularly interested in obtaining values for the magnitudes and relative signs of the cross-ring coupling constants.

The interpretation of the spectra was reasonably straightforward and was aided by spin decoupling experiments wherever possible and also by analogy with the chemical shifts and coupling constants obtained for various aza-substituted derivatives of the parent ring system, which we had previously studied. Selective spin decoupling experiments were performed to determine the relative signs of the coupling constants, most of which were found to be positive, except where indicated otherwise in Table 1. The iterative analysis (protons 1-5 treated as a 5-spin system, protons 4-9 treated as a 6-spin system, with the remaining small inter-ring couplings introduced by first order perturbation) led to the spectral parameters, in the two solvents, listed in Table 1 (shifts in Hz downfield from TMS).

The agreement between the coupling constants for the two solvents is reasonably good, the only major discrepancy being J_{59} , which in DMSO- d_6 is the least well-determined parameter because the lines for proton 9 are broad and relatively ill-defined. We regard the $CDCl_3$ value as the more reliable one.

The results indicate that cross-ring coupling in systems of this type is certainly significant and can even extend over seven bonds. We would not like to place too great an emphasis on their precise magnitude because we have found that in simpler, but related, systems the assumption that these small cross-ring couplings cause strictly first-order perturbations to the already complex multiplets is not quantitatively reliable.

Yours sincerely,

G. M. Irvine

M. L. Heffernan

Table 1
Spectral Parameters for
Pyrrolo-[1,2-a] quinoline (29°C)

Parameter (Hz).	5% in DMSO-d ₆	5% in CDCl ₃
ν_1	821.49	779 ^a
ν_2	677.26	676 ^a
ν_3	654.06	650 ^a
J_{12}	2.89	2.9 ^a
J_{13}	1.44	1.4 ^a
J_{14}	0.66	indeterminate
J_{23}	3.77	3.8 ^a
ν_4	740.01	726.92
ν_5	708.65	693.52
J_{45}	9.33	9.35
ν_6	774.80	758.64
ν_7	736.49	726.50
ν_8	755.80	744.17
ν_9	820.79	782.46
J_{46}	0.33	0.34
J_{48}	not resolved	0.29
J_{56}	-0.33	-0.37
J_{59}	0.62	0.74
J_{67}	7.87	7.83
J_{68}	1.52	1.50
J_{78}	7.24	7.27
J_{79}	1.08	1.11
J_{89}	8.42	8.38
J_{15}	0.25 ^b	--
J_{19}	0.25 ^b	--
J_{34}	-0.28 ^b	--
J_{35}	0.28 ^b	--

a These values are only approximate due to exchange effects involving protons 1 and 3.

b These values were not obtained by iteration and are only approximate.

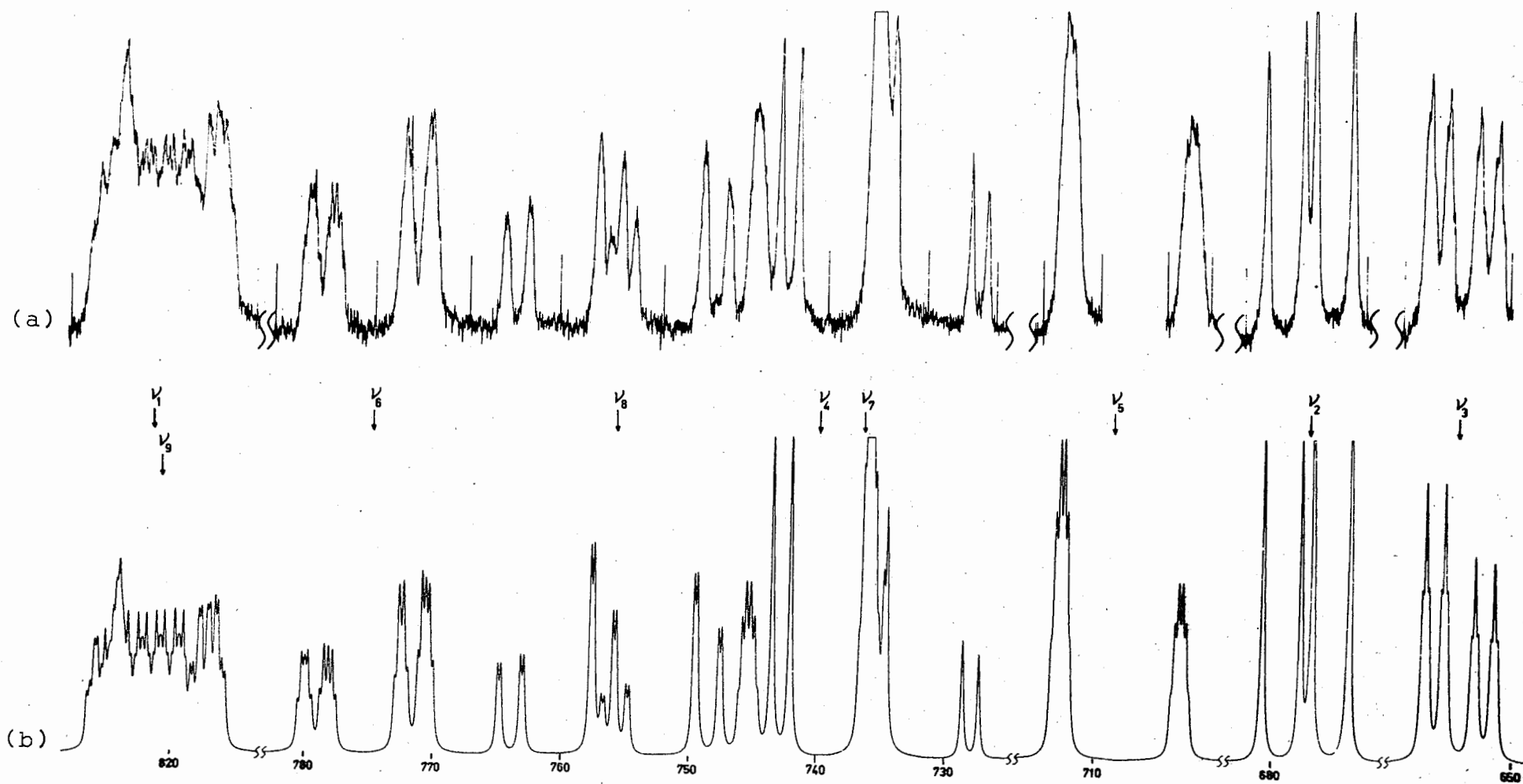


Figure 1. 100 MHz spectrum of a 5% w/v solution of pyrrolo[a]quinoline in DMSO-d₆ at 29°C.
 (a) experimental spectrum,
 (b) theoretical spectrum (including J₁₄, J₁₅, J₁₉, J₃₄, J₃₅, J₄₆, J₄₈, J₅₆ and J₅₉)

University of East Anglia

From The Dean
Professor N. Sheppard F.R.S.

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17th March, 1972

Dear Barry,

NMR Studies of Activation Parameters

and Energy Differences associated with Internal Rotation in

Substituted Ethanes

I am replying to your recent letter reminding me that another contribution is due from us for the NMR Newsletter.

Audrey Purdie and I have been looking at the variable-temperature NMR spectra of a series of ethanes substituted by Me or Cl groups with a view to determining the activation parameters of internal rotation, and the energy differences between spectroscopically distinguishable isomers.

Since starting this work, we have recently discovered two other groups which are interested in similar ranges of compounds under Professor J D Roberts of Cal Tech and Dr J E Anderson of University College, London. The table below gives the values of the free energy of activation ΔG^* at the coalescence temperatures, for the compounds where our work has overlapped. Results from different laboratories are approximately the same, taking solvent differences into account.

A surprising and somewhat disappointing feature about the values so far obtained is that they seem to lie within two ranges, namely 7 - 8.5 kcal/mole and 10 - 11.5 kcal/mole for the penta- and hexasubstituted ethanes respectively. We had hoped to see some well defined trends in the size of the ΔG^* as one type of substituent is systematically replaced by the other as an indication, for example, of the relative strengths of methyl...methyl, chlorine...chlorine and methyl...chlorine interactions across the central C-C bond. However, we have to bear in mind that ΔG^* is a relative energy term, dependent on the energy of the ground state conformer as well as that of the transition state. With interaction of the non-bonded substituents to be considered in both states, the overall picture is perhaps more complex than we originally envisaged.

We have been finding that in cases where the molecule has more than one isomer, the more stable form is the one in which the number of gauche interactions involving Me...Me and Cl...Cl is at a minimum, in favour of Me...Cl interactions. This tends to support the argument that the interaction between Me...Cl is less than that for Me...Me and Cl...Cl, as argued for data for energy differences in 1,2 disubstituted ethanes³.

Professor B L Shapiro,

17th March, 1972

We are continuing our NMR study of a number of related compounds as well as complementing this and previous work with Raman and infra-red studies. From the latter we hope to identify torsional frequencies, from which alternative data the barrier to internal rotation may also be determined.

Yours sincerely,



Norman Sheppard

COMPOUND	AP	Roberts	Anderson
$\text{Me}_3\text{C}-\text{CHMe}_2$	~7.4		7.1
$\text{Me}_3\text{C}-\text{CClMe}_2$	10.3	9.8	10.4
$\text{Me}_3\text{C}-\text{CCl}_2\text{Me}$	11.4	10.8	
$\text{Me}_2\text{CH}-\text{CCl}_2\text{Me}$	8.5		8.4
$\text{Me}_3\text{C}-\text{CMeCl}-\text{CMe}_3$		11.4	11.4

Values of ΔG^* in kcal/mole at the coalescence temperatures

1. J D Roberts et al, JACS 93, 4472 (1971)
2. J E Anderson and H Pearson, Chem Comm 871 (1971); JCS (B), 1209 (1971)
3. N Sheppard, Adv Spectroscopy (1959) 1, 288

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

OTTAWA CANADA
K1S 5B6

DEPARTMENT OF CHEMISTRY

March 17, 1972

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

Dear Barry,

Long range shielding effects of C-C single bonds

The simplest model using the point dipole approximation for calculation of magnetic anisotropy effects of bonds on the chemical shifts of nearby protons is the McConnell equation [1], modified by us in 1967 to include a correction for short distances where it seemed necessary to include a correction

$$[1] \quad \Delta\sigma = \frac{\Delta\chi}{3R^3} (1-3\cos^2\theta)$$

for a non-point dipole (1). The modified equation is [2].

$$[2] \quad \Delta\sigma = \frac{\Delta\chi}{3R^3} (1-3\cos^2\theta) + \frac{S^2}{R^5} \left[-\frac{X_I + 2X_T}{2} + 5(X_I \cos^2\theta + X_T \sin^2\theta) - 35(X_I \cos^4\theta + X_T \sin^4\theta)/6 \right]$$

We have recently been calculating the isoshielding curves for finite values of dipole length ($S = 0.6, 0.9$ and 1.2 \AA). These are shown (Figs. 2, 3 and 4) in comparison with those for equation 1 (fig. 1). In particular, we draw attention to the differences in shielding effects close to the bond in question when the dipole is considered to have a finite length.

Another exercise that we followed was to plot fig. 5 showing the variation of $\Delta\sigma$ with various values R making the angle θ indicated with an axis passing through 2 carbon atoms of the C-C bond.

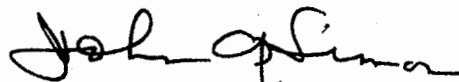
Using the McConnell equation [1] it is always possible to define R for given values of $\Delta\sigma$ and θ , such is not the case for the finite dipole model [2] for which there are certain regions forbidden for a proton having a downfield shift.

Prof. B. L. Shapiro
March 17, 1972

Practically, if it is remembered that for protons belonging to different molecules but defined by the same geometrical factors, measured $\Delta\sigma$ are often very different (1, 2), then one notes that for $S = 0.6$, the difference between models represented by equations [1] and [2] is less than the experimental error. This removes, at present any hope of determining χ_L and χ_T by nmr (3).

- (1) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders and W. B. Whalley, Tetrahedron, 1967, 23, 2339.
- (2) E. Pretsch, H. Immer, C. Pascual, K. Schaffner and W. Simon, Helv. Chim. Acta, 1967, 50, 105.
- (3) J. Elguero, A. Fruchier and R. Phan-Tan-Luu, to appear in the Journal de Chimie Physique.

Yours sincerely,


J. W. ApSimon


A. Fruchier

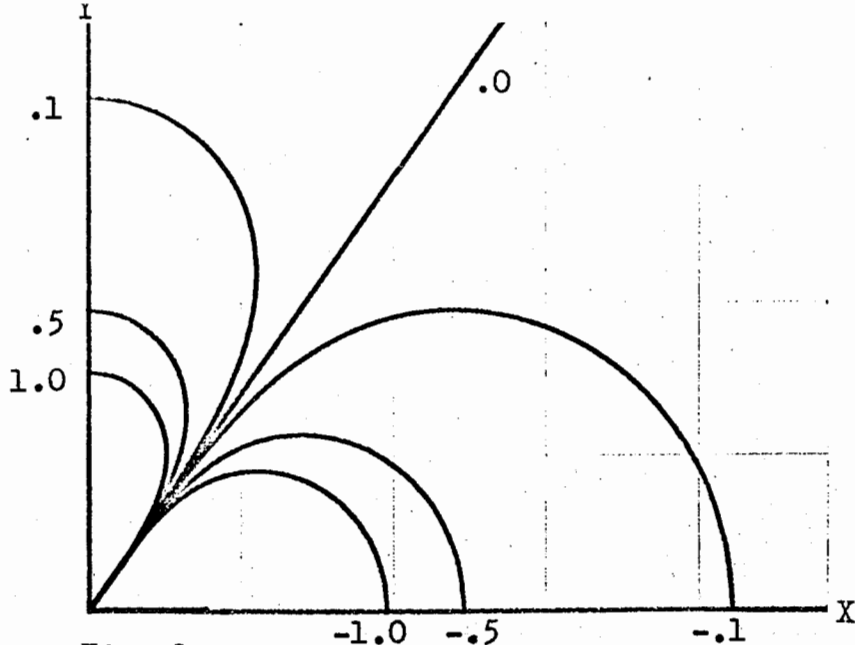


Fig. 1

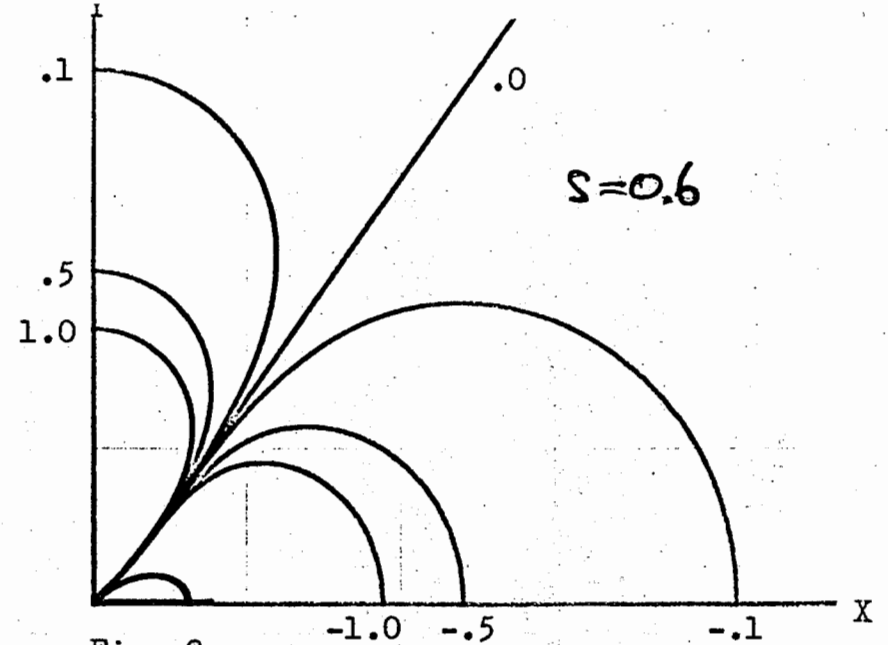


Fig. 2

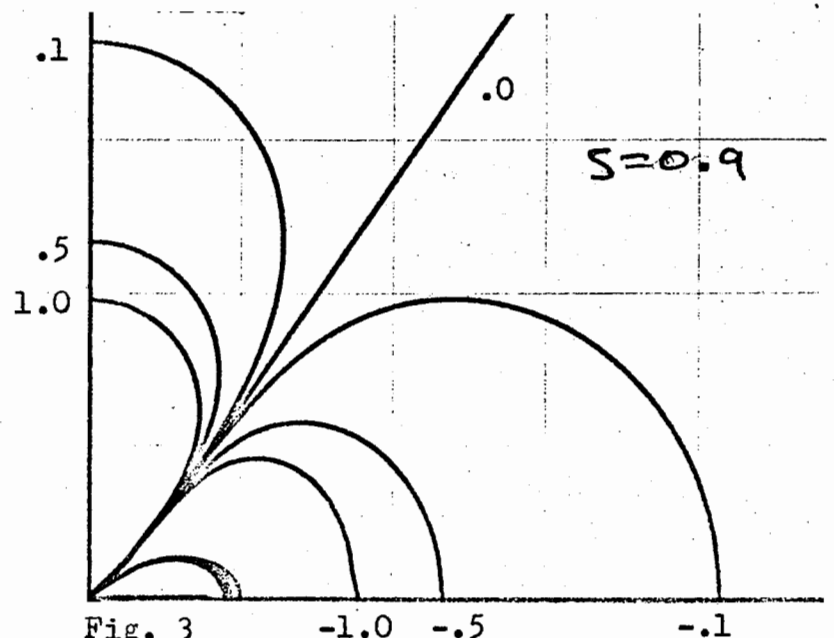


Fig. 3

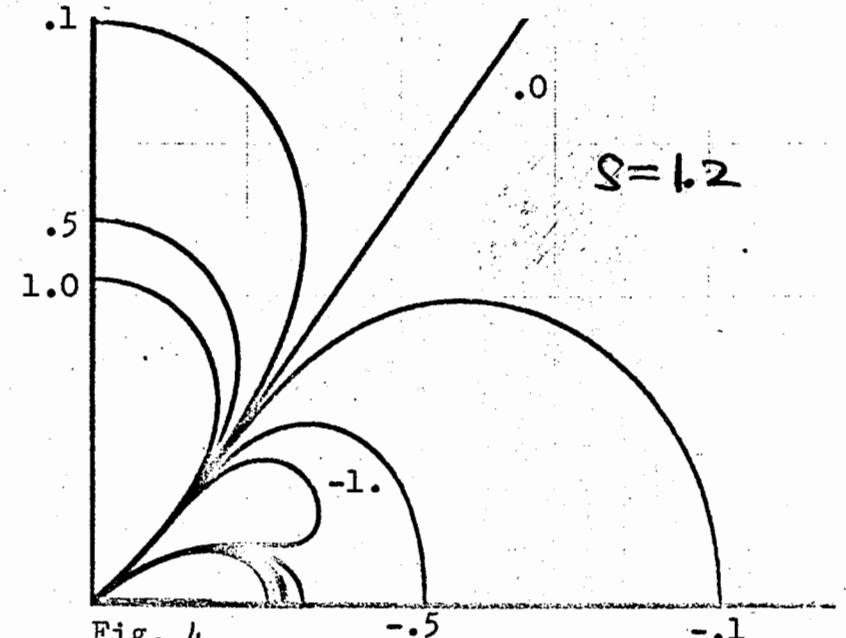
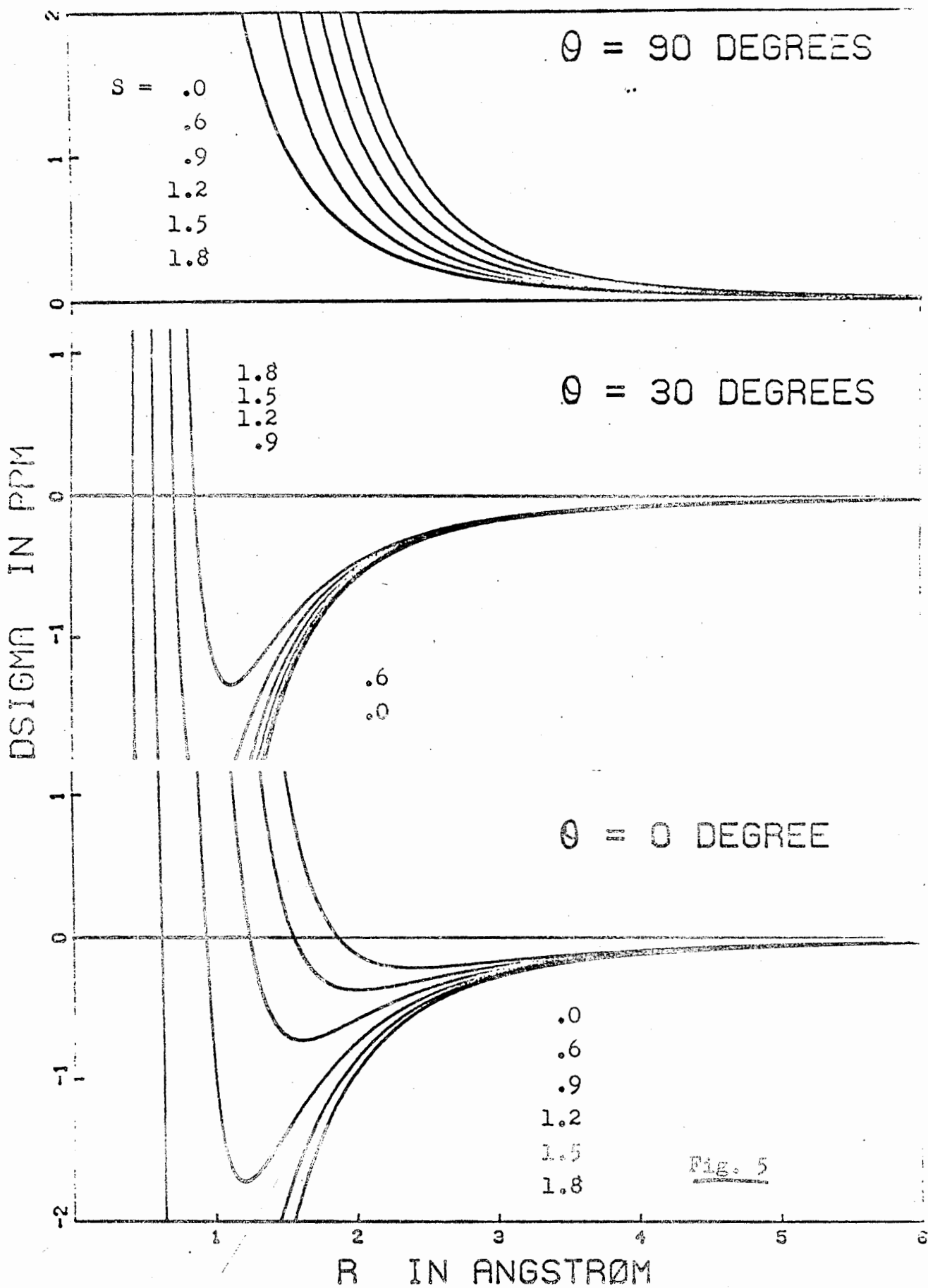
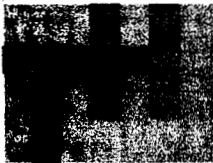


Fig. 4





Technische Hogeschool Delft

Laboratorium voor Technische Natuurkunde

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

Uw kenmerk

Uw brief van

Ons kenmerk

Delft, Nederland, Lorentzweg 1, tel. 01730-33222

23 March 1972.

toestel:

Onderwerp

Dear Professor Shapiro,

Thank you very much for your reminder of 7 March 1972, which caused us (J. Trommel and J. Smidt) to write the following contribution:

Title: 1. THD Research Fellowships.

2. Overhauser amplification of ^{13}C -resonance.

ad 1. There are possibilities of THD research fellowships (THD = Technische Hogeschool Delft).

Anyone who is interested to work in our group for a period of one year is invited to contact me (J. Smidt) for further information.

The group works in the field of nmr relaxation times in liquids and solids (research and building of apparatus). Moreover there is activity in the field of esr of liquids and of double resonance (Overhauser) in liquids. About the last topic Ir. Trommel has written the following:

ad 2. We have studied the dynamic nuclear polarization of ^{13}C -nuclei in some simple liquids. Measurements have been performed at two magnetic fields,

namely 3000 gauss and 8000 gauss. The corresponding ESR-frequencies are 9 and 22 GHz respectively. In most cases we used the following three free radicals: galvinoxyl, perchlorotriphenylmethyl (PCTM) and 1, 3, 5-triphenylverdazyl (TPV). TPV has an open structure with large spin densities on the four nitrogen atoms. These atoms are sterically good attainable for the solvent molecules. This is not the case for PCTM and galvinoxyl which have a more shielded spin distribution.

From dynamic polarization experiments of ^{13}C -nuclei it is well known at the moment that we have in many cases a mixture of dipolar interaction and scalar interaction between the unpaired electron and the ^{13}C -nucleus (1). The result is that we often find small enhancement factors. A condition for getting large enhancements is the existence of a pure dipolar interaction or a pure scalar interaction. In a given experiment the ratio of dipolar interaction and scalar interaction depends strongly on the used radical. The purpose of our research now was to find radicals which could satisfy the condition mentioned above as good as possible.

We performed experiments with simple liquids like CS_2 , C_6H_6 and some substituted benzenes. It was not possible to determine the enhancement factors directly because we could not detect the ^{13}C -signals without dynamic polarization. However, by comparing the enhanced signals with the unenhanced signals of ^{13}C -enriched acetic acid, we could roughly estimate the enhancement factors. In this way we found at 3000 gauss with the radicals PCTM and galvinoxyl enhancements in the range between -100 and -400. The interactions are in this case strongly dipolar. At 8000 gauss we found for the corresponding enhancement factors values between -15 and -80. Consequently, the negative enhancement factors decrease rapidly with increasing field. Two reasons can be responsible for this effect.

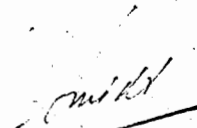
- a. The correlation time for the dipolar interaction is relatively long.
- b. There is always some scalar interaction with a correlation time shorter than the correlation time for the dipolar interaction. The influence of this scalar interaction increases then with increasing field.

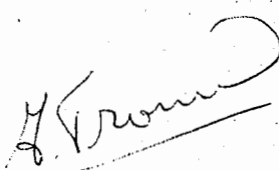
Within a few months we hope to perform experiments at 14000 gauss (corresponding ESR-frequency: 40 GHz.). On the ground of the results at 3000 gauss and 8000 gauss we expect to find with the radicals PCTM and galvinoxyl only small enhancements.

With the radical TPV we have measured at 3000 gauss small negative enhancements of about -20. At 8000 gauss we found for the corresponding enhancements values of about +50. Consequently, an important part of the interaction is now of the scalar type which becomes more important with increasing field. On the ground of these results we can perhaps expect reasonable positive enhancements at a field of 14000 gauss if we use the radical TPV.

- (1) H. Grützediek, W. Müller-Warmuth and R. van Steenwinkel.
Zeitschrift für Naturforschung 25a, 1703. (1970).

Yours sincerely,


Prof. dr. ir. J. Smidt.


Ir. J. Trommel.



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

March 30, 1972

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

Title: GINA - A sexy analysis program

Dear Barry:

We have recently rewritten the UEAITR analysis program to provide for display and plotting options. The program runs on a time sharing DEC PDP-10 computer and allows the user to look at the results of a zero initial fit and/or iterative calculation within seconds after the calculation is made. Provision has been made to vary the sweep width and/or sweep offset so that any portion of the spectrum can be viewed. Plots of the display screen or the standard Calcomp plots (with the plot being the same size as the chart paper) are readily obtained. We denote the composite of the original program, now capable of display and plotting of the initial fit and iterative calculations as GINA (Graphical Interactive NMR Analysis).

The program requires 48K of core for the analysis and plot, with up to 8K more for the display. Copies of the program can be obtained by writing Dr. A. W. Pratt, Director, DCRT, NIH, Bethesda, Maryland 20014.

Sincerely yours,

A handwritten signature in black ink, appearing to read "Steve".

Stephen R. Heller, Ph.D.
Heuristics Laboratory
Division of Computer Research
and Technology

P.S. Please credit this to Jim Ferretti's account.



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014
Bldg. 4, Room 135

March 28, 1972

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

NMR Spectra of Codeine and Isocodeine Derivatives.
The Magnetic Anisotropy of a Spiro Oxirane Ring.

Dear Professor Shapiro:

We have had occasion (using a secondhand HA-100 which we obtained recently) to compare the NMR spectra of a spiro oxirane (1) derivative of codeinone, codeine (2), isocodeine (3), 6-methylcodeine (4) and 6-methylisocodeine (5). An interchange of the chemical shifts of the olefinic protons in 1 was noted, as compared with those in all of the other compounds. This interchange could be attributed to the bond anisotropies of the oxirane moiety. NOE and double resonance experiments were used to confirm the conformation of 1, and the configuration about C-6 of 6-methylcodeine and 6-methylisocodeine. Table 1 lists the chemical shifts and coupling constants of the affected protons in the various compounds.

A more detailed description will be submitted for publication.

Sincerely yours,

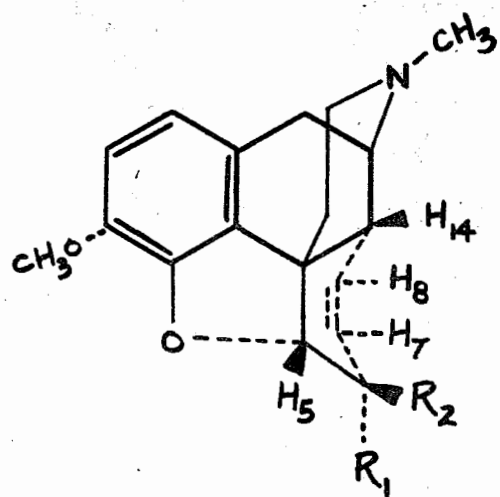
Herman J. C. Yeh
Herman J. C. Yeh, Ph.D.

Arthur E. Jacobson
Arthur E. Jacobson, Ph.D.

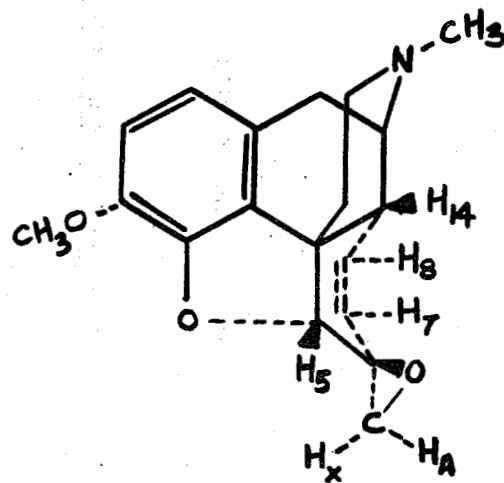
Lewis J. Sargent
Lewis J. Sargent, Ph.D.
Laboratory of Chemistry, NIAMD

TABLE 1

Compound	δ ppm								J (Hz)							
	5	6	7	8	14	HA	Hx	5,6	5,7	6,7	6,8	6,14	7,8	7,14	8,14	AX
Codeine (2)	4.85	4.14	5.67	5.26	2.66	-	-	6.4	1.3	1.8	3.1	2.6	10.0	3.0	2.3	-
Isocodeine (3)	4.77	4.21	5.94	5.58	3.08	-	-	1.2	1.0	5.7	-	0.8	9.6	2.8	1.8	-
6-Methylcodeine (4)	4.46	-	5.70	5.21	2.76	-	-	-	1.4	-	-	-	9.8	3.0	2.0	-
6-Methylisocodeine (5)	4.56	-	5.73	5.47	3.18	-	-	-	1.0	-	-	-	9.5	2.75	1.8	-
Spiro Oxirane (1)	4.47	-	5.26	5.82	3.08	2.08	3.31	-	0.9	-	-	-	9.8	3.0	1.8	4.8



	R_1	R_2
(2)	OH	H
(3)	H	OH
(4)	OH	CH ₃
(5)	CH ₃	OH



(1)

GORLAEUS LABORATORIA
DER RIJKSUNIVERSITEIT

Afd.: Org.Chem./Dr. J. Lugtenburg
Wassenaarseweg
Postbus 75
Leiden
Telefoon 4 83 33
Tst. 4468

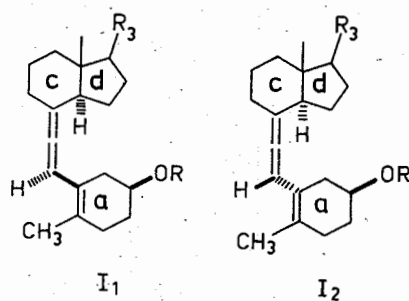
LEIDEN,march...23..... 19.....72

Professor B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
COLLEGE STATION TEXAS 77842.
USA

Dear Professor Shapiro,

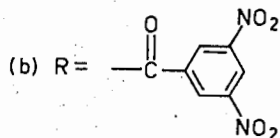
Assignment of configuration in two vinylallene derivatives.

Recently we were able to isolate two isomeric vinylallene derivatives out of the irradiation mixture of vitamin D₃ (dissolved in ethanol, 125 W. H.P. mercury arc $\lambda > 240$ nm). On basis of NMR, IR, UV, massspectra and degradation studies these compounds should correspond to the structures indicated in the figure as I1a and I2a.



R₃ = cholesteryl side chain

(a) R = —H



VERVOLGBLAD:

The problem left was the assignment of the correct configuration at the allene C-H atom. By esterification ^{with} 3-5-dinitro-benzoylchloride the esters I1b and I2b were obtained.

Comparison of the NMR spectra of these esters with those of the alcohol gave the following results: In I1b the 18 CH₃ signal is shifted 0.06 ppm to higher field than in I1a. In case of I2a and I2b the 18 CH₃ signals show no visible shift difference. Molecular models show the following features: In the case of the configuration where ring A is above the plane of the rest of the molecule the 18 CH₃ group can be situated on the axis of the benzene ring of the ester, giving rise to a shift to higher field for the 18 CH₃ signal. When ring A is below the plane of the molecule the 18 CH₃ and the ester group cannot come in each other's neighbourhood. No shift difference for the 18 CH₃ signal upon esterification is expected. On this basis we assign I1 to the configuration with the A ring β and I2 with ring A α to the rest of the molecule (as is already indicated in the figure).

Table of NMR values of Ia, I1b, I2a and I2b (100 MHz, J.E.O.L.-P.S. 100 CDCl₃ T.M.S. internal reference). The numbering is the usual steroid numbering

δ	I1a	I1b	I2a	I2b	shape of signal	coupling constant	number of H atoms	assignment
0.73	0.67	0.65	0.65	0.65	s		3	18 CH ₃
0.86	0.85	0.87	0.86	0.86	d	J=7Hz	6	26+27 CH ₃
0.91	0.90	0.91	0.91	0.91	d	J=7Hz	3	21 CH ₃
1.74	1.80	1.74	1.80	1.80	s		3	19 CH ₃
		2.61		2.47	m		1	4 βH
		2.68		2.55	m		1	4 αH
3.90	5.35	3.90	5.35	5.35	m		1	3 αH
6.18	6.30	6.14	6.27	6.27	t	J=4Hz	1	6 α or 6 βH

Sincerely Yours,



C. Erkelens



J. Lugtenburg

S.A. Bakker

The University of Oklahoma

620 Parrington Oval, Room 211

Norman, Oklahoma 73069

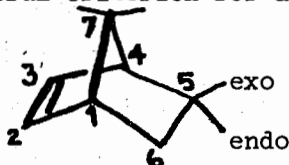
March 14, 1972

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

CHEMICAL SHIFT AND COUPLING CONSTANT VALUES AS CRITERIA FOR MAKING CONFIGURATIONAL ASSIGNMENTS IN 5-(EXO or ENDO) SUBSTITUTED NORBORNENES.

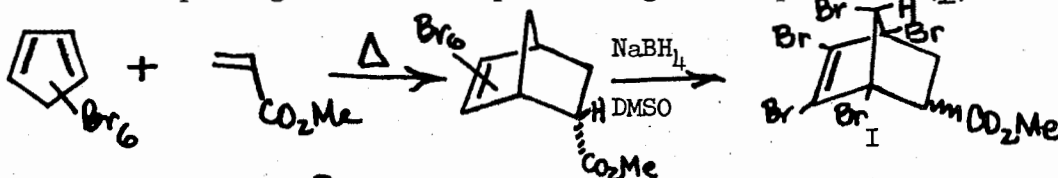
Dear Barry,

We are currently engaged in an nmr study of several series of halogenated exo- and endo-5-substituted norbornenes. An interesting point has emerged from this study which suggests that the magnitude of "internal chemical shifts" in these systems may provide a useful criterion for assigning configuration at the 5-position.



Utilizing the LAOCOON III computer program (1), we have calculated the proton chemical shifts and coupling constants of the series of compounds indicated in the accompanying two figures. These figures indicate linear correlations of coupling constants and internal chemical shifts (top and bottom figures, respectively) with electronegativities of the endo- or exo-5-substituents, X (2). Included for comparison with our data are Anet's (3) and Williamson's (4) results in similarly-structured systems.

Of particular interest to us are the results for 1,2,3,4, syn-7-pentabromo-endo (or exo)-5-carbomethoxynorbornene (I); this compound was prepared by reduction of the corresponding hexabromo-compound using Bell's procedure (5):



The calculated J and δ values for I prepared by this procedure have been included in the plots shown in the two accompanying figures. The J-values for I appear to fit the general correlations with electronegativity shown by the other compounds studied. However, the internal chemical shifts are not as well behaved. Concentrating on the boxed (dotted lines) area in the bottom figure, let us turn our attention to the data points for compound I (★) and for endo- (o) and exo- (x)



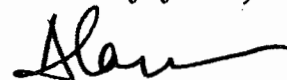
Department of
 Chemistry

March 14, 1972

5-carbomethoxy-1,2,3,4,7,7-hexadeuterionorbornene. While the endo- compound appears to fit the correlation line, the exo points (☆) and (x) do not, both sets of these points deviating to the left of the correlation line. Interestingly, for compound I we find $(\delta_3 - \delta_2) > (\delta_3 - \delta_1)$, whereas the inequality lies in the opposite sense for all of the other compounds studied!

We rationalize these observations by suggesting that endo \rightarrow exo epimerization of the COOMe group in I occurs concomitantly with reduction of the anti-7- (C-Br) bond. Preliminary chemical studies on this system have been performed, and the results reinforce this conclusion. We are now preparing a series of exo-5-substituted norbornenes to determine the nature and extent to which J and δ values in these systems correlate with substituent electronegativities. We hope to report the results of this study shortly.

Sincerely yours,

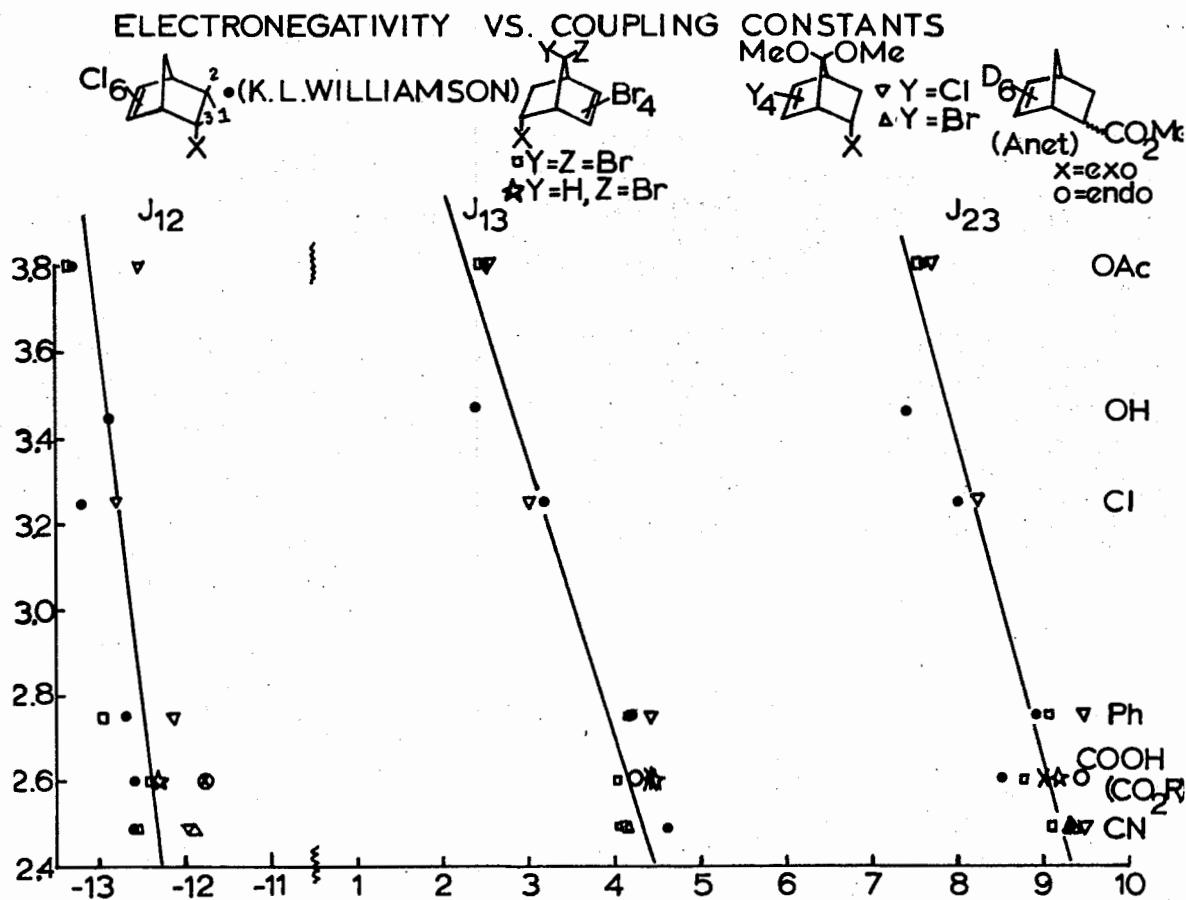


Alan P. Marchand
Associate Professor

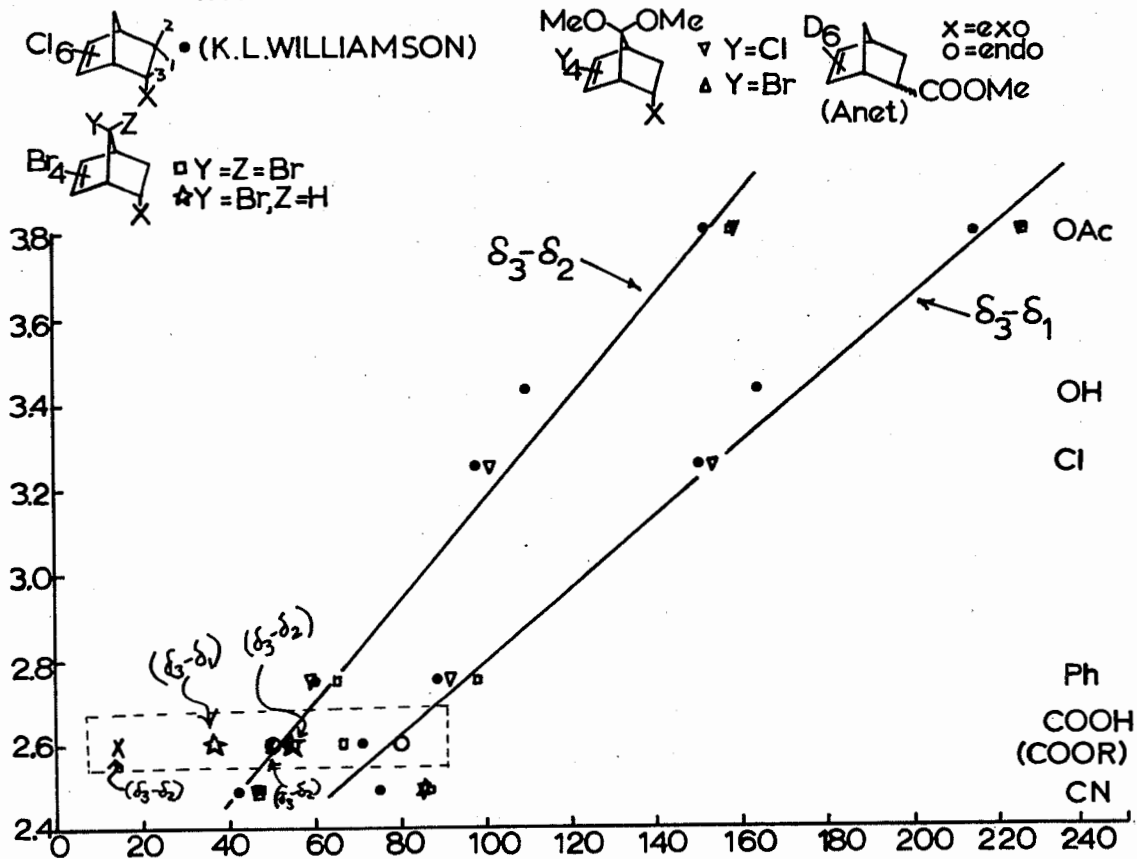
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1. S. Castellano and A. A. Bothner-By, J. Chem. Phys., 41, 3863 (1964).
2. J. R. Cavanaugh and B. P. Dailey, ibid., 34, 1099 (1961).
3. F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, J. Amer. Chem. Soc., 89, 4431 (1969).
4. K. L. Williamson, ibid., 85, 516 (1963).
5. H. M. Bell, et al., J. Org. Chem., 34, 3923 (1969).

ELECTRONEGATIVITY VS. COUPLING CONSTANTS



INTERNAL SHIFTS VS. ELECTRONEGATIVITY



DEPARTMENT OF THE AIR FORCE
AIR FORCE MATERIALS LABORATORY (AFSC)
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433



REPLY TO
ATTN OF: AFML/LPH (R. E. Rondeau/255-2280)

31 March 1972

SUBJECT: Internal Reports Available - Spectra
Digitization and Shift Reagent

TO: Dr. Bernard L. Shapiro
Texas A&M University
College of Science
College Station, TX 77843

Dear Dr. Shapiro:

Two internal Air Force Materials Lab reports have recently been published which may be of interest to TAMU Newsletter subscribers. The first, AFML-TR-71-273, is a 65 page report entitled, "EDREM, A Fortran IV Program to Identify Lines in Repetitively Scanned Digitized Spectra" by Dr. Vincent L. Donlan and me. Listings of Program EDREM were first made available through the Newsletter (TAMU-154). In this report, however, the program parameters of EDREM have been cast in more generalized units and are now suitable for other types of spectra in addition to NMR. One section of the report gives a detailed description of EDREM and serves as a user's manual for the program. Also included are a listing and computer output reproductions of EDREM's analysis of seven scans of benzoxazole including the digitized raw data, the smoothed and scaled data, the scan parameters and tables of peaks identified in each scan.

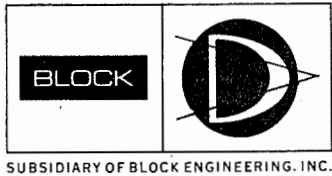
The second report, AFML-TR-71-282, is a 126 page job with the internal reportish title "NMR Spectral Chromatography - A Powerful New tool for Structure Determination." It was written by me and Captain Martin Berwick and summarizes our combined efforts in the area of shift reagents and how they've been applied to Air Force problems. After a short preamble which draws parallels between NMRSC and other "chromatographies," the report illustrates the use of lanthanide shift reagents [Eu(fod)₃, that is] in (1) monitoring the oxidation of azobenzenes; (2) analyzing liquid crystal mixtures; (3) elucidating structures of photolysis products; (4) preparing spectra for spin decoupling; and (5) obtaining input parameters for computer analyses.

Since few, if any, Newsletter subscribers are on our distribution list, either or both, reports can be obtained by dropping me a card.

Sincerely,

Roger E. Rondeau

ROGER E. RONDEAU
Exploratory Studies Branch
Materials Physics Division



DIGILAB INC

237 PUTNAM AVENUE, CAMBRIDGE, MASS. 02139
 TELEPHONE 617 868-4330
 TWX 710 320-0821
 TELEX 921481

April 3, 1972

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

Performance of an A-60A Spectrometer for
Fourier-Transform Spectroscopy

Dear Barry:

We thought your readers might be interested in some ^1H spectra obtained on an A-60A NMR Spectrometer, modified by our engineers for Fourier-Transform operation. The following Digilab NMR Components were used in this modification:

- A) NMR-3 Fourier Analysis and Display System
- B) Digilab 40-2 pulser and Digilab TR-100 (60 MHz transmitter-receiver)

In addition, the control loop of the A-60A spectrometer was modified so that it would operate while the sample channel was pulsed with the high power RF pulse. A gate was also inserted into the control receiver, which was triggered by a pulse from the data system which coincided with the gating pulse for the RF power amplifier.

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Dr. Barry Shapiro

4/3/72

The spectra shown in Figures A and B were obtained with 1 mg and 100 ug samples respectively of 3-Chloro-isopropyl Corban-itate dissolved in $DCCl_3/TMS$ in a standard 5mm tube.

The spectrum shown in Figure B (100 ug sample) indicates some "extra" resonance lines which are presumably due to impurities at this low concentration level. These spectra clearly illustrate the drastic improvement in sensitivity of an A-60A modified for the Fourier Transform mode.

Sincerely,

Charles T. Foskett *Rubelo Stuebel*

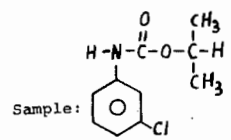
C. T. Foskett/R. Curbelo/G. Kneissl

DIGILAB, INC.

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Enclosures

A)



1 mg

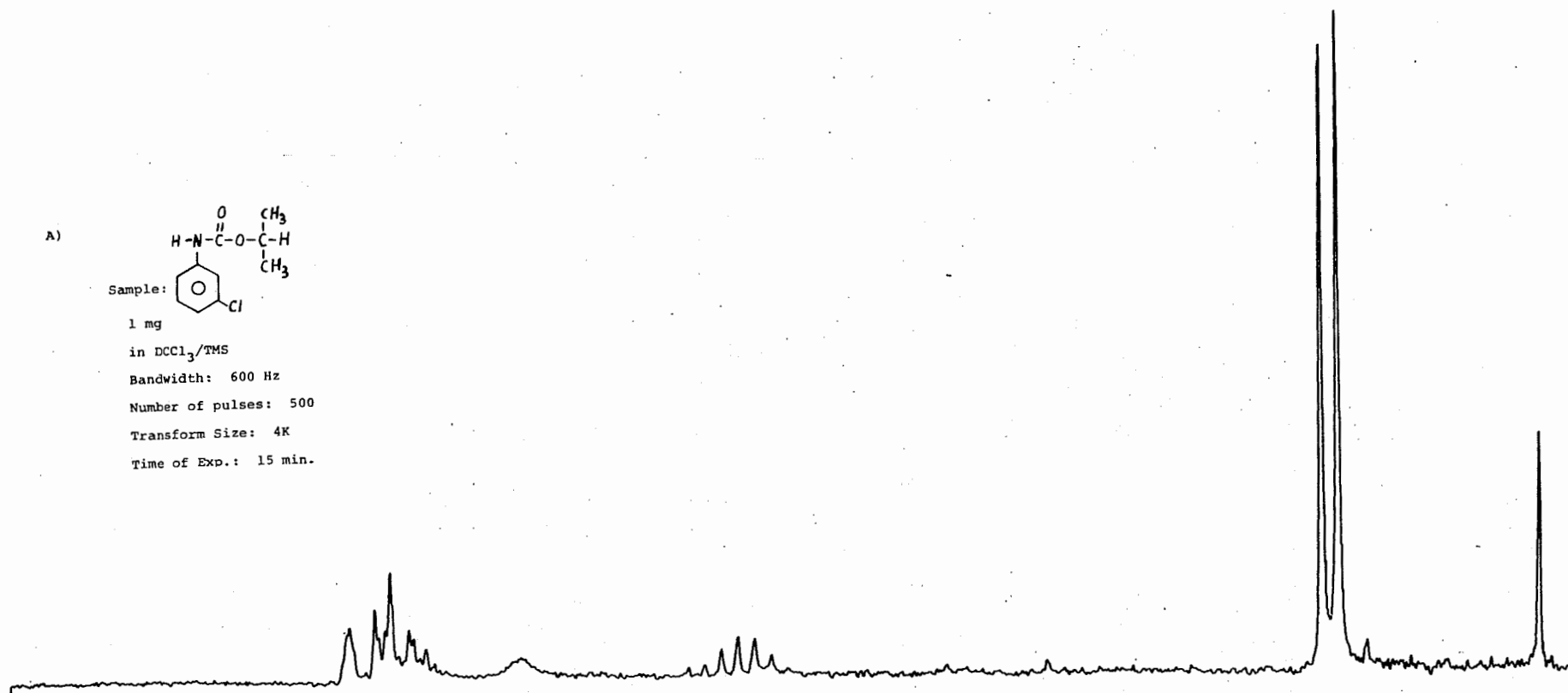
in DCCl_3/TMS

Bandwidth: 600 Hz

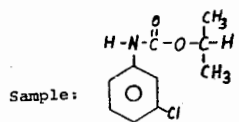
Number of pulses: 500

Transform Size: 4K

Time of Exp.: 15 min.



B)



100 μ g

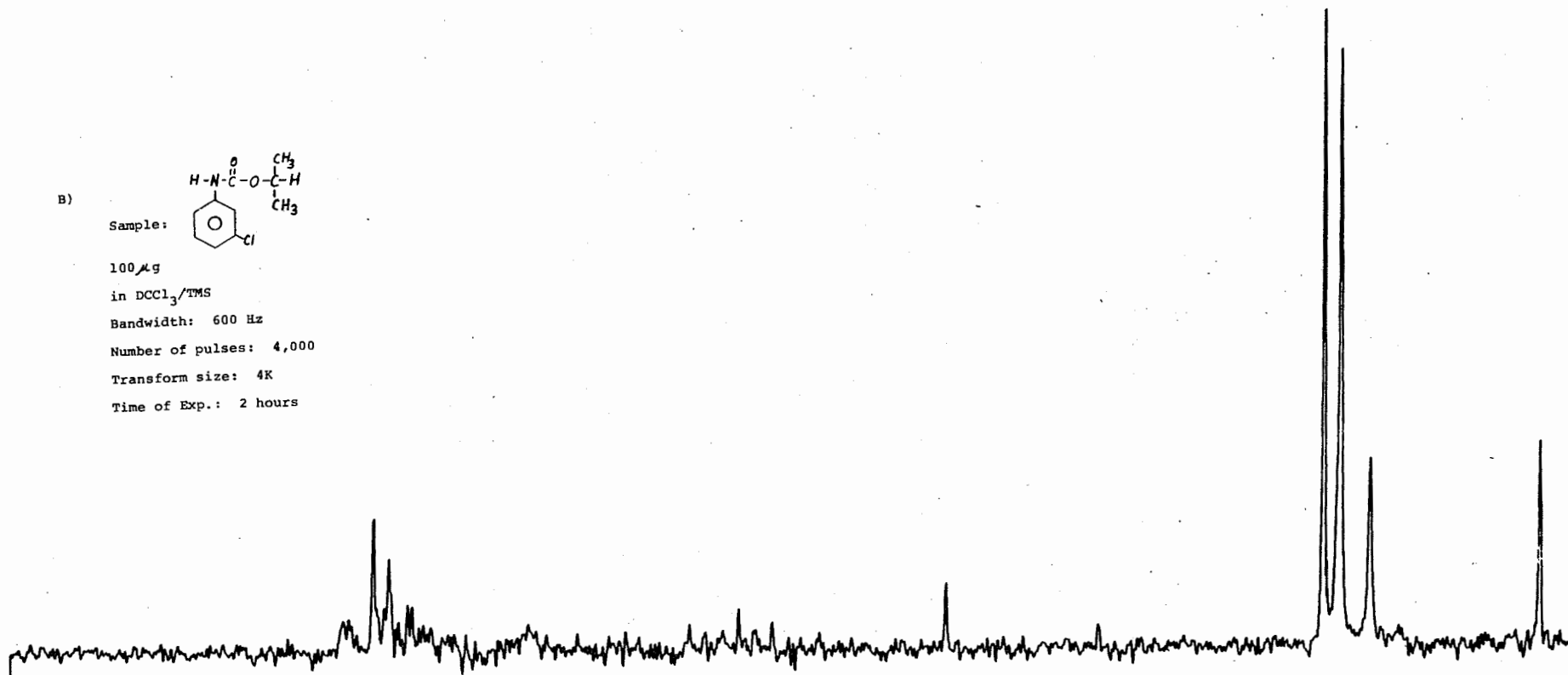
in DCCl_3/TMS

Bandwidth: 600 Hz

Number of pulses: 4,000

Transform size: 4K

Time of Exp.: 2 hours



Carr Laboratory, Department of Chemistry

MOUNT HOLYOKE COLLEGE

South Hadley, Massachusetts 01075

Telephone 413 538-2211



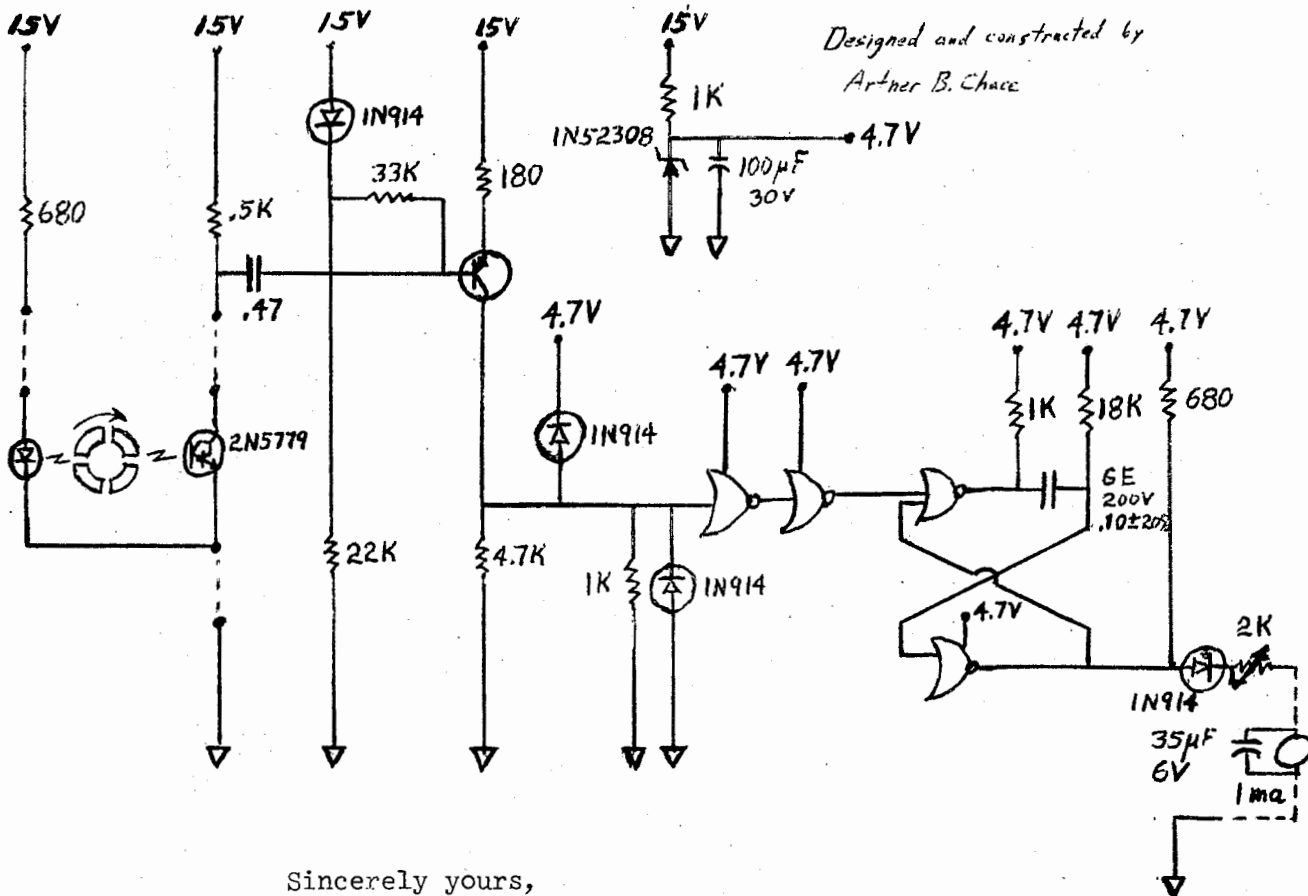
March 30, 1972

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

Dear Barry:

Spin Speed Indicator for HA-100

We have added this spin speed indicator to our HA-100. The slots in the top of the spinner serve to chop the light beam. The light emitting diode and the IR sensitive diode can be mounted directly on the probe or remotely using fiber optics.



Sincerely yours,

Ken Williamson

Kenneth L. Williamson
 Professor of Chemistry

Arther B. Chace

Arther B. Chace
 Electronics Technician

KLW/ak

TEXAS A&M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

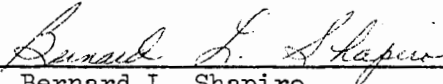
Department of
CHEMISTRY

POSITION WANTED

AVAILABLE: Spectroscopist with six years industrial and postdoctoral experience.

This person is presently employed as a Group Leader of Spectroscopy with supervisory and interpretive responsibilities in NMR, Mass Spectroscopy, IR, UV and ESR with a group of four persons. He has 12 publications and papers presented as well as many internal publications and reports of a confidential nature.

He desires either an academic or industrial position of an appropriate nature. Anyone interested in the possibility of making a position available to this man is invited to contact me at 713/845-6944. I will be happy to effect the appropriate connection.


Bernard L. Shapiro

THE UNIVERSITY OF CHICAGO

PHYSICS DEPARTMENT
5720 S. UNIVERSITY AVE.
CHICAGO, ILL. 60637

PHYSICS 351

PROBLEM SET 10: ELECTROSTATICS AND CAPACITORS

Due: 11/11/2020

1. A solid dielectric sphere of radius R and permittivity ϵ is placed in a uniform electric field E_0 directed along the z -axis. Find the electric field E and the potential V everywhere.

2. A dielectric slab of thickness d and permittivity ϵ is placed between the plates of a parallel plate capacitor.

(a) Find the electric field E and the potential V between the plates.

(b) Find the surface charge density σ on the top plate.

(c) Find the surface charge density σ' on the bottom plate.

(d) Find the electric field E and the potential V between the plates.

(e) Find the surface charge density σ on the top plate.

(f) Find the surface charge density σ' on the bottom plate.

(g) Find the electric field E and the potential V between the plates.

(h) Find the surface charge density σ on the top plate.

(i) Find the surface charge density σ' on the bottom plate.

(j) Find the electric field E and the potential V between the plates.

(k) Find the surface charge density σ on the top plate.

(l) Find the surface charge density σ' on the bottom plate.

(m) Find the electric field E and the potential V between the plates.

(n) Find the surface charge density σ on the top plate.

(o) Find the surface charge density σ' on the bottom plate.

(p) Find the electric field E and the potential V between the plates.

(q) Find the surface charge density σ on the top plate.

(r) Find the surface charge density σ' on the bottom plate.

(s) Find the electric field E and the potential V between the plates.

(t) Find the surface charge density σ on the top plate.

(u) Find the surface charge density σ' on the bottom plate.

(v) Find the electric field E and the potential V between the plates.