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Newsletter

No. 159

DECEMBER, 1971

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

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



The University of Western Ontario, London 72, Canada

Faculty of Science
Department of Chemistry

November 3, 1971.

Barry Shapiro,
College Station, Texas.

Dear Barry,

Some Current ^{13}C Work

In response to your blue and pink reminders I can outline the current status of our ^{13}C work.

After a few months of CW operation, our XL-100-15 was converted to FT mode for ^{13}C and, as Ian Smith pointed out in TAMU NMR 157-31, when it is operative it works very well indeed. Ours, like Smith's is not a production model, and, hopefully, this accounts for our difficulties. Since most of our problems have been of the intermittent sort these are difficult to trace and correct. Perhaps the set-up pains will soon be eliminated. When the instrument was CW only, it operated without any problems of any sort at a rate of 24 hours a day, 7 days/week for four months. I trust that this situation will soon be reestablished.

Probably the most interesting current work, chemically, is our use of ^{13}C NMR for tracer experiments employing ^2H labels. As Charlie Reilly recently noted (TAMU NMR 156-7), ^2H isotope shifts on ^{13}C shieldings are appreciable. Consequently, the incorporation of deuterium into, say, a methylene group gives rise to a 1:1:1 triplet for CHD which is nicely shifted from the residual CH_2 signal such that the relative amount is readily determined by integration of the whole pattern. In addition, the neighboring carbons often show a significant isotope shift which is helpful for confirmation of assignments. Methine incorporation can be assessed by comparison of intensities with that for a normal C-H signal. We have been examining homoenolizations of some bicyclic ketones to follow the sequential uptake of deuterium at various positions. For example, in fenchone, deuterium is most rapidly incorporated at C-6, as expected, and then at the exo-methyl and, at an even slower rate, at the endo-methyl. Comparison of the mass spectral data (as a check on the quantitative analysis) with the ^{13}C results shows good agreement. In a collaborative effort with Prof. Nickon, Johns-Hopkins Univ., I have been examining products in which deuterium is scrambled at various positions in tricyclic skeletons. On the basis of the preliminary results, ^{13}C NMR detection appears to be excellent for this as well. In each case, operating conditions were empirically found which give spectra for normal materials in which the signals for each carbon of interest are of equal intensity.

Another project involves the study of a series of organometallic materials for which both the ^{13}C shieldings and metal- ^{13}C coupling constants are desired. FT operation renders these spectra so much easier to obtain than the CW method that the scope of possible applications is markedly increased. Although the initial results of our work with some platinum compounds are not the first to be reported, we have submitted a note to Chem. Commun. showing substantial variation of $\text{J}_{\text{Pt-C}}$ with structure for the series trans $\text{Me}(\text{X})\text{Pt}(\text{AsMe}_3)_2$ where $\text{X} = \text{Cl}, \text{CO}, \text{CH}_3\text{NC}, \text{C}_6\text{F}_5\text{CN}, \text{C}(\text{OCH}_3)\text{CH}_3^+$. The one-bond Pt-C couplings vary over the range 360-1000 Hz and are at least crudely, related to bond hybridization variations.

Best regards,

Sincerely,

NANTES, le 6.10.71

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Professor B.L. SHAPIRO
Chemistry Department
Texas A&M University
College Station

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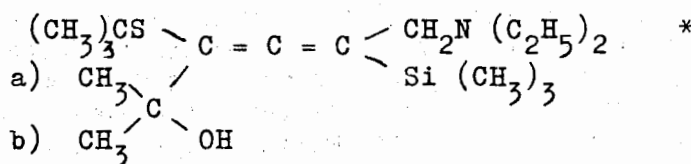
(DPM)₂ Eu (ou Pr) : stéréochimie de systèmes éthyléniques et non équivalences magnétiques

Cher Professeur SHAPIRO,

Les complexes de terres rares, en particulier les tris tétraméthyl 2,2,6,6- heptanedionates d'Europium ou de Praséodyme suscitant un enthousiasme communicatif, nous les avons utilisés à l'étude de la stéréochimie de systèmes éthyléniques et à celle de non équivalences magnétiques.

(X) (B) (A) Y
générale R CH(OH) CH = CH CH₃, le système ABX Y₃ fortement couplé est difficilement analysable. L'utilisation de complexes de Pr ou d'Eu augmente la non équivalence des protons A et B de l'isomère cis jusqu'à rendre le spectre analysable au premier ordre : on en déduit J_{AB} = 11,0 Hz pour R = (CH₃)₂CH. L'écart ν_A - ν_B est par contre diminué dans l'isomère trans. On dispose donc ainsi d'un moyen pour déterminer la configuration. La considération des proximités par rapport aux atomes Eu ou Pr explique ces comportements.

De même dans l'allène



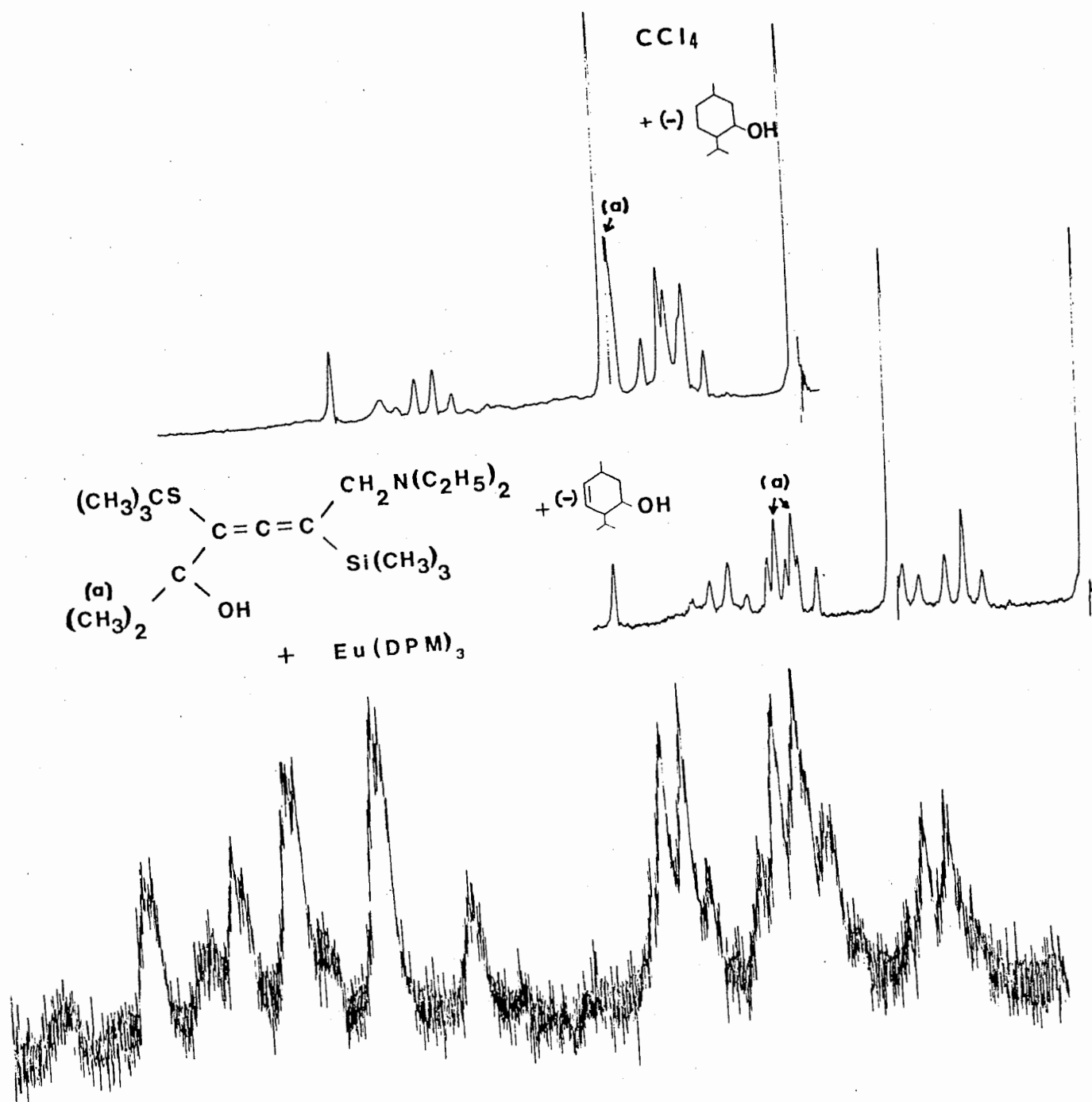
les deux groupements méthyles a) et b), en principe non équivalents du fait de la dissymétrie de type allénique, apparaissent en présence de CCl_4 sous forme d'un seul pic. L'addition de complexe d'Europium permet de révéler la non équivalence magnétique.

Veuillez croire, Cher Professeur SHAPIRO, à nos sentiments
 les meilleurs.

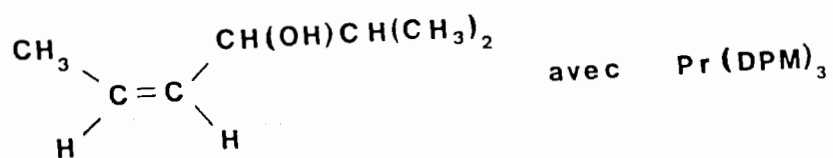
F. LEFEVRE

M.L. MARTIN

Produit synthétisé par R. MANTIONE, PARIS



ETALEMENT du MOTIF ETHYLENIQUE de



DOW CORNING

October 26, 1971

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

Lanthanide-Induced NMR Shifts (LIS): Characterization of Mixtures
 and of Polyfunctional Substrates

Dear Barry:

Although the LIS effect provides an effective way to distinguish between closely related structures, it is sometimes difficult to successfully apply to a mixture of substrates, since the LIS values depend on interacting equilibria. This difficulty is particularly evident when one attempts to use model compounds to assign LIS bands of a large polyfunctional substrate, and also when one wishes to study mixtures of "inseparable" substrates, e.g., labile isomers.

Recently, I found a way to avoid this difficulty by using an internal standard to determine intrinsic LIS parameters. A complexable internal standard (shift monitor) is added to a series of samples to be studied and some compositional variable (such as amount of LIS reagent) is adjusted so that the LIS value of the shift monitor has the same value in all samples. Under this condition, the LIS values of all other substrates in the series of samples will also be constant. Hence it becomes possible to use model compounds for line assignments.

A useful equation which should be obeyed rigorously only by monofunctional (one binding site) substrates was also derived:

$$\delta_j^{-1} = \delta_m^{-1} K_m \Delta_m / (K_j \Delta_j) + (K_j - K_m) / (K_j \Delta_j) \quad (1)$$

where m denotes monitor substrate, j denotes any other substrate; K denotes the formation constant for the reaction $L + S \rightleftharpoons C$ (L , S , C refer to LIS reagent, free substrate, and complexed substrate); δ is the observed shift of the appropriate substrate with respect to the shift of that substrate in the absence of LIS reagent, and Δ is the limiting shift of the completely complexed substrate with respect to the shift of that substrate in the absence of the LIS reagent.

Professor B. L. Shapiro
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October 26, 1971

Eq. (1) shows that when a series of solutions of some sample is prepared with varying amounts of the LIS reagent, then a reciprocal plot of the resulting LIS values will be a straight line for each substrate. This procedure has the advantage that the substrate is characterized by two parameters (slope and intercept, or K_j and Δ_j if K_m and Δ_m are known) rather than by just one.

I have tested this method on some substrate mixtures and obtained good agreement with theory. For example, the slope/intercept ratio of the two methyl groups and of the methylene group of ethyl acetate in the presence of varying amounts of methanol, ethanol, acetone, and Eu(DPM)_3 were all identical, demonstrating identical K values.

We have used this procedure to characterize ethylene oxide propylene oxide copolymer structure with good success. The line broadening displayed by polyfunctional substrates and which has been noted by others (Smith and Scahill, TAMUNMR-156-12; Friebolin, TAMUNMR-152-12) was not a serious problem in this case. Incidentally, the type of line broadening noted by Smith and Scahill does not occur when Eu(fod)_3 is used (R. T. Iwamasa, private communication).

I intend to publish a portion of this work in the near future.

Very truly yours,

Dwight Williams

Dwight E. Williams
Supervisor, Molecular Spectroscopy

gb



DEPARTMENT OF CHEMISTRY
THE UNIVERSITY
SHEFFIELD

29th. October 1971^{S3 7HF}

NMR OF BIO-MEMBRANES

Dear Dr. Shapiro,

As there is an increasing interest in applying NMR to biological systems, we thought that some of your readers might be interested in the NMR studies we've been carrying out on bio-membrane structure.

Membranes consist mainly of lipids, proteins and sterols. The lipids have polar headgroups and long hydrocarbon side chains, and form bimolecular leaflet structures in water. These may be either fluid liquid crystalline, or rigid gel phases. We recently showed that the PMR spectra of these systems are dominated by dipolar interactions¹, contrary to previous belief². We also reported the first CMR³ and DMR⁴ spectra of these molecules.

We've been extending the previous uses of DMR in biological systems (on D₂O), to a study of -CD₂- group mobility in liquid crystals and cell membranes. We already showed that in the model system lecithin-cholesterol, cholesterol increases the quadrupole splitting of the -CD₂- groups in a chain deuterated lecithin, the maximal splitting increasing from 27 to 49 KHz., a mobility decrease consistent with earlier ESR studies⁵.

Now we have successfully incorporated perdeuterated fatty acids ($nC_{12,14}$ and $_{16}$), biosynthetically, into natural cell membranes. We used the microorganism Acholeplasma laidlawii B. GC-MS indicates elongation of the C_{12} acid by 1 or 2 $^1H-C_2$ units. The DMR spectra indicate that the majority of the lipids are in a fairly rigid state, close to that of a gel. This surprised us a lot, since it has been fairly generally assumed that membrane lipids are "fluid".

We think that isotopically labelling bio-membranes with suitable nuclei (eg. ^{13}C and 2H) should give us a better insight into the mobility of the various membrane constituents, and further work is underway.

Yours sincerely,



Eric Oldfield.

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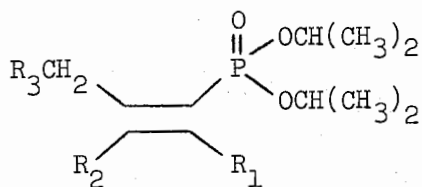
October 8, 1971

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

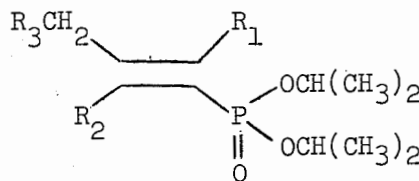
¹H-NMR Features of α,β -Unsaturated Phosphonates

Dear Professor Shapiro:

We have been able to assign isomeric structures, general structures I and II, to our series of α,β -unsaturated phosphonates from their ¹H-NMR spectra.



I (cis)



II (trans)

	<u>R₁</u>	<u>R₂</u>	<u>R₃</u>
Ia, IIa	Br	Br	H
Ib, IIb	H	Br	Br
Ic, IIc	Br	Br	Br
Id, IIId	I	I	I
Ie	H	I	I
If	H	H	H

Structures were assigned using three distinct features of the NMR spectra.

1. Differences between cis and trans allylic coupling constants ($^4J_{PH} \text{ cis } > ^4J_{PH} \text{ trans }$).
2. Differences in the chemical shift of cis and trans allylic protons ($\delta \text{ cis } > \delta \text{ trans }$).
3. Relative rate of change in the chemical shift of allylic protons upon addition of varying amounts of europium shift reagent (Eu(DPM)_3).

The NMR spectrum of analog If, cis isomer of known configuration, gives coupling constants which are consistent with literature data.¹⁻⁶ [$^2J_{PH} = 20 \text{ Hz (gem)}$, $^3J_{HH} = 13 \text{ Hz (cis)}$, $^4J_{HH} = 1.5 \text{ Hz (trans)}$, $^3J_{PH} = 52.5 \text{ Hz (trans)}$, $^4J_{PH} = 3.5 \text{ Hz (cis)}$]. Very little data on allylic or vinylic, J_{PH} , coupling constants could be found in the literature,²⁻⁶ however Martin, et. al.⁵ gives a reference to unpublished results of Wysocki and Griffin whereby they claim $^4J_{PH} = 1.2 \text{ Hz}$ and 3.2 Hz in diethyl β, β -dimethyl vinyl phosphonate [$\text{Me}_2 \text{C}=\text{CHP}(O)(\text{OEt})_2$].

In our series of halogenated phosphonate isomers we noticed a consistently larger $^4J_{PH} \text{ (cis)}$ vs. $^4J_{PH} \text{ (trans)}$ [$^4J_{PH} \text{ (cis)} = 1-3 \text{ Hz}$, $^4J_{PH} \text{ (trans)} = 0-2 \text{ Hz}$] and as would be expected,¹ the same analogy follows for $^4J_{HH}$ ($^4J_{PH}$ is the inverse of $^4J_{HH}$ in the same molecule). Since no $^3J_{HH}$ data exists in these molecules I (a-e), II (a-d), structures could be assigned only on the basis of their $^4J_{PH}$ and $^4J_{HH}$ coupling constants.

Allylic protons which are cis to P=O in I (a-d) are consistently farther downfield from the corresponding trans protons of II (a-d) due to the presumed anisotropy of the adjacent P=O . This difference in chemical shift can be enhanced as much as 5-fold by use of europium shift reagent. We presume that europium chelates with the P=O oxygen thereby causing the dramatic downfield shift of cis allylic protons. A recent publication noted this same analogy for six membered ring phosphorus heterocycles.⁷ We added varying amounts of Eu(DPM)_3 to 2 pair of isomers (Ia, IIa and Ib, IIb) and plotted the chemical shift of all protons vs. amount of europium added. A series of straight lines of varying slopes was obtained and by keeping the slope of the isopropyl methyl constant, we could see a 2.6 fold greater shift for cis vs. trans allylic protons in isomers Ia, IIa, and a 5 fold greater shift for cis vs. trans in isomers Ib, IIb. Compound IIc gave a downfield shift comparable to the trans isomers IIa and IIb, i.e. $\sim 1 \text{ X}$.

Other single isomers were assigned structures based on one or more of the NMR features common to the previously examined pairs of isomers.

Very truly yours,

G. O. Morton *J. E. Lancaster*
G. O. Morton and J. E. Lancaster

Table of NMR Data

Compound	$^3J_{HH}$	$^4J_{HH}$	$^2J_{PH}$	$^3J_{PH}$	$^4J_{PH}$	$^*\delta_{H\gamma}$	** Slope $\delta\Delta/\text{Amount}$ Eu(DPM)_3
Ia (cis)	-	-	-	-	3	2.91	2.6
IIa (trans)	-	-	-	-	2	2.63	1
Ib (cis)	-	0	7.5	-	2	4.83	5
IIb (trans)	-	1	8.5	-	0	4.28	1
Ic (cis)	-	-	-	-	2	5.17	-
IIc (trans)	-	-	-	-	0	4.55	0.9
Id (cis)	-	-	-	-	1	4.98	-
IId (trans)	-	-	-	-	0	3.93	-
Ie (cis)	-	0	9	-	2.5	5.00	-
If (cis)	13	1.5	20	52.5	3.5	2.07	-

* Chemical shift in CDCl_3 relative to TMS internal standard.

** Relative shift of isopropyl methyl taken as 1.

Coupling constants in Hz.

References

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2. S. L. Manatt, G. L. Juvinall and D. D. Elleman, JACS 85, 2664 (1963)
Coupling constants for $\text{P}(\text{CH}=\text{CH}_2)_3$, $J_{\text{trans}}=30.2$, $J_{\text{cis}}=13.6$, $J_{\text{gem}}=11.7$
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6. Y. Kashman and M. Sprecher, Tetrahedron 27, 1331 (1971).
7. K. C. Yee and W. G. Bentrude, Tet. Letters #29, 2775 (1971).



TEXAS CHRISTIAN UNIVERSITY

Fort Worth, Texas 76129

Department of Chemistry

November 8, 1971

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

Dear Barry:

As a natural response to the trend of throwing shift reagents into all samples we have tried $\text{Eu}(\text{DPM})_3$ on the C-13 spectrum of cholesterol. A 0.8 M solution in a mixture (0.7 ml benzene - 0.8 ml chloroform) was made 0.27 M in shift reagent. The benzene provided a lock signal, and TMS served as an internal standard. Proton decoupled spectra were determined at 25.1 MHz. Lines were assigned according to Reich, et al., J. Am. Chem. Soc. 91, 7445 (1969).

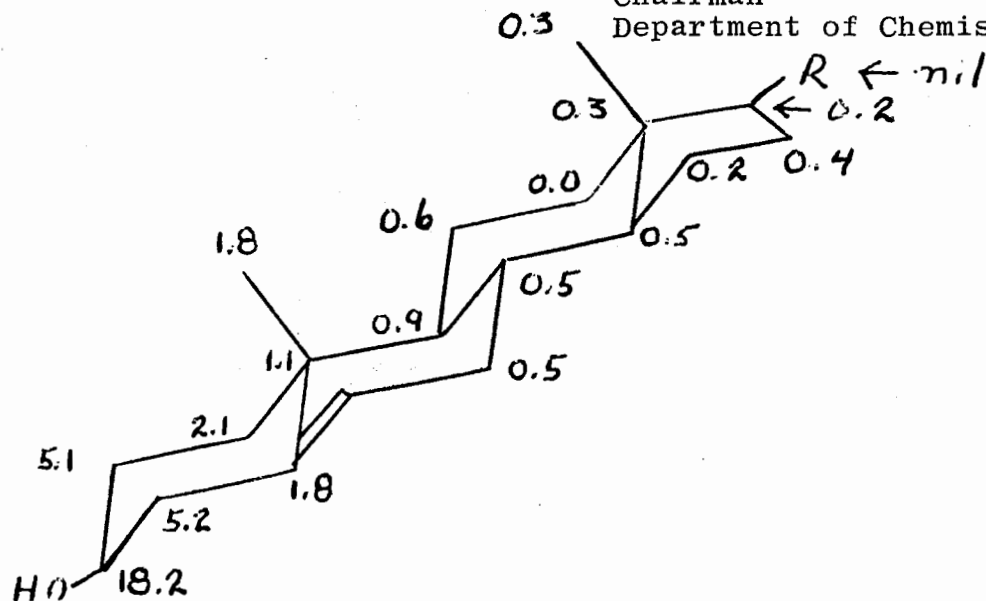
The diagram below gives the shift difference on adding the reagent. All shifts are to low field, and no doubt larger effects could be observed if one increased the concentration of reagent. I believe the results help confirm the literature assignments.

Best regards,

Bill

W. B. Smith
Chairman
Department of Chemistry

WBS/dc



THE UNIVERSITY OF GEORGIA

Department of Chemistry

ATHENS, GEORGIA 30601

November 9, 1971

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

Dear Barry:

Lithium-7 Shifts in Some Aromatic Dianion Systems

Since we have previously shown that information concerning the ring currents in planar aromatic anions and structural features of the ion pairs may be obtained from lithium-7 chemical shifts,¹ we have applied this technique to some dianions in the hopes of obtaining information concerning the electron delocalization in these systems.

The lithium-7 chemical shifts obtained from thirteen aromatic dianion systems (two electron reduction of the hydrocarbon lithium metal) in THF solution are given in the Table. With the exceptions of the dianions of azulene (IV) and 15, 16-dimethyl-dihydropyrene (V) the lithium-7 chemical shifts are upfield from the reference and the majority are clustered around +1.0 ppm. Various data indicate that these dianions form contact ion pairs in solution. Therefore, if the lithium cations are coordinated with the π -cloud of these dianions as was found for the anions, they should experience an upfield or downfield shift, due to their being located in the shielding or deshielding regions of the induced diamagnetic or paramagnetic ring current, respectively.

Of the dianions examined, only I-V are consistent with the periphery model for electron delocalization. The shifts for I-III indicate diamagnetic ring currents while IV and V indicate paramagnetic ring currents. The lithium-7 shifts for VI-XIII do not follow the above trends and their shifts are similar to that observed for allyl lithium. The fact that their lithium-7 chemical shifts are not shifted in either direction suggests the following possibilities: (1) the ions are solvent separated, (2) the periphery model is not an adequate model for electron delocalization in these systems or (3) the dianions possess essentially no induced ring current.

The first possibility is tentatively ruled out on the basis of the Coulombic attractions involved and on the basis of previous data concerning the ion pairing in these systems. A consistent explanation for both the proton² and lithium-7 spectra of the dianions (VI-XIII) is that the excess charge is delocalized around the periphery of the ring

Professor B. L. Shapiro

Page 2

November 9, 1971

systems with relatively large perturbations due to the cross links. Such perturbations of the delocalization would result in reduced paramagnetic ring currents in the dianions due to an increase in the splitting of the highest occupied and lowest unoccupied molecular orbitals. Evidence in support of reduced ring currents may be obtained by comparison of the lithium-7 and proton data of the dianions of 15,16-dimethyldihdropyrene (V) and pyrene (VI). The proton shifts of the exterior protons of V are shifted upfield approximately 12 ppm from their values in the neutral hydrocarbon.³ In contrast, the proton shifts of VI as well as some of the other dianions (VII-XIII) are only shifted upfield from 1-6 ppm from their values in the neutral hydrocarbons.² Thus, both the proton and lithium-7 data are consistent and supported the idea of smaller ring currents in VI-XIII.

Table

⁷Li Chemical Shifts in Some Aromatic Dianion Systems

Dianion	$\delta, ^7\text{Li}^a$
Cyclooctatetraene (I)	+8.55
Biphenylene (II)	+6.10
Acenaphthylene (III)	+4.13
Azulene (IV)	-2.05
15,16-Dimethyldihdropyrene (V)	-3.15
Pyrene (VI)	+1.10
Perylene (VII)	+1.33
Fluoranthene (VIII)	+0.93
3,4-Benzfluoranthene (IX)	+0.48
Anthracene (X)	+1.15
1,2-Benzanthracene (XI)	+0.94
Chrysene (XII)	+0.90
Tetracene (XIII)	+0.11

a. In ppm from external aqueous 1 M LiCl. A positive value denotes upfield. The formal concentration of the starting hydrocarbon is 0.3 M.

References:

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Sincerely yours,


Richard H. Cox
Assistant Professor

RHC:mjd

TO
PROFESSOR BERNARD L. SHAPIRO
DEPARTMENT OF CHEMISTRY
TEXAS A & M UNIVERSITY
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Abt.: PHYSIKALISCHE MESSTECHNIK
dd

Stöckheim, den NOVEMBER, 09.1971

DIRECT MEASUREMENT OF THE TEMPERATURE OF THE HA-100 MAGNETIC
COIL.

Dear Professor Shapiro,

Please excuse the delay in our contribution, which is due to the fact that the installation and testing of the magnet temperature measuring device took longer than expected.

As in our previous communication, we wish to report on technical changes on our HA-100.

More than a year ago, we were forced to exchange a magnet coil in our machine, a time consuming and expensive repair.

In contrast to the original magnet coil, the replacement coil did not have a built-in thermoelement for temperature measurement. Since we had often had defects in water cooling system, we wanted to utilize the temperature of the magnet coil as a corroborative check. Thus, because the replacement coil lacked a thermoelement, we sought a method which would measure the temperature of the copper coils directly.

The simultaneous measurement of the magnet's current and the applied voltage enables the ratio of these two quantities to be determined in a crossed coil meter. The reading yields the temperature directly. One can get around a calibration by marking only the operational temperature on the scale, which allows one to read just + or - deviations.

Future plans include the installation of an automatic switching-off device, which would be activated when a present value were exceeded.

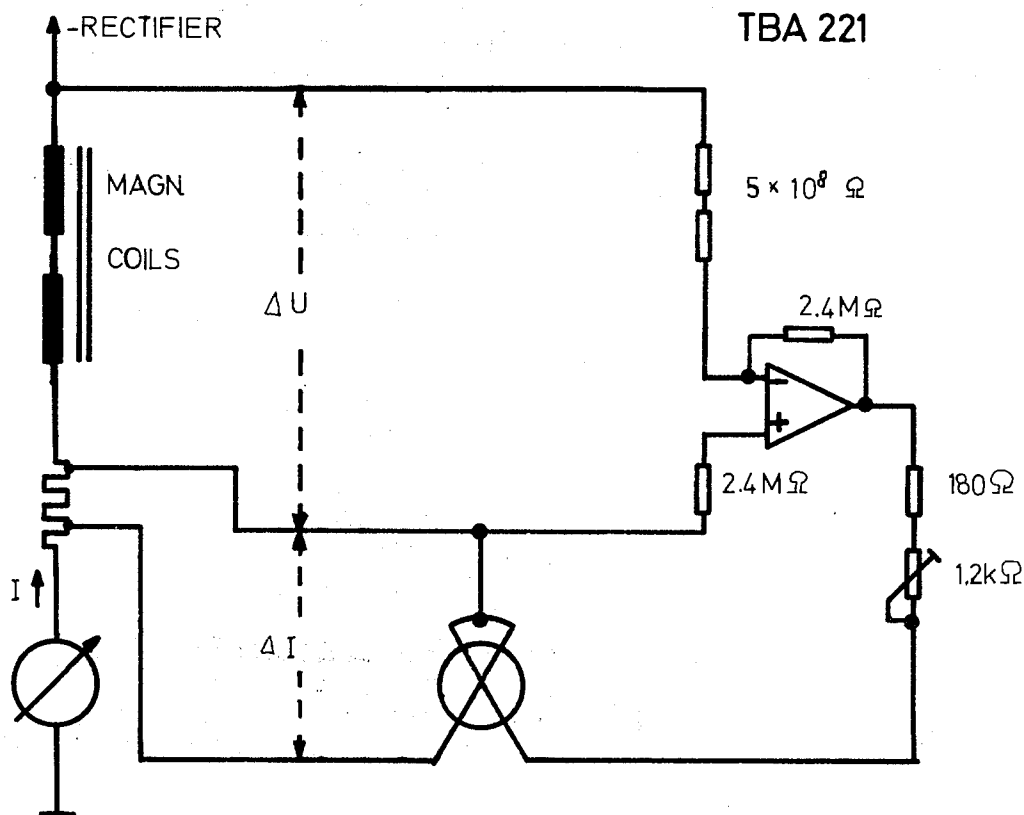
Yours sincerely



Peter Steyer



Horst Stegemann



CIRCUIT DIAGRAM

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DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

November 9, 1971

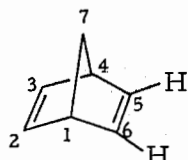
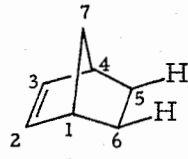
Professor B. L. Shapiro
 Department of Chemistry
 Texas A and M University
 College Station, Texas 77843

Problems with ^{13}C Integrals
in Rapid Sweep CW Operation

Dear Barry,

We offer a cautionary note to all who may be accumulating spectra of weak signals (^{13}C , ^{15}N), using continuous-wave, rapid-sweep procedures at high rf power levels. In ^{13}C spectra of certain chlorocarbons, we have noted that peak area measurements did not accord with simple expectations, with or without proton decoupling. While this is expected to be a common dilemma in spectra determined by pulse methods (unless there are appropriately long delays between pulses), we have seen no discussion to this effect for CW mode of operation. To focus more particularly on what happens, some representative peak area measurements are shown in Table I. We believe these abnormal integral ratios arise from relaxation effects associated with rapid-passage operation.

Table I. Some Representative Chlorocarbon Signal Integrals.

	Chemical shift ^a		Signal Integral ^{b, c} (±0.3)	
			Coupled	Decoupled
 C ₇ Cl ₆ H ₂	C-2, 3	51.7	1.0	1.0
	C-5, 6	55.0	4.7	8.5
 C ₇ Cl ₈ H ₂	C 2, 3	60.3	2.0	2.0
	C-7	93.8	1.0	1.0
	C-1, 4	110.3	2.0	2.0
	C-5, 6	128.1	4.1	5.8

- a) Chemical shifts in ppm upfield from CS_2 , measured from internal CHCl_3 at 115.4 ppm from CS_2 . b) Spectra accumulated at 40 Hz sec^{-1} (25 sec sweep time) at H_1 power level 10 db below maximum output of V4311. c) Operating conditions were below the saturation level of all signals.

Consider first the relaxation times for ^{13}C in the arrangements C-H and C-Cl. It is to be expected that $T_1^{\text{C-H}} \approx T_2^{\text{C-H}}$ when the relaxation is predominantly through the ^{13}C - ^1H dipolar mechanism, but that $T_1^{\text{C-Cl}} > T_2^{\text{C-Cl}}$ due to the greater effect of the scalar coupling mechanism "of the second kind" upon spin-spin relaxation. The absence of the ^{13}C - ^1H dipolar mechanism for carbon bonded only to chlorine suggests that $T_1^{\text{C-Cl}} > T_1^{\text{C-H}}$. These expectations are generally supported by experiment. (1) (cf. Table II).

Table II. Calculated Signal Integrals for Repeated Passage Through Resonance.

	T_1 sec	T_2 sec	Integral			
			Sweep 1	2	3	4
$^{13}\text{CHCl}_3$	33 ^a	0.35 ^a	1.880	0.930	0.961	0.961
$^{13}\text{C-H}^b$	10	10	3.309	2.768	2.812	2.808
$^{13}\text{C-Cl}^b$	150	1.0	2.315	-0.401	0.488	0.197

For all cases $H_1 = 10 \text{ rad. sec}^{-1}$. Spectra calculated for repetitive scans through resonance with 25 sec sweep times and 5 Hz sec^{-1} sweep rate.

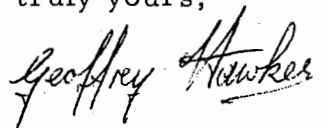
a) Values from T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, 1971. b) Hypothetical cases.

Whenever the relaxation times are rather long (and especially if they are very different), problems with signal intensities are to be expected as one approaches the realm of adiabatic rapid passage. Thus, in measurement of T_1 for ^{13}C in cyclohexane by the adiabatic rapid-passage method (cf. Grant and coworkers (2)), a single sweep through resonance at 40 Hz sec^{-1} , at an H_1 power level = 5 db below maximum output of our V4311 unit, effectively produces $\approx 65\%$ inversion of the equilibrium Z-axis magnetization. (cf. operating conditions in Table I). Consequently, for nuclei of T_1 ($\geq 50 \text{ sec}$), repetitive sweeps through resonance at 25-sec intervals can not realize the full signal intensity.

We have written a broadly useful program for numerical integration of the Bloch equations (based on the predictor-corrector cycle, (3) Ernst and Anderson (4) used the Runge-Kutta procedure). Calculated values of signal integrals for some T_2 , T_1 combinations for rapid-passage high-power levels (short of saturation) are shown in Table II. For the first sweep, the absorption-mode signal integrals are dependent on T_2/T_1 , but not in any very simple way. In successive sweeps, an equilibrium absorption-mode signal is quickly realized and the integral of this is strongly dependent on T_1 . Thus, to locate signals, it is fine to use the advantage of rapid-sweep operation but slow sweeps are necessary to obtain satisfactory integrals.

The work described here is a collaborative effort involving the undersigned and Robert A. Smith (first to experience these difficulties with chlorocarbons), David Doddrell (contributed a number of experimental data), and Donald W. Roberts (who wrote the computer program).

Very truly yours,



Geoffrey E. Hawkes



John D. Roberts

GEH/JDR:k

References

- (1) R. Freeman and H. D. W. Hill, J. Chem. Phys., 55, 1985 (1971).
- (2) T. D. Alger, S. W. Collins, and D. M. Grant, J. Chem. Phys., 54, 2820 (1971).
- (3) D. D. McCracken and W. S. Dorn, "Numerical Methods and Fortran Programming, John Wiley and Sons, Inc., New York, 1964.
- (4) R. R. Ernst and W. A. Anderson, Rev. Sci., Instr., 36, 1696 (1965).

Dr. Josef Brandt
MAX-PLANCK-INSTITUT FÜR KOHLENFORSCHUNG

MPI für Kohlenforschung, 4330 Mülheim-Ruhr, Kaiser-Wilhelm-Platz 1

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

4330 Mülheim a. d. Ruhr
Kaiser-Wilhelm-Platz 1
Telefon Sa.-Nr. ~~34021~~ 30 61
Durchwahl: 30 6 330

Ihr Zeichen

Ihre Nachricht vom

Unser Zeichen

Datum

11.11.1971

Dear Dr. Shapiro:

Connecting time averaging computers to a Varian XL-100

Although there is a TAC-connection cable delivered with every XL-100, connecting TAC's other than Varian's C1024 can be a nuisance, because there is nothing in the manuals to indicate which pin does what and at which voltage. You have to go all the way through the wiring diagrams.

It may therefore save others some work if I give here the functions, logical levels etc. on socket J030 together with those required at a TMC CAT 1000 (see Table!).

Please credit this contribution to the subscription of
Prof. Dr. E.G. Hoffmann.

Sincerely yours,

J. Brandt

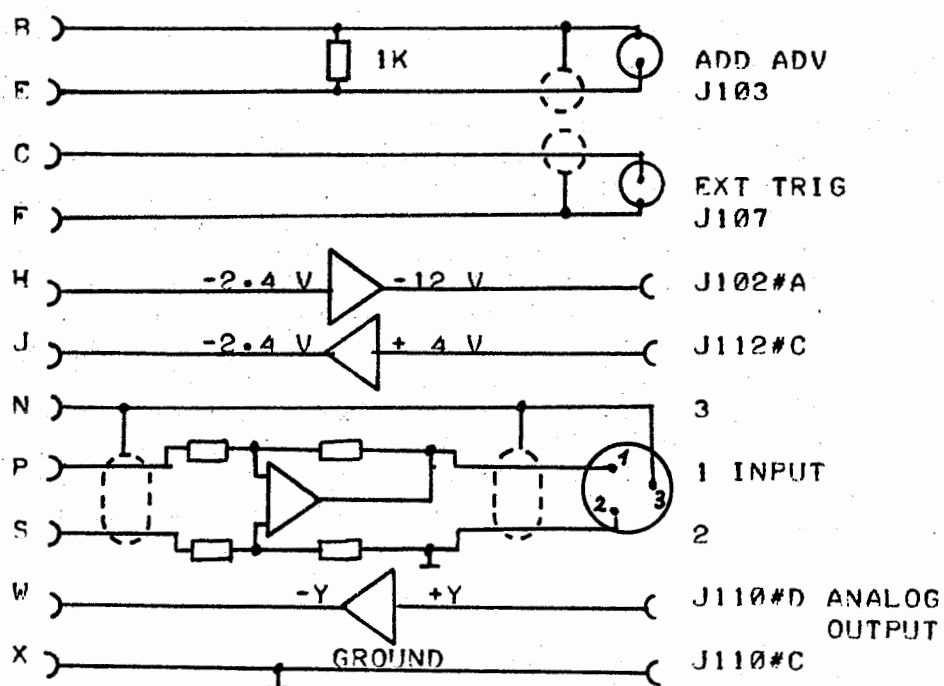
XL-100		TMC CAT 1000				
J030 pin						
hot ground	logical 1	logical 1	connector	hot pin ground	Function	re- marks
E	5V	5V	J103	BNC	Adress advance	1)
B						
F	same		J107	BNC	ext. Trigger (starts Sweep or Readout)	2)
C						
H	-2.4V	-12V	J102	A v.s.	Inhibit accumu- lation during readout	3)
(B,C)						
J	-2.4V	+ 4V	J112	C -	Control Flip- Flop (CFF),is "1" during sweep	
(B,C)						
P	analog -3V...+3V		INPUT 1	1 2 3	Analog Input to CAT (for accu- mulation)	4)
S						
N	Shield for 1 and 2					
W	analog		J110	D C	Analog Output (for Readout)	5)
X						

- 1) Insert 1 k load between E and B!
- 2) can be gated with a preset counter that is driven by CFF
- 3) we used small IC-opamps as level converters
- 4) insert non-inverting op-amp for level conversion and zero offset
- 5) insert inverting op-amp for level conversion and zero offset

Switch settings on CAT 1000 for Accumulation and Readout:

START, TRIGGER:EXT., ADDR. ADV.:EXT.

XL-100, J030



TEXAS A&M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

November 12, 1971

Department of
CHEMISTRY

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

Dear Barry,

Proton Nmr Investigations of the Environment of
 Aromatic Compounds in Micellar Solutions

We have been interested for some time in the utilization of H^1 and F^{19} nmr spectroscopy for the elucidation of the average environment of organic molecules in aqueous association colloidal, ie. micellar, systems in order to obtain a better understanding of the mechanism of micellar catalysis in these systems. Consequently we investigated the interactions of benzene, nitrobenzene, 2,4-dinitrophenyl sulfate, its *in situ* hydrolysis products, and 2,4-dinitrophenoxide ion with 0.50M zwitterionic micellar 3-(dimethyldodecylammonio)-propane-1-sulfonate, $CH_3(CH_2)_{11}N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$. The H^1 resonance frequencies of the solubilize protons as well as those of the micellar surfactant shift linearly upfield as a function of solubilize concentration. At least over a relatively low solubilize concentration range (0.01-0.18M), the data fit the usual equation

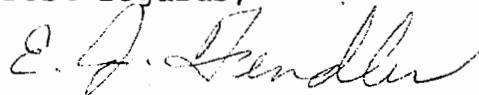
$$\nu = \nu_o + a[X]$$

where ν and ν_o are the observed and limiting resonance frequencies, respectively, and X is the solubilize. Comparison of the ν_o values for benzene and nitrobenzene in water, cyclohexane, in aqueous nonmicellar alkylammonium salts and in cationic, anionic, zwitterionic, and nonionic micellar solutions reveals that in all cases the ν_o values in the salt and micellar systems approach that in water rather than that in cyclohexane. Such results were previously misinterpreted in terms of solubilization at the micelle-water interface and due caution should be exercised in comparisons of extrapolated values for aggregated systems, which in the case of micelles and proteins often contain an appreciable amount of water. We have found that the a values are far more sensitive

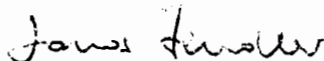
Professor Bernard L. Shapiro
November 12, 1971
Page 2

to and indicative of the average environment of the solubilizate in these systems. From these results it appears that both benzene and nitrobenzene interact primarily with the charged surface of the zwitterionic micelle, whereas the dynamic solubilization site for nitrobenzene is somewhat closer to the micelle interior than for benzene. Our pmr data for the benzene - sodium dodecyl sulfate (anionic micellar) system and those available for the benzene - hexadecyltrimethylammonium bromide (cationic micellar) system suggest that benzene is mainly in the interior of the anionic micelles but is located near the surface of the cationic and zwitterionic ones. More remarkably, 2,4-dinitrophenyl sulfate anion, whose hydrolysis is catalyzed by micelles, is located in the micelle interior whereas its in situ hydrolysis products and 2,4-dinitrophenoxide ion interact to a greater extent with the polar head groups.

Best regards,



E. J. Fendler



J. H. Fendler

EJF/dem

ANORGANISCH-CHEMISCHES LABORATORIUM
DER
TECHNISCHEN UNIVERSITÄT MÜNCHEN
Dr.K.E.Schwarzthans

8 MÜNCHEN 2, den 12.11.1971
Arcisstraße 21
Ruf-Nr. ~~XXXX~~ 330/331/332
333 (Prof. Fritz)

Herrn

Prof.Dr.B.L. S h a p i r o

Dept. of Chemistry,
Texas A and M - University,
College of Science,

College Station Texas, 77843

USA

^{199}Hg - ^1H -Kopplungskonstante in $\text{CH}_3\text{Hg}[\text{Co}(\text{CO})_4]$

Sehr geehrter Herr Professor Shapiro!

Bei unseren Arbeiten über Metallcluster der Hauptgruppen- und Übergangsmetalle erhielten wir auch die Verbindung $\text{CH}_3\text{Hg}[\text{Co}(\text{CO})_4]$. Dargestellt wurde dieser zweikernige Cluster durch Umsetzung von $\text{Na}[\text{Co}(\text{CO})_4]$ mit CH_3HgJ . Der Gang der ^{199}Hg - ^1H -Kopplungskonstanten von der Verbindung

$(\text{CH}_3)_2\text{Hg}$ mit $101,4^1)$ Hz über
 $\text{CH}_3\text{Hg}[\text{Co}(\text{CO})_4]$ mit 157 Hz zu
 CH_3HgNO_3 mit $258^2)$ Hz (gemessen in H_2O)

deutet in der angegebenen Reihenfolge auf eine beachtliche Zunahme der Orbitalüberlappung der Quecksilber-Kohlenstoff- σ -Bindung hin. Dies kann durch die Abnahme des Ionencharakters in $\text{CH}_3\text{Hg}[\text{Co}(\text{CO})_4]$ im Vergleich zu CH_3HgNO_3 erklärt werden.

Mit freundlichen Grüßen

Hans Stigge *K.E. Schwarzthans*

PS: Please credit this contribution to Prof.Dr.H.P.Fritz,
Anorganisch-Chemisches Laboratorium der Technischen Universität
München.

- 1) K.A.McLauchlan, D.H.Whiffen, L.W.Reeves, Mol.Phys., 10131(1966).
- 2) F.A.L.Anet, J.L.Sudmeier, J.Magn.Res.1, 124(1969)

UNIVERSITY OF CALIFORNIA, SANTA BARBARA

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA 93106

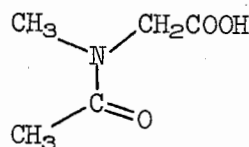
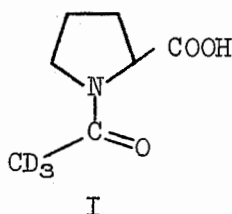
November 16, 1971

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

"Conformational Studies by Deuterium Magnetic Resonance"

Dear Barry:

As a continuation of previous work¹ we have examined the kinetics of amide group rotation in N-acetyl-L-proline(I). Analysis of the p.m.r. spectrum of this material for exchange effects was frustrated by the fact that signals from the acetyl methyl seriously overlap the resonances from the protons on the ring. The desired information was obtained by preparing the N-trideuterioacetyl derivative of I and obtaining the deuterium spectrum at 15.4 MHz. Some results are shown in the accompanying figure. The doublet separation (in p.p.m.) at low temperatures agreed well with that obtained from the p.m.r. spectrum and conventional lineshape analyses of these and related deuterium spectra led to acceptable estimates of the barrier to amide rotation. These are summarized below and compared to similar data for the acyclic model compound, N-acetyl sarcosine.¹



pH	1.6		
ΔG^\ddagger , kcal./mole		19.9	18.8
ΔH^\ddagger , kcal./mole		14.4	15.2
ΔS^\ddagger , e.u.		-16	12
pH	7.0		
ΔG^\ddagger , kcal./mole		21.1	20.5
ΔH^\ddagger , kcal./mole		26.1	21.1
ΔS^\ddagger , e.u.		14	2

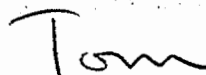
Professor B. L. Shapiro

Page Two

November 16, 1971

We have also used deuterium n.m.r. to determine the energy barrier to inversion in d_1 -cyclohexane with results that are in good agreement with Anet's values for d_{11} -cyclohexane, obtained by 1H spectroscopy. Conformational studies by deuterium spectroscopy can thus provide reasonable estimates of activation parameters and can offer some experimental advantages; such experiments at very low temperatures seem to be precluded by unfavorable quadrupolar effects, however.

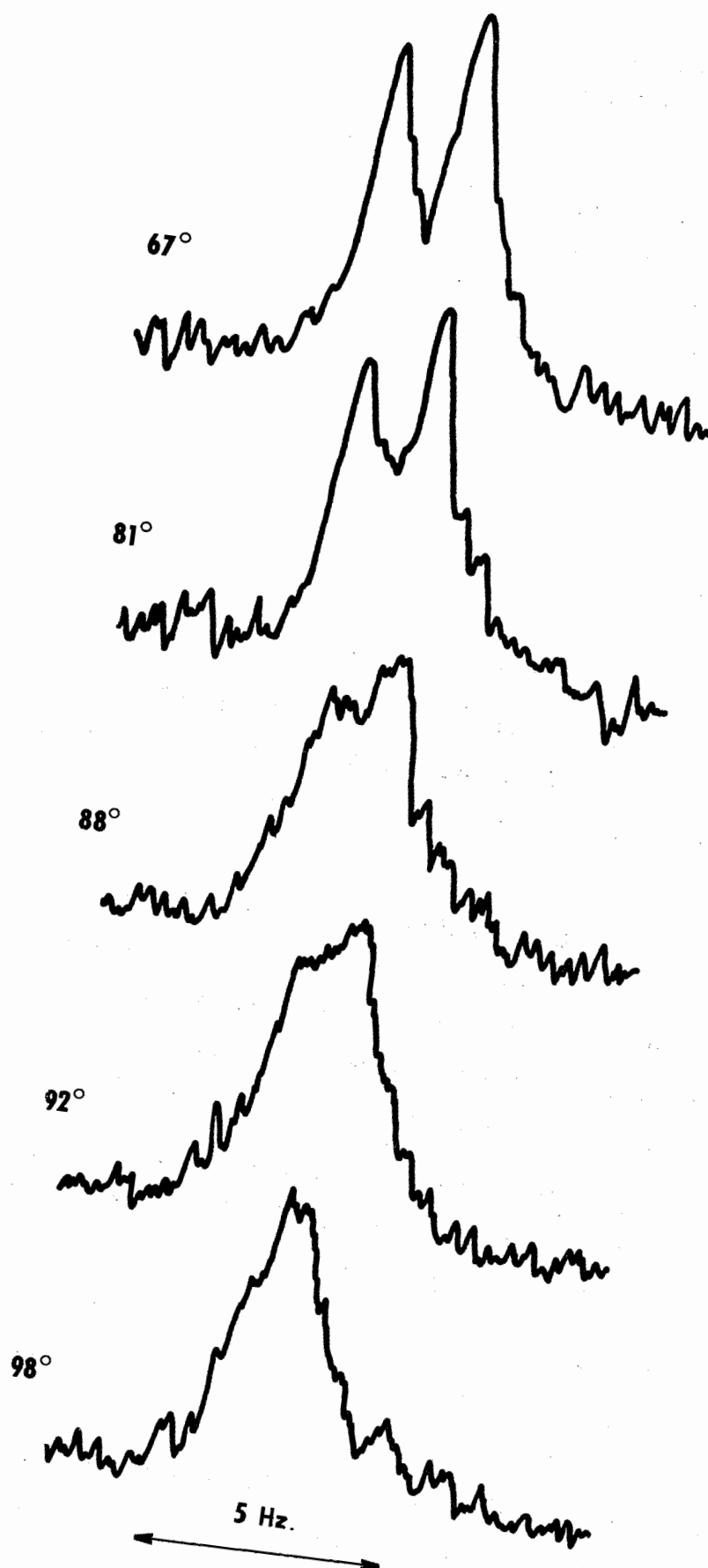
Sincerely yours,



J. T. Gerig
Associate Professor

¹ J. T. Gerig, Biopolymers, in press.

Figure 1. Single-scan deuterium magnetic resonance spectra of 1M N-trideuterioacetyl proline at pH 7.0 in H_2O . Spectra were obtained on a Varian Associates HA-100 operating at 15.4 MHz. and locked to D_2O in the solvent.



Iwan N. Stronski-Institut
II. Institut für Physikalische Chemie
der Technischen Universität Berlin
E. Lippert and W. Schröer

1 Berlin 12, den 16.11.1971
Straße des 17. Juni 112
Tel.: (0311) 314 (Dachwerk)
Az.: 3 S

Prof. B. L. Shapiro, Ph.D.

Texas A & M University
College of Science

College Station, Texas 77843
U.S.A.

Dear Barry,

Solvent shift and chemical reactivity

Variations of the chemical shifts and coupling constants in solution are caused by the polarisation of the electronic shell with the exception of magnetic anisotropic effects. Solvent shifts are, therefore, relevant when examining chemical reactivity.

It is, by nature of the problem, necessary to investigate a large number of the nuclei involved in order to clearly define the interactions of the molecule with its environment. In this way, solvent reactions of less significance can be separated from those of chemical relevance, where C^{13} is of vital importance. Some aspects of this problem are yet to be discussed [1].

We are analysing the interaction between the strong organic base hexamethylphosphorictriamid (HMPT) and the C-H bondings of various ethylenitriles in an inert solvent (CCl_4 , cyclohexane).

These molecules should be capable of forming associates having the same geometric structure as postulated for the transition states of nucleophilic reactions of α , β unsaturated carbonyl compounds.

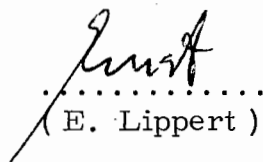
The ABC, ABCX and ABX_3 spectra have been analysed with LAOCOON III. By assuming independent associations at the centres an analysis of the acrylnitrile/HMPT/ CCl_4 system gives at 18 °C in the case of the α -proton-association an

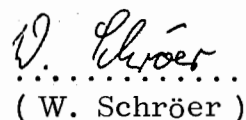
association constant of $K_x = 4,4$ and an enthalpy of $\Delta H = -0,63$ kcal/mol, while the values for the β -cic protons are $K_x = 9,1$ and $\Delta H = -1,1$ kcal/mol. The proton shifts are 1,03 and 0,305 ppm, respectively ; the C^{13} shifts are 0,49 and 2,99 ppm, respectively, toward lower field

Taking into account the magnetic anisotropy, the values of the associate shifts of protons agree with both , the approximate Lamb-formula calculations using CNDO electron densities and the electronic anisotropy calculations [2]. The C^{13} chemical shift calculations with the simple formula of Karplus and Pople [3] are unsatisfactory. We are, therefore, elaborating an approximation using more information from the CNDO calculations.

We expect a connection between the thermodynamic values obtained from NMR and the reaction rate as well as the activation energy and the yield of the corresponding chemical reactions. These investigations facilitates a clearer understanding of kinetic chemical reactions in liquids.

Sincerely yours


.....
(E. Lippert)


.....
(W. Schröer)

- [1] D. Ziessow, E. Lippert, Ber. Bunsenges. 74 , 13 (1970)
- [2] R.F. Zürcher, Prog. in NMR Spectroscopy 2 (1967) 205
- [3] M. Karplus and J.A. Pople, J. Chem. Phys. 38 (1963) 2803



הפקולטה לכימיה
DEPARTMENT OF CHEMISTRY

November 16, 1971

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

Dear Barry,

Interface between C-1024 CAT and P-120 Tally Punch.

Many nmr measurements require transfer of data from a CAT to paper tape or cards for further computer processing. An interface between our Varian C-1024 CAT and a Tally P-120 paper tape punch was designed by Eng. Y. Harlev and Mr. A. Peer. It is supplied commercially by ALEF Research and Development Ltd., P.O.Box 94, Kiriat-Haim, Haifa, under the trade name of "Alef Interface 300". The interface could be adapted to other tape or card punches.

The main technical features of the unit are: 1. DTL logic. 2. Adaptable to a serial output computer. 3. Generation of parity check. 4. Voltage supply to punch. 5. Organization of the information in ASCII code. 6. Preparation of format for printout with identification of experiment.

Admittedly this arrangement is inferior to any direct computer attachment to the nmr spectrometer. It is, however, a relatively cheap solution and may partially solve the problem.

Best regards.

Yours sincerely,

Aharon Loewenstein
A. Loewenstein



הפקולטה לכימיה
DEPARTMENT OF CHEMISTRY

TECHNION ISRAEL INSTITUTE OF TECHNOLOGY

November 17, 1971

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

Dear Barry,

Would you kindly enter the following announcement into the TAMU NMR Newsletter:

Postdoctoral Position Available

A postdoctoral position for the academic year 1972-3 is available in the nmr group here. The fellowship includes payment for a single return economy class air ticket and a monthly salary of about IL1350.- (tax free). Our equipment consists of a Varian DP-60, Bruker HFX-10, Bruker 322S pulsed, Varian A60 T-60 Spectrometers and various accessories. An IBM 370/165 computer on campus is available. The main current interest in my group is the study of molecular dynamics in liquids and liquid crystals. However, other suggestions are welcome.

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

Best regards,

Yours sincerely,

Aharon Loewenstein

A. Loewenstein

AL:kk

HARVARD UNIVERSITY
DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge, Massachusetts 02138
U.S.A.

November 18, 1971

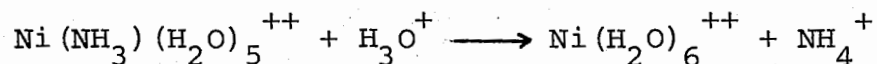
Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Barry,

Stopped Flow NMR

With the recent development of Fourier Transform techniques for rapid NMR spectrum acquisition, we became interested in applying rapid mixing techniques to NMR. With this in mind, a rapid mixing cell was designed in conjunction with the development of a stopped flow NMR spectrometer. Reported here are preliminary results obtained with this stopped flow NMR system.

Shown in Figure 1 is the oscilloscope trace of the reaction.



The reaction halftime is ~ 80 milliseconds and is in agreement with optical stopped flow measurements (G.A. Melson and R.G. Wilkins, J. Chem. Soc., 1962, 4209).

Yours sincerely,

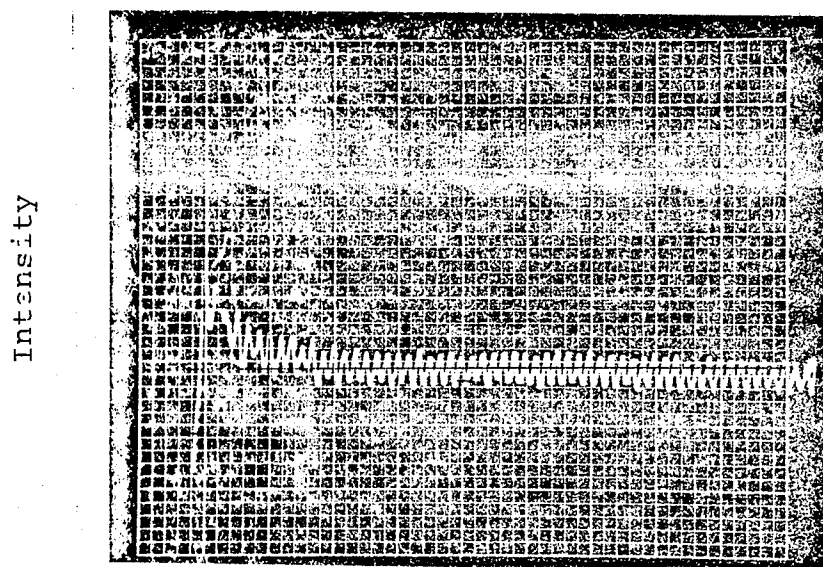
Brian

Brian D. Sykes

John Grimaldi

John Grimaldi

Figure 1



Time (1 CM = 0.1 sec)

DIVISION OF CHEMISTRY
DIVISION DE CHIMIE



CABLE ADDRESS
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"RESEARCH"

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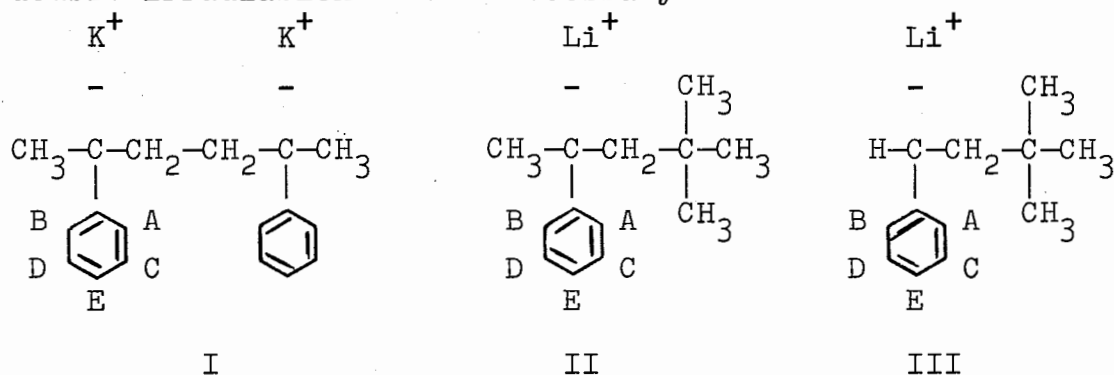
November 19, 1971

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

Hindered Rotation in Styryl Anions

Dear Barry,

The best I can do in answer to your blue letter is to give a few additional examples of hindered rotations about a phenyl carbon bond. In compounds I, II and III the hindrance presumably arises from charge delocalization into the aromatic ring with concomitant double bond character for the phenyl carbon bond. The only unusual aspect was the necessity to spin decouple the para proton in III to simplify the spectra so that theoretical spectra could be calculated for rate determinations. In II the ortho protons are sufficiently separated that they can be used for rate determinations and double irradiation is not necessary.



Yours truly,

S. Brownstein

SB/ldl

Compound	I	II	III
δ_A	4.855	5.18	6.050
δ_B	5.430	5.56	6.050
δ_C	5.937	6.06	6.434
δ_D	6.040	6.13	6.576
δ_E	4.235	4.45	5.385
J_{AB}	2.6		
J_{AC}	8.1	8	8.2
J_{AD}	0.5		
J_{AE}	0.9		1.0
J_{BC}	0.5		
J_{BD}	8.3	8	8.3
J_{BE}	0.9		1.0
J_{CD}	1.6		~ 2
J_{CE}	6.0	6	6.5
J_{DE}	6.0	6	6.5
E_D kcal/mole	Too large to measure	14 \pm 1	11.9 \pm 0.8
Charge on ring	0.89	0.80	0.61



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION
WASHINGTON, D.C. 20204
30 November 1971

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

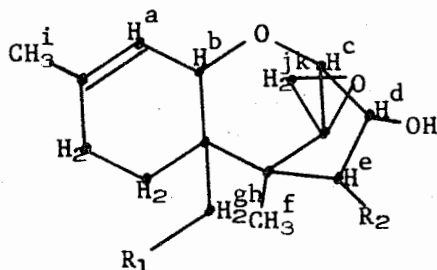
Natural Product Identification with Lanthanide Shift Reagents

Dear Barry,

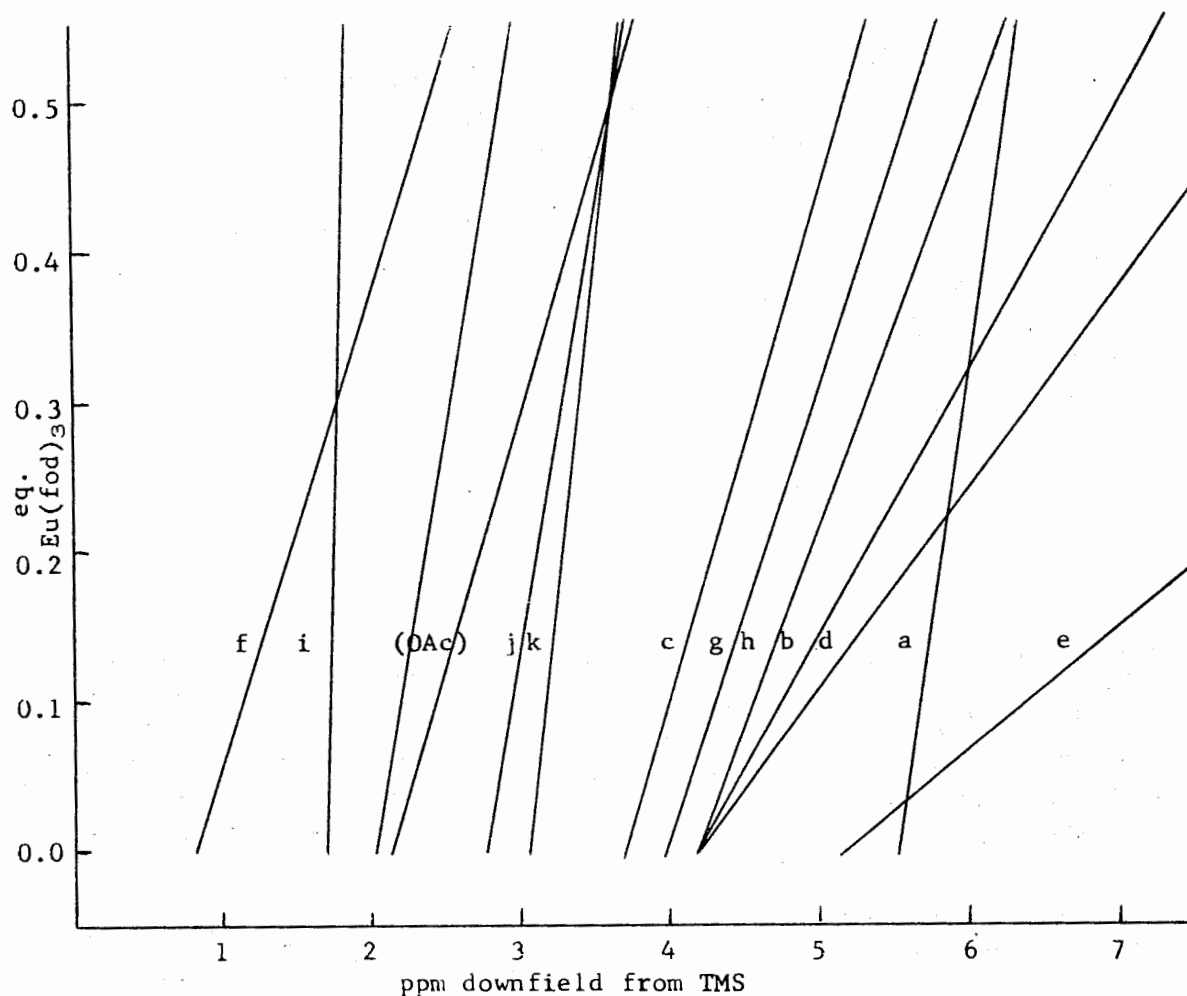
We at F D A are pleased to report an application of one of the new "wonder drugs". This curative from the "Lanthanide Complex" has greatly rejuvenated the capabilities of our HA-100 at a time when we feared that, due to the generation gap, its useful days were nearing their end.

Seriously, results with shift reagents, particularly $\text{Eu}(\text{fod})_3$, portend major breakthroughs for the identification and characterization of milligram quantities of natural product extracts, which are common and difficult requests made of the NMR group of the Bureau of Foods.

Our first substantial effort, still in its early stages, using shift reagents involves the identification of two previously unreported mold-metabolites, of which less than 20 mg of each have been laboriously isolated. Preliminary studies indicate that the unknowns are trichothecenes that possess the common backbone structure shown:



To see whether shift reagents would help in the analyses, diacetoxy-scirpenol ($R_1 = R_2 = \text{OAc}$) was studied as a model compound. Possible difficulties were anticipated because of the presence of the abundant supply of basic sites (oxygen on ester, ether, epoxide, and alcohol groups) which could bind with the shift reagent. The displacements of the shifts of all protons (excepting the ring methylene protons which are only slightly affected) are shown in the figure. As evidenced by the straight lines obtained well beyond 0.5 equivalents of $\text{Eu}(\text{fod})_3$, it appears that the predominant site of complexation is the alcoholic oxygen.



Thus the several bands of the spectrum could be assigned to the protons as shown by the superscripts in the structural formula. This result was easily obtained with 16 mg of the fairly high-molecular-weight (366) compound without any need for time-averaging.

Lanthanide-perturbed samples appear to be quite suited when the amount of available sample is small. The line-broadening permits the use of rather high rf power without appreciable saturation; because of the increased linewidths the inevitable losses in resolution occurring during prolonged time-averaging are quite insignificant.

We have high hopes that this method will enable us to perform some of the analyses which have heretofore been totally out of the question.

Sincerely yours,

D. N. Lincoln
D. N. Lincoln
BF-145

R. M. Eppley
R. M. Eppley
BF-146

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

DEPARTMENT OF CHEMISTRY
CAMBRIDGE, MASSACHUSETTS 02139

November 30, 1971

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843High Resolution ^{13}C NMR in Solids

Dear Barry:

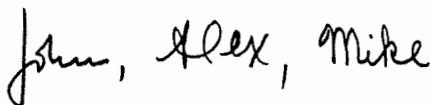
Nuclear magnetic resonance of natural abundance ^{13}C in solids is commonly thought to be prohibitively difficult for two main reasons: (i) Spin-lattice relaxation times are very long making signal averaging painful, (ii) Resolution is extremely poor due to broadening by abundant protons. By a sort of ass-backward adaptation of the Hartmann-Hahn and Lurie-Slichter experiments we have been able to overcome both these problems.

Figure 1 shows a spectrum of natural abundance ^{13}C in 50 mg of solid adamantane obtained in less than one second by our method, which we call "Proton-Enhanced Nuclear Induction in Solids". Basically, the technique consists of using the large proton polarization to enhance the ^{13}C signal by alternately observing the latter and establishing "thermal" contact with the protons. Resolution is attained by decoupling the protons during observation.

There are several advantages to extracting spectra from solid samples in this way as compared to spectra from liquid solutions: (i) signals are much stronger, (ii) There is more information in high resolution solid state NMR spectra.

Since we only wished at this stage to interest you in the preliminary results, the description of the experiment is of course somewhat cryptic. Details on the method and results on other compounds and nuclei will be published shortly.

Sincerely,

John S. Waugh
Alexander Pines
Michael G. Gibby

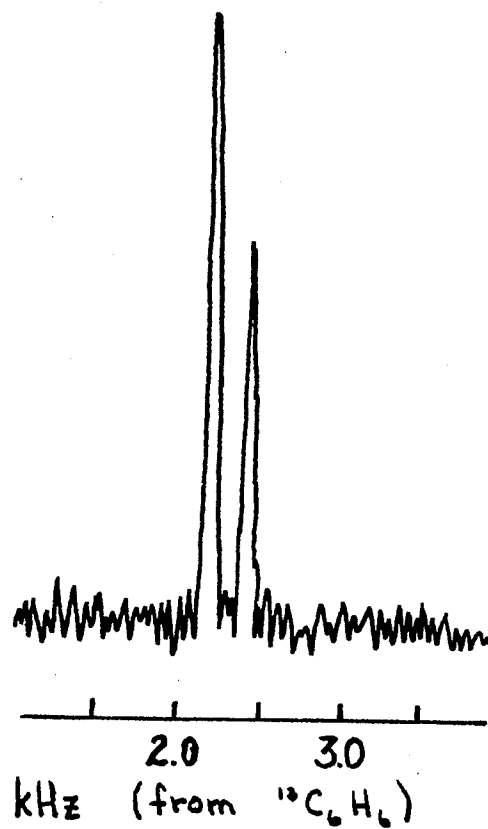


Figure 1

^{13}C NMR spectrum of solid adamantane
at room temperature (14 accumulations).



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ISTITUTO DI CHIMICA DELLE MACROMOLECOLE

20133 MILANO, 29.11.1971

VIA ALFONSO CORTI N. 12

TEL. 29.28.93 - 29.30.97 - 29.36.04 - 29.37.81

29.52.78 - 29.54.82 - 29.60.71

Ns. Rif. Prot. N.

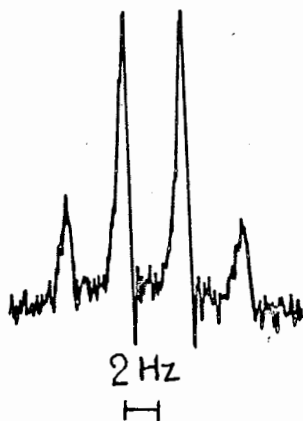
Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station
Texas 77843

Dear Professor Shapiro,

Once again our contribution has fallen due and to discharge it we would like to report on the long range ^{13}C -S-C-H coupling in dimethyl sulphoxide. We have measured this coupling at scale expansions of 4, 2 and 1 Hz/cm using our Bruker HF X90 spectrometer (32 accumulations) and obtained for all three expansions the value of $4.5 \text{ Hz} \pm 0.1 \text{ Hz}$ (see Spectroscopy Letters 1971, Vol. 4, No. 10) for neat D.M.S.O. containing ca 5% C_6F_6 .

Later we noticed a value of 6 Hz ($\pm ?$) reported (J. Amer. Chem. Soc. 1971, 93, 4294) for a sample almost identical to ours (n.l. + 10% C_6F_6) but however the scale expansion was not given, neither was any estimate of error. In view of the fact that we consider our value a good one (see figure) we would thus like to make the plea that when reporting long range ^{13}C -H couplings one should also report the scale expansion and an error value.

I hope this will fulfill our obligation for another year.



Yours faithfully

G. Gatti
(G. Gatti)

P. Swinton
(P. Swinton)

Southern Research Institute



KETTERING-MEYER LABORATORY
AFFILIATED WITH
SLOAN-KETTERING INSTITUTE
FOR CANCER RESEARCH

2000 NINTH AVENUE SOUTH
BIRMINGHAM, ALABAMA 35205
TELEPHONE 205-323-6592

December 1, 1971

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

A-60A FOR SALE

Dear Barry:

Here is an advertisement for the newsletter: We have a Varian model A-60A spectrometer for sale. It is six years old, serial number 756, and is equipped with variable temperature probe and controller, and with the homonuclear spin-decoupler V-6058A, serial number 311.

The system is in good working order, and any reasonable offer will be considered.

Sincerely,

Martha C. Thorpe
Senior Chemist

MCT:br

WESTERN
RESEARCH CENTER

Stauffer Chemical Company

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

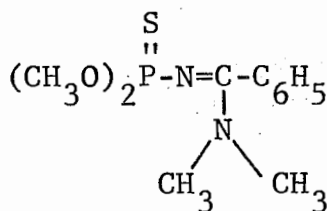
December 1, 1971

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

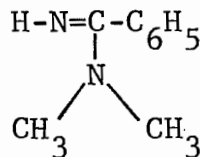
Dear Barry:

Hindered Rotation In Benzamidines

We have studied N,N-dimethyl-N'-[O,O-dimethylthio-phosphoryl]-benzamide (I) and have observed that the N-methyl groups of I give rise to a doublet at room temperature with chemical shift separation of 22.0 Hz in DMSO-d₆, 24.0 Hz in CDCl₃, and 37.2 Hz in C₆D₆ solution. The coalescence temperature is 80° and the free energy of activation calculated from these parameters is 18.0 kcal/mole. However, the N-methyl groups of N,N-dimethyl benzamide (II) exhibit a singlet both in CDCl₃ and C₆D₆ solution at room temperature. The high rotational barrier in I is believed to be the



I



II

result of p_π-d_π bonding in the P-N bond.

Sincerely yours,

C. K. Tseng
C. K. Tseng

TEXAS A&M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

2 December 1971

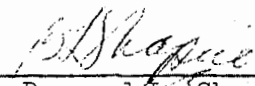
Academic Position Wanted

Available: Very Active Young (32) Researcher in Dynamic Organic and Inorganic Conformational Analysis

This individual is currently an Alfred P. Sloan Research Fellow (1971-73) who is directing the research of five (5) Ph.D. candidates and one (1) post-doctoral fellow. Over the past five years, he has published forty-three (43) papers and two (2) review articles concerning the dynamic conformational analysis of homocycles, heterocycles, acyclic amines, and boron hydride complexes. Support for his research has been obtained from The National Science Foundation (\$32,900; 1970-72), The National Cancer Institute (\$90,327; 1971-74; joint grant), Research Corporation (\$4,250; 1969-70), and The Alfred P. Sloan Foundation (\$17,500; 1971-73).

The main thrust of his research activities has been the synthesis of pertinent organic or inorganic systems and the application of DNMR spectroscopy to the study of nondestructive rate processes. He applies a sound working knowledge of current DNMR line shape calculation techniques.

He desires a position, starting in September 1972 or June 1973, in a larger university where research is given its proper place in the academic setting. 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

BLS:jch



"Anomalous Line Widths in Alcohols"

Dear Barry,

Peter Bladon and Keith Hardie (1) recently reported the line width variations in the proton spectrum of allyl alcohol, and mentioned that they were unable to find references to this effect in the literature. The answer, of course, is that a detailed density matrix treatment of such systems (including allyl alcohol) has recently been published by Yamamoto and Kamezawa (2) and an earlier paper by Arata et al. (3) describes similar effects in the methyl group spectrum of ethanol.

We have been interested in these "anomalous" broadening effects since observing the proton spectrum of propargyl alcohol in 1965 (see Fig. 1), realizing that although the effect was related to the line width variations observed by Arnold (4) and Anderson (5) there was more involved. Propargyl alcohol ($\text{H}-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$) is an AB_2X spin system in which the hydroxyl proton (A) is exchanging and $J(\text{AX})$ is essentially zero. Thus the shortened lifetime of the A proton can shorten T_2 of the B protons through the scalar coupling $J(\text{AB})$, but should only affect the X line-widths through "virtual coupling".

This rather glib description does not go very far in helping to understand the phenomenon, so we shopped around for a proper density matrix treatment, but by the time a volunteer had been conscripted, the paper by Arata et al. appeared and we abandoned the project. In any case closer investigation of the purified propargyl alcohol had indicated that the X region contained several "higher-order" lines which were now narrow and moved about as the AB shift was changed (6). The order in which these lines crossed as the AB shift was varied smoothly (by changing the temperature) gave the relative signs of $J(\text{AB})$ and $J(\text{BX})$.

These "labile" lines in the X spectrum seem to be the key to a physical picture of the anomalous broadening effects when the exchange rate is increased. Figure 2 shows the appropriate energy level diagram (the four "body diagonal" X lines are weak combination lines and may be ignored). We assume that the effect of exchange is to flip the A spin states after some random time interval, causing interchange of all X lines in pairs, for example 1-2 with 5-8. If the AB shift is small (comparable with $J(\text{AB})$), the X spectrum shows the "labile" lines as in Fig. 3(a) and these will be interchanged as indicated when the hydroxyl proton exchanges, leading to line broadening. However the two central lines 3-6 and 10-13 of the antisymmetrical levels are almost degenerate in frequency because $J(\text{AX})$ is vanishingly small, so no broadening occurs when they are interchanged. When the AB shift is large, as in Fig. 3(b), the "labile" X lines have moved back to near coincidence with the fixed X lines, and the same permutations caused by hydroxyl exchange do not broaden the X lines appreciably. Unless the AB shift is exactly zero, the line broadening will be unsymmetrical, indicating the relative signs of the coupling constants $J(\text{AB})$ and $J(\text{BX})$ as realized by Yamamoto and Kamezawa, and earlier by Diehl and Pople (7).

Kind regards,

Ray

Ray Freeman

- (1) Bladon and Hardie, *TAMUNMR*, 158, 18 (1971).
- (2) Yamamoto and Kamezawa, *J. Mag. Res.* 3, 269 (1970).
- (3) Arata, Fukumi and Fujiwara, *J. Chem. Phys.* 51, 859 (1969).
- (4) Arnold, *Phys. Rev.* 102, 136 (1956).
- (5) Anderson, *Phys. Rev.* 102, 151 (1956).
- (6) Freeman and Bhacca, *J. Chem. Phys.* 45, 3795 (1966).
- (7) Diehl and Pople, *Mol. Phys.* 3, 557 (1961).

Figure 1

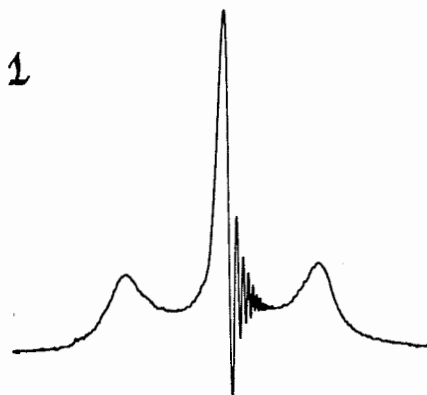
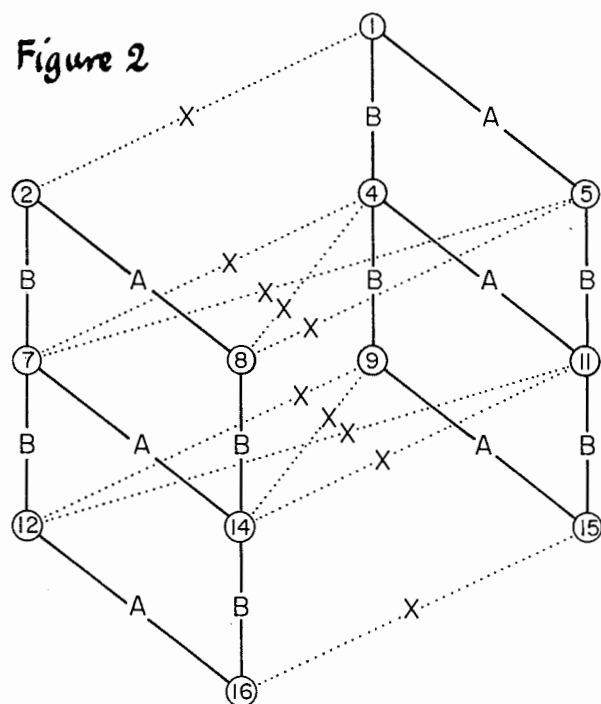
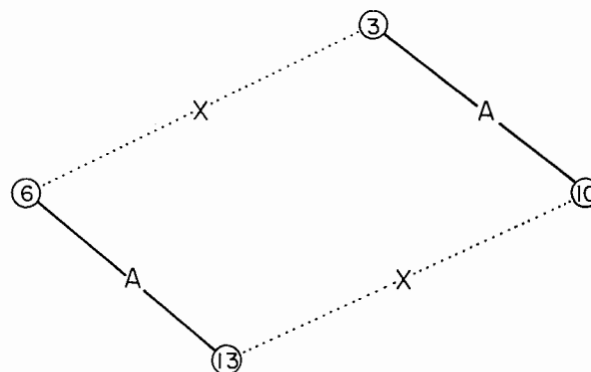
 $\equiv C-H$ 

Figure 2



SYMMETRICAL SET



ANTISYMMETRICAL SET

Figure 3(a)

$$\nu_{AB} = 0.6 \text{ Hz}$$

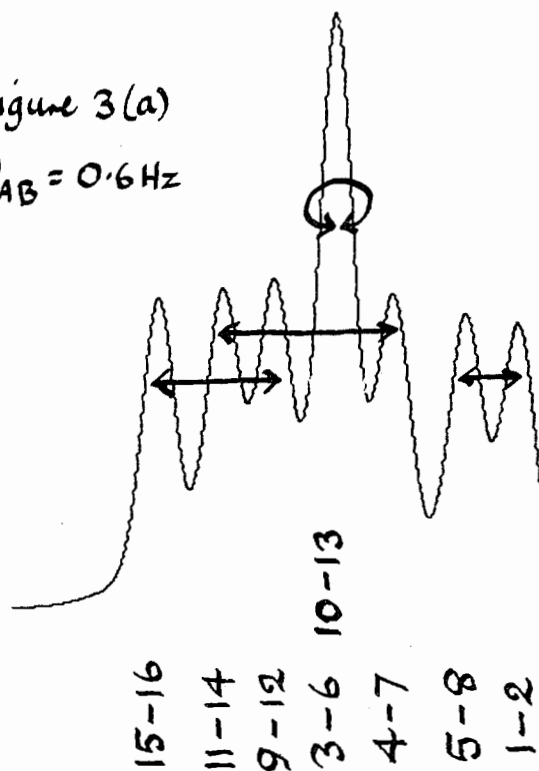
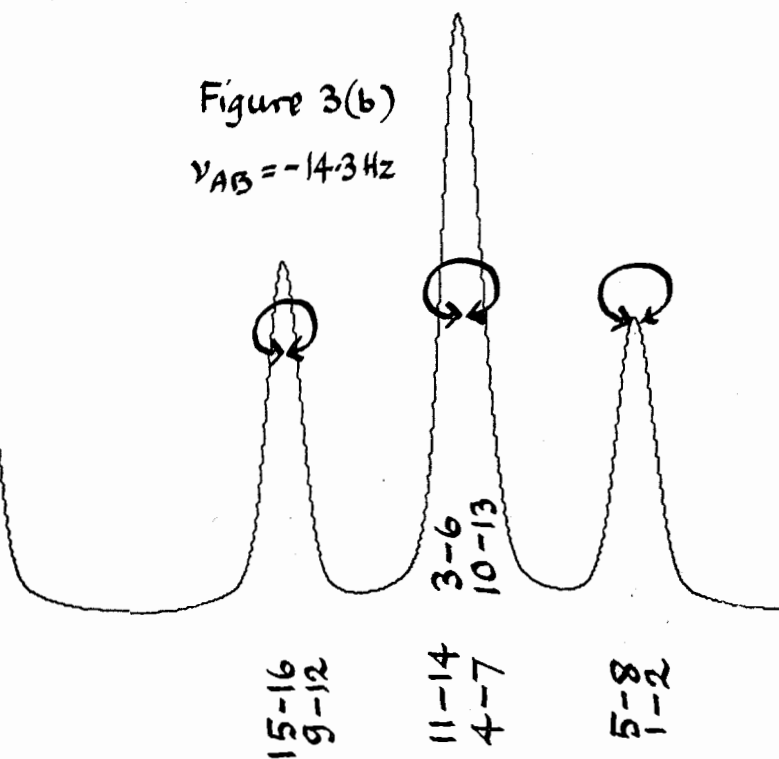


Figure 3(b)

$$\nu_{AB} = -14.3 \text{ Hz}$$



INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS
CZECHOSLOVAK ACADEMY OF SCIENCE
PRAHA 6 - SUCHBOL 2

December 2, 1971
A/2392/Schr

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

Dear Professor Shapiro:

Under the pressure of the pink reminder let me present the following frustrating results.

Recently, we had an opportunity to measure proton spectra of a series of $p-R^1R^2R^3Si-C_6H_4-CH_3$ compounds. Since the σ constants of some of these silyl substituents have not been determined we attempted to do so. Though the correlations with Hammetts constants, established for sixteen methyl $Cl^3 - H^1$ coupling constants and twenty two methyl proton shifts (Yoder C.H. et al.: J. Am. Chem. Soc. 91, 539 (1969)), have not high enough correlation coefficients and low enough standard deviations to permit their use for σ constant determination we hoped to get estimates which would show reasonable trends. But our results (a part of which is accompanied)

$R^1R^2R^3$	H_3	Cl_3	$MeCl_2$	Me_2Cl	Me_3	F_3	$MeFe_2$	Me_2F
$\sigma_{\text{from J}}$	+0.5	+0.1	0.0	+0.1	+0.7	-0.1	+0.5	-0.3
$\sigma_{\text{from } \delta}$	+1.0	-0.1	+0.4	+0.5	+0.7	+0.3	-0.5	+0.6

yielded not only unreasonable values of the constants but also definite trends opposite to our expectations.

With best regards,


Jan Schraml

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