Texas A&M University

N-M-R Newsletter

No. 225

June, 1977

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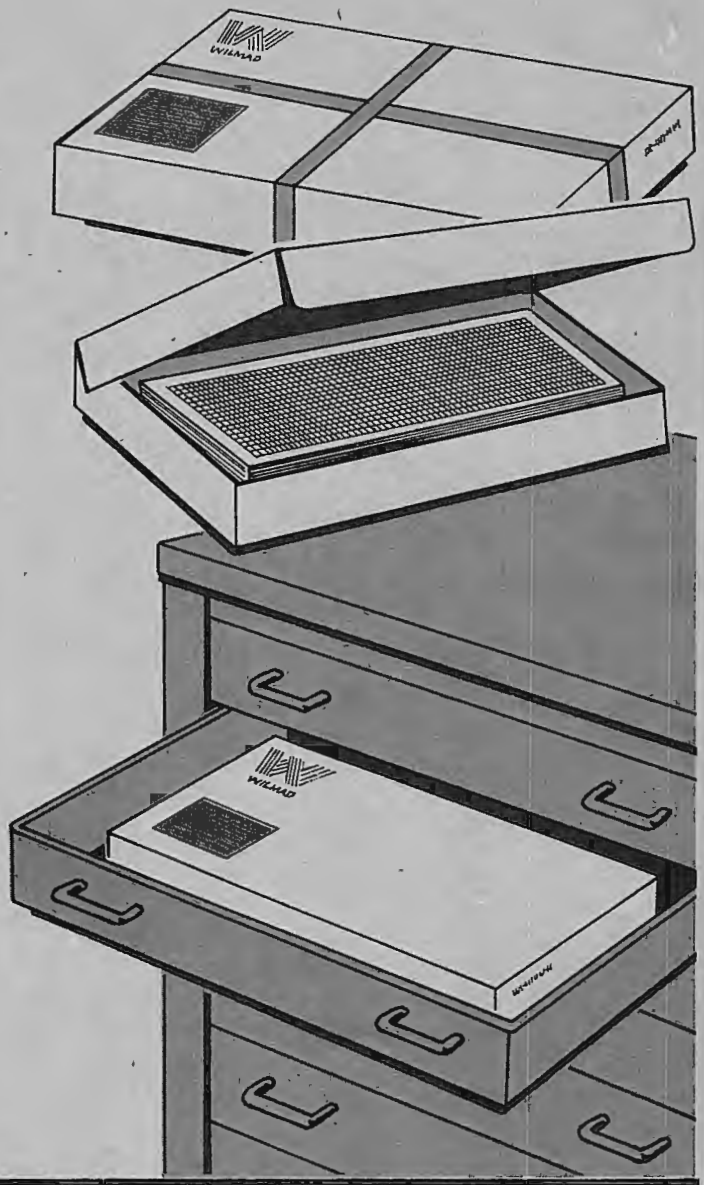

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DEADLINE DATES: No. 226: 5 July 1977
No. 227: 1 August 1977

All Newsletter Correspondence, Etc. Should Be Addressed To:

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 225

Hunter College

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

(212) 360-2351

May 5, 1977

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

Dear Barry:

Title: ^{15}N Chemical Shift Referencing

An increasing number of laboratories have been involved in ^{15}N chemical shift determinations, and as a result the measurement and reporting of these values in a manner which can be reproduced is of some importance. Until now, each laboratory has chosen its own reference, largely for convenience. We, for example, have used a capillary of 2.9 M ammonium chloride in HCl; other workers have used nitric acid, tetraalkylammonium salts, nitromethane, urea, and a variety of others. It is apparent to those carrying out such measurements that, for a variety of reasons, these reference materials do not give reproducible values in a reliable manner. Consequently, we explored the advantages and disadvantages of several references in some detail, to try to complement and clarify what is already in the literature. Here, we do not wish to elaborate on our findings, but merely state our recommendation, namely, that nitromethane in a capillary is the primary measurement reference substance of choice. Under these conditions, no solvent effects are exhibited either by the reference or the substrate, as in fact arises with an internal reference. In fact, even use of an internal deuterated lock solvent changes the resonance position of a series of typical compounds spanning a variety of structural types. To circumvent this, we have been using a 3-mm. capillary containing a mixture of $CD_3{}^{14}NO_2$, and $CH_3{}^{15}NO_2$, which provides both the internal lock signal and the reference. Chemical shifts are reproducible over long time intervals between measurements, there are no solvent effects (except, of course, those of self-association, which remains constant), and the deuterium resonance is strong and sharp enough to allow magnet homogeneity adjustment. The level of ^{15}N enrichment is adjustable according to whether time-averaging for short or long periods of time is expected. Indeed, in our laboratory, we keep capillaries with mixtures ranging from 20% to 90% ^{15}N enrichment; the chemical shifts are, naturally, independent of which one we use.

The disadvantage of using the low-field nitromethane reference is that most resonances will be at higher field, and if the sign convention accepted for ^{13}C and ^{1}H chemical shifts is adopted (which we urge), most nitrogen chemical shifts will have to be reported as negative. A possible way to circumvent this is to report

chemical shifts with respect to anhydrous liquid ammonia at 25°, whose value we have determined reproducibly as -380.2 ppm with respect to nitromethane. With this standard, almost all other shifts would be positive.

We point out that Dr. M. Witanowski has concluded that external nitromethane is the reference of choice for ^{14}N measurements, and for the same reasons. Some of our ^{15}N data are given in the attached Table, and full reports of both studies will appear shortly.

Sincerely yours,

P.R. Srinivasan

Robert L. Lichter
Associate Professor.

TABLE: ^{15}N Chemical Shifts of Model Organic Compounds[a]

Compound	^{15}N w.r.t. $CH_3{}^{15}NO_2$ (ext)	converted values w.r.t. NH_3(liq)[b]	NH_4NO_3	HNO_3, 9 M
N-Methylpiperidine	-340.84	39.36	17.79	-326.47
Sec-Butylamine	-339.82	40.38	18.81	-325.45
Aniline	-323.75	56.45	34.88	-309.38
Tetramethylurea(neat)	-317.73	62.50	40.90	-303.36
2-Methylindoline	-294.82	85.38	63.81	-280.45
N,N-Dimethylformamide	-276.42	103.81	82.21	-262.05
N-Methylacetamide	-272.75	107.45	85.88	-258.38
N-Methylformamide	-269.84	110.36	88.79	-255.47
Formamide[c]	-267.80	112.40	90.83	-253.43
Acetonitrile	-135.94	244.26	222.69	-121.57
Pyridine	-61.94	318.26	296.69	-47.47
Nitrobenzene	-10.07	370.13	348.56	-4.40

[a] In ppm; positive values denote shifts to lower magnetic field from the reference.
[b] At ca. 25°
[c] ca 10% acetone-d_6 was employed instead of benzene-d_6.

THE UNIVERSITY OF WINNIPEG
WINNIPEG, CANADA R3B 2E9

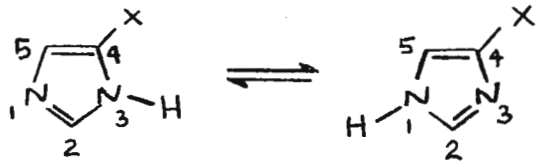
May 2, 1977

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

TITLE: Imidazole Tautomerism

Dear Barry:

There are few reliable methods available for measuring the relative populations of I and II.



I II

A couple of years ago Reynolds and co-workers (1) introduced a simple dependable technique which involves measuring the ^{13}C chemical shifts of C_4 and C_5 as a function of pH.

Here we wish to briefly discuss a complementary method which involves measuring $^3J(C_5,H_2)$ at any value of pH as long as pH $\geq$ pk_a (imidazole ring) + 1.0. We find

$$^3J(C_5,H_2)_{obs} \simeq 10.4 - 6.1\ X_{II} \qquad [1]$$

hence $$X_{II} \simeq 1.705 - 0.164\ ^3J(C_5,H_2)_{obs} \qquad [2]$$

where X_{II} is the mole fraction of the 1-H tautomer in the equilibrium mixture. Equation 1 was derived by noting that in substituted imidazoles $^3J(\underline{C}, N(\text{lone pair}), C,\underline{H})_{trans} >> {}^3J(\underline{C}, N(R), C, \underline{H})_{trans}$.

For example in 1-methylimidazole $^3J(C_4, H_2)$ = 10.4 ± 0.2Hz while $^3J(C_5, H_2)$ is only 3.3 ± 0.2 Hz. In toluene $^3J(C_6, H_2)$ decreases by about 1 Hz compared to the corresponding three-bond coupling in benzene (2). Assuming a similar substituent effect for the 1-methylimidazole - imidazole pair, $^3J(C_5, H_2)$ is taken as 4.3 Hz in II, and as 10.4 Hz in I, thus

$$^3J(C_5, H_2) = 10.4\ X_I + 4.3\ X_{II} \qquad [3]$$

For histidine, $^3J(C_5, H_2)$ = 4.7 ± 0.2[5] Hz and X_{II} = 0.9. Similarly for histamine, $^3J(C_5, H_2)$ = 4.3 ± 0.3 Hz and $X_{II} \simeq 1.0$. Both these results are in good agreement with those obtained by the method of Reynolds and co-workers (1, 3, 4). The technique based on coupling constants should be useful in studying non-aqueous solutions. Other examples and further details will appear in the Canadian Journal of Biochemistry (4).

Yours sincerely,

Rod Wasylishen

Rod Wasylishen
Department of Chemistry

RW/eh

References

(1) W. F. Reynolds, I. R. Peat, M. H. Freedman and J. R. Lyerla, Jr., J.A.C.S. 95, 32B (1973)

(2) M. Hansen, and H. J. Jakobsen, J. Mag. Res. 20, 520 (1975).

(3) W. F. Reynolds, and Tzeng, Can. J. Biochem., in press.

(4) R. E. Wasylishen and G. Tomlinson, Can. J. Biochem., in press.

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Professor B.L. Shapiro
Department of Chemistry
Texas A and M University
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5 May 1977

Dear Professor Shapiro,

N.M.R. Spectra of N-Benzoyl Imino Acids

Cis-Trans-Rotational isomerism about the amide bond of proline derivatives has been well documented[1] using n.m.r. techniques and in general the trans form predominates over the cis. The diamagnetic anisotropy of the carbonyl group is reflected in the chemical shifts of the α-proton and the δ-protons having different values in the two

Trans ⇌ Cis

rotamers. A requirement for N-benzoyl imino acids for a study of n.m.r. techniques in the assessment of racemisation[2] has led us to investigate the spectra of these derivatives. Rotamer peak assignment was a little difficult since the shielding effect of the benzene ring could modify the effects of the carbonyl group on the neighbouring atoms.

The characteristic cis-trans pattern of peaks[1] shown by the β and γ carbons in the ^{13}C spectra should however be fairly independent of the acyl substituent, and in N-benzoylproline we see a predominantly trans pattern. Extrapolation of this information to the p.m.r. spectrum indicates that the trans α-proton is downfield of the cis, while the trans δ-protons are upfield of the cis (in $CDCl_3$ solution). This situation implies that in proline the shielding effect of the benzoyl group is consistent with the data on aliphatic acyl substituents. Similar effects are seen in the pipecolic acid analogue.

It does not necessarily follow, however, that we should see the same shielding effects in the p.m.r. spectra of acyclic N-methyl amino acids since the relative conformation of the protons near the benzoyl group would be altered. On the other hand it is plausible that the methyl carbon of a N-methyl group in e.g. N-benzoyl-N-methylalanine would have the same relative position to the benzoyl group as the ε-carbon in N-benzoyl pipecolic acid, and similarly the α-carbons would be expected to bear the same relationship. On the basis of this comparison we see a similar pattern in the ^{13}C-spectra of (4), (5) and (8), where the smaller signal for the α-carbon is downfield of the larger signal. We have assigned the α-carbon in the cis-form to these downfield

signals as in proline and pipecolic acid. Compound (6) and to a lesser extent compound (7) are anomalous and show the more deshielded carbon as the stronger signal. N-Methyl

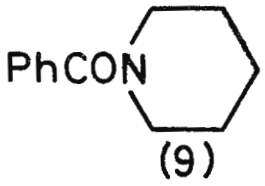
Compounds	(1)	(2)*	(3)*	(4)	(5)	(6)	(7)	(8)
N-Benzoyl	Pro	Pip	Az	Sar	MeAla	MeVal	MeNorVal	MeLeu
Cis/Trans Ratios($CDCl_3$)	20/80	25/75	0/100	40/60	45/55	60/40	55/45	47/53

*Pip = Pipecolic acid, Az = Azetidine-2-carboxylic acid

carbons also show a similar cis-trans effect, the cis being at higher field than the trans, with (6) and (7) again being anomolous.

In the p.m.r. spectra of the acyclic imino-acid derivatives the more intense α-proton multiplet was generally downfield of the weaker signal, while the smaller of the N-CH_3 proton signals was upfield of the stronger. The latter result implies that a benzoyl group has a different effect on these, from that previously established for aliphatic acyl derivatives. Combining these results we have estimated the cis/trans ratios to be as shown in the table. In all the spectra analysed the valine derivative (6) gave a much higher amount of cis isomer than other members of the series.

Another unusual feature in the p.m.r. spectra of the benzoyl derivatives (2), (4), (5), (6) (7) and (8) is the appearance of the aromatic protons as a 5-proton singlet at 7.4 ppm, i.e. the ortho protons are not deshielded relative to the others. As this phenomenon is also found in the spectra of Ph $CO.NMe_2$ and (9), but not in Ph CO.NHMe, (10), or the proline (1) and azetidine (3) derivatives where the ortho protons are ca 0.2 ppm to lower field, we conclude that the angle Ø (12) is important in deciding whether the aromatic ring can be accommodated in the plane of the aromatic ring, or whether non-bonded interactions with the N substituents force it to prefer the out of plane conformation (e.g. (11)).



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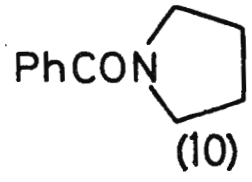

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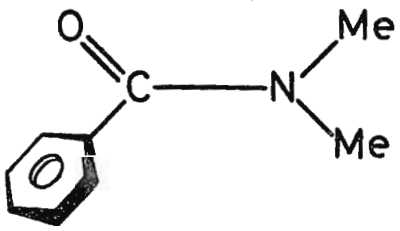
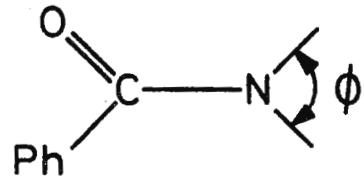


(11)



(12)

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2. J.S. Davies, R.J. Thomas and M.K. Williams, Chem.Comm. 1975, 76.

Yours sincerely,

John S. Davies

W.A. Thomas, Roche Products Ltd., U.K.

John S. Davies

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V/RÉF.

N/RÉF. GJB/cc

Professeur B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College of Science
College Station Texas
77843

U.S.A.

Genève, le 1er juin 1977

Cher Professeur Shapiro,

Merci de votre lettre de rappel du 16 mai 1977.

1. Application du magnétisme nucléaire dans le champ terrestre au diagnostic médical

a) Note au C.R. de l'Académie des Sciences de Paris, t.284 p. 141 - 143 Série B - 1977 -
"Magnétographie nucléaire en champ faible. Résultats préliminaires" de Georges J. Béné, Bernard Borcard, Emile Hiltbrand, Patrick Magnin et Robert Séchehaye transmise par Monsieur Pierre Grivet.

This paper gives the first observation of the proton free precession on parts of the thorax and the abdomen of a living man by external exploration. Our results show the possibility to detect pathological diseases as serosities or malignant tumors.

b) Perspectives nouvelles en magnétographie nucléaire

G.-J. Béné, Département de Physique de la Matière Condensée de l'Université de Genève.

Plusieurs auteurs ont envisagé l'emploi du magnétisme nucléaire (notamment de la RMN) comme méthode de détection du cancer ou d'autres états pathologiques par mesures de certaines constantes (temps de relaxation, diffusion...) des protons des molécules d'eau engagées dans les tissus malades. Nous discuterons l'avenir de cette méthode, par comparaison avec les techniques en cours (rayons X, ultrasons) pour la détection in situ de maladies par exploration externe chez l'homme ou d'autres systèmes biologiques de grande taille.

2. Prochains Meetings du Groupement Ampère

a) Third Specialized Colloque Ampère
"Optical Techniques in Magnetic Resonance Spectroscopy"
Trinity College Dublin - August 29 - September 1 1977 -

Plenary Lectures

S. Geschwind (Bell Laboratories) : Probes to electron dynamics in CdS using resonant spin flip raman spectroscopy

C.A. Hutchinson (Chicago) : EPR in optical excited states of transition metal and rare earth metal ions

J. Schmidt (Leiden) : ODMR in triplet states of polyatomic molecules

B.P. Zacharachenya (Leningrad): Optical nuclear polarization in semiconductors

Keynote Lectures

J.J. Davies (Hull) : Excited states of defects in semiconducting phosphors

W. Hayes (Oxford) : ODMR of defects in ionic solids

C. Herman (Palaiseau) : Optically detected CESR and NMR in semiconductors

R. Romestain (Grenoble) : Jahn-Teller effects in excited triplet states

J.U. von Schütz (Stuttgart) : Proton spin relaxation by optically excited triplet states

D. Stehlik (Berlin) : Optical nuclear polarization by level anticrossing

b) XXth Congress Ampère
Tallinn (R.S.S. d'Esthonie)
21 - 26 august 1978)

Avec mes sentiments très cordiaux.

Prof. G. J. Béné

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You can be sure that we are actively working on new "firsts." For example, we'll be demonstrating a complete Fourier Transform Mass Spectrometer very soon. To repeat the closing statement from our original ad—write or call collect to discuss your requirements. Maybe we can work together to add another "first."

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DEPARTMENT OF ORGANIC CHEMISTRY
THE ROBERT ROBINSON LABORATORIES P.O. BOX 147 LIVERPOOL L69 3BX TEL: 051 – 709 - 6022

The University of Liverpool

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

13th May, 1977.

Dear Barry,

Ring-current calculations[1].

Our recent studies on the aggregation behaviour of metalloporphyrins in which large shifts are observed, indicative of "tight aggregates", made it necessary to develop a better ring current model of the porphyrin ring than those at present available.

We considered first the two simple models, i.e. the equivalent dipole approximation versus the current loop approach, as applied to the benzene ring current. To my astonishment, for all inter-molecular distances these are identical (figure). This has the rather useful consequence in that as the equivalent dipole formulation is of course the same as that used for lanthanide shifts calculations, all the sophisticated L.I.S. search programmes can be used unchanged for benzene-substrate geometries and we have made use of this recently.

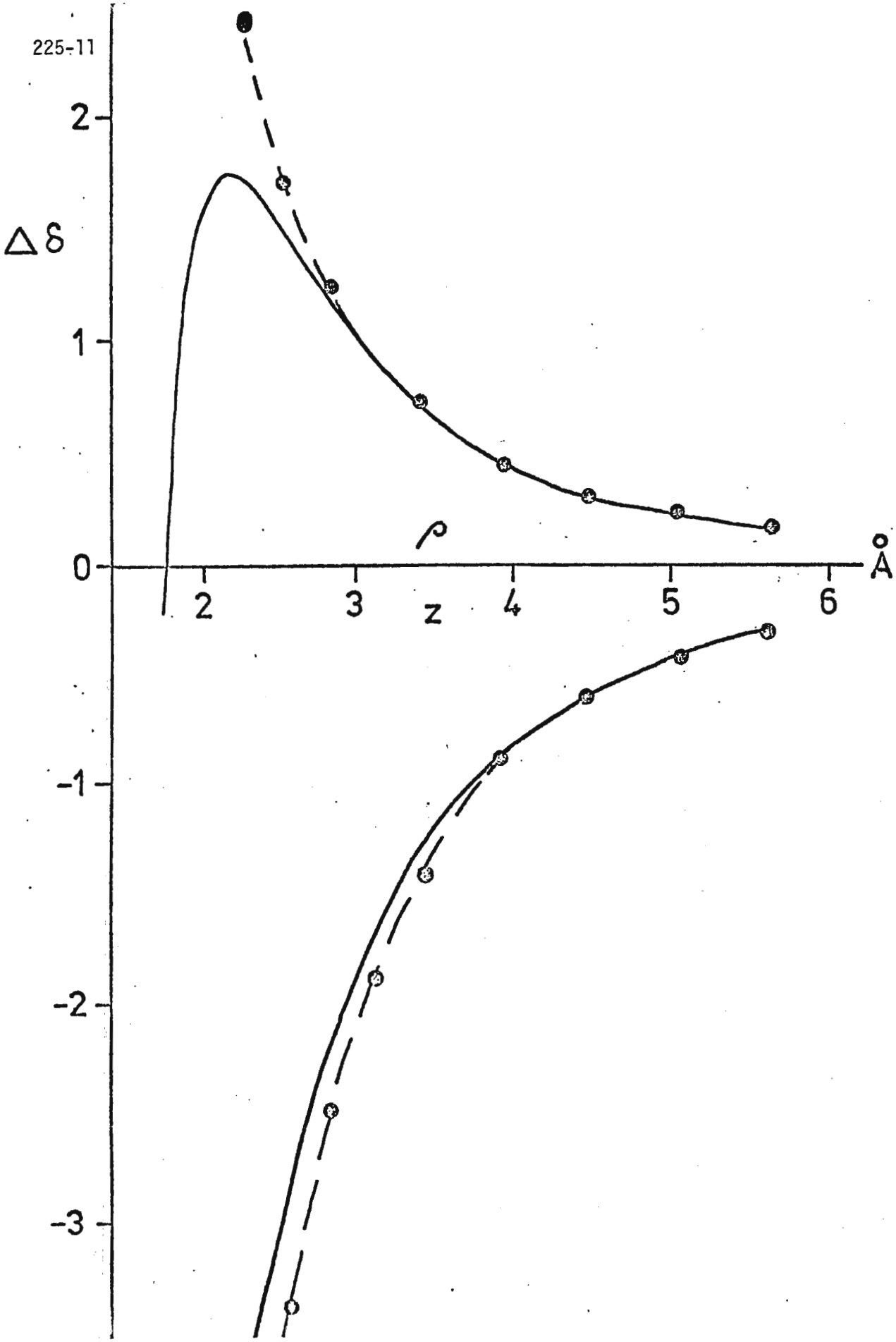
We therefore decided to update my old network model of the porphyrin ring current. A simple extension of this model to the "double-dipole" model, gives good agreement with the observed ring current shifts of nuclei both within and above the porphyrin ring plane. (c.f. table). The only serious disagreement is with the α-protons of pyridine co-ordinated to zinc porphyrin, and these hydrogens are only 2.67Å above the ring plane, well within Van-der-Waals interactions.

One great advantage of this model over the current loop approach is that it can be simply adapted to the unsymmetrical chlorin ring and the observed ring current shifts in chlorins vs porphyrins are again nicely predicted on our model. Space is too short to give you these details, but preprints are available on request.

With best wishes,

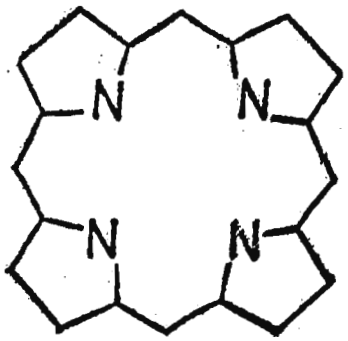
Yours sincerely,

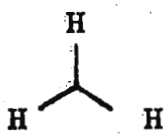
Dr. R.J. Abraham.



CALCULATED SHIELDING CONTRIBUTIONS, ABOVE (Z) AND IN THE PLANE (p) OF THE BENZENE RING, DUE TO THE RING CURRENT. SOLID LINE CURRENT LOOP; BROKEN LINE EQUIVALENT DIPOLE.

CALCULATED AND OBSERVED RING CURRENT SHIFTS IN METALLOPORPHYRINS



PROTON		RING CURRENT SHIFTS (PPM) CALCULATED		OBSERVED
meso-H		5.30		5.2
β-H		4.40		4.4
β-Me	Av. pos^n	2.32		
(β-CH_2)		1.97		
		2.48	2.17	2.13
		2.05	2.27	2.06
β $CH_2\underline{C}H_3$		0.94 1.06 0.91	0.97	0.86
Zn-pyridine	α - H	-7.93		-6.30
	β - H	-2.27		-1.93
	γ - H	-1.74		-1.78
Zn-picoline	γ - CH_3	-1.29		-1.29

1. R.J. ABRAHAM, S.C.M. FELL AND K.M. SMITH, ORG.MAG.RES.(IN PRESS).

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May 9, 1977

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

Dear Barry:

With the advent of programmable pocket calculators, much of the drudgery and tedium of routine laboratory calculations has been eliminated. One application of these calculators which may be of interest to *Newsletter* readers is their uses in NMR spectral analysis.

Generally, what one wishes to do in analyzing spectra is to take a set of lines, feed them into a program, and have the program return a set of shifts and coupling constants. For several small systems of nuclei (AB, A_2B, and ABX along with some special "lucky" cases) it is possible to do such calculations on programmable calculators such as the HP-67 and HP-97. I have worked out a few of these and interested readers may obtain the programs from me (listings and descriptions).

The basic idea behind such calculations is given below. First, one obtains equations which give the best shifts and couplings (in the least-squares sense) and puts these into a form suitable for programming. Second, equations giving the line frequencies and intensities are programmed to allow the user to check his results. In the case of AB analysis, both sets of equations fit on one card. Other cases require more cards but, I have found, surprisingly complicated systems can be handled with two or three cards.

Without further ado, here are the forms best suited for programming onto an HP-67-type calculator:

AB ANALYSIS:

I. *Shifts and coupling constants from the four lines (in Hz):*

Designate the lines as ℓ_1, ℓ_2, ℓ_3, and ℓ_4. Then, from a least-squares fit, the best values for the spectral parameters are

$$\nu_A = R + \tfrac{1}{2}\Delta,$$

$$\nu_B = R - \tfrac{1}{2}\Delta,$$

and $$J = \tfrac{1}{4}(\ell_1 - \ell_2 + \ell_3 - \ell_4),$$

where $$R = \tfrac{1}{4}(\ell_1 + \ell_2 + \ell_3 + \ell_4)$$

and $$\Delta = \tfrac{1}{2}[(\ell_1 + \ell_2 - \ell_3 - \ell_4)^2 - 4J^2]^{\frac{1}{2}}.$$

Use of the above equations is quite simple in practice. One simply enters all line frequencies (in Hz) into the stack, pushes a button, and obtains the shifts and coupling constant.

II. Obtaining the four lines from the shifts and coupling constant:

(These reverse formulas are, of course, well-known. However, they are given to show the obvious "subroutine" structure needed in saving programming steps.)

The lines come immediately from

$$\ell_1 = R + A,$$

$$\ell_2 = R + B,$$

$$\ell_3 = R - B,$$

and $\ell_4 = R - A,$

where, $A = C + J/2,$

$$B = C - J/2,$$

and, in turn,

$$C = \tfrac{1}{2}(\Delta^2 + J^2)^{\frac{1}{2}},$$

with $\Delta = \nu_A - \nu_B$

and $R = \tfrac{1}{2}(\nu_A + \nu_B).$

* *

The above sample case should give the reader a good idea as to how to proceed with more complicated cases. Analyses of simple spin systems can be obtained with pocket calculators in a matter of seconds at one's desk.

Sincerely yours,

Milt

Milton D. Johnston, Jr.
Assistant Professor of Chemistry

Suggested title: *"Pocket Calculator NMR Spectral Analysis (LACOON½?)"*

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NMR Probe Protection

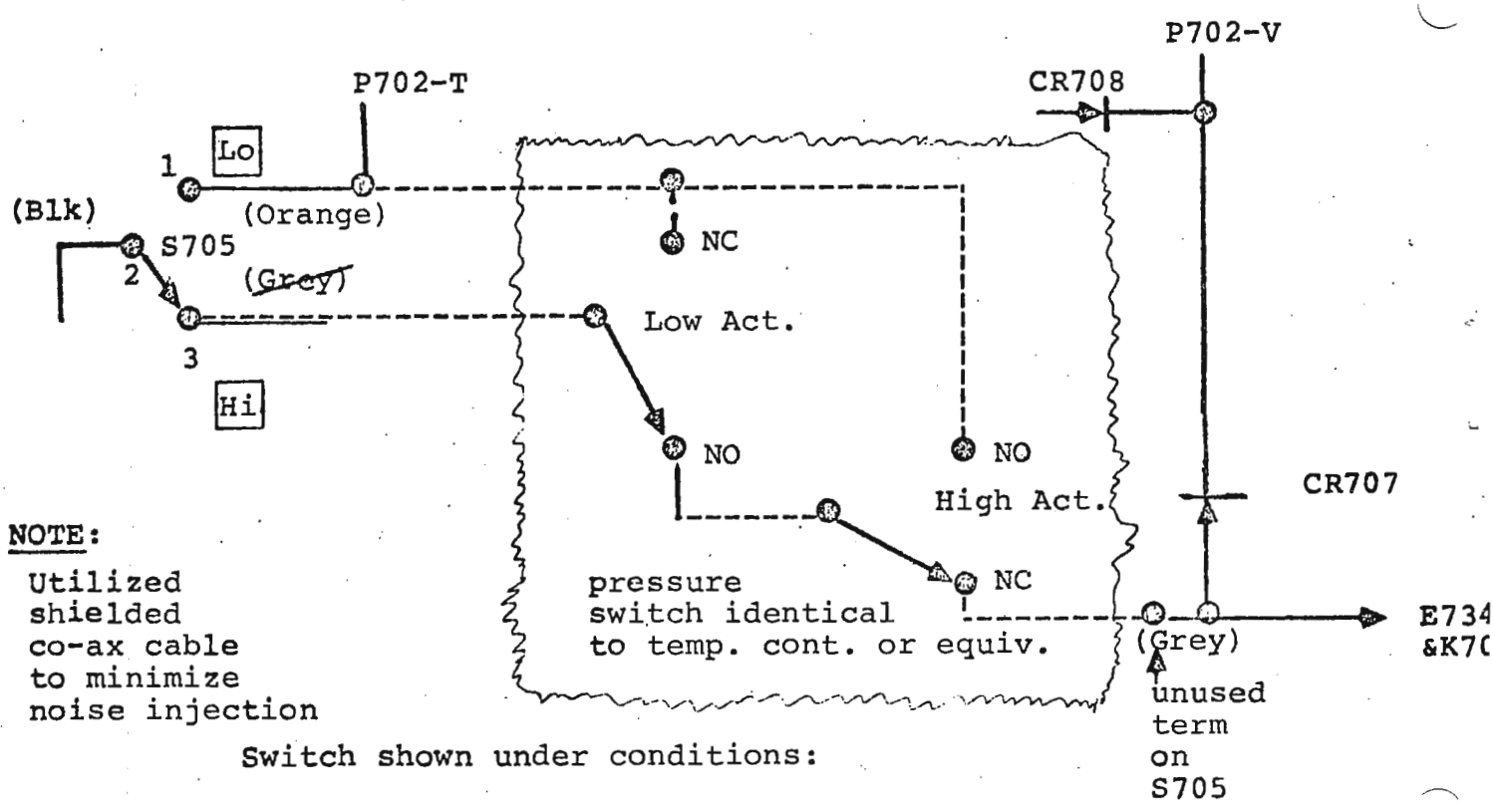
CORRECTION

A regrettable error was introduced and was missed at proofreading in the circuit diagram. The correct diagram is as shown here. Please correct your old version (TA&M-NMR-Newsletter #217 and Varian "Interface" #3) since its implementation may cause damage to the instrument.

We are extremely grateful to Dr. Robert Santini of Purdue University for pointing out this error.

CIRCUIT MODIFICATION[2]

Low Level - High Level Gas Pressure Protection



Switch shown under conditions:

Low pressure $< N_2$ Pressure $<$ High Pressure

Sandra Barcza

John H. Eckhardt

MONTEDISON

May 8, 1977

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

DIPE/CER/PM
Stabilimento Petrolchimico
Via G. Motta
30175 Porto Marghera
(Venezia) ITALY

Dear Professor Shapiro,

Title:

QUANTITATIVE ANALYSIS OF POLYETHER AND POLYSILOXANE BLOCK COPOLYMERS

Surface-active agents at very low concentrations are very often employed in the preparation of flexible and rigid polyurethane foams. These agents are liquid block copolymers of polyethers and polysiloxanes, the employment of which is related to some of their well-established physico-mechanical features; they are also used as control agents of foam cell size (1). A series of these block copolymers of different origin have been analyzed by 60 MHz ^1H NMR spectroscopy roughly defining their structure.

The solutions of the liquid copolymers at concentrations of 40 ÷ 50% v/v in $CDCl_3$ have been examined and the main chemical shifts related to TMS have been determined (see Table 1).

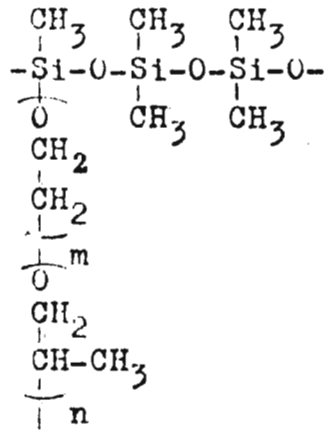
TABLE 1

Chemical shifts in ppm	Coupling constants	Chemical groups
$\delta_1 = 0.08$	singlet	$-Si(\underline{CH}_3)_2O-$
$\delta_2 = 1.15$	$J(CH_3-CH) = 6$ Hz	$-CH_2-CH(\underline{CH}_3)O-$
$\delta_3 = 3.0 \div 3.7$	not determined	$-\underline{CH}_2-\underline{CH}(CH_3)O-$
$\delta_4 = 3.6$	singlet	$-\underline{CH}_2-\underline{CH}_2-O-$

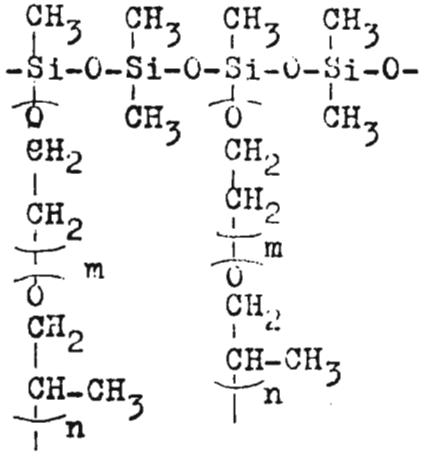
The assignement of the c.s. of CH_3 for the dimethylsiloxane unit has been effected on the basis of the I.R. analysis of the silicon oil 200/50 DC, which compared with (2) presents a polydimethylsiloxane structure, and of the NMR spectrum compared with the Viscasil silicone-dimethylpolysiloxane spectrum (3).

Models A, B and C have been introduced based on considerations reported in (1) (4) (5) as well as concerning the syhthesis.

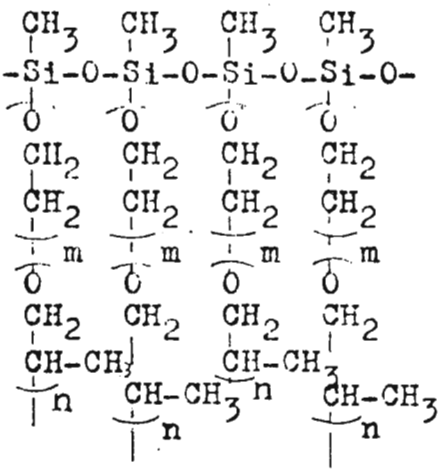
A)



B)



C)



The A model is practically related to the hypothesis of a linear copolymer

$$-(-Si(CH_3)_2O)_p-(CH_2-CH_2O)_m-(CH_2-CH(CH_3)O-)_n-$$

The weight % composition in oxyethylene, oxypropylene and methylsiloxane units was calculated from the NMR spectra according to A and C models for a series of different samples.

The B model is related to a structure calculated with some difficulty through NMR.

The silicon percentages calculated according to A and B limit models from the weight compositions of the methylsiloxane units were compared with the fluorescence spectrometric X-ray data (FRX). Model A resulted the best. The results obtained are reported in Table 2.

I repute that model A is only a fair approximation to calculate the polymer composition, which does not necessarily involve a completely linear structure. The analysis of a typical copolymer of this group (no. 19) with ^{13}C NMR FT spectroscopy at 22.6 MHz confirmed the composition obtained with ^{1}H spectroscopy.

I hope to be able to extend the method to the analysis of more complex block copolymers with different aliphatic and aromatic substituents to the silicon atom by using ^{1}H, ^{13}C NMR and possibly mass spectroscopy data.

I am indebted to dr. A. Perazzolo for FRX analysis.

Yours sincerely

Giorgio Gurato

(Giorgio Gurato)

References

1) R. BOUDREAU, Mod. Plast., 44, 133 (1967)
2) HUMMEL-SCHOLL Atlas der Kunststoff-Analyse, C. Hanser Verlag, Band I, Teil 2, München, 1968, 1397 Spectrum
3) SADTLER Standard Spectra C 372 M
4) KIRK-OTMER, Encyclopedia of Chemical Technology, vol. 18, 231
5) C.U. PITTMANN Jr,, W.J. PATTERSON, S.P. McMANUS, J. of Polym. Sci., 14, 1715 (1976)

Table 2

Sample n°	$-CH_2-\underset{CH_3}{CH}-O-$	$-CH_2-CH_2O-$	$(CH_3)SiO-$	Si_{NMR}	Si_{FRX}
1	47.7	37.8	19.4	7.3	6.1
2	90.9	0.5	8.6	3.2	2.8
3	4.5	64.4	31.1	11.8	10.1
4	4.9	69.2	25.9	9.8	8.3
5	49.2	33.2	17.6	6.7	6.4
6	26.9	54.3	18.8	7.1	6.8
7	50.6	31.1	18.3	6.9	6.1
8	22.2	65.9	11.9	4.5	4.7
9	78.7	14.7	6.6	2.5	1.8
10	46.4	33.0	20.6	7.8	8.6
11	95.4	1.1	3.5	1.3	1.2
12	65.3	16.3	18.4	6.9	7.2
13	52.8	31.3	15.9	6.1	7.2
14	46.0	32.7	21.3	8.1	9.6
15	48.6	29.4	22.0	8.3	7.9
16	50.9	34.3	14.8	5.6	5.6
17	45.9	36.4	17.7	6.7	6.7
18	48.0	32.1	19.9	7.6	7.2
19	52.4	30.2	17.4	6.6	6.0
20	50.6	33.3	16.1	6.1	5.6
21	45.8	31.5	22.7	8.5	7.2
22	77.8	12.9	9.3	3.5	2.9
23	41.4	40.6	18.0	6.8	5.4
24	42.5	40.9	16.6	6.3	5.6
25	43.1	38.4	18.5	7.0	5.7

225-19

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Klingelbergstrasse 82, Telefon 061 - 44 20 40

CH - 4056 Basel (Schweiz)May 10, 1977/ho

Prof.Dr.P.Diehl

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

Continuum of parameters reproduces the same ABC-spectrum

Dear Barry,

During various tests of our program for the automatic analysis of NMR-spectra[1]) we found that quite often more than one set of parameters reproduced the same spectrum, linepositions and intensities, within very small deviations of the order of 10^{-1} Hz in position and 10^{-2} in intensities.

To our surprise we lately also discovered a case in which a continuum of parameters reproduced the same spectrum. It looks like an AB_2-spectrum but can be interpreted as a continuum of ABC-spectra in which certain relations between the parameters are approximately fulfilled as follows:

$$\begin{aligned} |J_{AB} + J_{AC}| &\approx \text{constant} \\ (\nu_B + \nu_C) &\approx \text{constant} \end{aligned} \qquad \text{(I)}$$

Eleven such sets of parameters are shown in the Fig.. The range of J_{AB} and J_{AC} is surprisingly large covering the whole region between -7 and +4 Hz. Of course we tried to find a general proof that any AB_2-spectrum may be interpreted as an ABC-spectrum with a continuous range of parameters, however, we did not succeed. (Perhaps somebody reading this letter has more success).

Qualitatively we found an explanation for the phenomenon. If the elements of the Hamiltonian for an ABC-system are derived on the basis of symmetrised AB_2 -functions and subsequently the observed conditions (I) are introduced (Table) one finds that the variations of J_{AB}, J_{AC}, ν_B and ν_C affect the problem only as perturbations of the order of δ^2/J_{BB}' and ε^2/J_{BB}'.

Summarizing the situation it seems that the uniqueness of NMR-spectra is certainly theoretically fulfilled but in praxis there may be large continuous ranges of parameters leading to practically undistinguishable spectra.

1) J. Magn. Res. 19, 67 (1975).
OMR 8,638 (1976).

Yours sincerely

Peter

P. Diehl

Fig. Spectrum for parameters ① - ⑪

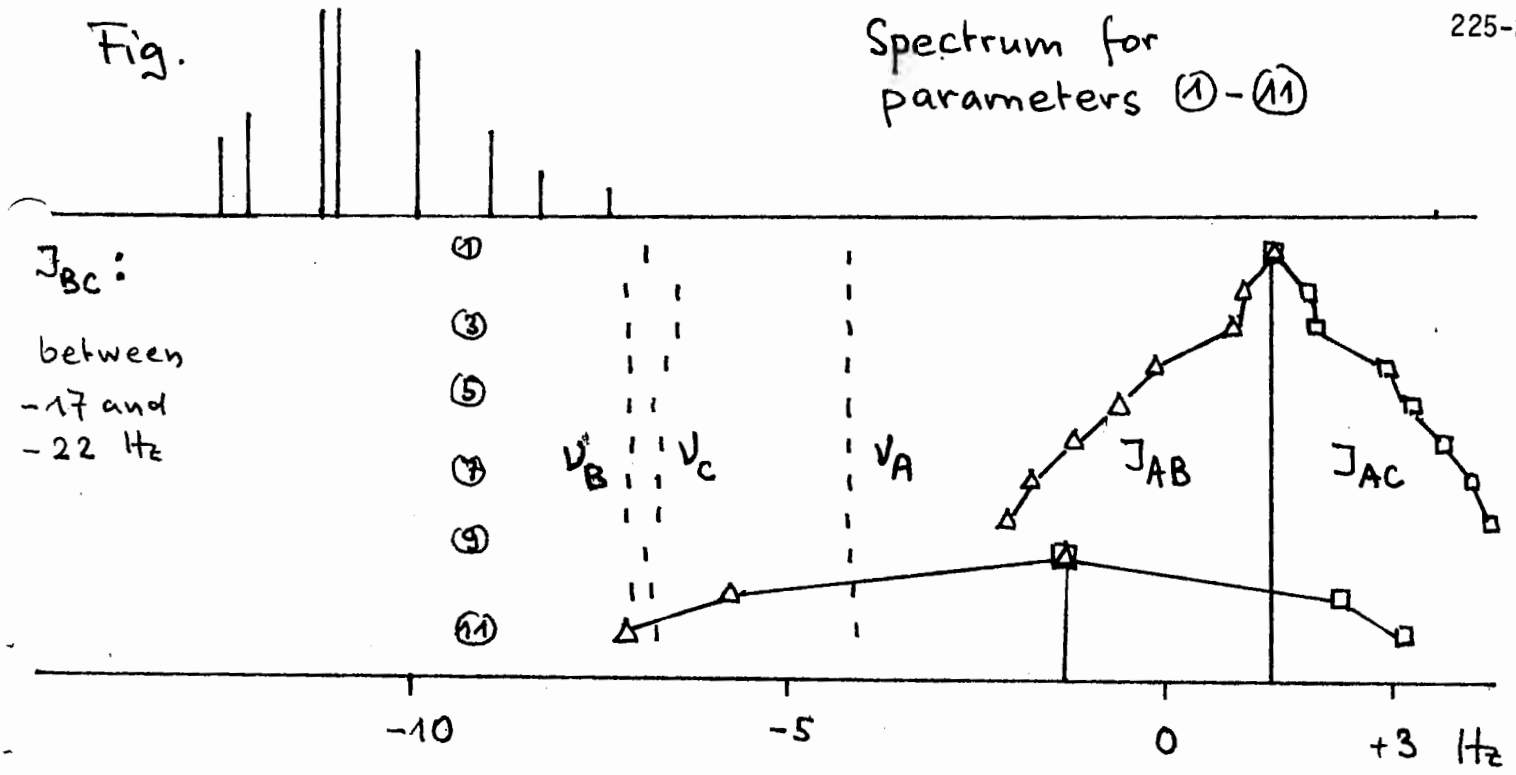

Table:

Special ABC (approx. ABB') →

$\nu_A \rightarrow \nu_A$	
$\nu_B \rightarrow \nu_B' + \varepsilon$	
$\nu_C \rightarrow \nu_B' - \varepsilon$	
$J_{AB} \rightarrow J_{AB'} - \delta$	
$J_{AC} \rightarrow J_{AB'} + \delta$	
$J_{BC} \rightarrow J_{BB'}$	

$\frac{1}{2}(\nu_A+\nu_B+\nu_C)+\frac{1}{4}(J_{AB}+J_{AC}+J_{BC})$	H_{11}	$\frac{1}{2}(\nu_A+2\nu_B')+\frac{1}{4}(2J_{AB'}+J_{BB'})$
$\frac{1}{2}(-\nu_A+\nu_B+\nu_C)+\frac{1}{4}(-J_{AB}-J_{AC}+J_{BC})$	H_{22}	$\frac{1}{2}(-\nu_A+2\nu_{B'})+\frac{1}{4}(2J_{AB'}+J_{BB'})$
$\frac{1}{2}\nu_A+\frac{1}{4}J_{BC}$	H_{33}	$\frac{1}{2}\nu_A+\frac{1}{4}J_{BB'}$
$\frac{1}{2}\nu_A-\frac{3}{4}J_{BC}$	H_{44}	$\frac{1}{2}\nu_A-\frac{3}{4}J_{BB'}$
$\frac{1}{2\sqrt{2}}(J_{AB}+J_{AC})$	H_{23}	$\frac{1}{2\sqrt{2}}(2J_{AB'})$
$\frac{1}{2\sqrt{2}}(J_{AB}-J_{AC})$	H_{24}	$\frac{1}{2\sqrt{2}}(-2\delta)$
$\frac{1}{2}(\nu_B-\nu_C)+\frac{1}{4}(J_{AB}-J_{AC})$	H_{34}	$\varepsilon-\frac{1}{2}\delta$

ABC-Hamiltonian for transition: ABC → → ABB' → AB_2

δ and ε appear only in off-diagonal elements, affect spectrum as per-
turbations: $\delta^2/4\nu_{AB}$, $\delta^2/4J_{AB}$

ISTITUTO SUPERIORE DI SANITA'
ROMA

May 12th 1977

Viale Regina Elena,299
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Telegr : ISTISAN-ROMA

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

^{1}H and ^{13}C magnetic relaxation studies of non-ionic detergent inverted micelles.

Dear Prof. Shapiro,

we should start apologising for the delay of the present note. An extensive reorganization of the Departments of our Institute, that has taken place in the last few months, has demanded sustained contributions of time and energy from all of us.

It is known that detergent molecules in hydrocarbon solvents are able to form aggregates termed "inverted" micelles, in which the polar or ionic region of the solute comprises the interior (hydrophilic) core, while the non polar tails are exposed to the solvent. Although inverted micelles have been little characterized so far in terms of molecular structure and local mobility, these aggregates have been considered as simplified and useful models for studying non-covalent interactions in a number of biological systems, including mechanisms of hydration in macromolecular solutions and in whole cells.

The use of several physical techniques have suggested that at least three broadley defined types or classes of water can be identified in biopolymer systems: a) water tightly bound to the macromolecular surface; b) water participating in loosely defined hydration shells; c) bulk water (1).

As already reported in one of our earlier notes (2), NMR techniques may provide a useful tool for elucidating some of these mechanisms of hydration at a molecular level(3).

We have been able to study by PMR the dynamical properties of water molecules of the second class ("loosely" bound water), isolated within the interior of inverted micelles formed by polyoxyethylene 20-sorbitan-monooleate (TWEEN 80) in toluene (20% w/w), containing various amounts of water. Upon increasing the content of solubilized water an increasing number of oxyethylene units are driven into the internal core of the micelle, where these units experience various degrees of hydration (as indicated by the presence of various-CH_2CH_2O- signals in the PMR spectra; an example is reported in ref. 2). Peak area analysis showed that in two micellar systems, in which the ratio (r) of water molecules to oxyethylene

units was 0.34 and 0.48 respectively, the internal oxyethylene chains were surrounded on the average by no more than one hydration shell. In both systems it was found that the most internal (and most highly hydrated) region of the micellar core was formed by about 35% of the hydrat oxyethylene units.

Proton spin-lattice relaxation times and spectral analyses at 100 and 220 MHz (4) have indicated that at 30°C the average rotational correlation time of water molecules in these systems was about 10^{-11} s. Water molecules exchanged with an "intermediate" rate between two main states of hydration, identified with the inner and the peripheral region of the hydrophilic core respectively. The exchange lifetime was evaluated to be of the order of 10 ms. in the sample with r=0.34 and shorter than 3 ms. in the sample with r=0.48.

^1H spin-lattice relaxation times, measured at 100 MHz on the various chemical groups of the detergent molecules, have indicated a progressive T_1 reduction for the oxyethylene units in the direction going from the periphery towards the most internal region of the micelle. From a comparison of ^1H (100 MHz) and ^{13}C (25 MHz) relaxation times measured on the oxyethylene chains, we have concluded that the presence of water in the micellar core restricts the intramolecular mobility of the polar chains, likely through hydrogen bonding between the oxyethylene units and water.

Sincerely yours,

Franca Podo Francesco Paolo Gentile

Franca Podo* Francesco Paolo Gentile+

* Laboratorio di Biologia Cellulare e Immunologia;
+ Laboratorio delle Radiazioni;
Istituto Superiore di Sanita', Rome, Italy.

---

1 - R. Cook and I.D. Kuntz, (1974) Annual Review of Biophysics and Bioengineering, 3, 95-126.
2 - F.F. Ricci, E. Masimov, F.P. Gentile, P.E. Giua and F. Podo, TAMU NMR Newsletter, (1974), 192, 10.
3 - F.P. Gentile, F.F. Ricci, F. Podo, P.E. Giua,(1976) Gazzetta Chimica Italiana, 106, 423-430.
4 - 220 MHz NMR spectra were taken at the Middle Atlantic Regional NMR Facility, which is supported by NIH Grant RR 542 at the University of Pennsylvania.

Diamond Shamrock

T. R. Evans Research Center

May 16, 1977

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

Dear Barry:

Subject: Quantitative Analysis by ^{13}C FT NMR

In a recent evaluation of ^{13}C FT NMR as a quantitative analytical tool [B. Thiault and M. Mersseman, Org. Mag. Res., 8,28(1976)], it was reported that peak intensities were reduced substantially with increasing distance from the rf carrier. An essentially linear attenuation from 100 to 50% intensity was seen as the distance between the rf carrier and the ^{13}C resonance of interest varied from 0 to about 6 kHz. The instrument used was a Bruker HFX-90. The authors contend that this phenomenon cannot be due to inadequate transmitter power, and they attribute it to either a frequency-dependent amplification or a filtering effect. In any case, the presence of such an effect complicates the use of ^{13}C FT NMR for quantitative analysis, since a "frequency normalization" curve must now be established for an instrument.

We have performed a similar experiment to ascertain if such an effect occurs on our Bruker WH-90. The integrated intensity (by computer) of the ^{13}C resonance of ethylene glycol (4:1 in acetone-d_6) was measured as a function of frequency and each value normalized to the intensity 0.3 kHz from the rf carrier. The results are given below.

Δf (EG-rf carrier) (kHz)	Normalized Area
0.3	1.00
0.7	1.00
1.2	1.00
2.2	0.97
3.2	0.99
4.2	0.97
5.2	0.95
5.8	0.96

Dr. Bernard L. Shapiro

May 16, 1977

(Conditions: 4 transients, spectral width = 6.02 kHz, 16 k FT, added line broadening 2 Hz, 12 kHz audio filter)

Clearly, little, if any, attenuation is seen on the WH-90 over the frequency range studied. The changes seen are of the order of the size of the errors arising from such things as inadequate digitization in the frequency domain, slightly improper phasing, or signal-to-noise limitations of typical ^{13}C spectra. This result allows us to confidently compare resonance intensities in different portions of the spectrum. Of course, the usual precautions relating to variable NOE and attenuation of peaks with T1's $\geq$ the pulse delay must still be observed.

Sincerely,

Richard A. Komoroski

Richard A. Komoroski

Université de Lausanne — Faculté des Sciences

INSTITUT DE CHIMIE MINÉRALE ET ANALYTIQUE

Place du Château 3, 1005 Lausanne (Suisse)

Lausanne, May 31, 1977

Dear Professor Shapiro and colleagues,

I am soliciting your aid in obtaining a good candidate for a post-doctoral position. A good knowledge of relaxation theory and possibly electronics is expected. The research topics concern the use of high pressure high resolution multinuclear NMR in chemical kinetics.

The salary after taxes amounts to $ 11'500-13'500/year.

Thank you for your cooperation and please notify interested parties that two letters of recommendation should be sent to me directly.

Sincerely yours

A. Merbach

A.E. Merbach

Professor

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91125

June 5, 1977

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

Title: Natural Abundance N-15 NMR Studies of the α-Helical Formation of Poly-γ-benzyl-L-glutamate in $CDCl_3$/TFA

Dear Barry:

Recently we have studied the effect of the formation of an α-helical coil in poly-γ-benzyl-L-glutamate (PBLG) on its N-15 NMR spectrum. Literature H-1 and C-13 NMR studies show that in 100% $CDCl_3$, PBLG with a molecular weight of about 60,000 exists as an α-helix, and as trifluoroacetic acid (TFA) is added (12-18%), it uncoils to a random coil. [Conditions for N-15 spectra were: 1.0g of PBLG (ca. 60,000 MW) in 17 ml of solvent; 70° pulse angle; 0.34 sec acquisition time and repetition rate; broad band proton decoupling; spectrometer frequency of 18.25 MHz.]

In 80% $CDCl_3$/20% TFA where PBLG should exist as a random coil, a good signal was obtained in about 20 min. At this concentration of TFA, the NOE was about -4.7 (theoretical max = -5) and the T1 was about 0.3 ± 0.1 sec. A series of spectra were taken at TFA concentrations of 20, 19, 18, 16, and 14%. As the TFA concentration was lowered, the signal became harder to obtain yet always remained 20-30 Hz wide with a constant chemical shift of 253 ppm upfield of external HNO_3 (at 14% TFA, 9 hr was required for a marginal signal).

Reference to a standard plot for dipolar relaxation of T1 vs. correlation time (τ) showed that a T1 of 0.3 sec corresponds to a τ of about 10^{-9} sec. A similar plot of NOE vs. τ showed that there should be very nearly a full NOE for this τ. Furthermore, according to the plot, as τ is lengthened slightly, the NOE should begin to diminish rapidly. If this is correct, then going from the random coil to the α-helix (longer τ) should lead to a diminished NOE which could make the signal quite small or even nulled. The longer τ should also shorten the T2, thereby compounding the problem with more broadening. In fact, we have never obtained a signal which is reliably attributable to the α-helix.

Sincerely yours,

Glenn

Glenn R. Sullivan
Present address: Stanford
Magnetic Resonance Lab,
Stanford, Ca. 94305

Jack

John D. Roberts

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July 47, 3549

Prof. B. L. Shapiro, CCXLVI
Department of Chemistry and Stellarometry
The Alpha Centauri A&M University
University Station, New Texas 78695095867493940586

Dear Barry the two-hundred-forty-sixth:

We just received your pink notice that this contribution was overdue. Surely, you realize that hyperspace communications are not what they used to be and that, at least in this part of the galaxy, the Romulans have caused untold havoc in communications. But, in the spirit of better-late-than-never we shall tell you what has been going on in our laboratory lately.

1. Our new 14,349,456,200 Gauss FT spectrometer arrived last week. When we first turned it on, all wrist-watches were destroyed in this solar system. However, our spectra are so much simpler than ever before, it is certainly worth it. However, with only 556K of memory for our transforms, resolution is suffering. Also, we have found that liquid sodium does not work well in cooling the magnet system. However, we shall not discuss how we got around this problem since magnet cooling systems are not allowed in the Newsletter. Finally, you will note that we report the field strength in Gauss. The recently adopted cgs system of units is probably confusing to some, but we believe strongly that those unwieldy SI units should go.

2. The newly discovered element, no. 4539 (Nixonium), has very interesting properties in the NMR. So far, we have had superb spectra from the isotopes of spin 78, 45, and 33-1/3. The coupling patterns, especially across 48 bonds are magnificent.

3. Gamma-ray excited carbon-12 NMR seems to be a thing of the past. I have not seen any papers in the last 3 or 4 years employing this technique. Are any of your readers still active in this area?

4. Eka-eka-eka-eka-ekalanthanide shift reagents look to be very promising. Especially interesting is element no. 456. Those half-filled g and h orbitals give rise to shifts approaching 33,456.009 ppm. This should greatly help people studying conformations on the surfaces of black holes.

5. We recently discovered that hydrogen (element no. 1) has a nuclear spin. (So far, we can say it is only less than 3.5.) It has coupling patterns more complex than any seen recently. We are confident that this will present a great breakthrough and are proceeding with this work with a great deal of excitement. Unfortunately, the Galactic Academy has refused to fund the work until we have given further demonstration of its feasibility. Probably, the work would have been funded if we had not simultaneously mentioned a new technique we used in obtaining the spectra. It seems that sweeping with a slowly varying magnetic field gives spectra directly WITHOUT USING A FOURIER TRANSFORM. This upset the academy greatly; also, the computer companies were up in arms.

Well, nothing further to report. I hope that you can stop by sometime. After all, we are only 5000 light years from you.

Sincerely yours,

Bela Oxnyx, Director, Iotian-Arcturan Academy

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

May 18, 1977

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

EXTENDED TRANSMITTER OFFSET ON THE CFT-20

Dear Dr. Shapiro:

In conjunction with Tobin Marks' work on organoactinide compounds,[1] we have found ourselves limited by the transmitter offset range of the Varian CFT-20, which is nominally 4 KHz to either side of TMS. An additional 1 KHz of range may be obtained by shifting the frequency of the lock transmitter, thus slightly changing the magnetic field strength. This method is fast, inexpensive, and requires no modifications of either the lock or the observe transmitter cards.

The lock frequency in the CFT-20 is generated from a 5.355 MHz voltage-controlled crystal oscillator. This frequency is mixed down to 2 KHz, which is compared to a 2 KHz reference signal from the master clock by a phase detector that sends an error voltage to the VCXO. If the 2 KHz reference signal is replaced by a frequency that can be varied, the frequency of the oscillator and ultimately the lock transmitter can be varied within the limits determined by the phase-locked loop. It is important that this frequency source be stable relative to the observe transmitter frequency. A frequency synthesizer that can be phase locked to the 1 MHz reference signal from the CFT-20 master clock meets this criterion. We used a Hewlett-Packard 3320 A synthesizer commonly used for homonuclear decoupling on the CFT-20. The synthesizer output was converted to a TTL-compatible signal with an LM 311 voltage comparator, which operates using the +5 V supply on the lock transmitter card.

The 2 KHz reference signal from the master clock is disabled at pin 20 of the lock transmitter card. The frequency synthesizer output from the LM 311 comparator is put into pin 4 of U3 on the lock transmitter card,[2] which is a NAND gate prior to the phase detector. The +5 V and the ground for the LM 311 supply may be picked up from pins 14 and 7 of U3. The lock frequency may then be slowly walked up or down from the 2 KHz reference. The phase lock light on the spectrometer console will go out when the end of the range of the phase-locked loop has been reached. On our system, a shift of 1.0 KHz to lower field and 1.3 KHz to higher field in the proton spectrum can be obtained. Additional capacitor tuning on the lock transmitter may be used to extend this range somewhat. Tuning on the observe transmitter card, combined with software modification to permit transmitter offsets greater than 99 or less than 0, may be used for further extension of the range of transmitter offsets available.[3] The stability of the system as determined by the proton linewidth is equivalent to the standard system over one hour of data acquisition.

I wish to acknowledge helpful discussions with Chuck Shires of Varian Associates.

Please credit this contribution to Joe Lambert's subscription.

Sincerely,

Kenner Christensen

Kenner Christensen

1. T. J. Marks, Acc. Chem. Res., 9, 223 (1976).

2. Varian schematic 87-144-717.

3. Suggested by Steve Patt of Varian Associates.

Hunter College

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

(212) 360-2353

May 23, 1977

Dear Dr. Shapiro:

We would be grateful if you could include this request in your next nmr newsletter. We are interested in purchasing a used nmr magnet as soon as possible with the following rough specifications:

9" or 12" pole diameter, min. 2" air gap, field strength at 2" air gap is 10 kG or above, e. g. Varian V-7200.

Thank you for the use of this service.

Sincerely,

Robert A. Marino

Robert A. Marino
Associate Professor

CHEMICAL CENTER
PHYSICAL CHEMISTRY 2

Lund, May 23, 1977

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

Title: ^{113}Cd NMR. Chemical shifts of individual complexes

Dear Prof. Shapiro,

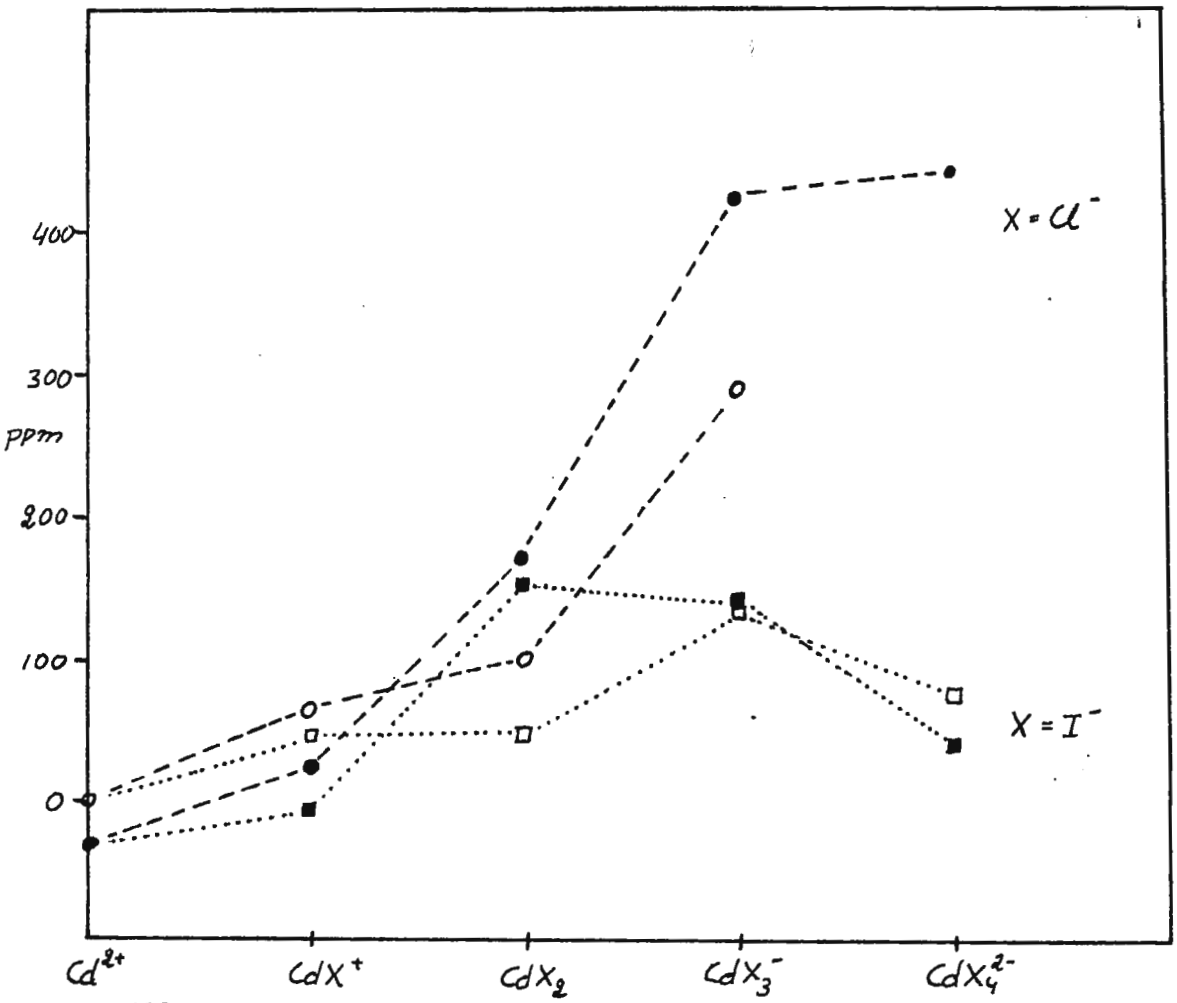
We have for some time been using a Traficante type modification on our XL-100 to make the observation of various frequencies possible. This modification has been used to study ^{113}Cd in systems, where several complexes are present in mixtures and it is thus necessary to know all the complex constants in order to obtain the ^{113}Cd chemical shifts of the various complexes.

In collaboration with Prof. S. Ahrland at the division of inorganic chemistry in Lund we have studied some cadmium-halogen systems using either water or DMSO as solvent. This work was started to investigate if it is possible to monitore the change in coordination number, from six to four, of cadmium with increasing halogen concentration. For these systems the complex constants are well known and it is thus possible to determine the chemical shifts of the individual complexes from the dependence of the ^{113}Cd shift on the halogen concentration. In figure 1 is shown the shifts for the various complexes in water as well as in DMSO. Based on calorimetric studies it has been sugested that the switch from octahedral to tetrahedral complexes should take place between the second and third complex in water solution and between the first and second in DMSO. This is indeed in agreement with our ^{113}Cd chemical shifts that shows a large downfield shift for the third complex in water and the second in DMSO.

The results indicates that the chemical shift of the metal nucleus can be used to follow the change in coordination number and that the shift of ^{113}Cd in tetrahedral complexes is downfield to those in octahedral.

Sincerely yours

Torbjörn Drakenberg



^{113}Cd chemical shifts of the individual complexes in the Cd - Cl and Cd - I systems. Filled symbols for DMSO and non-filled for water solution. Shifts in ppm downfield from 0.1 M $Cd(ClO_4)_2$ in water.

University of Illinois at Urbana-Champaign

School of Chemical Sciences
DEPARTMENT OF CHEMISTRY
Roger Adams Laboratory
Urbana, Illinois 61801

May 12, 1977

Dear Barry:

As I mentioned during our last telephone conversation, I have a postdoctoral opening in my group starting September 1977. Salary: $12,000. Possible projects: NMR relaxation in supercritical dense fluids at high pressure; rotating frame experiments on disordered organic materials; high resolution spectroscopy on liquids at high pressures. I shall send a detailed outline of the projects to interested candidates.

Best regards.

Sincerely yours,

J. Jonas
Professor of Chemistry

225-33

TITLE: STEREOCHEMICAL ELUCIDATIONS OF ORGANOMETALLIC CARBONYL EXCHANGE REACTIONS BY C-13 FT-NMR.

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

May 24, 1977

North Texas State University
Denton, Texas 76203
Department of Chemistry

Dear Barry:

Recent evidence indicates that 5-coordinate intermediates arising through metal-carbon bond fission in substitution reactions of octahedral metal carbonyl derivatives are fluxional.[1,2,3] Thus, in molecules containing chemically non-equivalent carbonyls the site of carbon-metal bond fission cannot be inferred on the basis of product stereochemistry.

The site of M-CO bond breaking has been determined by Atwood and Brown for the $BrM(CO)_5$ systems (M = Mn, Re).[4] However, the method employed by those workers is complex, and has, in other systems, led to equivocal results.[5] This method involves direct ^{13}CO enrichment of the substrates and a kinetic accounting of the rates of appearance and disappearance of the possible enrichment products. In the $BrM(CO)_5$ systems, there are twelve such species.

We have developed an alternate, simpler approach which has been applied successfully to three systems which were not amenable to unequivocal solution through use of the methods of Atwood and Brown.[5] This approach, which employs ^{13}C Fourier-transform NMR spectroscopy and/or infrared spectroscopy, we illustrate here for $(phen)Cr(CO)_4$ (phen = o-phenanthroline)(see the figure). Kinetics results indicate $(phen)Cr(CO)_4$ reacts exclusively via CO-dissociation to afford the cis-$(L)(phen)Cr(CO)_3$ product.[6] It has also been reported that various L can be displaced from these products under conditions milder than those required for replacement of CO from the substrate.[7] The replacement of L by ^{13}CO is stereospecific, and affords (b). The site of initial Cr-C bond-breaking can now be adduced through reaction of (b) with L and subsequent replacement of L by unlabeled CO. The extent of label loss and the distribution of the label in (c) provides this information. For example, the results reveal loss of half of the label and a statistical distribution of that label at one axial and two equatorial positions. Thus, the intermediate is fluxional, and Cr-C bond-breaking occured exclusively cis to the phen nitrogens (axial loss).

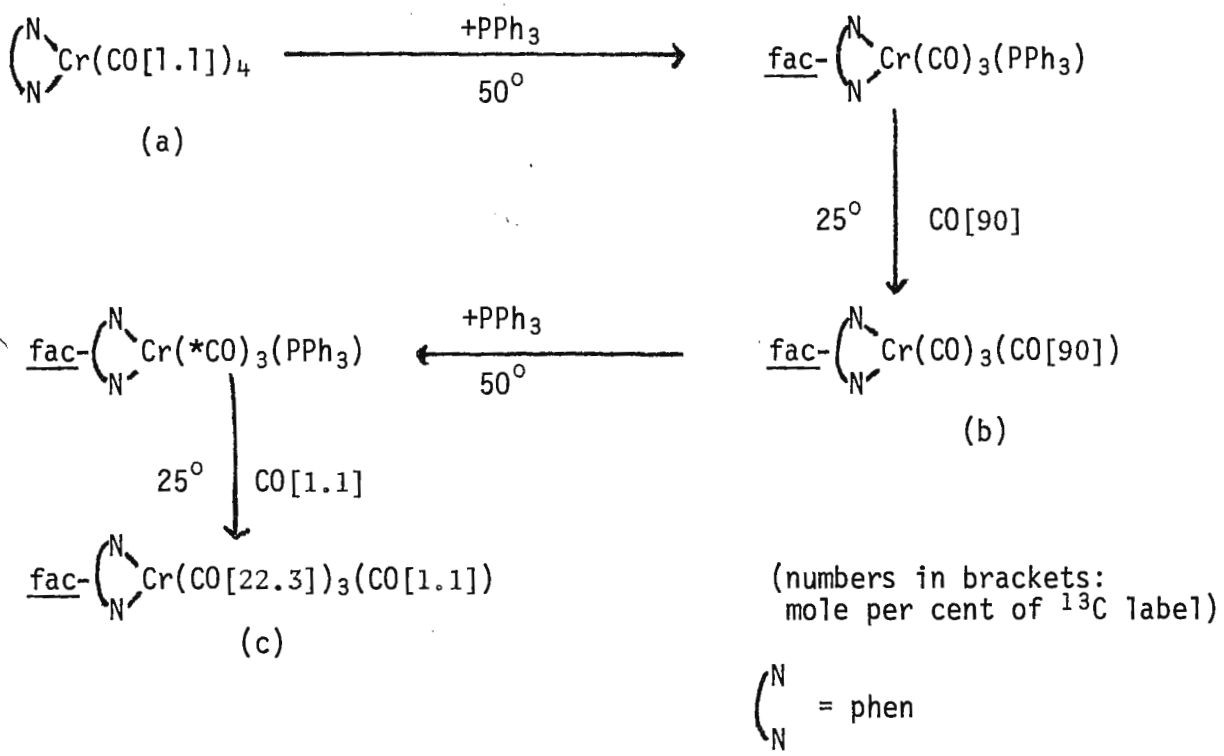
A key to the applicability of the approach being described here is that since replacement of L by CO occurs under milder conditions than does replacement of CO in the substrate, only enriched species containing a single label will be obtained. In $(phen)Cr(CO)_4$, for example, while the Brown method involves nine different species of varying isotopic distribution, the present method involves only three, greatly simplifying data analysis. Further, only the determination of the distribution of the label in species (a-c) is required to determine the stereochemistry of bond-breaking and possible fluxionality of the resulting intermediate. The Brown approach requires the determination of the rates of formation and disappearance of the isotopically-labeled species.

In metal carbonyl complexes which are quite soluble and stable in $CDCl_3$ (the solvent of choice), integration of the ^{13}C Fourier-transform spectra of (a), (b) and (c)

provides this information. This has been found to be the case for (diphos)$Mo(CO)_4$ (diphos = 1,2-bis(diphenylphosphino)ethane), which exhibits reactivity analogous to (phen)$Cr(CO)_4$.[8] The twenty-four phenyl carbons in this complex offer an attractive, natural isotopic abundance internal standard with which abundances of ^{13}C in carbonyls *trans* and *cis* to P can be compared.

In the (phen)$Cr(CO)_4$ case, sparing solubility and relative instability, as well as the lack of a convenient internal standard of reasonable intensity in complexes (a-c) permit the determination only of the degree of label scrambling in (c), and thus only the result that the (phen)$Cr(CO)_3$ intermediate is fluxional on the time-scale of the substitution process could be obtained. With this information, however, the site of CO loss can readily be determined through careful analysis of the carbonyl stretching spectra of (a-c).

These methods are currently being applied to other systems.



1. G. R. Dobson, Accounts Chem. Res., 8, 300 (1976)
2. J. D. Atwood and T. L. Brown, J. Amer. Chem. Soc., 98, 3160 (1976)
3. E. J. Darensbourg, A. Moradi-Araghi, and G. R. Dobson, J. Organomet. Chem., 116, C24 (1976)
4. J. D. Atwood and T. L. Brown, J. Amer. Chem. Soc., 97, 3380 (1975).
5. M. A. Cohen and T. L. Brown, Inorg. Chem., 15, 1417 (1976).
6. R. J. Angelici and J. R. Graham, Inorg. Chem., 6, 988 (1967).
7. G. R. Dobson and L. A. H. Smith, Inorg. Chem., 9, 1001 (1970).
8. G. C. Faber and G. R. Dobson, Inorg. Chim. Acta, 2, 479 (1968).

Sincerely,

G. R. Dobson
Professor of Chemistry

J. L. Marshall
Professor of Chemistry

UNIVERSITÉ DE DROIT, D'ÉCONOMIE ET DE SCIENCES D'AIX-MARSEILLE
FACULTÉ DES SCIENCES ET TECHNIQUES DE SAINT-JÉROME

Laboratoire des Organométalliques
J. C. MAIRE, Professeur.

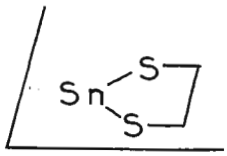
25th May 1977

Dear Prof. Shapiro,

Confirmation of dimethyl-2,2 dithia-1,3 stanna-2 methyl-4 cyclopentane : variable temperature ^1H NMR study.

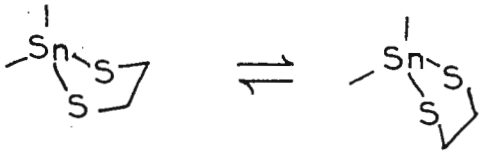
We reported earlier that dialkyl-2,2 dithia-1,3 stanna-2 cyclopentane compounds (alkyl group = Me, Et, nBu, Ph) have a monomeric structure (1) instead of the dimeric similar compounds including oxygen atoms in the ring (2).

PMR spectra of methylenic protons presents a single sharp peak corresponding to a A_4 type consistent with :

- either a planar conformation for the  moiety

(symmetry C_{2v})

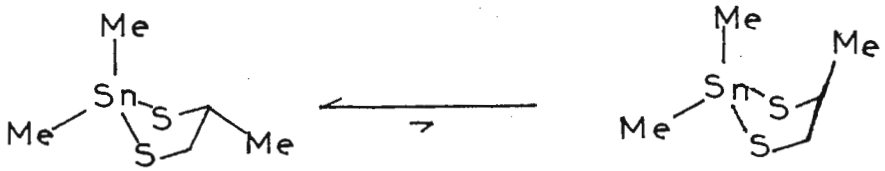
- or a non planar conformation with rapid exchange



(symmetry C_s)

In the way to determine the conformation of the stannacyclopentane skeleton we synthesize the corresponding compound substituing the ring with a methyl group.

Fortunately the dimethyltin compound shows an interesting PMR spectrum (fig.1) corresponding to the equilibrium :



(I) (II)

The heteronuclear coupling constants Sn, H allows to assign without any incertainty the position of the signal corresponding to the methyl groups linked to tin atom.

At low temperature (-45°C) the only conformation (I) is present, with a sharp signal for each methyl group. The signal becomes more complex as the temperature increases. The conformation (II) thus becomes more predominant, confirming the hypothesis for a non-planar cycle.

^{1}H NMR spectra were recorded in $CDCl_3$, on a Varian XL 100 spectrometer at 100 MHz.

Sincerely yours.

M.A. DELMAS

J.C. MAIRE

(1) M.A.DELMAS, J.C.MAIRE, W.McFARLANE, Y.RICHARD, J.Organometal.Chem., 87 (1975) 285.
(2) JC.POMMIER, J.VALADE, J.Organometal.Chem., 12, (1968) 433.

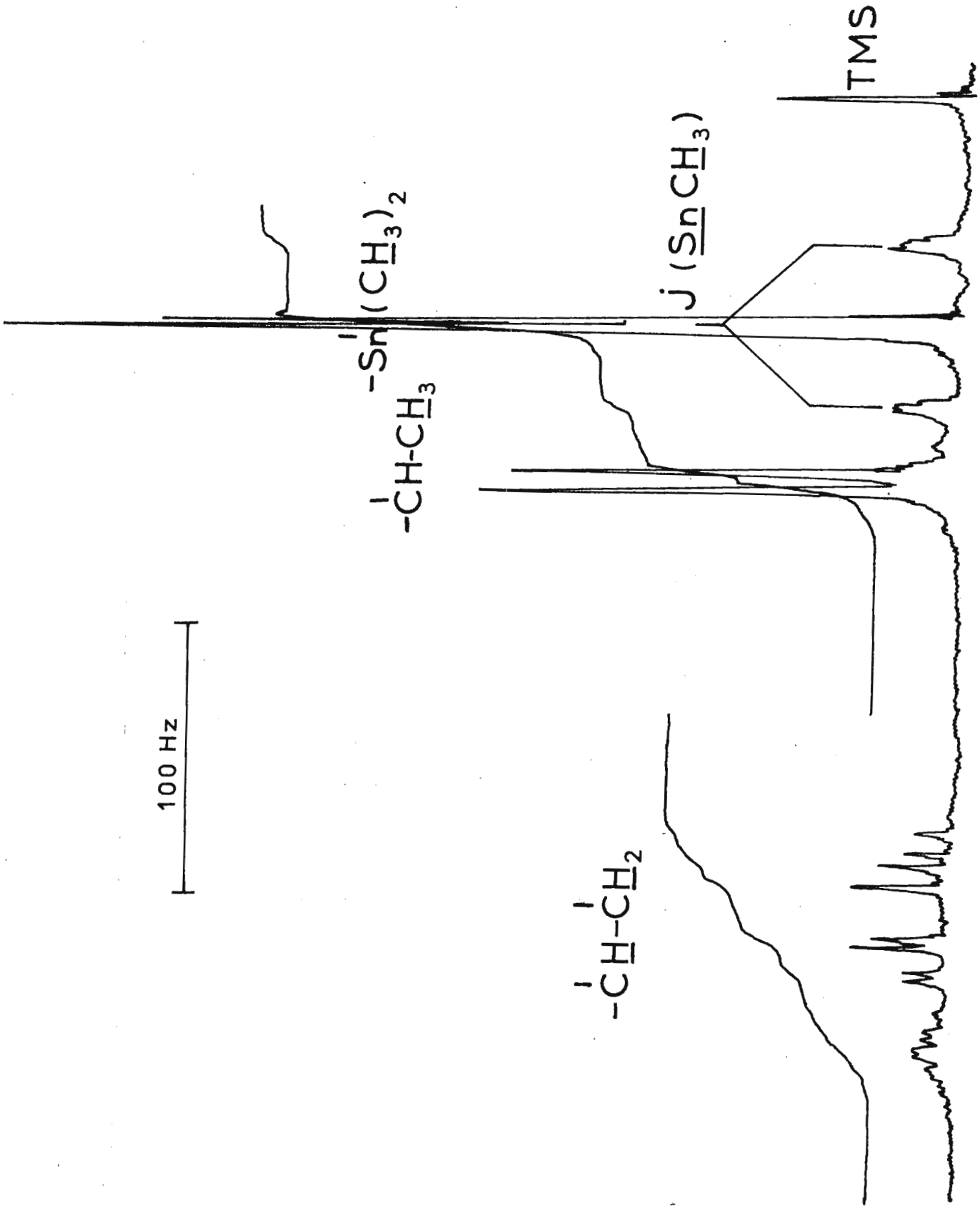


FIG 1

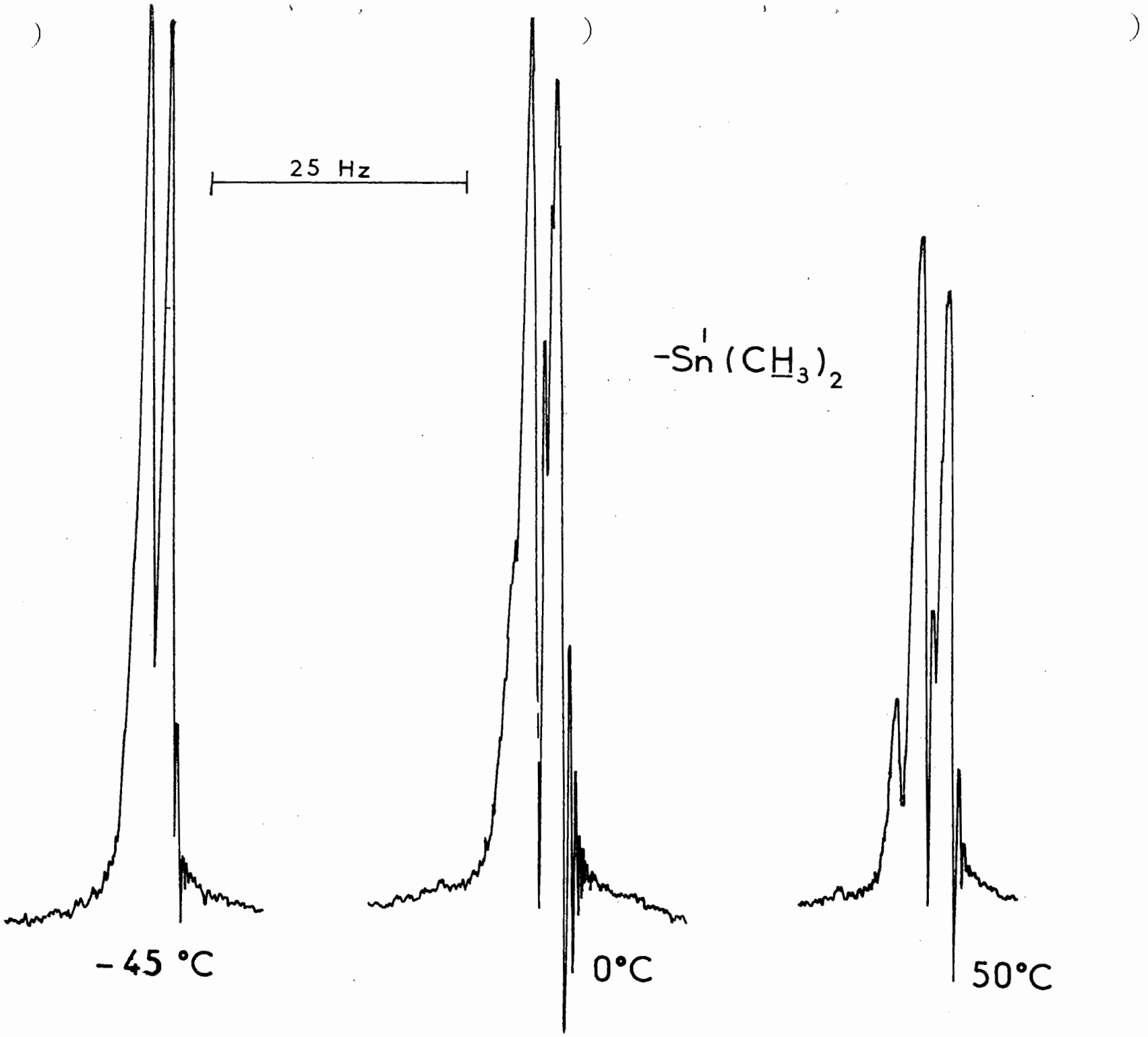


FIG 2

WAYNE STATE UNIVERSITY
COLLEGE OF LIBERAL ARTS DETROIT, MICHIGAN 48202

DEPARTMENT OF CHEMISTRY

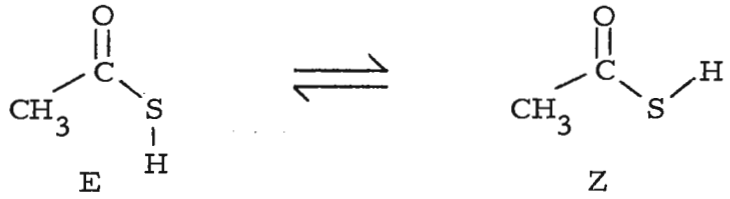
May 26, 1977

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

Title: Carbon-Sulfur π-Bonding

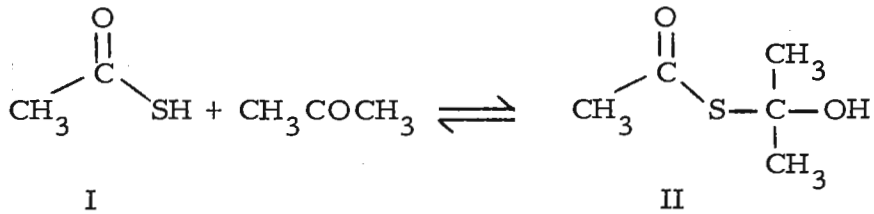
Dear Professor Shapiro:

In a recent communication,[1] the temperature dependence of the pmr spectra of thioacetic acid (I) was described. In either acetone-d_6 or $CHClF_2$ as solvent, two peaks of unequal intensities were observed for the methyl protons at low temperatures and were attributed to slow interconversion of E and Z isomers.



E Z

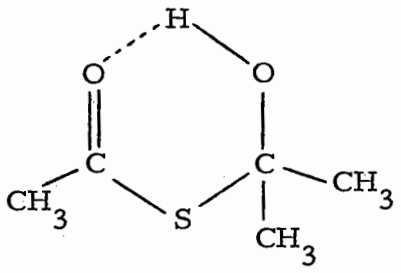
Further work, including a low-temperature ^{13}C nmr study, has now shown that the changes observed in acetone at relatively high temperatures are due to reaction of the thioacetic acid with the solvent, probably as outlined below.



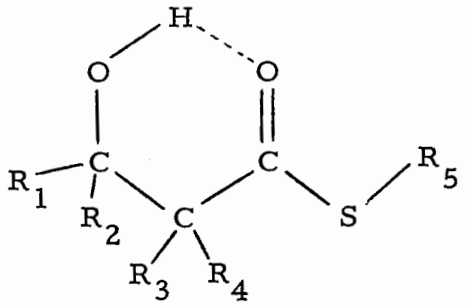
I II

The ambient-temperature ^{13}C spectrum of thioacetic acid in acetone (720 mg of I in 2.4 g of unlabelled acetone containing 2.5% TMS by weight) shows peaks at δ205.8 and 30.5 for CH_3COCH_3 and at δ195.0 and 33.2 for CH_3COSH. External methanol-d_4 was used for the lock signal. At this temperature, reaction with the acetone probably occurs to only a very small extent. At -90°, peaks assigned to II are observed at δ199.7, 86.1, 31.4, and 30.4. The carbonyl carbons of S-methyl, S-ethyl, S-propyl, S-isopropyl, S-butyl and S-tert-butyl thiolacetates were all

found[2] to absorb in the narrow range of 194.4 to 195.6 ppm in DMSO-d_6. The lower value observed for II could be due to formation of an intramolecular hydrogen bond (III), although hydrogen bonding to the solvent is also possible.



III



IV

A study[2] of several β-hydroxy thiol esters in DMSO-d_6 and $CDCl_3$ has provided evidence that intramolecular hydrogen bonding in these compounds (IV) can result in a downfield shift of several ppm for the carbonyl carbon.

Pmr spectra of solutions of I in unlabelled acetone provide further evidence for the formation of II; peaks assigned to the methyl protons of the complex appear at δ1.67 and 2.30.

A lower limit for the barriers to cis-trans isomerism of I can be calculated from the data obtained in $CHClF_2$[1]. Further work on this and related problems is in progress.

Sincerely,

Eric Noe

Eric Noe

References

1) E. A. Noe, J. Amer. Chem. Soc., 99, 2803 (1977).

2) C. M. Hall and J. Wemple, J. Org. Chem., in press.

225-41

מכון ויצמן למדע
THE WEIZMANN INSTITUTE OF SCIENCE
REHOVOT · ISRAEL רחובות · ישראל
Prof. M. Raban
DEPARTMENT OF STRUCTURAL CHEMISTRY המחלקה לכימיה מבנית

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

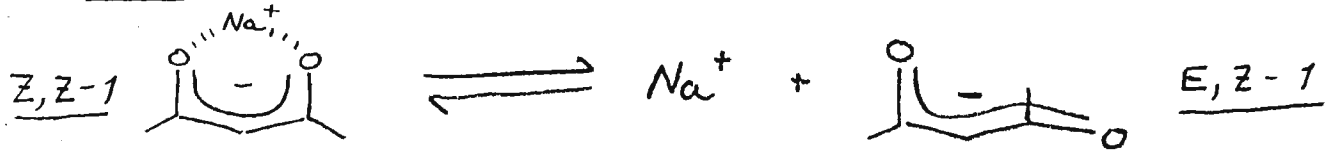
May 26, 1977

CMR Spectra of Acetylacetone Enolates.

Dear Prof. Shapiro,

We have begun over the past months to apply ^{13}C n.m.r. spectroscopy to our research interests in the area of configurational analysis of imides and enolate anions using our new JEOL FX-60 spectrometer. We have been pleased with the results and have found that cmr spectroscopy provides a valuable adjunct to our previous pmr studies. Two new results on acetylacetonates will serve as examples.

We have measured the cmr spectrum of sodium, acetylacetonate (acacNa), at low temperature in methanol containing 10% deuterated acetone and 10% TMS. The spectrum features two methine carbon resonances at 102.5 and 99.4 in a ratio of about 4:1 indicating that two species are present in equilibrium. Previous pmr studies have demonstrated that they must arise from the chelated ion pair Z,Z-1 and the dissociated ions E,Z-1. That the downfield (major)



resonance arises from E,Z-1 is apparent from the carbonyl region of the spectrum which features two equally intense resonances at 194.8 and 193.1 (from the diastereotopic carbonyl groups of E,Z-1) and a single less intense resonance at 190.8 (from the homotopic carbonyl groups of ZZ.1). Thus, it may be seen that dissociation of the chelate to solvent separated ions results in downfield shifts (ca. 3ppm) of both the methine and carbonyl resonances.

CABLE ADDRESS: WEIZINST (Israel) :מען למברקים PHONE: 956444 :טלפון TELEX: 31934 :טלקס

This is in sharp contrast to the behavior of acetophenone enolate as reported by House and co-workers.[1] They state that increasing dissociatic (in the series of Li,Na and K salts) results in upfield shifts of both resonances. While there are considerable differences in the two experiments, we do note that the arguments used by House and co-workers to rationalize their results, when applied to acacNa, afford predictions which are at variance with experiments.

We have also investigated the ^{13}C spectra of the complexes of diethylamine (DEA) triethylamine (TEA) with acetylacetone in chloroform. Of particular interest were the shifts of the β(methyl) carbon atoms of the amines. The β carbons of amines are known to exhibit upfield shifts on protonation.[2] These were observed, in our case, by addition of 1 equivalent of benzoic acid to produce the chloroform soluble benzoates which exhibit upfield shifts of 4.1ppm(DEA) and 3.2ppm(TEA). The DEA complex of acetylacetone also exhibits an upfield shift (0.9 ppm) while that of TEA is almost unchanged (downfield shift of 0.2ppm). This suggests that the two complexes are different: the DEA complex can be thought of as a hydrogen bonded salt ($acac^{-}...H.DEA^{+}$) while that of TEA is a non-ionic hydrogen bonded complex (acacH...TEA). This behavior reflects the difference in basicities of the two amines and could possibly serve as a diagnostic for differentiating between these two functional groups in assignments of CMR spectra of compounds containing one or both functional groups.

I will be returning from sabbatical leave in the fall and will have to fill one or two positions for post-doctoral research associates then. Interested candidates are encouraged to write to me at 335 Chemistry Wayne State University, Detroit MI 48202.

Sincerely yours,

Morton Raban.

1. H.D. House, A.V. Prabhu and W.V. Phillips, J.Org.Chem., 41, 1209 (1976).

2. K.F. Koch, J.A. Rhoades, E.W. Hagaman and E. Wenkert, J.Am.Chem.Soc., 96, 3300 (1974).

225-43

INDIANA UNIVERSITY
Department of Chemistry
CHEMISTRY BUILDING
BLOOMINGTON, INDIANA 47401

TEL. NO. 812— 337 5513

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

May 31, 1977

Detection of the Furanose Anomers of D-Mannose in Aqueous Solution

Dear Barry:

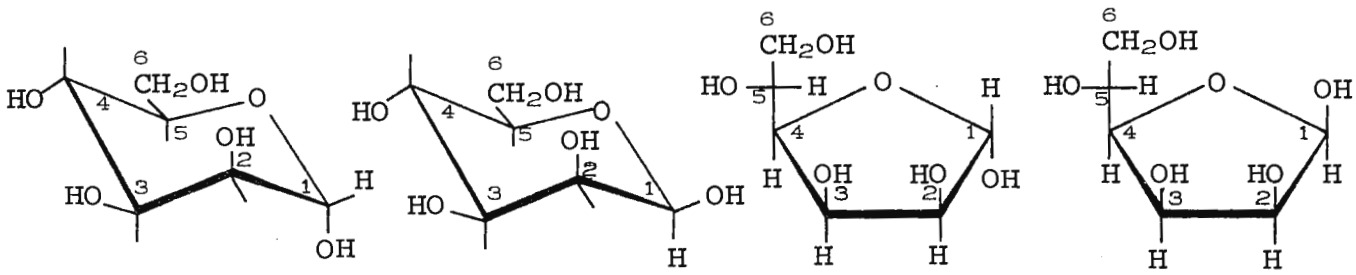
In the past, proton NMR spectroscopy has been used extensively to determine the proportions of the predominant (pyranose) anomers of various common aldohexoses in aqueous solution, by taking advantage of the relatively resolved resonances of the anomeric hydrogens.[1,2] Some aldohexoses have also yielded observable resonances for the anomeric hydrogens of the furanose anomers.[2] Notable exceptions are glucose and mannose. Angyal and Pickles[2] estimated that the proportion of the furanose forms in the anomeric equilibrium of each of these sugars in water is considerably less than 1%. My coworkers, Dr. David J. Wilbur and Ms. Carol Williams, have found that ^{13}C NMR spectra at 67.9 MHz (63.4 kG) yield identifiable resonances of five carbons of α-D-mannofuranose (1c, Figure 1) and three carbons of β-D-mannofuranose (1d, Figure 1). A spectrum is shown in Figure 2. Integrated intensities indicate the presence of 0.6±0.1% α-D-mannofuranose and 0.3±0.1% β-D-mannofuranose.

1. R. U. Lemieux and J. D. Stevens, Can. J. Chem., 44, 249 (1966).
2. S. J. Angyal and V. A. Pickles, Aust. J. Chem., 25, 1695 (1972).

Best regards,

Adam

Adam Allerhand
Professor of Chemistry



1a 1b 1c 1d

Figure 1. Structures of α-D-mannopyranose (1a), β-D-mannopyranose (1b), α-D-mannofuranose (1c), and β-D-mannofuranose (1d).

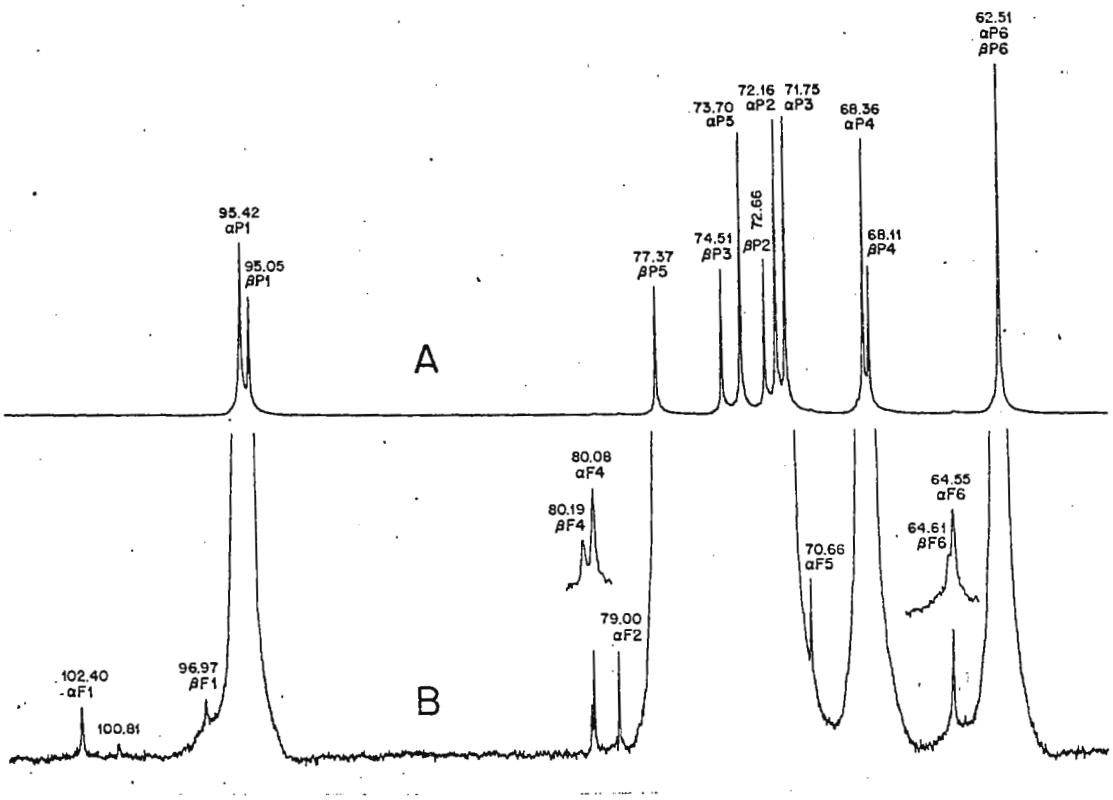


Figure 2. Proton-decoupled natural-abundance ^{13}C NMR spectrum (at 67.9 MHz) of 4 M D-mannose at anomeric equilibrium in H_2O at 36°, after 5 h of accumulation. Spectrum B is the same as A, but with a 32-fold vertical expansion. The insets in spectrum B present a 4-fold horizontal expansion. Numbers above indicated assignments as chemical shifts in ppm from Me_4Si. The anomeric carbon resonances are somewhat broader than other peaks, as a consequence of differences in the effectiveness of proton-decoupling.

PURDUE UNIVERSITY DEPARTMENT OF CHEMISTRY

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

3rd June, 1977

Dear Barry,

Practical Guide to INDOR

I presume a few of your readers are still interested in obtaining cw INDOR spectra as an aid to spin analysis etc. Unfortunately many chemists still regard INDOR as a black art devoid of practical utility, despite the efforts of the faithful[1-3]. Hopefully this empirical guide might help to lighten the darkness. The following points should be considered.

1. INDOR is a population transfer phenomenon and requires times of the order of T_1 for measurable response. Thus slow decoupler sweeps are essential.

2. The selection of power levels for both the observing (H_1) and decoupling (H_2) fields are critical. H_1 should be set to give maximum equilibrium peak height for the monitored peak. This provides best signal/noise as it generates the maximum steady state X magnetization. The optimum H_2 power is a balance between two effects:- the need for maximum population transfer which requires large H_2 and line splitting distortions resulting from spin tickling effects.

3. Additional responses may be observed arising from through-space population transfers which are not related to progressive and regressive transitions.

The following procedure has proved practical.

1. Adjust the H_1 frequency and power for maximum response at the peak to be monitored (no sweep).

2. Select a progressive response and adjust the H_2 frequency and power level for maximum positive response (No sweep). For most proton INDOR work a standard compound such as styrene oxide may be used to select the appropriate range of power level for other systems.

3. Use slow sweep rates - for instance 1 Hz/sec is usually too fast.

Similar observations have been made by Wagner and Philipsborn[4]. Some practical examples obtained with a Perkin Elmer R-32 spectrometer employing the vinyl region of ethylvinyl ether are shown.

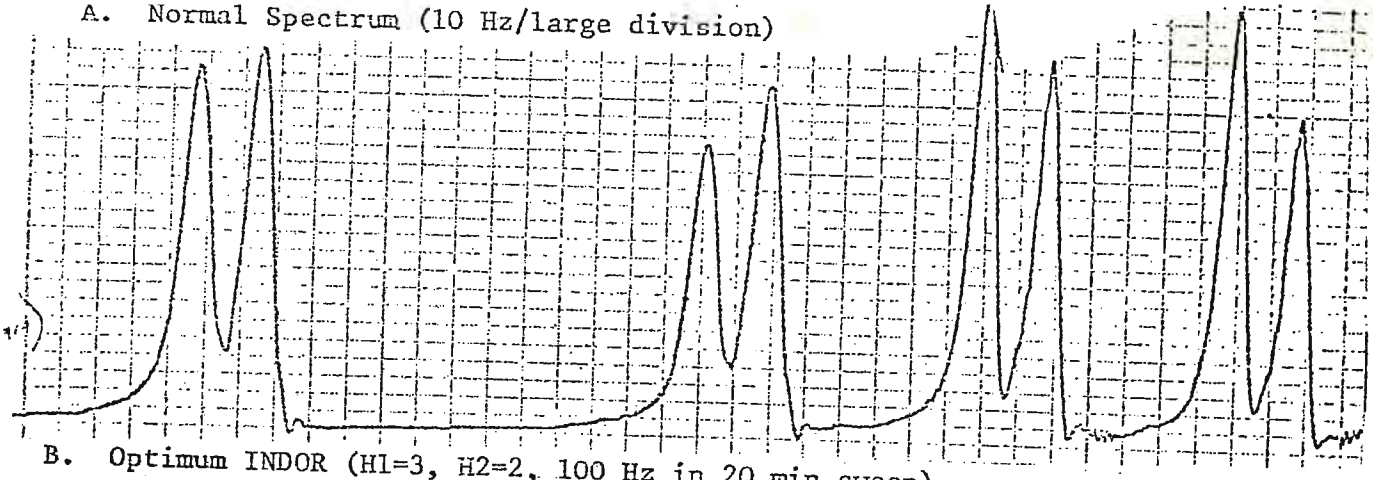
1. W. von Philipsborn, Angew. Chemie. 83, 470 (1971).
2. R.A. Hoffman, S. Forsen and B. Gestblom, "NMR Basic Principles and Progress" Vol.5, p.45, 1971.
3. J.A. Ferretti and R. Freeman, J. Chem. Phys., 44, 2054 (1966).
4. R. Wagner, Ph.D. Dissertation, University of Zurich, 1972.

Chemistry Building
West Lafayette, Indiana 47907

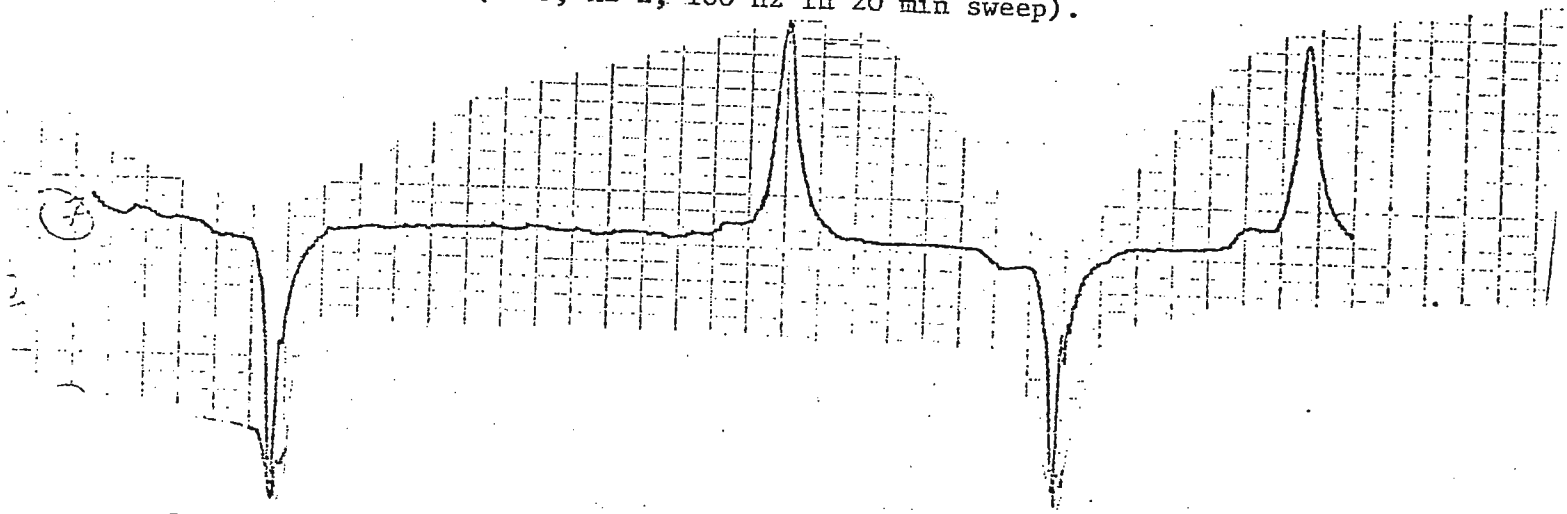
Yours sincerely,
John B. Grutzner

John B. Grutzner

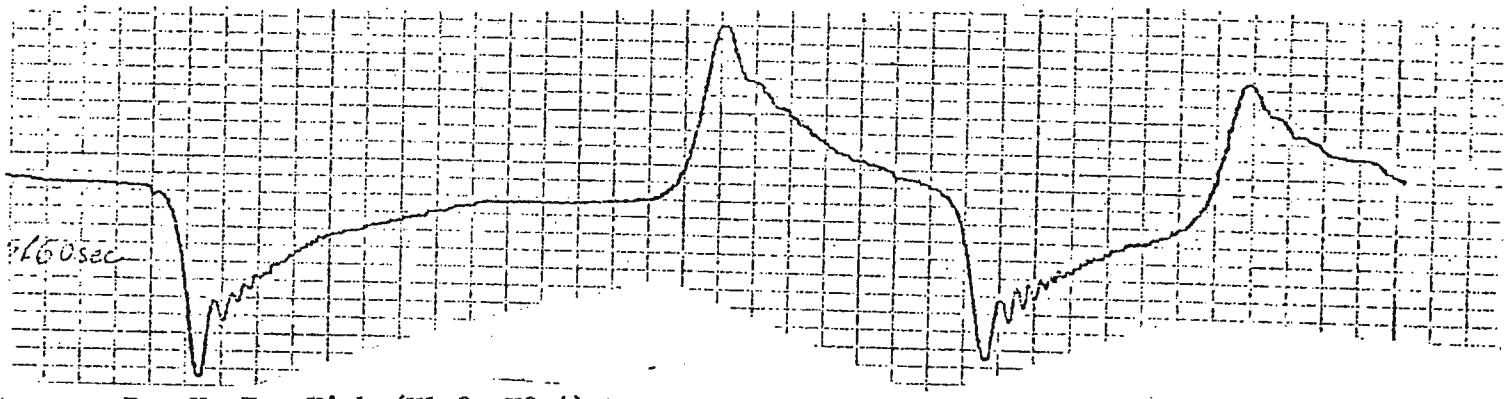
A. Normal Spectrum (10 Hz/large division)



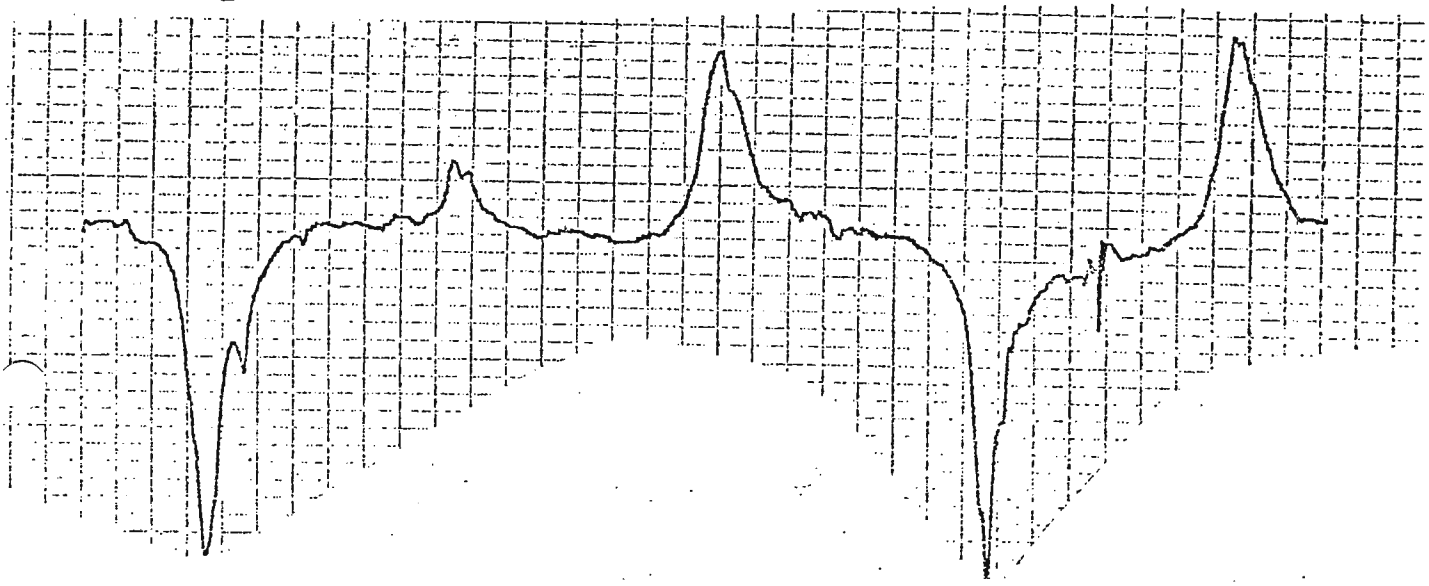
B. Optimum INDOR (H1=3, H2=2, 100 Hz in 20 min sweep).



C. Sweep Rate Too High (same as B but sweep time 180 secs).



D. H_2 Too High (H1=3, H2=4)



UNIVERSITY OF VIRGINIA
DEPARTMENT OF CHEMISTRY
CHARLOTTESVILLE, VIRGINIA 22901

June 6, 1977

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

Dear Dr. Shapiro:

Recently we have found through nuclear relaxation and kinetic studies that Li-7 can be an effective probe of monovalent cation binding sites of enzymes. Li-7 is easily observed using a JEOL-PS-100P/EC-100 Fourier transform spectrometer with a standard carbon probe by dropping the field to 1.52 T. Observing Li-7 at 25 MHz in this fashion precludes the use of the H-2 lock. However, as can be seen in the accompanying figure we have obtained usable signal-noise using 25-50 mM LiCl and a single transient. Since the enzyme systems we have studied (pyruvate kinase, $Na^+ + K^+$-ATPase) bind Mn^{2+}, titration with Mn^{2+} increases the $1/T_1$ of $^7Li^+$ and the usual formalism can be applied to derive Mn^{2+} - Li^+ distances. Space limitations prevent going into the details, but our results show that Li-7 is a viable, and in some cases preferable, alternative to using Tl-205 nmr in these systems. Linewidth changes were ignored since preliminary experiments showed $T_1/T_2 > 1.16$ and hence dipolar broadening is not dominant. Li-7 nmr has the following advantages over Tl-205.

1.) Li-7 is much more sensitive.

2.) Tl-has a non-trival toxicity and must be handled accordingly.

3.) TlCl is insoluable in H_2O and nitrates or other salts not native to many systems must be used.

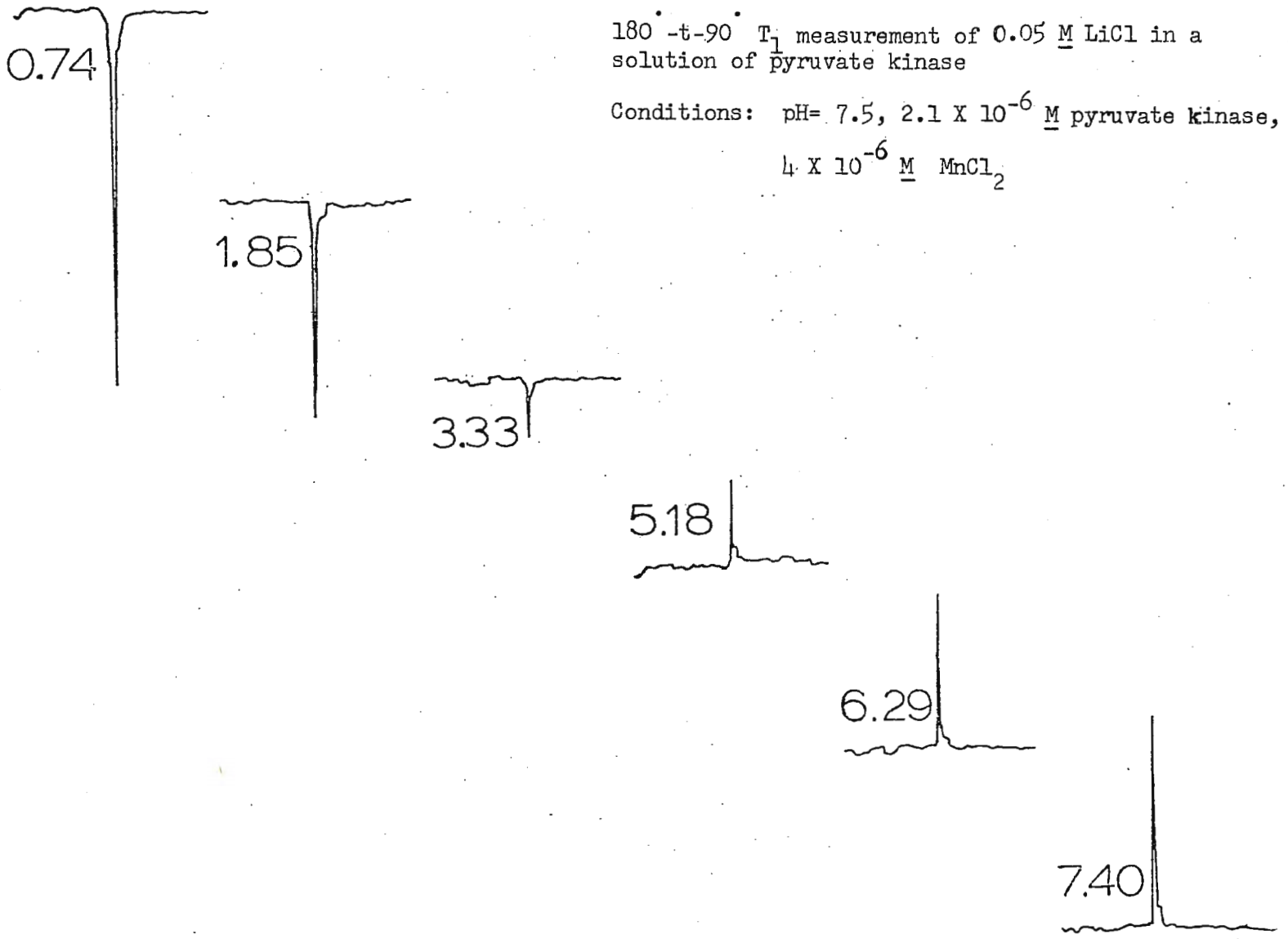
Please credit this letter to Dr. Bruce Martin's account.

Sincerely,

Charles M. Grisham

Charles M. Grisham
Assistant Professor

William C. Hutton
Research Assistant



180°-t-90° T_1 measurement of 0.05 M LiCl in a solution of pyruvate kinase

Conditions: pH= 7.5, 2.1×10^{-6} M pyruvate kinase, 4×10^{-6} M $MnCl_2$

225-49

UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

DEPARTMENT OF CHEMISTRY
(803) 777-5263

June 8, 1977

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

Dear Barry,

Selenium-77 Spin-Lattice Relaxation

As part of our continuing interest in the applications of multinuclear NMR to biological systems we have turned our attention to selenium-77. Since the observation of a rare nucleus present in the low concentrations usually encountered in biological studies will tax the NMR instrumentation considerably, it is desirable at the outset to have an estimate of T_1 in order to optimize the recycle time of the PFT NMR experiments. Accordingly we have begun our investigations of selenium-77 with a study of T_1's in simple organoselenium compounds and report herein some preliminary results.

The temperature dependence of the spin-lattice relaxation times displayed in the Table are indicative of a dominant spin-rotation relaxation mechanism for Se-77. Thus, as depicted graphically for ethylselenol and dimethylselenide in the Figure, the Arrhenius plots have a negative slope. In addition, a proton-selenium nuclear Overhauser effect enhancement was not observed for any of the compounds, not even at the lowest temperatures where the dipole-dipole mechanism is expected to compete more favorably with spin-rotation. This observation, along with the linearity of the Arrhenius plots attests to the dominance of spin-rotation.

The remarkable absence of dipole-dipole relaxation from the directly bound proton in the selenols (in which $^1J_{Se-H}$ is 43 Hz) can be attributed to the relatively long (1.44 Å) Se-H bond distance and the $1/r^6_{SeH}$ dependence of the dipole-dipole mechanism.

$T_1(DD)$ may be calculated from the observed value of T_1, the observed NOE enhancement, n, and the maximum n_o of 2.61. For example, using an arbitrary n of 0.10, a lower limit for $T_1(DD)$ of 637 sec for dimethylselenide and 248 sec for ethyl selenol at -60°C are obtained. These values will be even larger at room temperature.

All spectra were obtained on a Varian XL100-15 spectrometer operating at 19.1 MHz in the Gyro Observe mode. During the course of this work we encountered a technical difficulty, namely the inability to noise or square-wave modulate the proton decoupling signal without introducing a prohibitive amount of electronic noise in the receiver. Sufficient coherent decoupling power was obtained only after inserting an ENI model 320L amplifier between

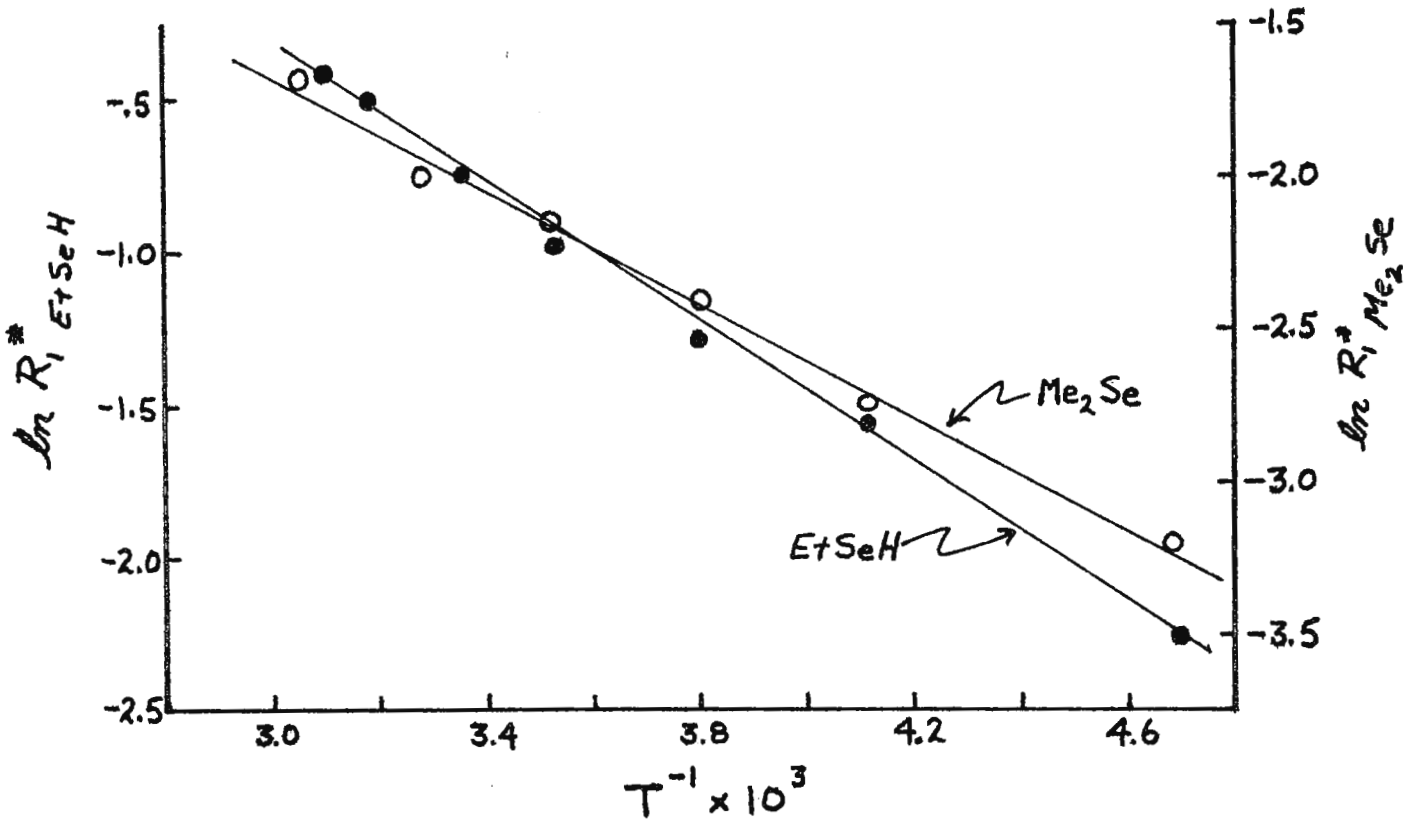
Professor B. L. Shapiro June 8, 1977

the output of the Gyrocode Spin Decoupler and the decoupler matching network. Since we were unable to determine the origin of this problem we would welcome all comments or suggestions.

The technical assistance of R. Andrew Byrd was greatly appreciated.

Compound	T_1(sec)	T(°C)	Compound	T_1(sec)*	T(°C)
dimethylselenide	24.4	-60	dibenzyldiselenide	31	18
	7.5	32		27	55
ethylselenol	9.5	-60	diphenyldiselenide	31	0
	1.6	40		20	45
methylselenol	4.3	-45	dimethyldiselenide	13	0
	1.4	40		9	45

* in $CDCl_3$ solution



Please credit this contribution to the account of Paul Ellis.

W. H. Dawson J. D. Odom

CENTRO DE INVESTIGACION DEL IPN

APARTADO POSTAL 14-740

MEXICO 14, D. F.

DEPARTAMENTO DE QUIMICA

May 12, 1977.

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

Further advantages of gated proton decoupling during carbon magnetic resonance

Dear Professor Shapiro:

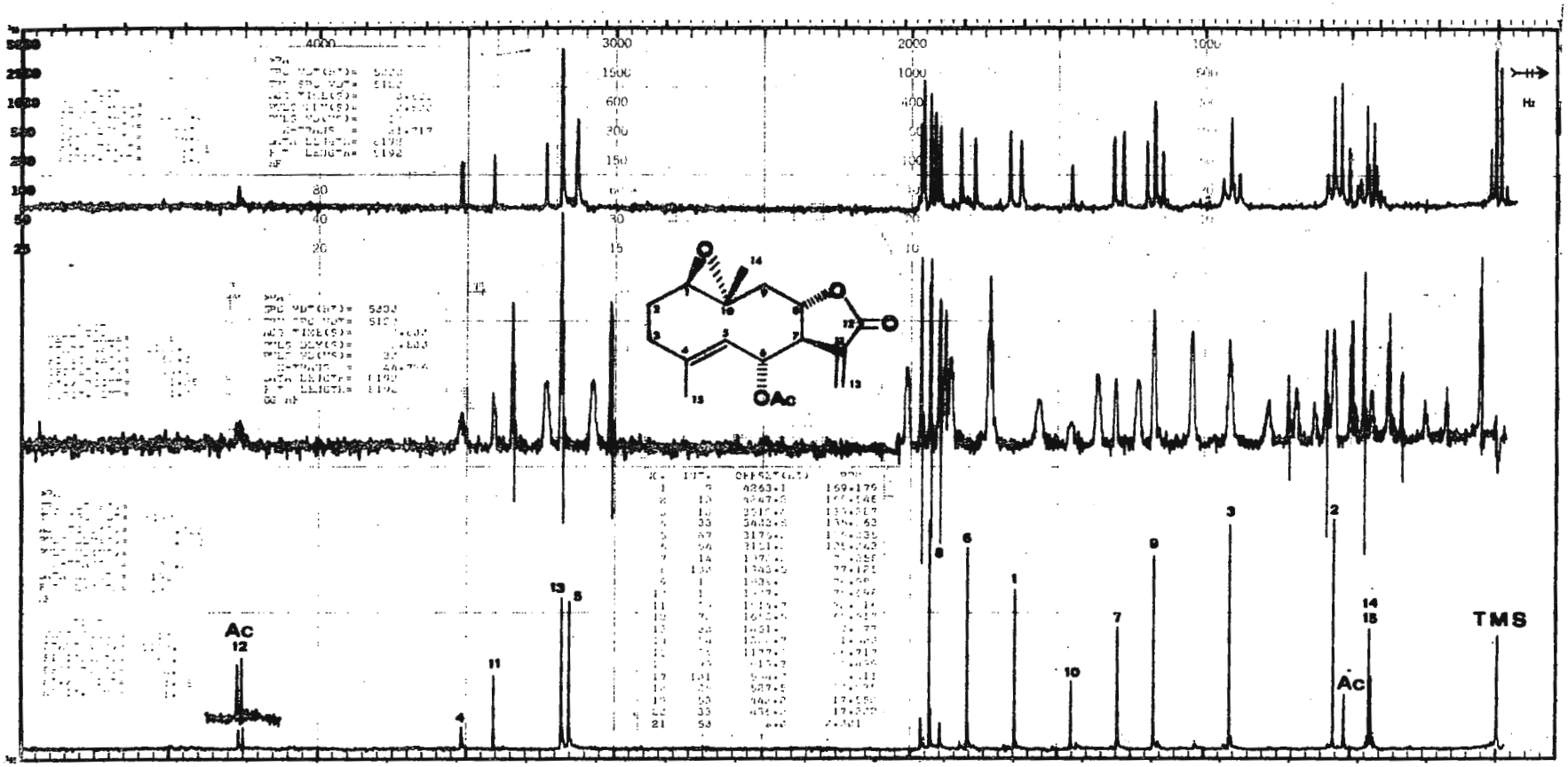
In the previous contribution, the assignments of the carbon signals of a pseudoguaianolide natural product were described with the aid of gated decoupling. TAMU NMR, 215, 20 (1976).

This technique has been further explored and results for the germacranolide chrysantin, isolated from Chrysantemum cinerariaefollium, a compositae widely distributed in Ecuador, South America, are now described.

In order to obtain better signal to noise ratios, the long term gated decoupling experiments were now performed incorporating pulse delays. It was found that when the delay was greater then 0.2 sec, the Fourier transformed spectrum started to contain negative contributions in some specific signals, which do not increase further after a delay of 0.6 sec.

The central trace of the enclosed figure corresponds to a gated spectrum obtained with AT = 0.8; PD = 0.8. It can be seen that the deuterochloroform triplet and some other specific peaks show this contributions. One group corresponds to the exocyclic methylene triplet and the other to the acetyl methyl quartet, which obviously is much easily recognized in this situation.

Furthermore, on analizing the upper trace of the figure, which corresponds to an off resonance cw decoupling experiment, one can see that specifically for the right portion signals, the small chemical shift differences between the various carbons, make quite difficult the assessment of their individual multiplicities, this being also quite difficult to achieve by single frecuency decouplings, since in the corresponding proton spectrum of this molecule[1], the signals appear close together. Therefore the gated experiment provides much more information.



Proton noise, gated and off-resonance cw decoupled carbon-13 spectra of chrysantin.

Bernard L. Shapiro.-

Although the negative peaks look real, a good explanation for them appears misterious. Its origin was found to be due to ground loops in the probe of our XL-100 spectrometer which results in a momentary perturbation of the lock signal during decoupling gating, as can clearly be seen on the scope during the experiment. This can be eliminated by connecting a solid copper wire between the connector J006 on the right side of the XL-100 console (preferentially inside the cabinet) and one of the non painted screws going to the chassis. However, if the benefit of the ground loops is desired for some measurements, then a very low resistance knife type switch as those used in old domestic electrical installations should be connected in place.

The assignment of the signals in the spectrum of chrysantin are given in the figure.

Sincerely yours,

Dr. Pedro Joseph-Nathan
Professor of Chemistry

1.- H. Yoshioka, T.J. Mabry and B.N. Timmermann, Sesquiterpene Lactones. Chemistry, NMR and Plant Distribution, University of Tokyo Press, p. 186, Tokyo (1973).

PJN/psp

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

June 7, 1977

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

^{15}N and ^{111}Cd NMR Studies of ^{111}Cd meso-tetraphenylporphyrin-^{15}N

Dear Professor Shapiro:

Dr. Michael King (The George Washington University) and I have been interested in the ^{15}N and metal nuclides NMR studies of metalloporphyrins. Recently we have prepared a ^{111}Cd and ^{15}N doubly labeled ^{111}Cd meso-tetraphenylporphyrin-^{15}N (91% ^{111}Cd and 95% ^{15}N enriched) as part of these studies. Using the $\{^{111}Cd\}$-^{1}H and $\{^{15}N\}$-^{1}H INDOR experiments we are able to obtain the ^{111}Cd and ^{15}N spectra of this compound at 5-10 mg quantity in few hours on our modified Varian HA-100 spectrometer.

The ^{111}Cd INDOR spectrum of this compound in $CDCl_3$ with a trace of pyridine shows a quintet (centered at 21.210954 MHz in a magnetic field where the ^{1}H resonance of TMS is exactly 100 MHz) with the peak separation of 144 Hz attributing to the one bond coupling between ^{111}Cd and the four ^{15}Ns of the porphyrin. In a careful examination, each of the quintet can be further resolved into 9 lines arising from the four bond coupling (J=4.5 Hz) between ^{111}Cd and the eight β-protons of porphyrin. Thus, the ^{111}Cd spectrum of ^{111}CdTPP-^{15}N consists of 45 lines.

The ^{15}N INDOR spectrum shows a doublet (centered at 167 ppm upfield from $CH_3{}^{15}NO_2$) with a one bond ^{15}N-^{111}Cd coupling constant of 143.5 Hz which is in agreement with the number determined from the $\{^{111}Cd\}$ -^{1}H INDOR experiment.

We are currently investigating the effect of ligands on the ^{15}N and ^{111}Cd NMR spectra.

Sincerely,

Herman Yeh

Herman J. C. Yeh

225-55

The University of Western Ontario

Department of Chemistry
Chemistry Building
London, Canada
N6A 5B7

8 June 1977.

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

Dear Barry:

USEFUL MICKEY-MOUSE MODIFICATIONS to the old T_1 PROGRAM

Your recent pink letter apparently demands some action and I wonder if the following suggestion would satisfy that demand.

Some months ago, some modifications were written into our old Freeman-Hill inversion recovery program as an approach to averaging instrumental variations through the course of a long experiment. Many of our T_1 experiments require a day or two of instrument time and it was thought that a better mode of operation would be desirable. Consequently, the program was altered in two ways. First, the cassette is not nearly full with 10τ values so we increased this to 18 as a maximum. Secondly, we modified the program so that a given number of transients is collected and stored for each τ value and a number of passes through the series of τ values is performed adding each additional "block" of transients to those collected in the initial pass. This block approach has the advantage of averaging the long-term instrumental variations over all τ values employed. Also, the number of blocks originally requested may be more than is required so that the experiment can be interrupted after a given set and all τ values utilized in the T_1 measurements.

Although this is a very simple-minded modification, we feel that it is worthwhile. With up to 18τ values available one can collect a reasonable number of points in one experiment for nuclei with significantly different T_1 values. Of course, the time taken up transferring the individual blocks from core to cassette and vice versa is not trivial but for a long experiment this becomes a relatively small portion of the total period. Our approach utilizes a cassette formatted for the 18τ values and the modified program is that for an XL100-cassette arrangement. Perhaps some readers may want to modify their experiments in a similar fashion but I would be happy to provide a listing of the changes required for our system if anyone wishes to have these alterations.

Sincerely,

Jake

JBS/co

J.B. Stothers
Chairman.

May 31, 1977

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

Dear Barry:

Solvent Suppression on the CFT-20

We have recently installed the capability for proton observation on our CFT-20. As we did not get the homonuclear decoupling accessory, however, we cannot generate simple selective pulses for solvent suppression. We do have a number of aqueous samples in which the solvent peak is a problem, though.

At the suggestion of Steve Patt, I have modified program 994130-07D (the difference program) to allow a train of excitation pulses preceding the standard non-selective excitation pulse. As was described by Bodenhausen, Freeman and Morris,[1] such a pulse train selectively excites signals whose frequency separations from the carrier are integral multiples of the repetition frequency of the pulse train.

For our purposes, I substituted the pulse train for the first two pulses of the normal three-pulse sequence. The routine works in nulling a solvent through a selective 180° pulse train followed by the appropriate delay or by a very long saturating pulse train. It also can be used for observation of carbon, for which a variety of experiments have been suggested.[1]

I would be happy to send a description of the program changes with instructions for use to anyone who can use them.

Sincerely yours,

Mark Henrichs

PMH:nc

P. M. Henrichs
Chemistry Division
Research Laboratories

[1] G. Bodenhausen, R. Freeman, and G. A. Morris, J. Mag. Resonance, 23, 171 (1976)

225-57

TEXAS A&M UNIVERSITY
COLLEGE OF SCIENCE
COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

6 June 1977

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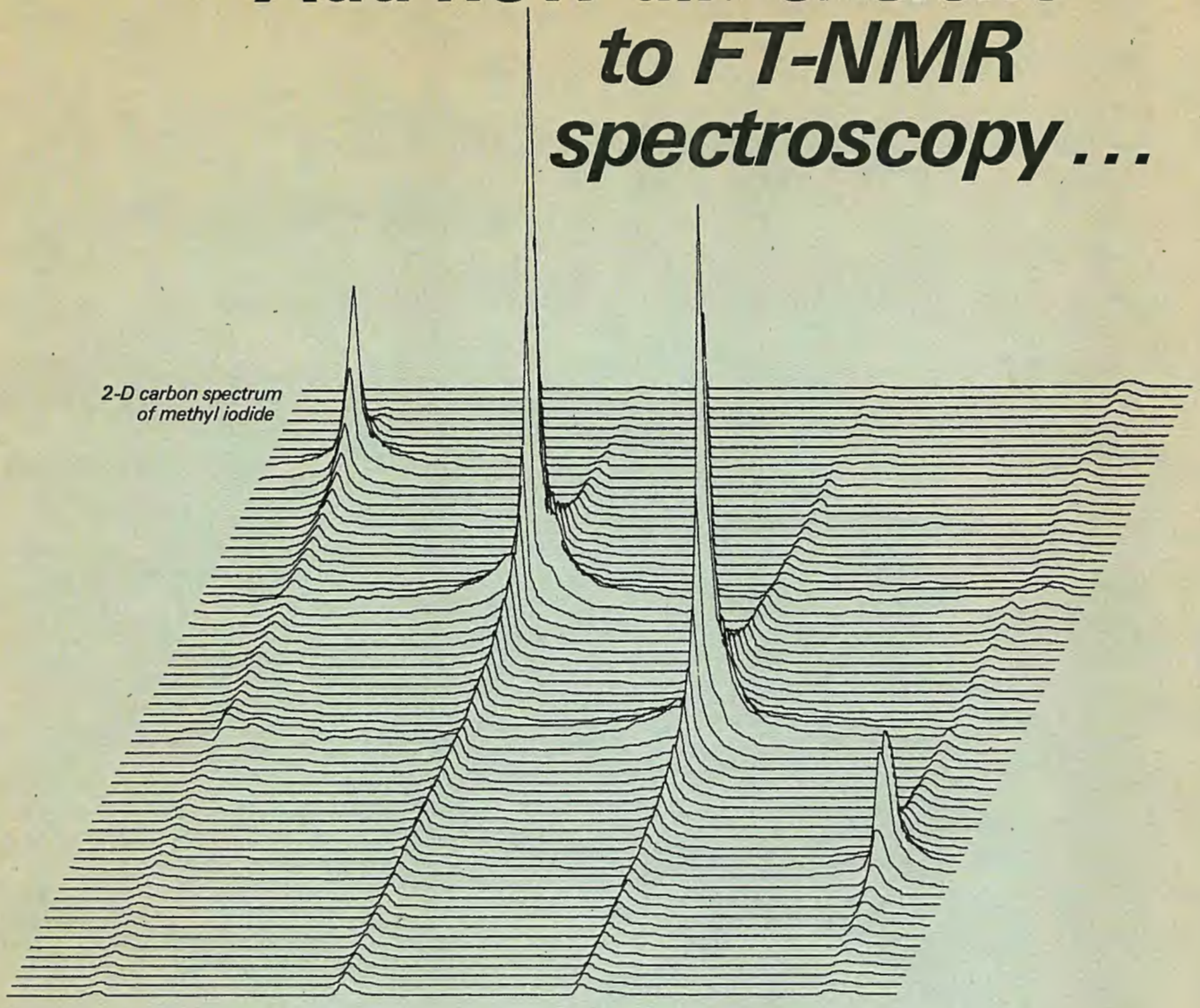
B. L. Shapiro

Add new dimensions to FT-NMR spectroscopy . . .



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- plot/print/CRT display
- spin simulation

examples of acquisition:
- $T_1/T_1\rho$
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- kinetic
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