Texas A & M University N-M-R Newsletter

No. 276

September, 1981

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DEADLINE DATES:		
	No. 277	5 October 1981
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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. 276

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Waterloo, Ontario, Canada
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Faculty of Science
Department of Chemistry
519.885-1211

July 20, 1981

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

Dear Barry:

I am hampered by our regular seasonal postal strikes, but now the University has opened up an illegal mail run to Niagara Falls twice a week. The mounties have not yet stopped the truck. Following on from the last letter, I can release the abstract of a paper to appear in J. Phys. Chem. in November, which shows that we really did know how to manipulate the diamagnetic anisotropy of disk shaped micelles.

Abstract

The diamagnetic anisotropy of magnetically aligning disc micelle lyotropic liquid crystals has been reversed by the inclusion of aromatic amphiphiles. This reversal occurs without a phase change and at the point of transition a non-aligning Type 0 disc micelle mesophase is formed. Different host mesophases have been taken through the change in sign of the diamagnetic anisotropy, and the effects of temperature variation investigated. The rate of alignment of the Type I disc micelle mesophases is a linear function of aromatic amphiphile concentration.

The figure from the paper is instructive. It shows the velocity constant of alignment of a type I DM mesophase as a function of mole-fraction of potassium heptyloxy-benzoate (an aromatic amphiphile) in sodium lauryl sulphate. The dependence is linear, extrapolating to 0 rate constant at a mesophase that is diamagnetically isotropic, a Type 0 DM. Diamagnetism is a molecular property and mixing aromatic and aliphatic chains in a micelle, with of course appropriate relative alignment, leads eventually to diamagnetically isotropic micelles that dispose in orientational order to give a liquid crystal. Kind regards.

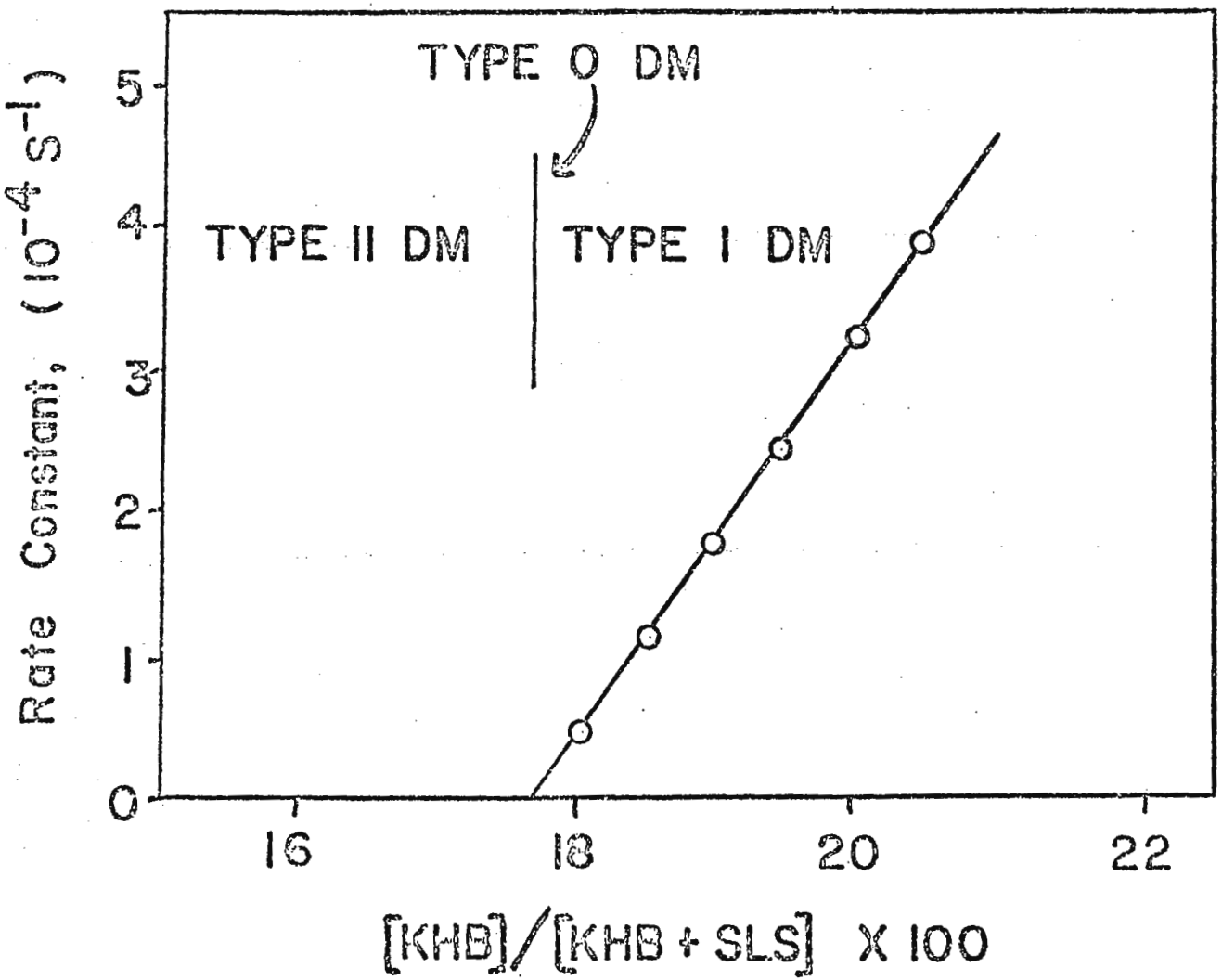
Yours sincerely,

Len Reeves

L.W. Reeves
Professor of Chemistry

LWR/dv

ALIGNMENT RATE VS. AROMATIC CONTENT



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

RÉFÉRENCE A RAPPELER
G/DRF/CH/81-242/mjc

VOTRE RÉF.

VOTRE LETTRE DU

GRENOBLE, LE 24 juillet 1981

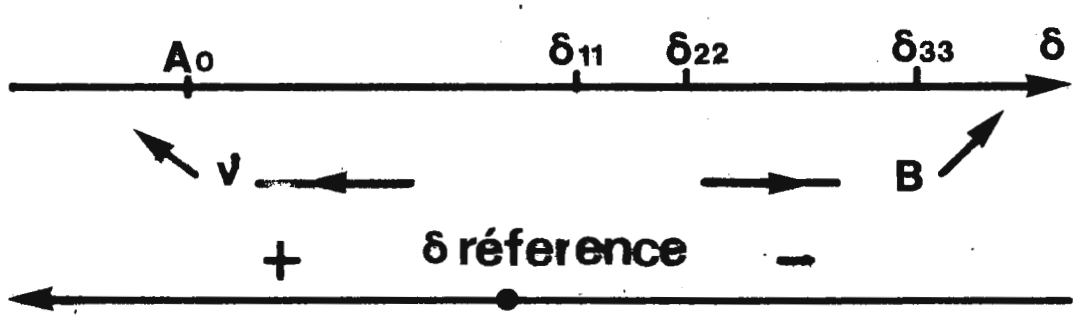
Dear Dr. Shapiro,

More and more data concerning the n.m.r. chemical shift are obtained now from solid state studies. Thus, using the measurement of the constant of spin rotation and ab initio calculation on a reference compound, it is possible to determine the magnetic shielding tensor components of the recorded nuclei on an absolute scale with respect to the bare nucleus. In a n.m.r. experiment, the bare nucleus N_0 experiences a field B which will in general be greater than the one experienced by the same nucleus N_c involved in a chemical bond. With spectrometers operating in the F.T. mode, i.e. at constant field and variable frequency, the bare nucleus N_0 most frequently resonates at higher frequency than chemically bonded nuclei N_c. Thus we suggest to adopt a scale increasing from high to low frequency for the components of the magnetic shielding tensor components σ_{rr}, even if the values are given with respect to a reference and not in absolute scale. Such a suggestion is not in agreement with the I.U.P.A.C. recommendation for the chemical shift sign scales.

Sincerely,

J.B. ROBERT

L. WIESENFELD



C.E.N.G. IMP. N° 1 - 11-77

UNIVERSITY OF UMEÅ
Department of Organic Chemistry

August 3, 1981

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

Dear Barry,

Ockham´s Razor Again - SSP vs DSP.

As expected, there has been some response to my last contribution in TAMU (no 265), which concerned the necessity of testing the degree of parameterization using NMR SCS correlation models. Sardella suggested (TAMU no 269), that if a single substituent parameter equation (SSP) and a dual substituent parameter model (DSP) gave an identical fit, one should use the latter, since the DSP model permits a detailed partitioning of effects. This proposal was exemplified by treating the individual C4 -C7 C-13 NMR shifts of 1-substituted azulenes.[1]

First of all, five 1-substituted azulenes are too few compounds to be a basis for a meaningful SCS data analysis(minimum 6-7[2]) and besides, correlation coefficients get larger with decreasing sample size. Moreover, his choice of substituents is hardly representative for the whole substituent domain (CH_3, H, Cl, CH_3CO, NO_2). However, ignoring this sad fact for the moment, I consider the azulene data set as a typical multivariate data analysis problem, i e we want to find out how many " uncorrelated effects" are needed to account for all four C4- C7 C-13 NMR SCS. If one analyses such a matrix (preferably a larger data set than the 5x4 matrix) it could very well be that on a statistical basis (F-test) a two-component model is superior to a single component model. Of course, this does not exclude that one could find individual positions showing an acceptable correlation to a single scale. I can mention, that in a very similar study of 2-substituted indenes[3] we found, that a two-component model was necessary to account for the total C4 -C7 C-13 SCS variation, although for some individual carbons only one "effect" was significant. So I do not think there is a need for a re-examination of " Ockhams Razor ". If a two-component

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is necessary, it will be revealed when we treat the complete shift matrix with a multivariate data analysis method.

One must also keep in mind that correlation models can operate either on a descriptive or explanatory level. Especially in the first case there exists statistical tools for the selection of those variables or shifts with relevance to the actual problem. We have exemplified this approach by considering three classes of α-substituted styrenes (α-H, α-Me and α-t-Bu series)[4], each class consisting of seven 4-substituted derivatives. Based on those NMR parameters (Cl, Cβ and $H_a\beta$ and $H_b\beta$) which had relevance to our classification problem, we then tried to classify " unknown α-substituted styrenes" and to probe the substituent trend in each class. A single component (θ) model was found to be sufficient in each class. Since the selection of variables partly was determined by our classification problem and since we were afraid that the component values (θ) should be misused as a general substituent scale, we did not publish these values for the separate classes. The flood of scales is large enough without our contribution. However, in one case, after having merged the α-Me and α-H classes, the component values were given. We thought, that component values based on such a structurally hetereogenous class (14 α-H and 7 α-Me structures), based on both H-1 and C-13 varibles with relevance to our classification problem etc., would prevent the use of these values as a general substituent scale. But contrary...

Reynolds et al recently used these component values in a study of a subset of our matrix (12 α-H structures) to prove the superiority of the σ_I, σ_R^o model to SSP scales (θ and σ_p).[5] Our θ values for the merged class are of course of a very local validity and strongly related to our classification problem. Therefore, these values should not be used on other data sets or subsets of our shift matrix. Reynolds concluded from this study that " a DSP treatment is not only sufficient but also sufficient to interpret the styrene magnetic resonance parameters ".

A completely contradicting result was quite recently reported by Laszlo et al[6] They analysed four series of styrene derivatives and they found by a rigorous statistical treatment, that

there exists no statistical superiority in general of a DSP to a SSP treatment in these four series. Moreover, if DSP approaches were applied, the inductive effect was found to be more sensitive to configurational differences.

Does it seem confusing? No wonder that one sometimes have a wish, that organic chemists should not go beyond variable-by-variable plots.

Best regards

Ulf Edlund

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6. A. Cornélis, S. Lambert, P. Laszlo and P. Schaus, J. Org. Chem.,1981,46,2130 and personal communications.

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August 12, 1981

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

Nitrogen Metabolism by CPMAS N-15 NMR

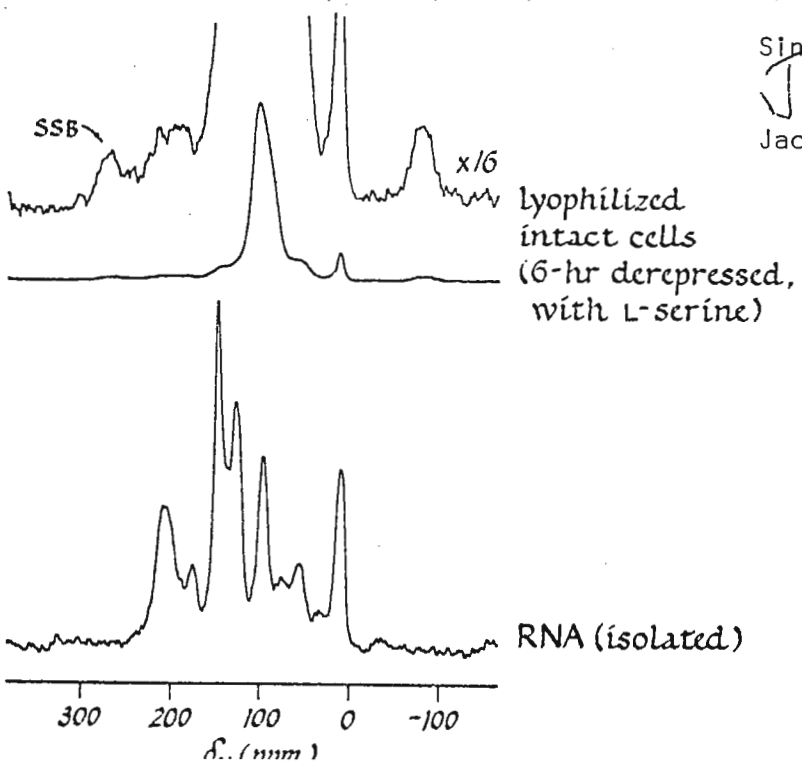
Dear Barry:

Cross-polarization magic-angle spinning (CPMAS) ^{15}N nmr of intact lyophilized *Neurospora crassa* grown in ^{15}N-nitrate medium as a function of time showed the incorporation and subsequent metabolism of label, with, for example, individual lines observed for nitrogen in lysine, arginine, and histidine residues. The time dependence of the intensity of each of these lines over an eight-hour period resulted in a detailed budget for nitrogen metabolism impossible to achieve with a nitrogen radiolabel (^{13}N halflife of 10 minutes). We have extended these experiments to studies of nitrogen fixation by *Klebsiella pneumoniae* introducing label uniformly via $^{15}N_2$. An unexpected result of some early experiments is the observation of a separate resonance associated with purine nitrogen of ribosomal RNA (δ_N=200 ppm, top spectrum). We are in the process of performing various relaxation experiments which will allow our using this peak to quantify the extent of label directed into RNA synthesis. Ultimately we hope to perform these experiments on intact viable cells.

Sincerely,

Jake

Jacob Schaefer



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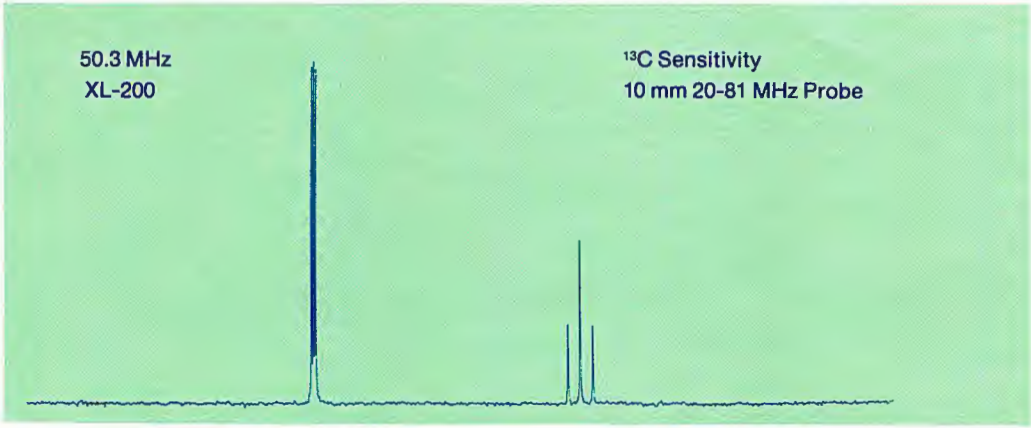
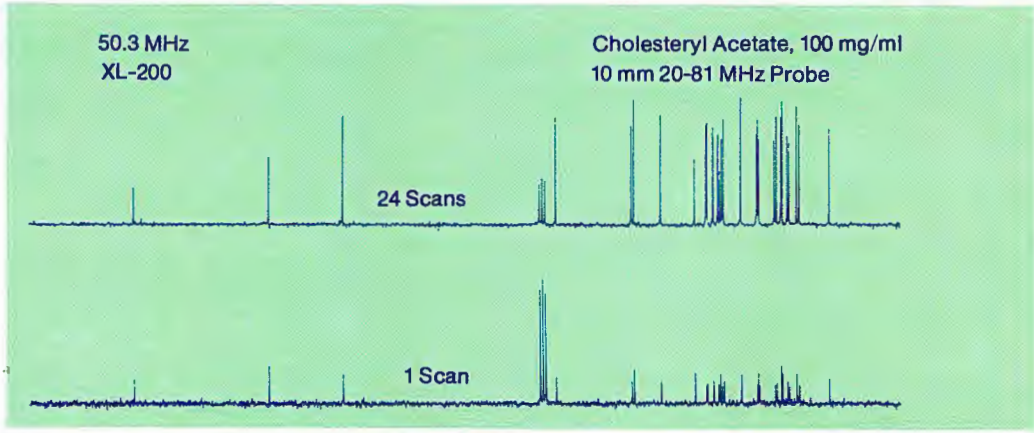
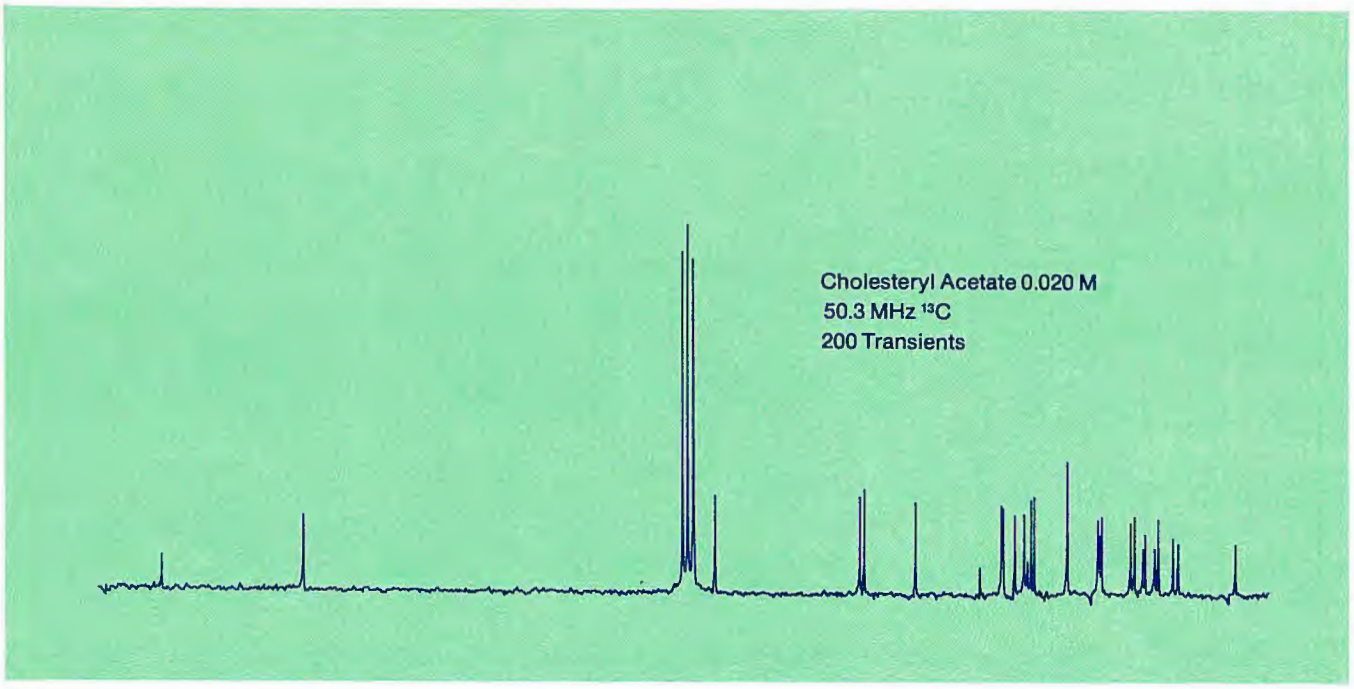


^{13}C Sensitivity Test: Single transient following 90° pulse on 60% C_6D_6/40% dioxane using the 10 mm 20-81 MHz broadband probe.

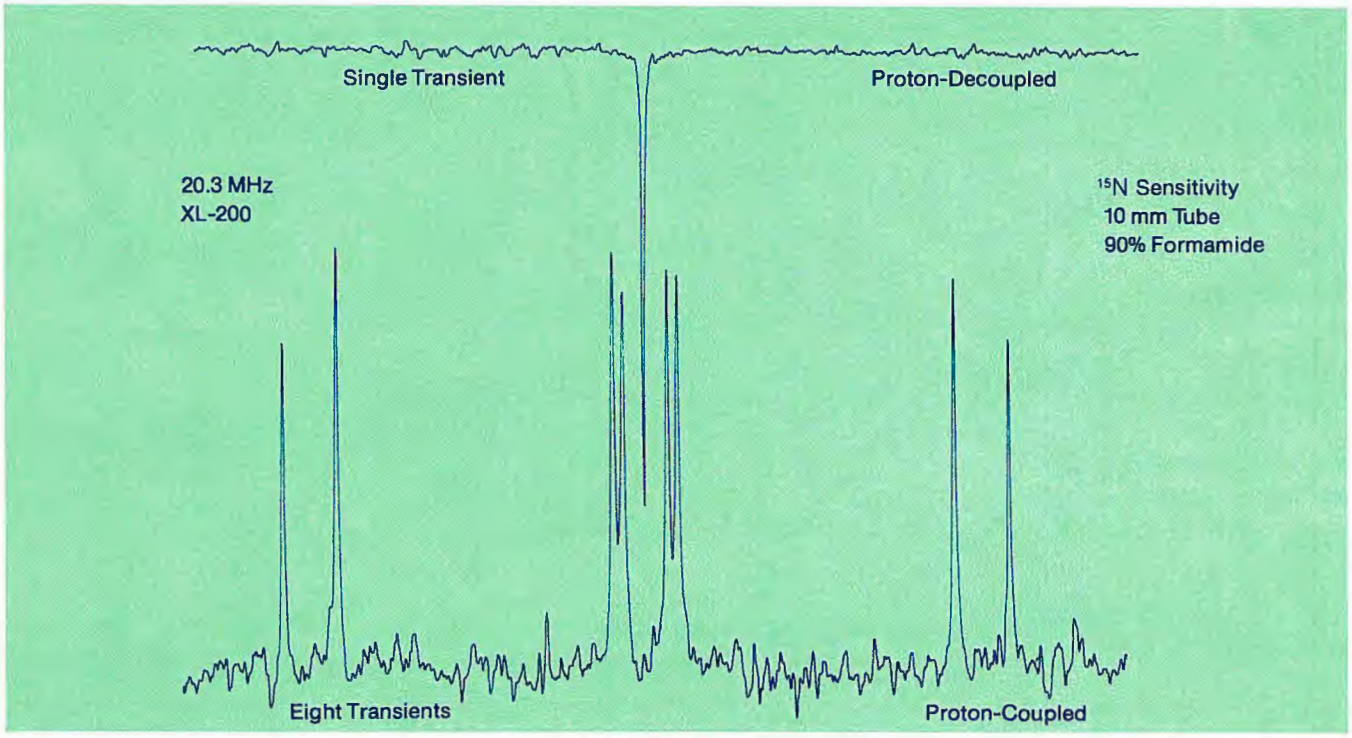


^{13}C Sensitivity Test: Cholesteryl acetate, 100 mg/ml, 10 mm broadband probe. Transients accumulated using 90° pulses every 2.28 seconds with 0.5 Hz line-broadening.

Additional spectra appear on the following page



^{13}C Sensitivity Test: 0.02 molar cholesteryl acetate in a 16 mm tube, 200 transients.



^{15}N Sensitivity Test: 90% Formamide in dmso-d_6, 10 mm 20-81 MHz broadband probe. Upper trace: single-transient (with NOE) proton-decoupled. Lower trace: eight transients, coupled (with NOE) 8-second acquisition time, 20-second delay time.

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

August 3,1981

Title: Selectively Fluorine and Spin Labeled Neurotoxin

Dear Barry:

To evaluate intramolecular distances in the spatial structure of polypeptide neurotoxin in solution (1) we incorporate selectively two different labels in the Central Asian Naja naja oxiana neurotoxin II (NT-II).

Firstly, the mono-spin labeled (SL) derivative was prepared by treating NT-II with one equivalent of 2,2,6,6-tetramethyl-4-carboxymethylpiperidyl-1-oxyl N-hydroxysuccinimide ester. The individual [SL-Lys-27]NT-II product was treated with excess of trifluoroacetic acid phenyl ester and two derivatives were isolated: (A) tetra-trifluoroacetyl[Leu-1, Lys-15, Lys-26, Lys-47]-[SL-Lys-27]NT-II, and (B) penta-trifluoroacetyl[Leu-1, Lys-15, Lys-26, Lys-45, Lys-47]-[SL-Lys-27]NT-II.

Fluorine resonances in the spectra of the spin label quenched A and B compounds were identified by comparison with assigned signals and their chemical shift vs. pH dependencies of hexa-trifluoracetyl-NT-II (2).

The fluorine spectra of A and B derivatives were decomposed by iterative procedure on a HP-computer with plotter as shown in the Figure. Calculated line widths of the individual resonances were used in calculation of apparent distances between the spin label on Lys-27 and corresponding fluorine groups by Bloembergen equation. The results are shown in the Table together with the data obtained previously from EPR spectra of di-spin labeled NT-II derivatives at liquid nitrogen temperature (3) and

TABLE

Residue	Paramagnetic Line Width, Hz	Distance from Lys-27, nm		
		F-19 NMR	EPR	X-Ray
Leu-1	<0.5	>1.8	-	1.9
Lys-15	6.5 ± 0.5	1.35 ± 0.06	1.42	2.1
Lys-26	8.5 ± 0.5	1.25 ± 0.05	1.53	1.4
Lys-45	4.5 ± 0.5	1.45 ± 0.07	1.45	1.1
Lys-47	27 ± 3	1.0 ± 0.1	1.3	0.8

from the X-ray crystallography of homologoues erabutoxin b (4).

The pronounced difference in the Lys-27 — Lys-15 distances could be easily realised on the three-dimensional molecular model as being due to local conformational mobility of the corresponding side chains.

Sincerely yours,

Vladimir

Vladimir Bystrov

References:

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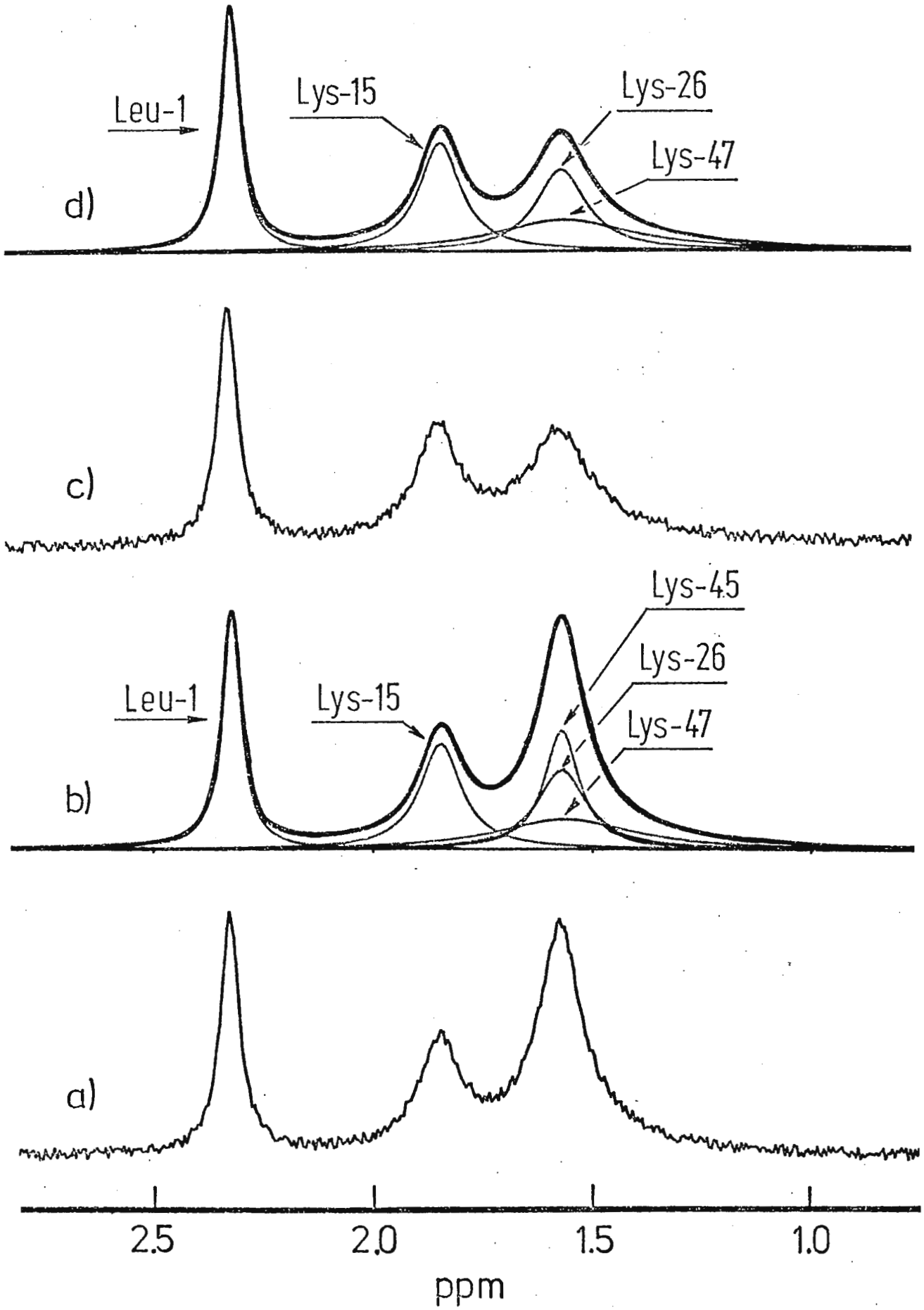
FIGURE : a) and c) - F-19 NMR spectra of A and B derivatives, respectively.
b) and d) - Their computer decomposition.


Leu-1
Lys-15
Lys-26
Lys-47
d)
c)
Lys-45
Lys-26
Leu-1
Lys-15
Lys-47
b)
a)
2.5
2.0
1.5
1.0
ppm

Princeton University DEPARTMENT OF CHEMISTRY
PRINCETON, NEW JERSEY 08544

August 5, 1981

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

Title: ^{13}C Investigation of Mesoionic Compounds

Dear Professor Shapiro:

A certain J. S. Baum (well-known to this author) published some work on cycloaddition reactions of activated isocyanates with anhydro-4-hydroxythiazolium systems (1).[1] These reactions were claimed to give cycloadducts of structure 2, but a recent paper[2] cast some doubt on the structure of these compounds, and further head scratching afforded two possible mesoionic structures 3 and 4 for the products of these reactions. As these compounds proved to be quite stable over the years, and since Baum and Potts have a good pack rat instinct and never discard anything, it was decided to reinvestigate the ^{1}H, and investigate the ^{13}C NMR spectra to clear up all doubt.

The ^{1}H spectra pointed toward the mesoionic compounds right away, with the N-CH_3 chemical shifts at 4.20δ for the a structures, and 4.21δ for the b structures, leading one to postulate a methyl group on positively charged nitrogen. The ^{13}C spectra (coupled and decoupled; chemical shifts are shown on the structures 4a and 4b) are consistent with structures 4a and 4b, as the singlets at 113.1δ and 113.0δ showed. The $^{1}J_{CH}$ coupling constants for the N-CH_3 groups again indicated substantial positive charge on nitrogen, these values being 145.8 Hz for 4a and 145.7 Hz for 4b.

I trust this contribution will serve to reinstate me in the good graces of the TAMUNN after a too-long hiatus.

Sincerely yours,
Mary W. Baum
Mary W. Baum

[1] K.T. Potts, J. Baum, S. K. Datta and E. Houghton, J. Org. Chem. 41, 813 (1976).

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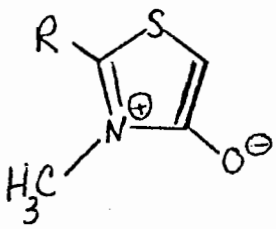
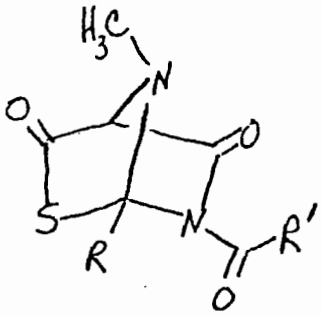
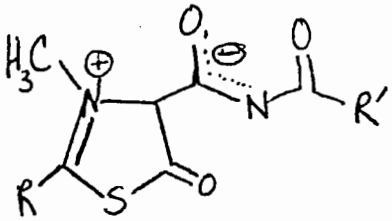


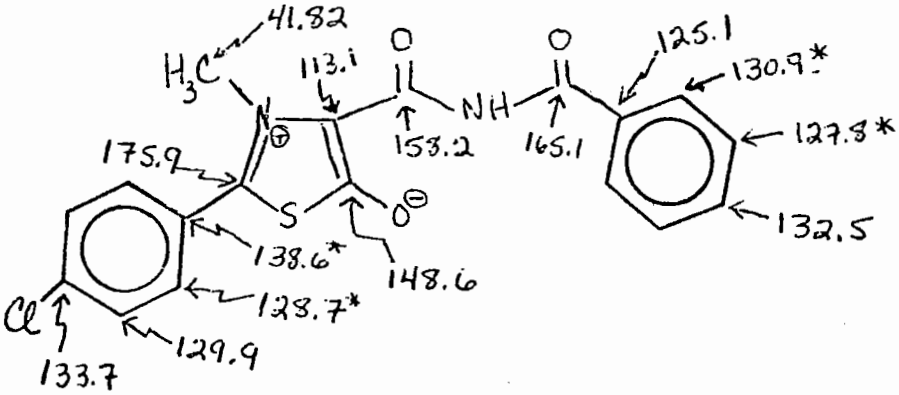
1 a, b



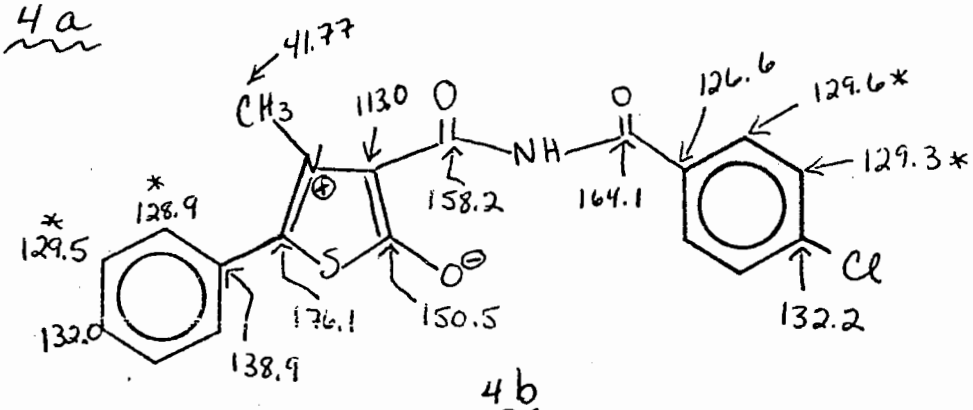
2 a, b



3 a, b



4 a



4 b

* On each compound, shifts bearing * may be incorrectly assigned.

University of East Anglia

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

12th August 1981

SOLID-STATE ^{13}C NMR OF PLATINUM COMPOUNDS

Dear Barry,

For a number of years we have been operating a home-built spectrometer for high-resolution ^{13}C NMR studies of solids at 22.6 MHz using the high-power-decoupling, cross-polarization and magic-angle rotation suite of techniques [1]. Recently we have been looking at a number of samples of platinum complexes supplied by the Johnson Matthey Research Centre. We have now become accustomed to seeing effects which differ from those in solution, and, indeed, we are puzzled by some of the features displayed by the platinum compounds. However, we feel the attached spectrum might interest TAMUNMR readers, since it provides a clear NMR example of the freezing of molecular motion in the solid state, and we believe it is the first observed example for metal compounds using high-resolution ^{13}C NMR. In this case the solid-state structure is known from X-ray studies [2], and the ring conformation ensures the two CH_2 groups bonded to the six-membered ring are non-equivalent, giving ^{13}C resonances at 35.7 and 28.4 ppm from TMS. In solution, of course, rapid inversion of the six-membered ring results in equivalence of these two CH_2 carbons. The solid state thus gives better structural information and also allows shielding effects to be better related to molecular geometry.

Our spectra should show splittings due to (Pt,C) coupling, but clearly this is not so for the attached Figure. However, splittings of 72 Hz and 46 Hz are shown for the methine and methyl carbons, respectively, of platinum bisacetylacetonate. These values relate well to those found [3] in solution.

We hope this keeps us "solvent" with respect to TAMUNMR.

Best wishes

Robin Ken Chris.

R.K. HARRIS K.J. PACKER C.J. GROOMBRIDGE

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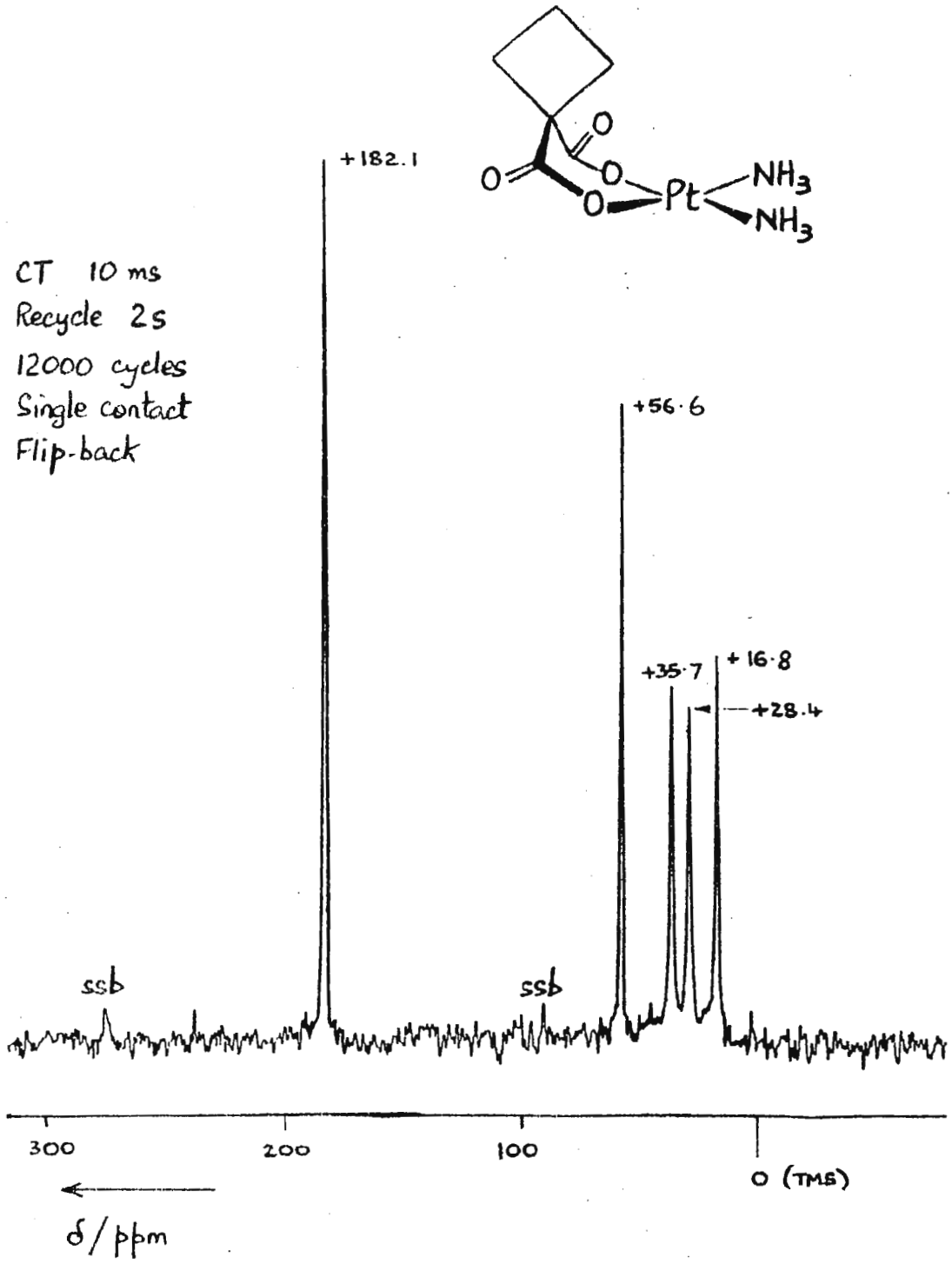
CP-MAR ^{13}C NMR SPECTRUM

of cis-(diammino)(1,1-cyclobutanedicarboxylato) Pt(II)



276-17

The University of Connecticut

STORRS, CONNECTICUT 06268

THE COLLEGE OF
LIBERAL ARTS AND SCIENCES
Department of Chemistry

August 13, 1981

Dear Professor Shapiro:

Recently we reported the observation of quadrupolar splittings for deuterated solvents in swollen, uniaxially strained elastomers.[1] We are currently restricted to examining such materials in a single orientation with our iron-magnetic high resolution spectrometer: the strain direction is at right angles to the field $\vec{H}$. However, this summer Bertrand Deloche and I were able to devise a technique for examining such samples in uniaxial compression. Moreover, we could rotate the sample within the 5mm sample space to specified orientations of the compression direction $\vec{c}$ relative to $\vec{H}$. When $\theta = 90°$, $\vec{H}$ is in the plane of the compressed elastomer and the translational diffusion of the solvent appears to be insufficient to completely average the quadrupolar interactions to a discreet dublet. The resulting spectrum is remeniscent of those observed in cholesteric liquid crystals for slowly diffusing species.[2] We are pursuing these studies to probe "nematic-like" arrangements of the polymer chains in deformed elastomers.

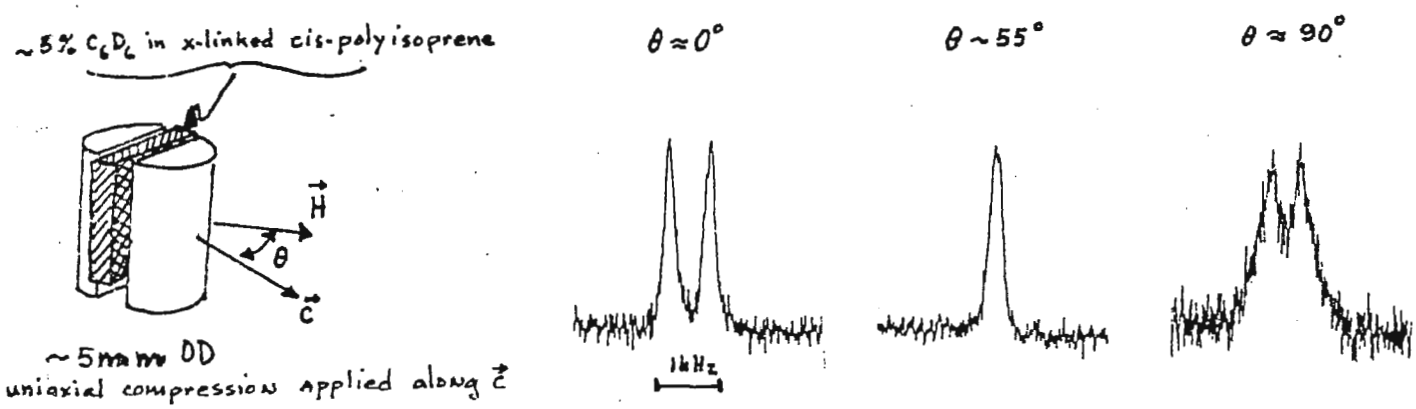
Very truly yours,

Edward T. Samulski

ETS:mr

References:

1. B. Deloche and E. T. Samulski, Macromolecules 14, 575 (1981).
2. Z. Luz, R. Poupko and E. T. Samulski, J. Chem. Phys. 74, 5825 (1981).



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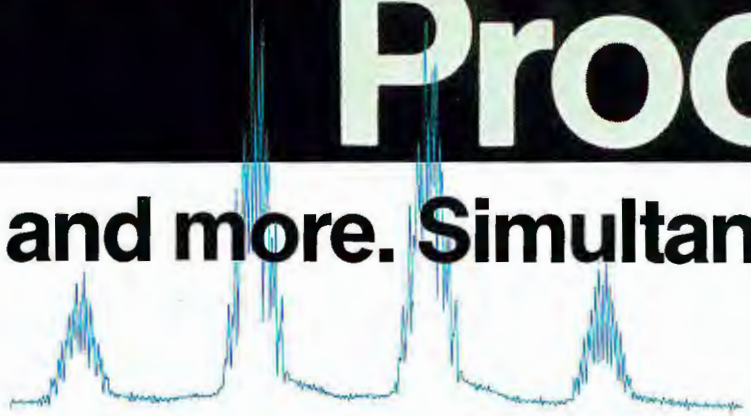

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July 30, 1981

Professor Bernard Shapiro
Dept. of Chemistry
Texas A & M University
College Station - TX 77843 - USA

MONTEDIPE/PM/CER
Stab. Petrolchimico
via della Chimica
30175 Porto Marghera
(Venezia) Italy

Dear Professor Shapiro,

Title: ^{13}C chemical shift assignements, spin-lattice determination and quantitative analysis of a model elastomeric polyurethane

We have analyzed in our laboratory a number of linear elastomeric polyurethanes by ^{13}C pulsed NMR spectroscopy using a Bruker WH90.

The aim of this work was to check the quantitative NMR analysis according to the data from laboratory synthesis. We chose a sample amid these polyurethanes (PIPNEG) that was of a particular interest by virtue of its components: neopentylglycol (NEO), hydroxy pivalic acid (PIV), butanediol (BUT), adipic acid (ADA) and methane-bis (p-phenyl-isocyanate) (MDI). A 11% (w/v) solution was used in 10 mm. o.d. tubes at 112°C under the following experimental conditions: pulse angle=55°, cycle time: 7sec, sweep width: 6000 Hz, memory: 8K. About 2000 sweeps were needed to obtain a satisfactory signal to noise ratio in the decoupled spectrum. To justify the cycle time we report a list of T_1 values of the different carbons of the copolymer (Table 1). From the comparison of the experimental chemical shifts with those of model compounds and of other polyurethanes, the lines of the spectrum were assigned and it was possible to obtain a quantitative analysis of the components. For the determination of the T_1 values the following experimental conditions were adopted using the usual inversion recovery method: cycle time: 15 sec, number of spectra: 8, delay between 180° and 90°pulse: 12 sec, 12/1.85, 12/1.85[2], etc. We remember that the T_1 values determined at 130° C for another polyurethane sample[1] (BUT/MDI/ADA) of similar molecular weight: $\bar{M}n$=25000, as reported in a previous letter (1), were much higher for the corresponding carbon atoms.

This was partially justified from the different nature of the copolymer and the higher temperature. The T_1 values of the carbon atoms corresponding to the lines used for the quantitative determination are in the range 0.6-1.4 sec. We calculated the molar percentages of the comonomers on the basis of the following chemical shifts: δ_1 for NEO, δ_2 for PIV, δ_4 and δ_8 for BUT δ_3 and δ_5 for ADA and δ_{12}, δ_{13} for MDI (Table 2). Data are reported from the 100 and 10 Hz/cm integrals together with the syntesis data.

TABLE 1

^{13}C Chemical shifts (EMDS = 0)	Assignements	T_1 (sec)
δ_1 = 19.43	CH_3 NEO	1.3
δ_2 = 20.08	CH_3 PIV	
δ_3 = 22.03	β CH_2 ADA	1.4
δ_4 = 23.53	β CH_2 BUT	0.9
δ_5 = 31.325	α CH_2 ADA	1.0
δ_6 = 32.885	C NEO	4.4
δ_7 = 40.55	C PIV	(*)
δ_8 = 61.935	α CH_2 BUT	0.6
δ_9 = 66.81, δ_{10} = 67.39, δ_{11} = 68.01	α CH_2 NEO + CH_2O PIV	0.7
δ_{12}=117.05	CH m,o of MDI	1.0
δ_{13}=126.86	CH o,m of MDI	1.0
δ_{14}=133.68	j,j of MDI	5.1
δ_{15}=135.31	j,j of MDI	4.6
δ_{16}=151.88	OCO NH	undet.
δ_{17}=170.21, δ_{18}=170.40	COO ADA	undet.
δ_{19}=172.6	COO PIV	undet.

(*) Undetermined because of overlapping with $dmso_{d6}$

TABLE 2

% Moles	100 Hz/cm		100 Hz/cm		Syntesis data	
W' MDI	18.5	38.6	20.0	38.7	17.1	37.9
W' ADA	20.1		18.7		20.8	
W' PIV	24.7		23.5		24.2	
W' BUT	15.1	36.7	13.4	37.8	13.7	37.9
W' NEO	21.6		24.4		24.2	

We can observe that the relationship $W'_{MDI} + W'_{ADA} \simeq W'_{BUT} + W'_{NEO}$ is obeyed and that we obtained a satisfactory fit with the synthesis data.

Yours sincerely

Giorgio Gurato — G. GURATO

Gianfranco Lunardon — G. LUNARDON(°)

Giorgio Rigatti — G. RIGATTI(°°)

(°) Montepolimeri SpA/URI/PM

(°°) Istituto di Chimica Fisica of the University, via Loredan 2, Padova

References

(1) G. Gurato and G. Rigatti. TAMUNN n°250 July 1979, pag.41

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

14th. August 1981.

Dear Professor Shapiro

$^{35}Cl/^{37}Cl$ and $^{79}Br/^{81}Br$ Isotope effects.

In responce to the letter from Dr. Brevard (TAMU No. 272) we note that the additional fine structure he observed in the ^{103}Rh spectrum of $RhCl_6^{3-}$ from $^{35}Cl/^{37}Cl$ isotope effects is identical to our observation of the same effect in the ^{195}Pt spectra of $PtCl_6^{2-}$ and $PtBr_6^{2-}$ (1).

It would seem that under favourable conditions small isotope effects such as these can be readily detected in both organic and inorganic molecules. A recent example of this comes from work undertaken in this laboratory on the ^{31}P spectra of PCl_3 and PBr_3 where the isotope effects can be readily seen (Figure 1) (2). The increasing use of high field instruments will undoubtedly reveal more such effects and n.m.r. spectroscopists should consider the possibility of isotope shifts before seeking alternative explanations (mass spectroscopists have recognised these splitting patterns for some time).

Please credit this contribution to the ULIRS/Ed Randall account.

Best Wishes.

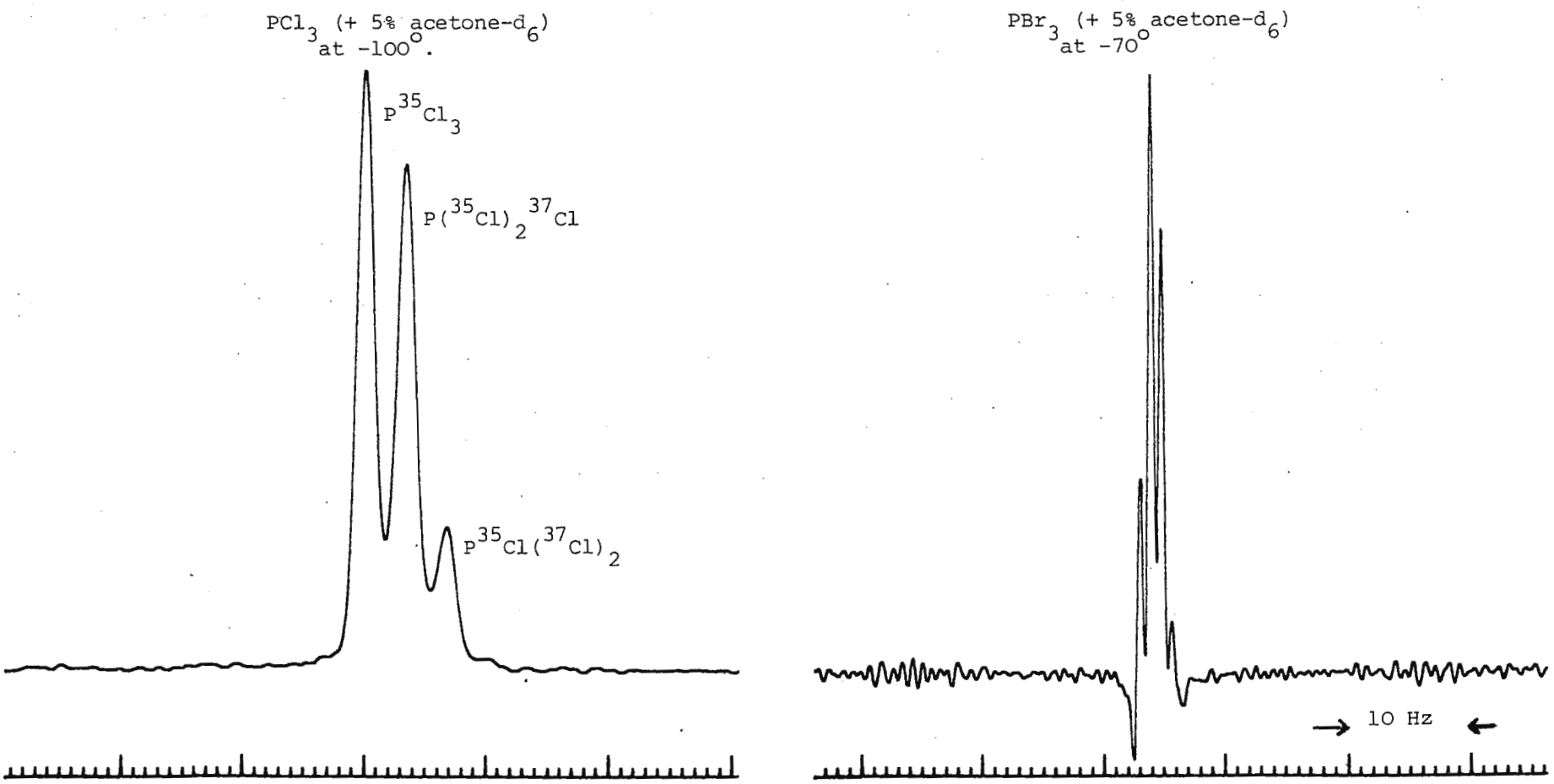
Yours Sincerely,

Peter Sadler — P.J. Sadler
I.M. Ismail — I.M. Ismail
G.E. Hawkes — G.E. Hawkes
M.J. Buckingham — M.J. Buckingham

REFERENCES. 1. I.M. Ismail, J.S. Kerrison, and P.J. Sadler, J.C.S. Chem. Comm., 1175, (1980).

2. I.M. Ismail, P.J. Sadler, M.J. Buckingham, and G.E. Hawkes, Unpublished results.

^{31}P spectra at 162 MHz from ULIRS WH-400 NMR Service at Queen Mary College.



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Uppsala 17/8 1981

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

"Size-resolved NMR"

Dear Professor Shapiro,

Thank you for your yellow reminder. The pulsed-gradient spin-echo experiment, when performed in the FT mode(*) is remarkably useful in providing quantitative physico-chemical information in the form of molecular self-diffusion coefficients (D) for complex systems in solution(**). We have even noted that it may be of use as an analytical tool.

With the 90°-t-δ-t-180°-t-δ-t-acquisition sequence (t-δ--t=Δ) the Fourier-transformed spin-echo signals decay with increasing δ according to

$$A_i = c_i \cdot \exp(-(\gamma G \delta)^2 D_i (\Delta - \tfrac{1}{3}\delta))$$

if Δ is kept constant. Regardless of any J-modulation or T_2 effects this will be true for each part of an NMR signal if there is only one component in solution, because all nuclei in a molecule necessarily diffuse at equal rates on the time-scale of the experiment. Therefore (apart from a common amplitude factor) the whole bandshape is constant for all δ-values under these conditions. An experiment (G ≈ 1 Gauss/cm) is illustrated in figure a (neat decanol). Even at high gain the decanol difference spectrum is essentially zero. (These spin-echo spectra are recorded at arbitrary vertical gain, and the difference spectra have been obtained through data manipulation so as to null the $C\underline{H}_2OH$ signals by subtraction in memory.) Note that the bandshape from a multicomponent sample necessarily must change during an experiment of the present kind (unless all molecules have equal self-diffusion coefficients). This is illustrated in b (50/50 decane-decanol). Nulling the H_2OH band (and thus the whole decanol bandshape)

leaves only the decane spin-echo spectrum. The same procedure could , of course , be extended to more than two components, provided that each component gives at least one isolated NMR band.

A longer version of this letter will appear in Anal. Chem. in the near future. With best wishes.

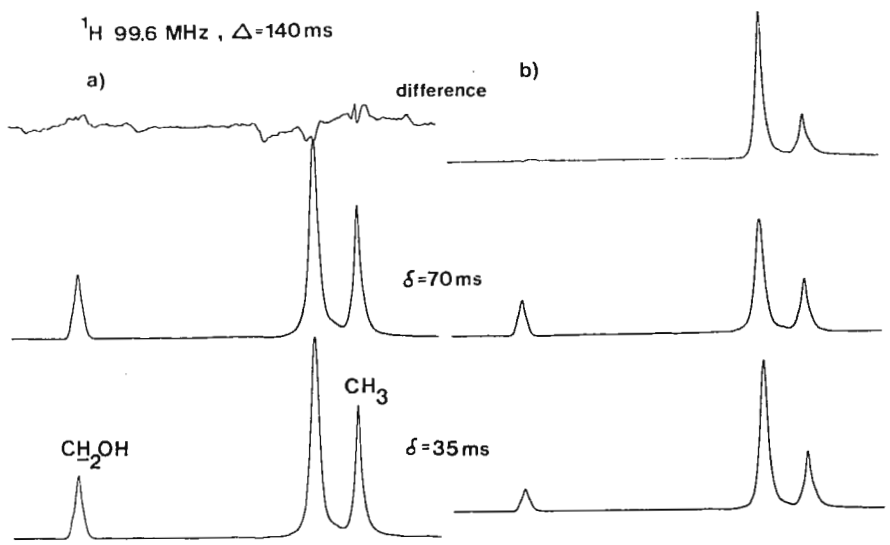
Yours sincerely

Peter Stilbs

/Peter Stilbs/

(*) The idea on which FT-PGSE is based originates from a paper by Vold, Waugh, Klein and Phelps, J. Chem. Phys. 48 (1968) 3831. The first experiments were apparently made by James and McDonald in 1973.

(**) See e.g. recent and forthcoming papers in J. Magn. Res., J. Phys. Chem., Polymer, J. Colloid Interface Sci. and Chemica Scripta, co-authored by B. Lindman, M.E. Moseley, J. Roots and B. Nyström.



Dr. Ludger Ernst
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Professor B.L. Shapiro
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Texas A & M University

College Station, TX 77843
USA

GBF
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Dr. Ernst Lustig

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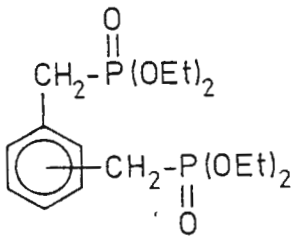
		05 31/70 08 306	18. August 1981 E/ud

Determination of the relative signs of interbenzylic $^{31}P,^{31}P$ spin coupling constants from SPI difference spectra

Dear Dr. Shapiro:

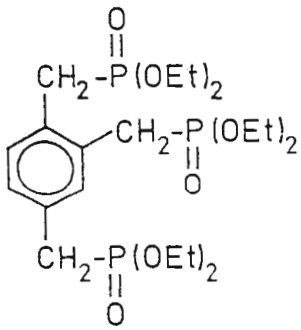
some time ago[1] we reported interbenzylic P,P spin coupling constants over five, six, and seven bonds in the xylylene diphosphonates 1.



1

isomer	$\lvert J_{PP} \rvert$ [Hz]
ortho	9.0
meta	3.1
para	7.8

These J_{PP} are thought to be transmitted mainly through the aromatic π-system, as are the corresponding J_{CH_3,CH_3} in the xylenes[2]. One expects opposite signs for the couplings over an even and over an odd number of bonds. Because the spectra of the series 1 are not suitable for double resonance experiments, we synthesized 2, which contains the three types of J_{PP} in the same molecule and which gives a nice three spin system of ^{31}P nuclei when the protons are broadband decoupled (Figure 1a). Having no triple resonance facilities on our WM-400 spectrometer (^{31}P at 162 MHz), we used the INDOR-like selective population inversion difference



2

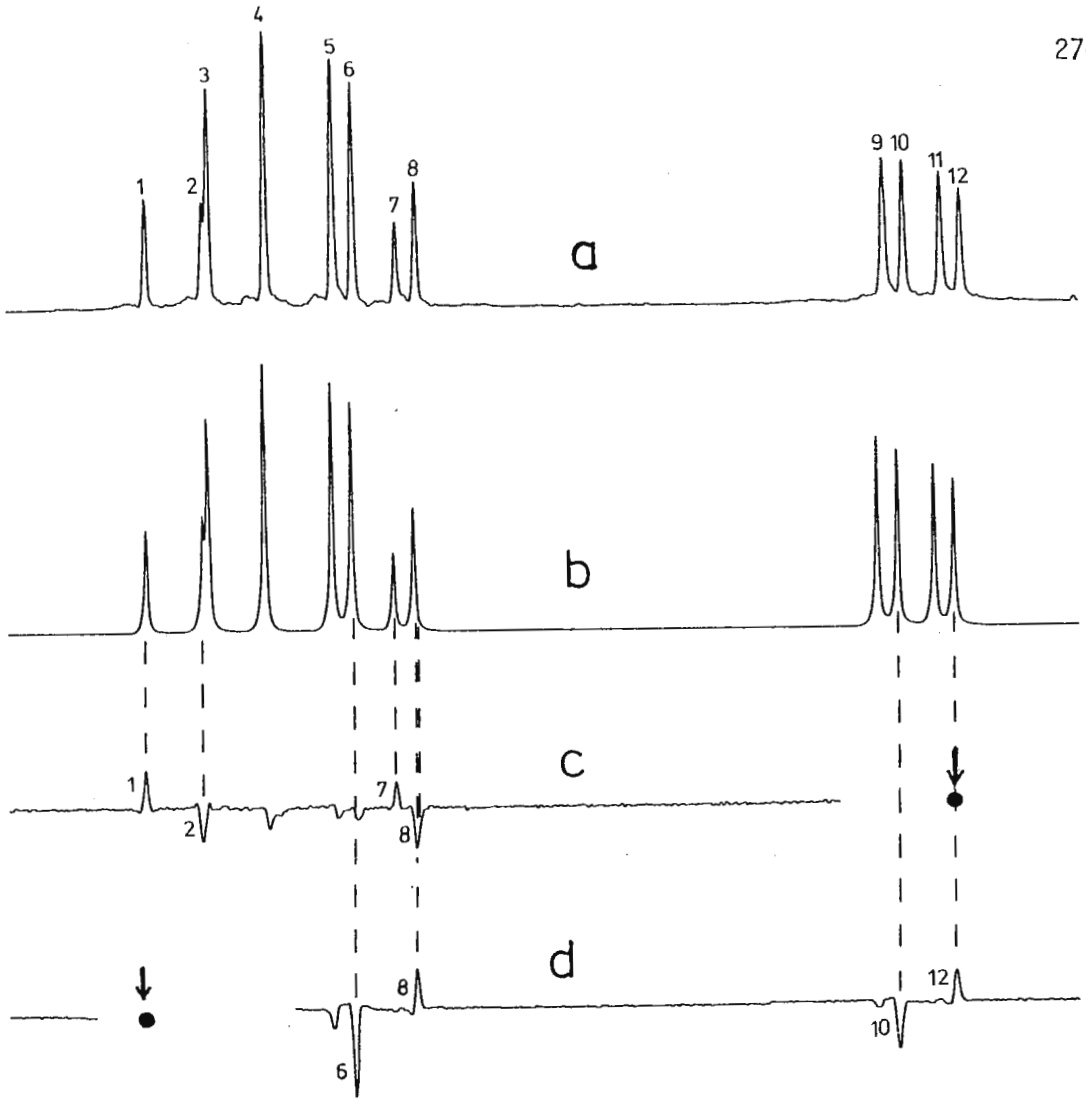


Fig. 1. (a) 162 MHz $^{31}P\{^{1}H\}$ NMR spectrum of 2 (d_6-acetone solution); (b) simulated; (c) SPIDIF spectrum with inversion of transition 12; (d) as in (c) but inverting transition 1.

spectroscopy[3] instead. We inverted a ^{31}P transition by applying a selective pulse (to line 12 in Fig. 1c; to line 1 in Fig. 1d) followed by the nonselective observing pulse. From the resulting FID the normal FID was then subtracted. The broadband ^{1}H decoupler was permanently on. The pseudo-INDOR spectra in Figures 1c and 1d show that the sign of the smallest coupling, $^{6}J_{PP}^{meta}$, is opposite to those of the two larger ones, $^{5}J_{PP}^{ortho}$ and $^{7}J_{PP}^{para}$, as expected. The simulated spectrum is shown in Fig. 1b.

1. Ernst, J.C.S. Chem. Commun. 375 (1977).
2. Macdonald & Reynolds, Can. J. Chem. 48, 1002 (1970).
3. Pachler & Wessels, J.C.S. Chem. Commun. 1038 (1974).

Yours sincerely,

Ludger Ernst

JEOL (U.S.A.), INC. • ANALYTICAL INSTRUMENTS DIVISION
235 BIRCHWOOD AVENUE • CRANFORD, NEW JERSEY 07016
TELEX NO. 13-8840 • (201) 272-8820

August 25, 1981

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

Dear Barry:

USE OF THE DIXON SEQUENCE FOR SUPPRESSION OF
SPINNING SIDEBANDS IN SOLID STATE SPECTRA

We recently have been using the Dixon[1] sequence for spinning sideband elimination on the FX-200 equipped with CP/MAS solids accessory. Our initial experiments indicate this technique will prove quite useful in removing spinning sidebands which are inevitable in high field solid state spectra. The ^{13}C CP/MAS spectrum of vanillin is depicted in Figure 1a complete with complicating spinning sidebands (ν_{rot} = 3630 Hz, Kel-F rotor). Figure 1b shows the addition spectrum of the same sample which removes the first order spinning sidebands as a result of the Dixon sequence. Solid state spectra of hexamethylbenzene in Figures 2a - c show the "normal" spectrum, 180° phase inverted 1st order SSB spectrum and the addition spectrum (a-b), respectively.

Note the presence of 2nd order SSB's in the HMB spectrum which may be removed either by additional applications of the Dixon technique or, from a practical viewpoint, by rapid spinning rates (∿ 4 KHz). Quantitation using this technique may prove difficult due to the substantial delays required in the pulse sequence and we are investigating these possibilities as well as the use of SSB free spectra for other nuclei (e.g. ^{31}P).

We feel the Dixon sequence will become a very useful technique in solid state NMR and we tip our rotors to Dr. Dixon for development of this clever approach.

Sincerely yours,

H. Cecil Charles
Applications Chemist

Michael J. Albright
NMR Product Manager

HCC:MJA/mjd

1. Dixon, W. Thomas, J. Magn. Res., 1981, 44, 220.

Vanillin

"NORMAL"
Spectrum

↑ = SSB

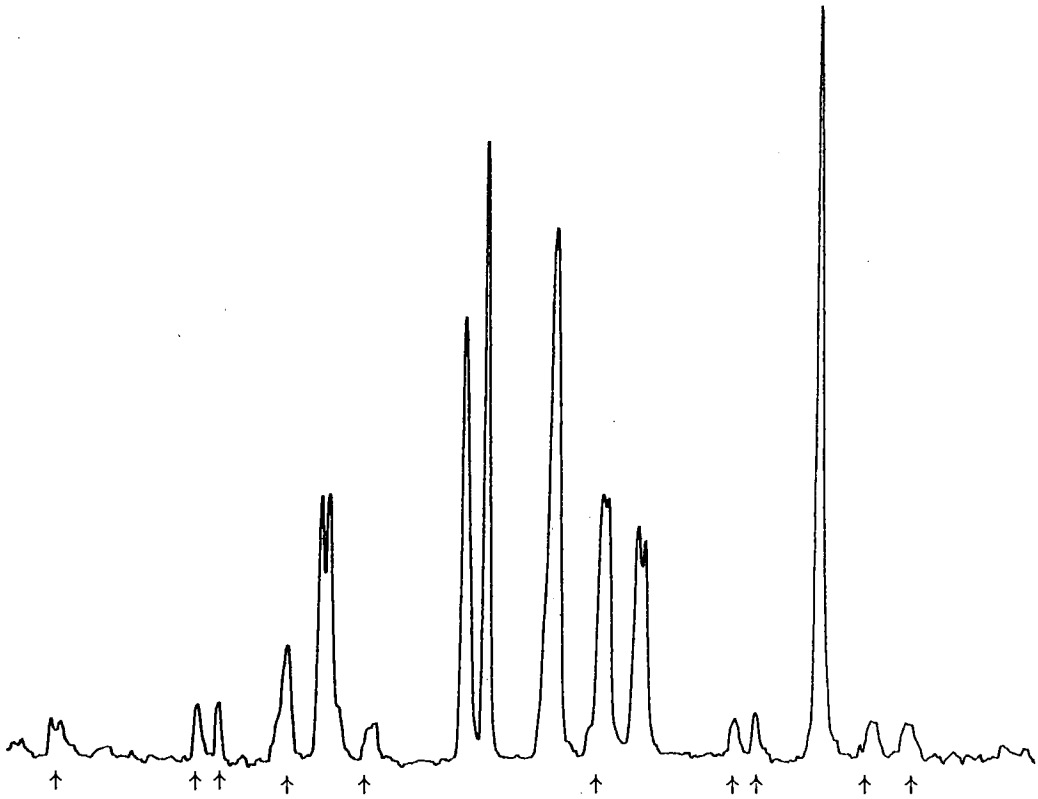


Fig. 1a

SSB FREE
Spectrum

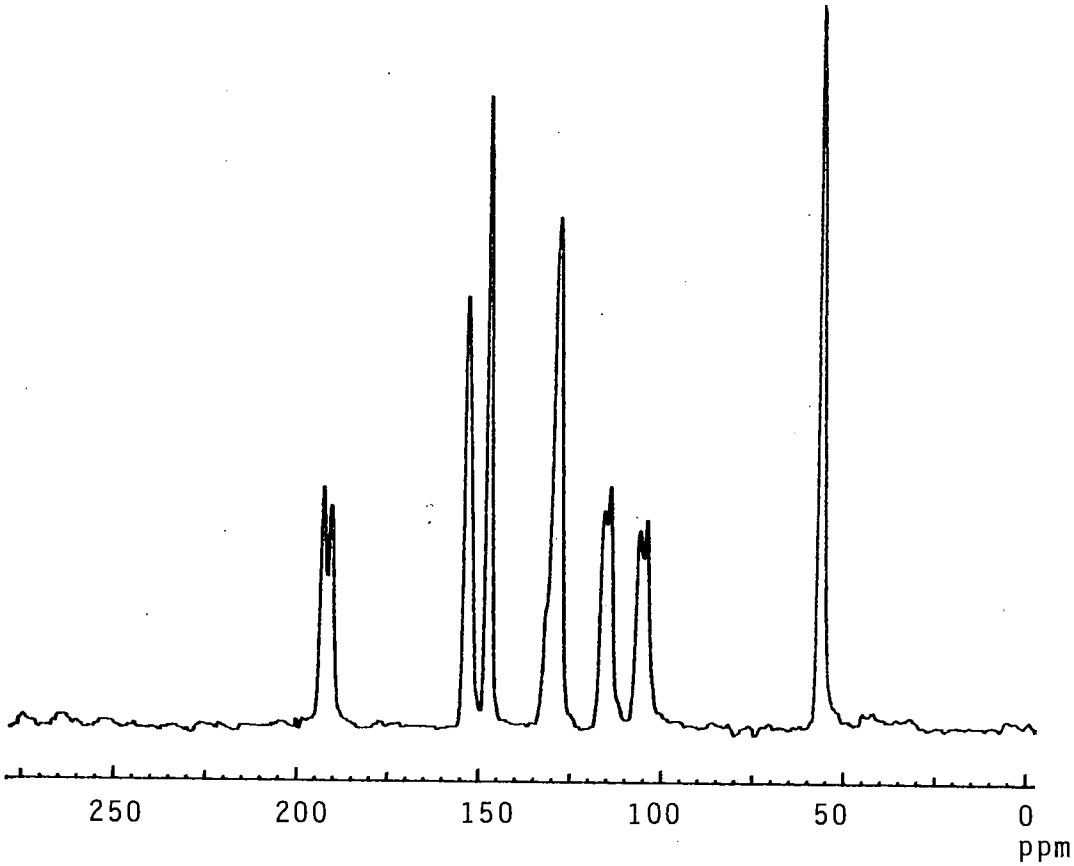


Fig. 1b

Hexamethylbenzene

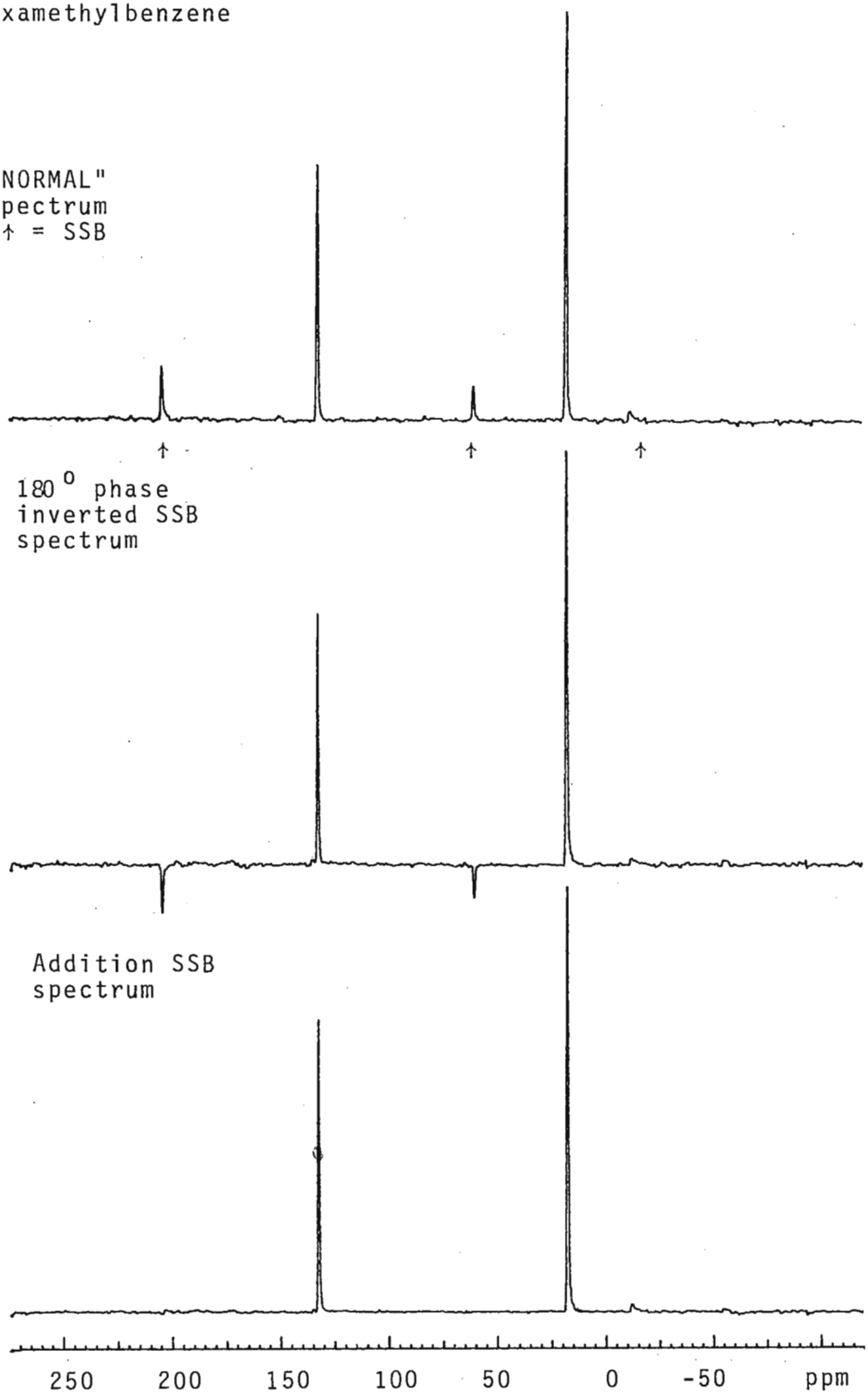


Fig. 2a

Fig. 2b

Fig. 2c

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	Noise Floor:	— 135dBc/Hz
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Texas A & M University
Department of Chemistry
College Station
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U. S. A.

5900 Siegen 21, August 21, 1981
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Postfach 210209
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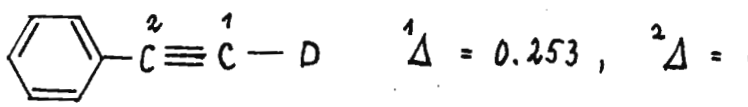
Durchwahl 740 4390/4400

More $^{2}H/^{1}H$ Isotope Effects on ^{13}C Chemical Shifts

Dear Barry,

we are again behind schedule with our contributions, and I hurry up to inform your readers that another rule generally accepted for deuterium isotope effects on carbon-13 chemical shifts has been found violated. In phenylacetylene we observed that the isotope effect over two bonds is nearly twice as large as that over one bond:



$^{1}\Delta = 0.253$, $^{2}\Delta = 0.426$ ppm

This is, to our knowledge, the first exception to the rule formulated by Batiz-Hernandez and Bernheim,[1] and frequently cited by Jameson,[2] that the isotope effect is decreasing with the number of bonds between the two atoms involved.

We are presently engaged in a more complete study of structural effects and hope to find other interesting information from molecules with large structural differences (hybridization, bond angles etc.).

Sincerely yours,

H. Günther J. Wesener

1) H. Batiz-Hernandez and R. A. Bernheim, Progr. Nucl. Magn. Reson. Spectrosc., 3, 63 (1967).

2) See e.g. Specialist Periodical Report, NMR, Vol 10, The Royal Society of Chemistry.

Wageningen
Department of Molecular Physics

Your reference BLS/lmk
Your letter of July 8, 1981
Our reference 81/397 dJ/jbw
Date August 21, 1981
Enclosures

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

Subject Improvement of the Redfield sequence

Dear Professor Shapiro,

In biological samples exchangeable protons are interesting. When the exchange is fast, these protons can only be detected in H_2O as the solvent. The concentration of the relevant protons is very low. The problem is the measurement of these weak resonances in the presence of the nearby, strong water peak.

The Redfield sequence (J. Magn. Res. 19, 114 (1975)) is one of the best solutions for the problem. With this pulse sequence the watertransient on our CXP 300 is about 100 times noise. Our improvement reduces the watertransient to less than 2 times noise. The phase and amplitude of the watertransient is more or less random. This is the reason for the distortion free baseline.

The Redfield sequence consists of a 2(+x)1(-x)4(+x)1(-x)2(+x) pulse. The length of this pulse is optimized for a minimal watertransient. The improvement consists of optimizing the length of the pulse and the phase of (-x). This is easily done on our CXP 300 by minimizing the watertransient by alternately turning the knob of the pulse length and the knob of the phase of (-x).

Please credit this contribution to the account of Prof. T.J. Schaafsma.

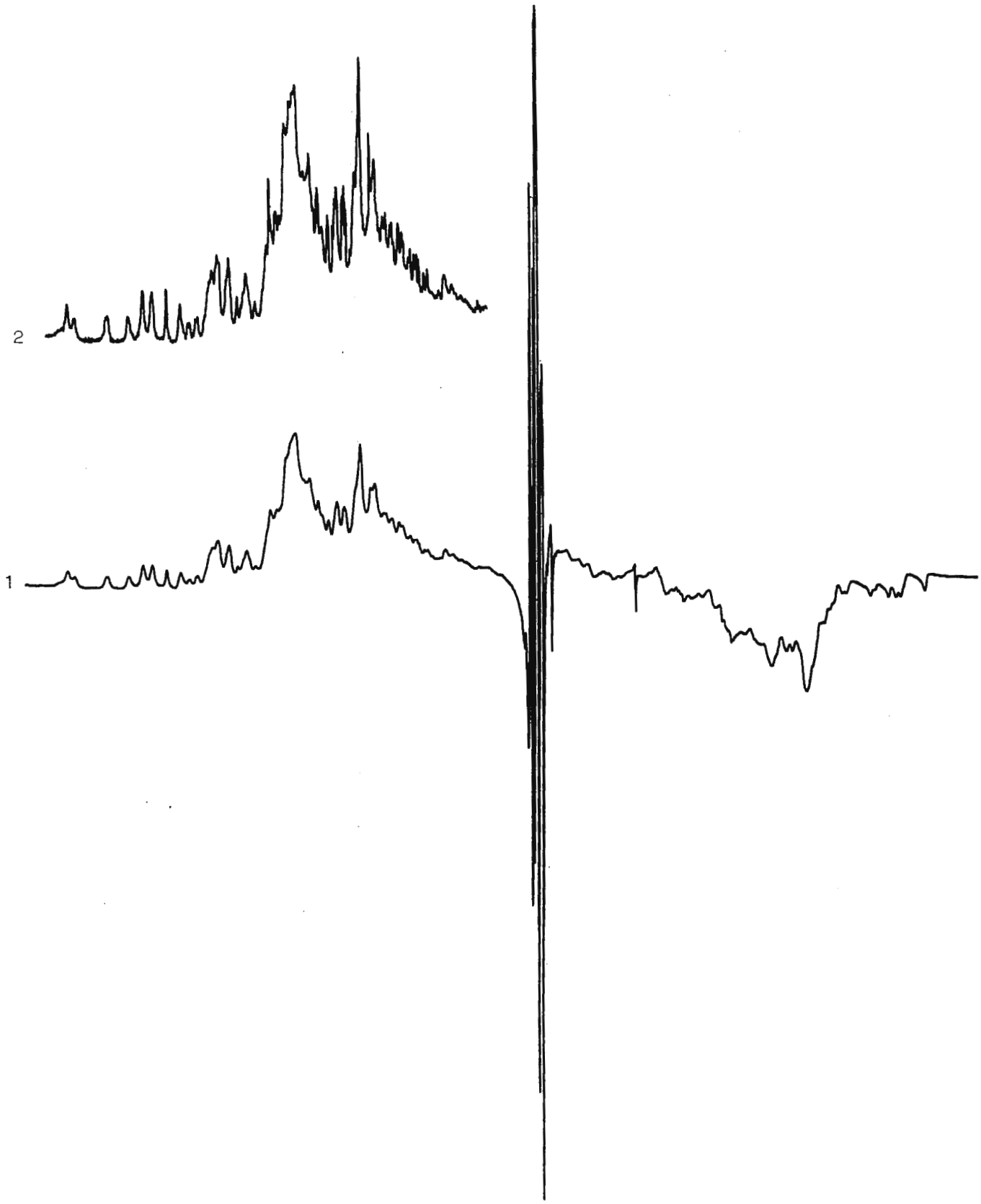
Adrie de Jager
Dept. of Mol.Physics

Chrit Moonen
Dept.of Biochemistry

Agricultural University/Transitorium, De Dreijen 11/6703 BC Wageningen/The Netherlands/Tel. (08370) 82044/82634

Figure 1. 1mM Flavodoxine (MW 15.000) in 90% H_2O 10% D_2O; spinning 5 mm tube; 20.000 transients of 0.5s; no data-manipulating; 12 to -1.5 ppm.

Figure 2. Part of 1 with Gaussian multiplication.



UNIVERSITY COLLEGE OF SWANSEA

Department of Chemistry

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F.R.S.C

F.R.S.C

Professor of Chemistry

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

27th August, 1981.

Dear Dr. Shapiro,

We have used n.m.r. to follow the rates of solvolytic reactions over several hours in a thermostatted HA100 n.m.r. probe at 25°C. The "standard" procedure we tried initially utilised liquid nitrogen as the coolant, but careful adjustment of the settings for flow and heater controls was required to obtain specification precision (±0.5°C) over several hours. These settings varied siginficantly from day to day. Some kinetic runs were spoiled by temperature drifts of several degrees - temperatures were determined using the temperature dependent OH signal of methanol and checked using calibrated thermistors after rapidly removing the solution from the n.m.r. probe.

As only slight cooling of the probe is required to obtain 25°C we tried ice/water as the coolant. This leads to both more reliable and more convenient thermostatting of the n.m.r. probe.

The reactions we are examining are displacements of alkyl halides or esters (RX where X = halogen, sulfonate, phosphonate) by solvent (ROH where R = H, alkyl or fluoroalkyl). Such reactions are usually followed kinetically using conductometric or titrimetric techniques. The advantages of n.m.r. are: (i) strongly acidic reaction media, e.g. aqueous sulfuric acid, can be employed; (ii) small amounts of solvent are required - important for fluorinated alcohols as reaction media;[1] (iii) several signals of starting material or products can be monitored readily; (iv) theoretical "infinity" values for disappearance of starting materials can be

obtained easily. The main disadvantage of n.m.r. is that lower precision kinetic data is obtained because relative signal heights or areas cannot be obtained precisely and gases provide less precise thermostatting than liquids ($\pm 0.01^{\circ}C$ or better).

This work is being carried out by S. Jackson and S.J. Morris and we are grateful for skilled technical assistance from G. Llewellyn and M. Nettle.

Please credit this contribution to the account of Dr. J.M. Williams.

References.

1. T.W. Bentley, C.T. Bowen, W. Parker and C.I.F. Watt, J.Amer.Chem.Soc., 1979, 101, 2486.

Yours sincerely,

T W Bentley

T.W. Bentley.

Columbia University in the City of New York | New York, N.Y. 10027

DEPARTMENT OF CHEMISTRY
(212) 280-2577

Havemeyer Hall

August 11, 1981

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

Dear Professor Shapiro,

We have an opening for an NMR spectroscopist to manage the NMR facilities at Columbia. We would very much like to hear from anyone you feel would be a suitable candidate for the job.

The position involves serving as a consultant in NMR problems to our various inorganic and organic research groups as well as carrying out cooperative research with them. We are looking for someone with a thorough grasp of NMR experimental technique and spectral analysis. While a sound understanding of NMR equipment is highly desirable the candidate would not be responsible for more than routine maintenance repairs to the spectrometers. Assistance in running routine spectra would also be available.

Salary depends on experience and qualifications and eventual promotion to the level of Senior Research Associate would be possible.

Applications are to be sent to me and should include a curriculum vita, a list of publications and the names of two referesnces.

Your help is greatly appreciated.

Sincerely yours,

W. Clark Still
Professor of Chemistry

WCS:jb

SYRACUSE UNIVERSITY

DEPARTMENT OF CHEMISTRY | 108 BOWNE HALL | SYRACUSE, NEW YORK 13210

TELEPHONE 315/423-2925

August 27, 1981

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

Subject: BRUKER HX-60 SPECTROMETER FOR SALE

Dear Barry,

We have a Bruker HX-60 NMR Spectrometer for sale at a price of $5,000 plus removal and shipping costs (est. $2,500). This spectrometer is a CW instrument but it can be upgraded for FT or solids NMR. The configuration follows:

1. HX-60 console
   ^2H lock
   H^1 observe module

2. Magnet
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   with power supply

3. Probes 3 each 5 mm H^1 insert
   2 each 10 mm H^1 insert

Any interested parties should write to me at the above address or call (315) 423-4026 or 423-1021.

Yours sincerely,

George C. Levy
Professor

GCL:jrd

276-41

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College of Arts and Science

Department of Chemistry

123 Chemistry Building
Columbia, Missouri 65211
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Expertise in NMR in the physical, biophysical or biochemical areas is required in both positions. For inquiry or application (please submit c.v., references, and a list of publications) should be made to:

Professor T.C. Wong
Department of Chemistry
University of Missouri
Columbia, MO 65211

or call: 314-882-7725
or 314-882-2439

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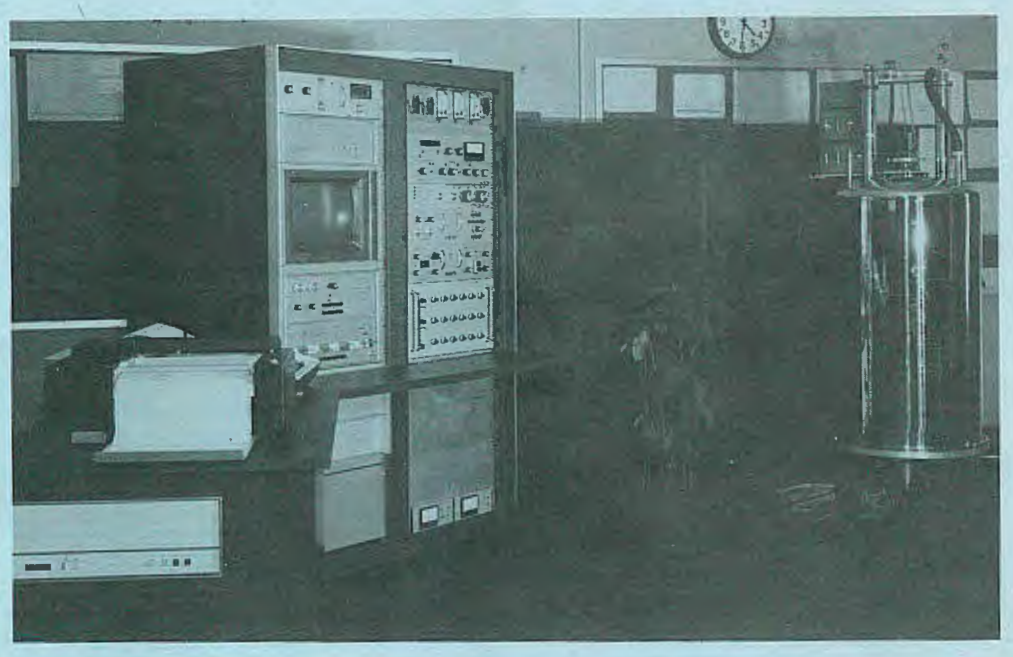

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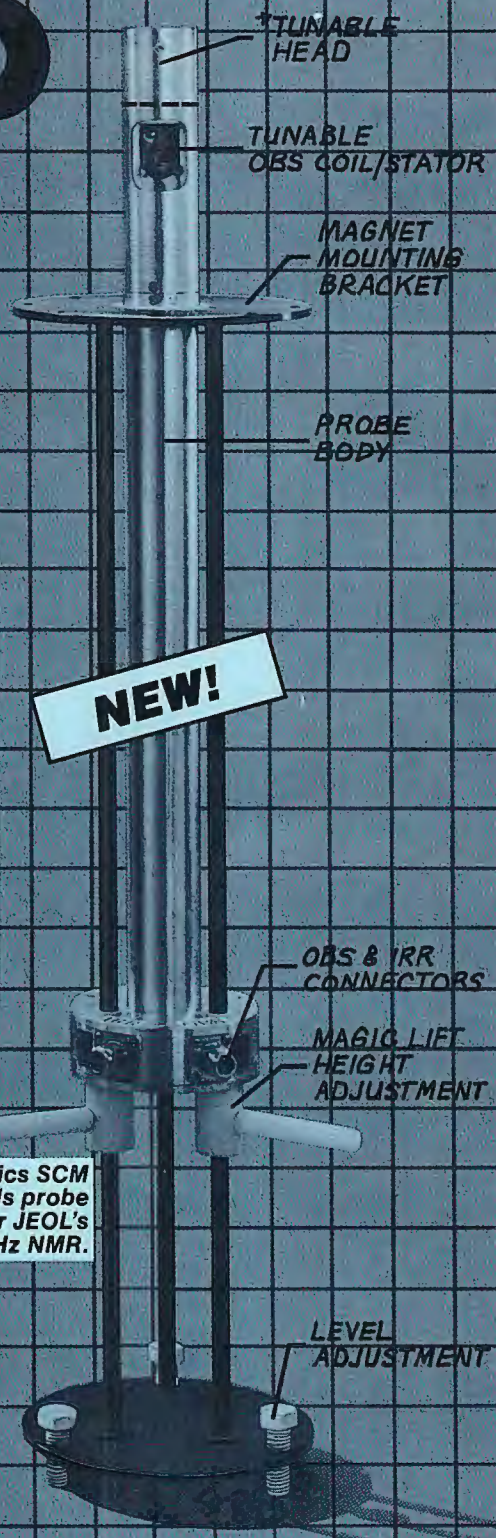

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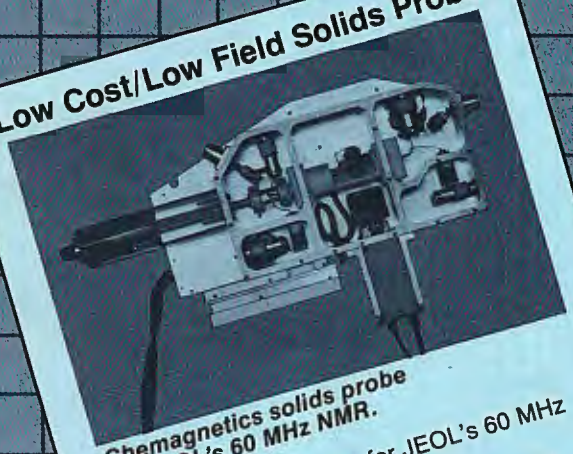

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