Texas A&M University
N-M-R Newsletter

No. 269

February, 1981

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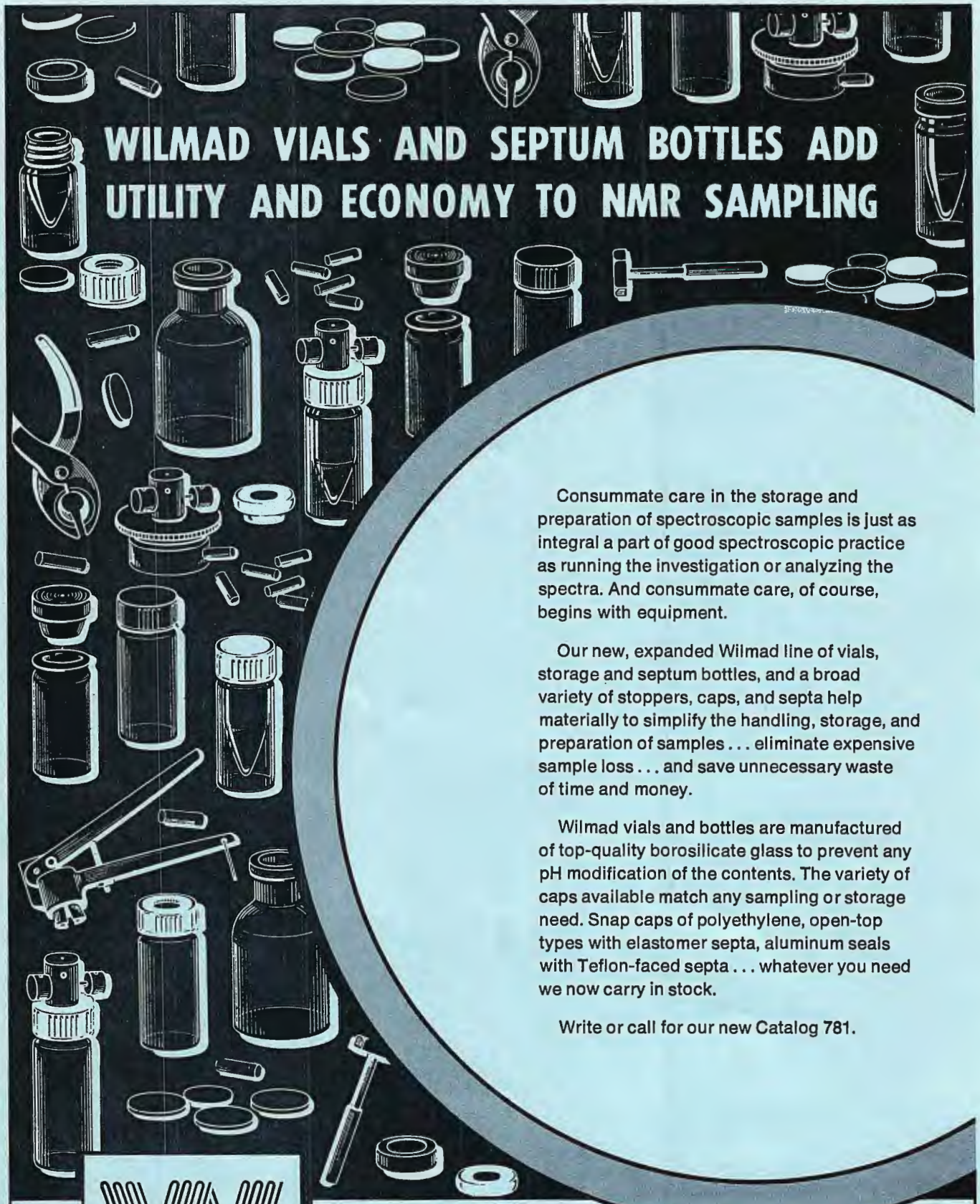

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DEADLINE DATES: No. 270 2 March 1981
No. 271 6 April 1981

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. 269

FT NMR was never "hard," only certain samples were.

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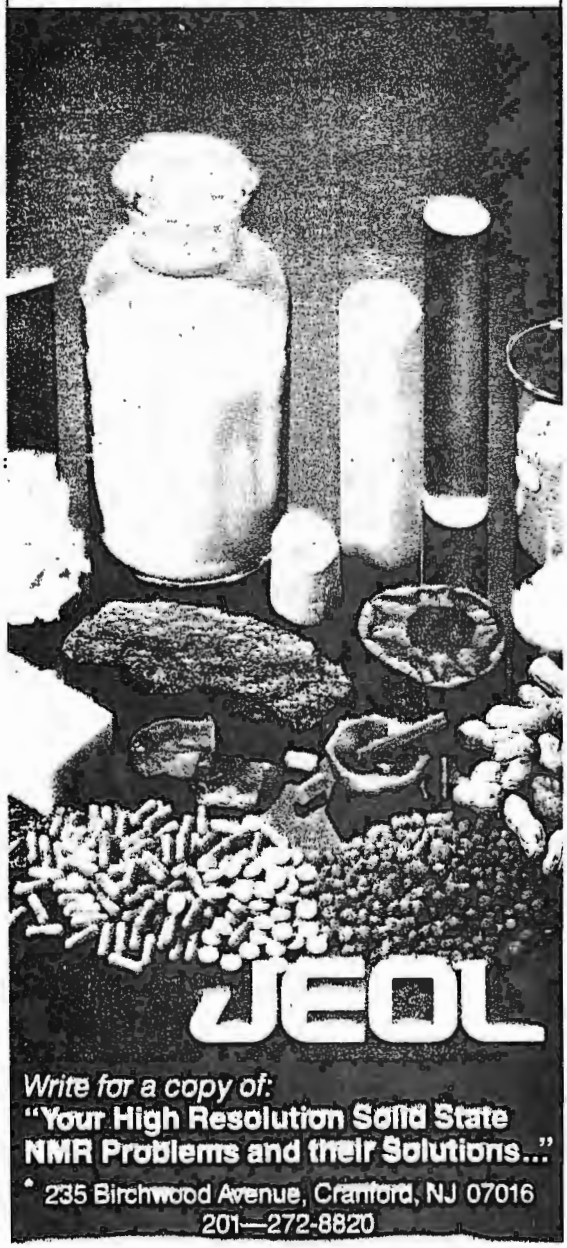

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November 15th, 1980

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

Title: ^{19}F NMR Study of Competitive Interaction of Metabolites and Drugs with Human Serum Albumin.

Dear Prof.Shapiro,

according to the method indicated by Gerig et al. (1) we have selectively labelled Human Serum Albumine on a lysine (probably Lys 199), that is located in the proximity of the main binding site for Bilirubin.The used label is Sodium 2,6-dinitro-4-trifluoromethylbenzenesulfonate and in fig.a the ^{19}F NMR spectrum of HSA at physiological conditions is shown.

By incubating the arylated HSA with Bilirubin we can observe (fig.b) a narrowing in linewidth(from 136 to 72 Hz)which is accompanied by an upfield shift (0.32 ppm).

A similar line-narrowing (from 136 to 88 Hz), without any variation of chemical shift, is observed when the arylated HSA is incubated with Penicillin G (fig.c).

On the other hand, after addition of Penicillin G to HSA already incubated with Bilirubin the signal is shifted downfield to its original position, while the linewidth corresponds to the value found in the presence of Penicillin G alone(fig.d).

This last result indicates that, under the present conditions, the spectral features of the sample which contains both Bilirubin and Penicillin G are the same as that which contains Penicillin G alone.

Yours sincerely

Anna Giuliani** Laura Guidoni*

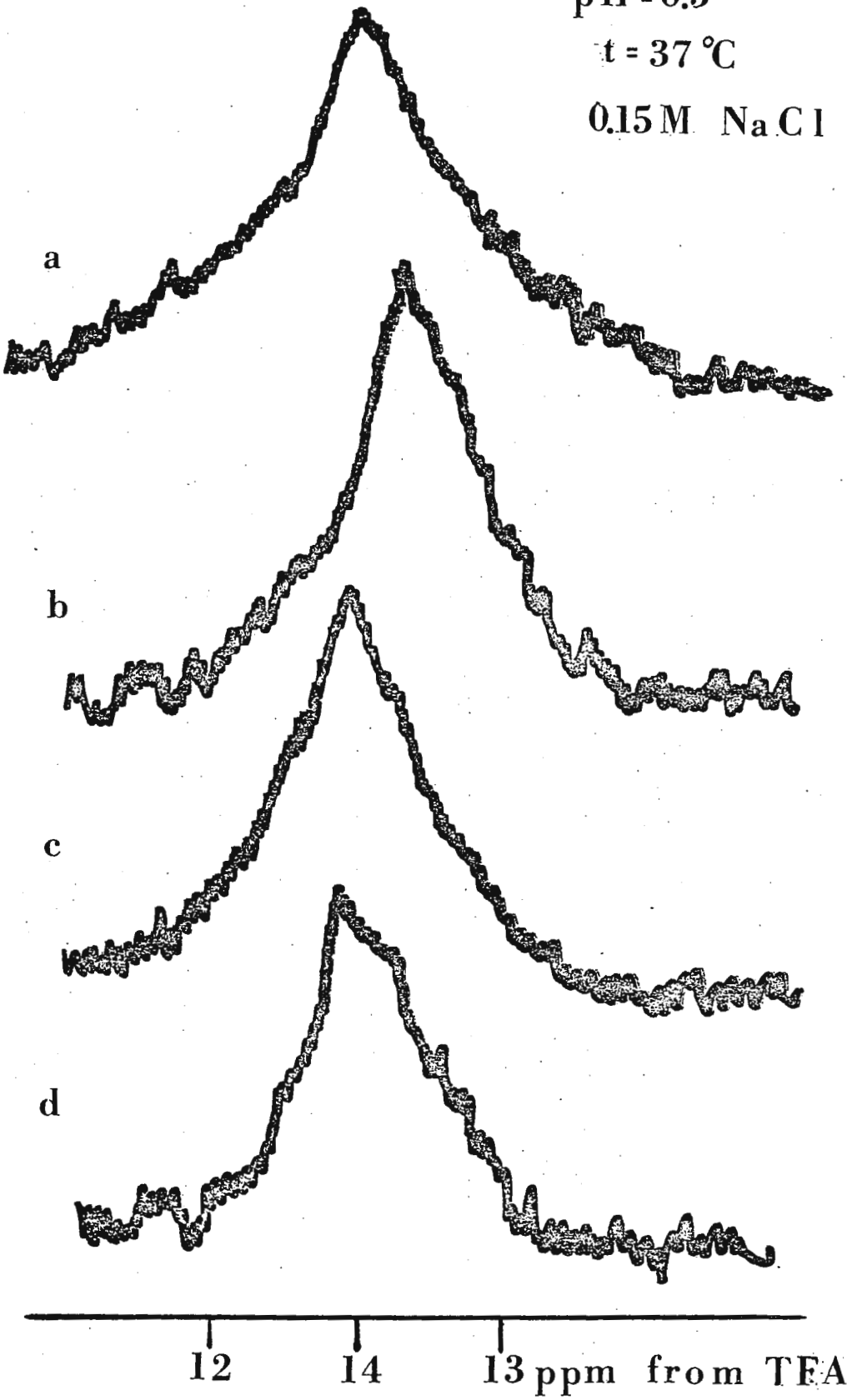
Donatella Maffi** Vincenza Viti*

(1) J.T.Gerig,K.E.Katz,J.D.Reinheimer -(1978) Biochim.Biophys.Acta 534, 196-209.

* Lab.Biol.Cell. e Immunol.,Ist.Sup di Sanità, Roma (Italy)

** Lab.diPatologia non Infettiva,Ist.Sup.di Sanità,Roma (Italy).

Please credit this contribution to the account of dott.F.Podo.


pH = 6.5
t = 37 °C
0.15 M NaCl
a
b
c
d
12
14
13 ppm from TEA

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.

November 21, 1980.

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

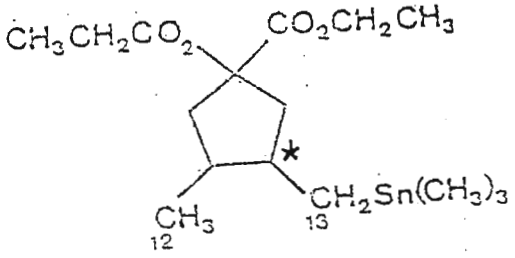
TITLE : Magnetic non-equivalence in a CH_2 group in α position to an asymetric center.

Dear Professor Shapiro,

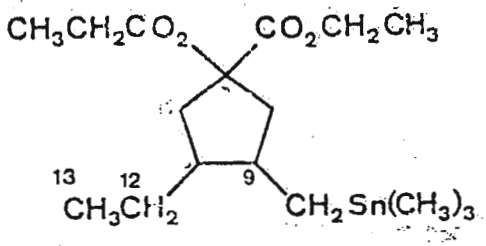
In the NMR spectrum of the cis isomer of (I), even at 250 MHz, it is not possible to definitely assign the signals of the H_1 and H_2 methylene hydrogens in α position with respect to asymetric carbon C_9. These protons should be unequivalent and give rise to an ABX patteron which is only observed for the trans isomer. The same is observed for(II).

This is probably due to the relative γ gauche positions of the CH_3 (or C_2H_5) group and the carbon bearning the H_1 and H_2 protons, in the trans isomer.

In that case, on the basis of measured coupling constants, the CH_2-$Sn(CH_3)_3$ group is pseudo-equatorial ; the ring strain reduces the diedral $^{12}CH_3$-ring ^{10}C-ring ^{9}C-$^{13}CH_2$- angle, bringing $^{13}CH_2$ in closer interaction with $^{12}CH_3$ group, which accordingly makes the $^{13}CH_2$ protons more unequivalent. That could be used to estimate the effect of substituents on the strain (or the planarity) of the ring . However replacing CH_3 by C_2H_5 does'nt change significantly the corresponding chemical shift difference.



(I) cis-trans



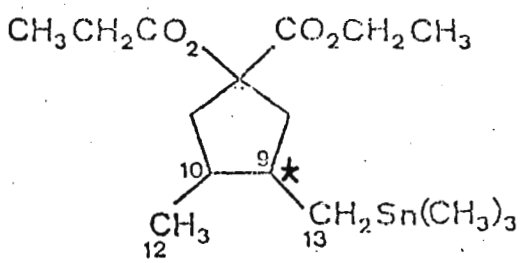
(II) cis-trans.

Sincerely yours.

Y.LIMOUZIN-MAIRE

J.NECCIARI

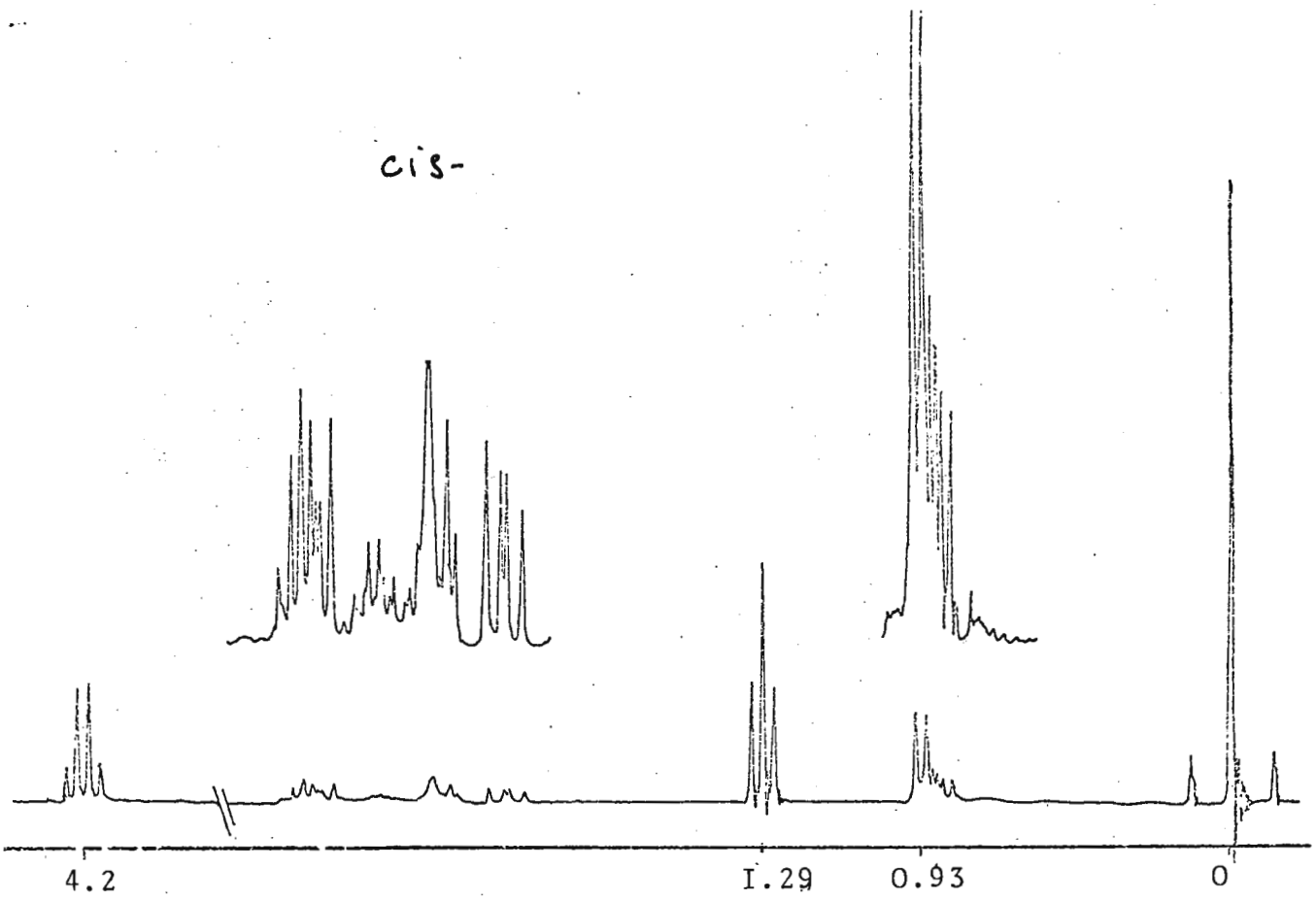
rue Henri Poincaré - 13397 MARSEILLE Cedex 4
tél.: (570).
98 90 10


CH3CH2CO2
CO2CH2CH3
10
9
*
CH3
12
CH2Sn(CH3)3
13

trans-

4.2
I.2
0.88
0

cis-


4.2
I.29
0.93
0

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

Datum 19 January 1981
Uw kenmerk
Ons kenmerk
Onderwerp Nomogram for O1 or O2 determination in a Bruker spectrometer for various lock-solvents.
Automatic acquisition of a number of T_1 measurement series.

Dear Prof. Shapiro,

We just received your final warning, so we hope that this contribution will reach you in time for an uninterrupted subscription to and delivery of the Newsletter.

We run our WP-200 NMR-spectrometer in a multi-user environment and noticed that a number of these users continuously had problems in determining the correct offset-frequencies O1 and O2 when the lock solvent was changed or a new decoupling frequency had to be entered. As these users find a careful reading of the manual obviously a bore, we designed for them a nomogram from which they can read the desired frequencies. The nomogram, which might be of use to the Newsletter readers is practically self-explanatory (see figure), and easily adapted to other spectrometers.
Example: Decoupling at 4 ppm in CD_2Cl_2 requires an O2 of 3480.

In our research we are interested in determining Spin-Rotation interactions for small molecules. This requires large T_1 measurement series at various temperatures, in order to obtain the various contributions to T_1. We designed a microprogram for our Bruker disk-equipped system, which automatically performs such a measurement series. In this way we can i.e. obtain an inversion recovery sequence at 16 τ_i values, with two independent S_∞ and NOE-suppressed values that are acquired evenly spaced throughout the total measuring time and which each have twice the number of scans of an τ_i value. The series is repeated at a predetermined number of temperatures.

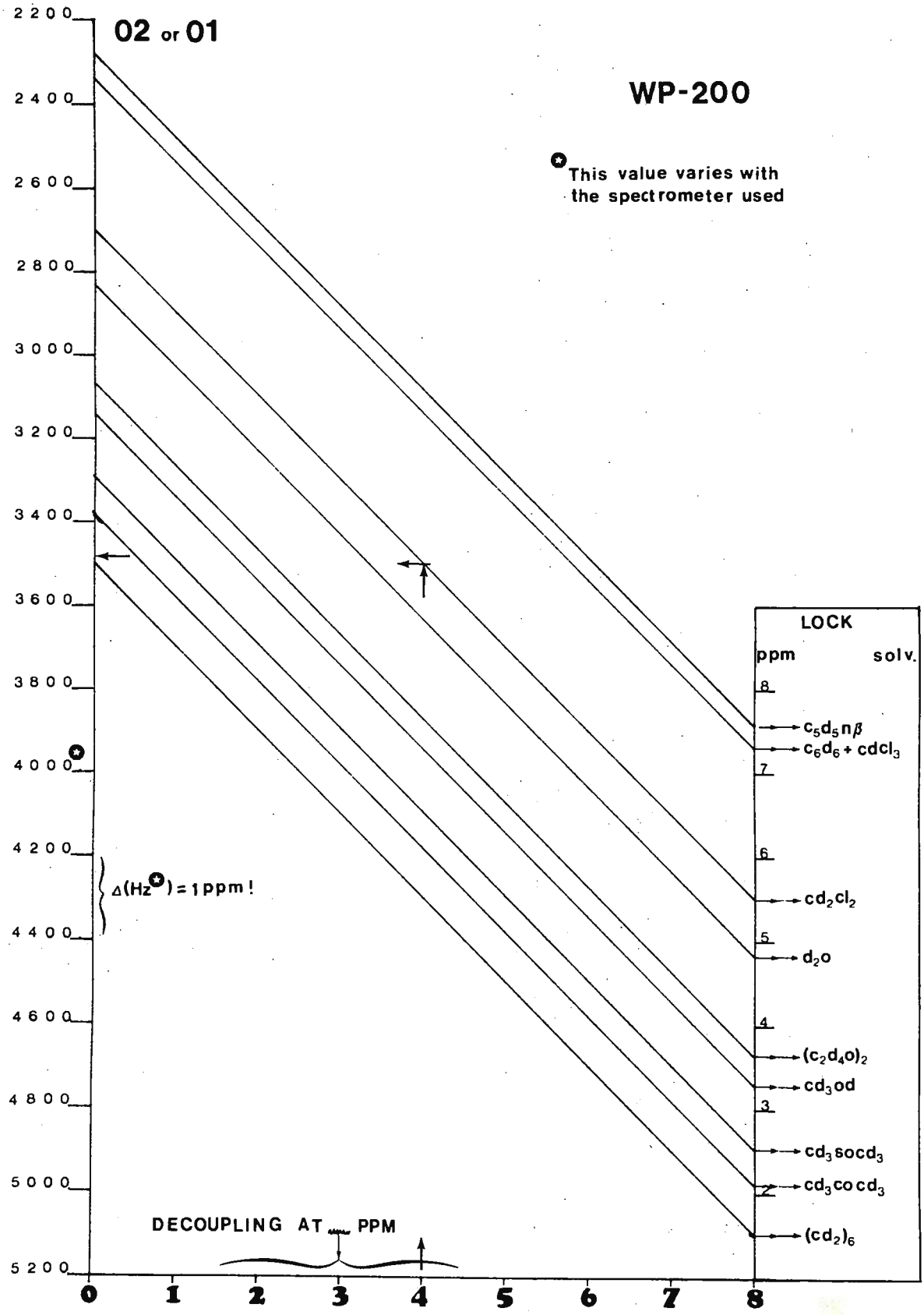
The program, as submitted with this letter, consists of four parts:
- A file space creator FISPCRE
- The acquisition module IRT1
- The automatic plot of spectra in IR-presentation APOSIR
- A plot routine for the S_∞ and NOE suppressed data SINOPL

These programs are easily adapted for other plotting modes such as MIR. By a judicious use of the NE (number of experiments) and VC (variable) counters, it is possible to manipulate each data set independently.

Yours Sincerely,

M.J.A. de Bie

D. Seykens


02 or 01
WP-200
This value varies with the spectrometer used
2200
2400
2600
2800
3000
3200
3400
3600
3800
4000
4200
4400
4600
4800
5000
5200
Δ(Hz) = 1 ppm !
LOCK
ppm
solv.
8
7
6
5
4
3
2
$c_5d_5n\beta$
$c_6d_6 + cdcl_3$
cd_2cl_2
d_2o
$(c_2d_4o)_2$
cd_3od
cd_3socd_3
cd_3cocd_3
$(cd_2)_6$
DECOUPLING AT ___ PPM
0
1
2
3
4
5
6
7
8

FISPCRE

```
 1 RF SINF                 11 DF NOE                 21 ZE
 2 RF NOE                  12 LO TO 10 TIMES 2       22 WR SINF
 3 RF T1                   13 DF T1                  23 IF SINF
 4 IF SINF                 14 LO TO 13 TIMES 16      24 WR NOE
 5 IF NOE                  15 RE T1                  25 IF NOE
 6 LO TO 4 TIMES 2         16 ZE                     26 LO TO 22 TIMES 2
 7 IF T1                   17 WR T1                  27 IN = 15
 8 LO TO 7 TIMES 16        18 IF T1                  28 EXIT
 9 LO TO 4 TIMES C         19 LO TO 15 TIMES 16
10 DF SINF                 20 RE SINF
```

For n experiments NE has the value n and VC the values 1,2,....,n
To manipulate only i.e. series 3, VC = 3 and NE = 1, or VC = 3,5 and NE = 2.
The program is designed for 16 τ_i values.

IRT1

```
 1 TE                      11 LO TO 7 TIMES 4        21 IN = 2
 2 RE SINF                 12 WR T1                  22 IF SINF
 3 D1                      13 RE NOE                 23 IF NOE
 4 GO = 3                  14 DO                     24 DF T1
 5 WR SINF                 15 D1                     25 LO TO 24 TIMES 16
 6 RE T1                   16 BB                     26 LO TO 2 TIMES 2
 7 D1                      17 D2                     27 TE
 8 P1                      18 GO = 14                28 LO TO 2 TIMES C
 9 VD                      19 WR NOE                 29 EXIT
10 GO = 7                  20 IF T1
```

NE is the number of runs through the series for each temperature, divided by 2.
Each SINF and NOE file has two times the number of scans of an τ_i file.

APOSIR

```
 1 RF T1                    6 LO TO 5 TIMES 16       11 PK
 2 IF T1                    7 RE T1                  12 PL  (or PX)
 3 LO TO 2 TIMES 16         8 IF T1                  13 LO TO 7 TIMES 16
 4 LO TO 2 TIMES C          9 EM                     14 IN = 1
 5 DF T1                   10 FT                     15 EXIT
```

For comment see FISPCRE

SINOPL

```
 1 RF SINF                 11 IF SINF                21 PK
 2 RF NOE                  12 EM                     22 PL  (or PX)
 3 IF SINF                 13 FT                     23 LO TO 17 TIMES 2
 4 IF NOE                  14 PK                     24 IN = 1
 5 LO TO 3 TIMES 2         15 PL  (or PX)            25 EXIT
 6 LO TO 3 TIMES C         16 LO TO 10 TIMES 2
 7 DF SINF                 17 RE NOE
 8 DF NOE                  18 IF NOE
 9 LO TO 7 TIMES 2         19 EM
10 RE SINF                 20 FT
```

For comment see FISPCRE

The number 16 determines the number of τ_i values in these programs.
For a new series of experiments FISPCRE has to be used first, as there is no reset of the file-contents to zero in any of the other programs. This means that experiments can be selectively continued or restarted for the different temperatures.

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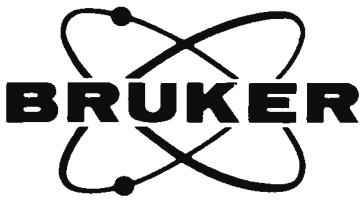

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Department of Chemistry

1/20/81

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

Dear Barry:

Over the course of the past year I have been taking a detailed look at the uranyl tricarbonate system in collaboration with Tom Strom and Don Woessner at Mobil Laboratories. It goes without saying that we were very interested in the observations of Henrikson and Grenthe (Newsletter, 262-29). Here we shall extend their observations somewhat.

At room temperature the ^{13}C-NMR spectrum of a solution 0.0295M in UO_2^{++} and 0.242M in HCO_3^- with a 10% ^{13}C lable at pH 8.84 in 75%- 25% H_2O-D_2O shows two peaks at 162.3 ppm(larger) and 168.9 ppm (an external methanol refence was taken as 49.3 ppm from TMS). If the uranyl ion complexes with three carbonates this solution should be 0.0885M in the complexed carbonate of the uranyl tricarbonate ion and 0.1535M in bicarbonate. In simpler solutions uncomplexed bicarbonate falls at 162.1 and carbonate at 169.6 ppm respectively. Carbonate-bicarbonate mixtures give a singlet spectrum whose apparent chemical shift is a weighted average of the composition.

With increasing temperature the two peaks in the uranyl-bicarbonate system above draw together and merge about 58°. Based on the chemical shifts above and the calculated composition of the solution, one can calculate the position of the fast exchange singlet as due at 164.7 ppm. The experimental value is 164.8. After a detailed temperature study and line shape analysis, Don calculated an Arrhenius activation energy of 13.0 Kcal with a pre-exponential factor of 9.24 x 10 exp 10.

The rate of carbonate transfer increases markedly upon lowering the pH. At room temperature and pH 7.06 the spectrum is almost a singlet, but separate peaks are cleanly resolved at 16°. Interestingly, at this pH one can see nicely the dissolved carbon dioxide at 125.8 ppm.

Yours sincerely,

Bill

William B. Smith
Chairman

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Professor B.L. SHAPIRO
Dpt of Chemistry
Texas A and M University

COLLEGE STATION Texas 77843
USA

N./Réf. 80 12 554 CB/RS/MCH
V./Réf.

Wissembourg, le December 23, 1980

Dear Prof. Shapiro,

13C Solvent Suppression from Triplet to Septuplet

In reference to the letter of Prof. D. Leibfritz (TAMU NMR n° 264), we would like to present a pulse sequence we are using in our application laboratory, for 13C solvent peak suppression.

The procedure we use, permits selective elimination during the relaxation delay of normal acquisition. It may be very advantageous, specially when recording polymers or biological samples spectra.

The method allows for successive saturation of each solvent peak resonance via a selective 90° pulse train and then full spectrum recording with a non selective pulse (SEPIA like sequence in BRUKER terminology).

For ASPECT 2000 users, the sequence is written as follow :

```
 1   ZE
 2   J1
 3   O1
 4   P1
 5   D1
 6   LO to 4, TIMES 100
 7   LO to 3, TIMES 14
 8   J2
 9   GO = 2
10   EXIT
```

O1 à 1000 Hz
déplacer du solvant
O1
1/1L
1/0,1 10 Hz

with P1 = 1 us D1 = 0,001 s.

JOB 2 parameters are normal 13C acquisition ones. Frequency list (FL) contains each solvent peak offset ± 1000 Hz (1/D1).

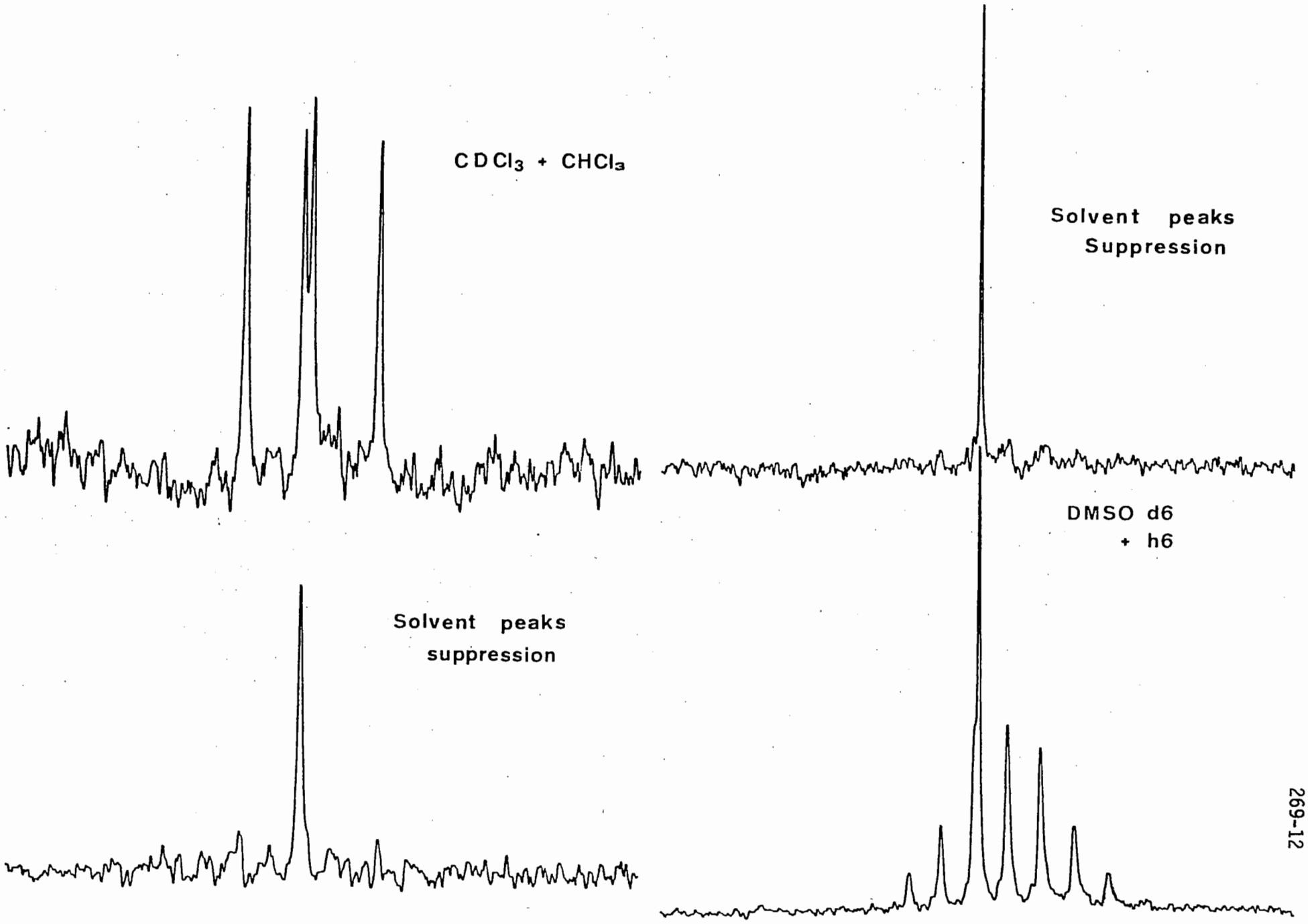
The spectra shown were obtained on a WP 80 SY standard system, with 17 dB attenuation on the emitter (90° pulse = 100 µs).

Note the selectivity of the method which will prove usefull for DMSO solutions of polypeptides.

Happy New Year !

Sincerely yours,

R. SCHIMPF C. BREVARD


$CDCl_3$ + $CHCl_3$
Solvent peaks
Suppression
DMSO d6
+ h6
Solvent peaks
suppression
269-12

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CHESTNUT HILL, MASSACHUSETTS 02167

(617) 969-0100

DEPARTMENT OF CHEMISTRY

January 6, 1981

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

Dear Barry:

"Ockham's Razor revisited; All that glitters..."

The recent letter by Edlund (TAMUNMRN #265) prompts the following two comments:

1) When should DSP analyses be used?

Edlund appears to suggest that DSP analyses should only be used when they give a correlation superior to a single-parameter (SSP) fit (e.g. vs. σ_p). While this appears reasonable, I disagree. If the object is simply to obtain a correlation, then certainly the SSP fit is to be preferred to the DSP fit, if both work equally well - the guiding principle being Ockham's Razor. However, whole being "neater" the SSP fit conceals detail, because the blend of "resonance" and nonresonance" effect is unknown. Since $\mathcal{F}$ and $\mathcal{R}$ (to choose one pair of parameters) were derived from σ_p, SSP and DSP fits of equal quality should be entirely equivalent, except that the DSP analysis would permit more detailed partitioning of effects.

To test this, I analyzed ^{13}C shift for 1-substituted azulenes from our recent paper [J. Org. Chem., 45, 2400 (1980)] using both SSP (σ_p) and DSP ($\mathcal{F}$ and $\mathcal{R}$). Using the regression equations of the form

$$\delta_{C_i} = f\mathcal{F} + r\mathcal{R} + \delta_0$$

$$= \rho\sigma_p + \delta_0$$

I derived relations between σ_p and $\mathcal{F}$, $\mathcal{R}$ for several carbons. The DSP analyses for C-5 and C-7 were significantly better than the SSP fits, and the relations derived from the data are:

Prof. Shapiro January 6, 1980

$$\sigma_p = 0.47\,\mathcal{F} + 1.33\,\mathcal{R} \qquad \text{(C-5)}$$

$$\sigma_p = 0.38\,\mathcal{F} + 1.65\,\mathcal{R} \qquad \text{(C-7)},$$

in poor agreement with the relations derived by Swain and Lupton. However, for C-4 and C-6, where DSP and SSP correlations are of identical quality, the derived relations are

$$\sigma_p = 0.56\,\mathcal{F} + 1.02\,\mathcal{R} \qquad \text{(C-4)}$$

$$\sigma_p = 0.58\,\mathcal{F} + 0.95\,\mathcal{R} \qquad \text{(C-6)}$$

in excellent agreement with Swain and Lupton's

$$\sigma_p = 0.56\,\mathcal{F} + 1.00\,\mathcal{R}.$$

So, it seems to me that DSP fits should only not be done if they give a worse correlation than SSP fits (which seems difficult to imagine, given the principle that with enough parameters one can build an elephant!).

2) How far should one "believe" the regression parameters?

The fact that a given regression parameter is not zero has to be treated cautiously, as we found out when analyzing π-electron density data from CNDO calculations on p-substituted trans, trans-1-phenyl-1,3,5-hexatrienes. The π-densities are well correlated by an equation of the form $\rho = f\mathcal{F} + r\mathcal{R} + \rho_o$, implying both resonance and "nonresonance" effects to be involved. To separate them we zeroed the π-overlap between C-1 and C-7 while leaving everything else fixed. To our surprise, "r" did not go to zero as one might have expected, but decreased to about half its original value, while the number of π-electrons remained at 6.00 in the hexatriene moiety, confirming that resonance effects were absent. We conclude that (a) X interacts with the aromatic ring, causing development of a charge at C-1 whose magnitude is governed by both $\mathcal{F}$ and $\mathcal{R}$; (b) this charge polarizes the hexatriene π-system, redistributing the electron densities. Thus, since the magnitude of the polarization is governed by q-1, which in turn is governed by $\mathcal{F}$ and $\mathcal{R}$, the π-densities appear to be determined by resonance interactions with X, when in fact they are not, an example of the well-known dictum that "correlation does not imply (direct) causability". Due caution should obviously be exercised in interpretations of DSP fits.

Aphoristically yours,

D.J. Sardella
Associate Professor

DJS:af

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

PRE-SPINNING THE SAMPLE:
CONCENTRATION OF MACROMOLECULES INTO D_2O BY ULTRACENTRIFUGATION

Dear Barry,

Many macromolecules (in our case, 11S acetylcholinesterase, AchE, MW = 330000) cannot be concentrated into D_2O simply by lyophilizing an H_2O sample and dissolving the powder in D_2O, because the enzyme denatures. Moreover, ultrafiltration can result in large activity losses (>35% for AchE) when such hydrophobic proteins contact the dialysis membrane.

Figure 1 shows another method, suggested by the higher specific gravity (1.108 vs. 0.997 at 25°C) of D_2O compared to H_2O. A concentrated sample of AchE in slightly trititated H_2O was carefully layered on top of protein-free D_2O buffer in a centrifuge tube. After 20 hr at 40,000 rpm in a Beckman 23-50 ultracentrifuge, aliquots withdrawn from the tube showed the ^3H and AchE activities plotted in the Figure. Note that most of the AchE has sedimented to the bottom of the tube (i.e., D_2O), with negligible diffusion of H_2O (as shown by ^3H activity) to that region.

In practice, this method is made difficult by convection currents from non-uniform tube temperature, and by the need to calibrate the run so as to stop the centrifuge at the moment when the enzyme is well-concentrated near the tube bottom but not yet pelleted against it. However, we have made the method work, and offer it for consideration when (as in this case) other techniques are not suitable.

Sincerely,

Alan G. Marshall
Professor of Chemistry and Biochemistry

AGM:agm

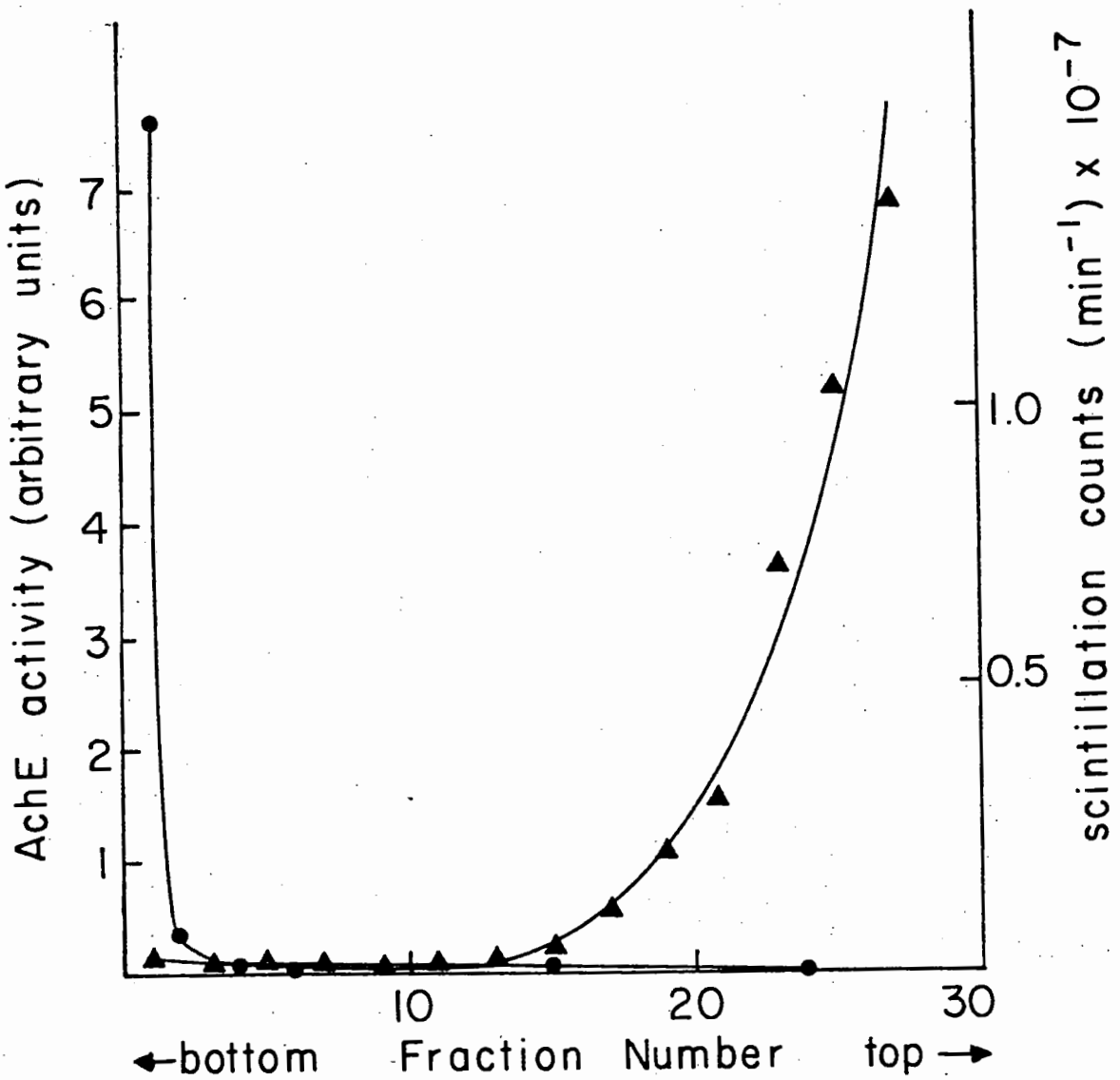

Figure 1. Concentration of acetylcholinesterase (AchE) into D_2O buffer. AchE concentration (●) is reflected by the activity assay scaled by the left-hand axis. Diffusion of tritiated H_2O in the centrifuge tube is reflected by the radioactivity profile (▲) scaled by the right-hand axis. Fractions are numbered starting from the bottom of the centrifuge tube.

269-17

ENC Inc. **Twenty-second Experimental Nuclear Magnetic Resonance Spectroscopy Conference**

Asilomar, California, April 5-9, 1981

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22nd ENC

January 6, 1981

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

Dear Barry:

A tentative program for the 22nd ENC to be held in Asilomar, California, April 5-9, 1981, is given below. Requests for information pertinent to preregistration should contact Prof. A.A. Bothner-By, Department of Chemistry, Carnegie-Mellon University, 4400 Fifth Ave., Pittsburgh, Pennsylvania 15213. Here is the tentative program:

	Morning	Afternoon	Evening
Monday	NMR in Solids-CP/MAS (D. VanderHart, Chair) D. VanderHart, C.S. Yannoni, R.A. Wind	Computers in NMR (E.D. Becker, Chair) D.J. Ruben; Panel Disc. "Data Systems for Multipurpose NMR Facilities"	New Methods (H.D.W. Hill, Chair) I.M. Campbell, D. Shaw, J.J.H. Ackerman
Tuesday	Multiple Quantum NMR (A. Pines, Chair) R.R. Ernst, G. Bodenhausen, S. Vega, G. Drobny, R.L. Vold	Poster Session (D. Dalrymple, Chair) Wine Tasting	NMR Of Biomolecules (B.D. Sykes, Chair) E. Oldfield, R. Kaptein, I. Morishima, S.J. Kohler
Wednesday	2D FTNMR (R.R. Vold, Chair) R. Freeman, L. Müller, R.G. Griffin	Poster Session (D. Dalrymple, Chair) Nicolet Technology, 145 E. Dana St., Mountain View, Ca. 94041 (Poster Abstract should be on one 8½" x 11" page.)	
Thursday	In Vivo Studies (D.I. Hoult, Chair) G.K. Radda, P.C. Lauterbur, L.E. Crooks, T.R. Brown		

Sincerely,

Gerd N. La Mar
Chair, 22nd ENC

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DEPARTMENT OF MEDICINAL CHEMISTRY

December 2, 1980

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

Dear Barry:

REMOVAL OF OIL AEROSOLS FROM COMPRESSED AIR

The air supplied by many in-house compressed air systems is contaminated with oil; I know ours is. This oil, present as a very fine aerosol, will pass completely through air filters such as those supplied by Varian. We made several attempts to remove the oil, buying and installing two different filters purported to remove oil aerosols, with results as described below.

The first commercial filter that we tried did not work in our laboratory. After only a short period of time, less than two months, an oil film coated and discolored the insides of the tygon tubing air lines. This filter uses a rolled rayon element.

The second type of commercial filter we tried was a Series I Vape-Sorber from the Selas Corporation, Huntingdon Valley, Pennsylvania. After ca. six months in service, it seems to be working satisfactorily. We have observed no oil in the air lines even at bends where the aerosol normally condenses fastest. Installation consisted of simply adding the Vape-Sorber filter on to the end of the existing air filter system, although information supplied by the manufacturer suggests it might work more efficiently on the high pressure side of the regulator.

We also tried a third, non-commercial, method of oil removal. We installed a glass drying column filled with silica gel, followed by an 5-micron filter after the pressure regulator. This did seem to work for the short time we used it before installing the Motor Guard unit.

Please credit this contribution to the account of Dr. Byron Arison.

Sincerely,

David W. Cochran

David W. Cochran
Senior Research Chemist

/rjh

Carleton University
Ottawa, Canada K1S 5B6

January 9, 1981.

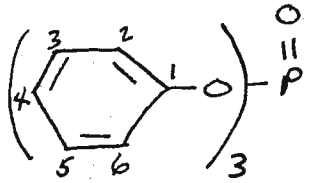
Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas
77843 U.S.A.

^{13}C NMR of triaryl Phosphates

Dear Barry:

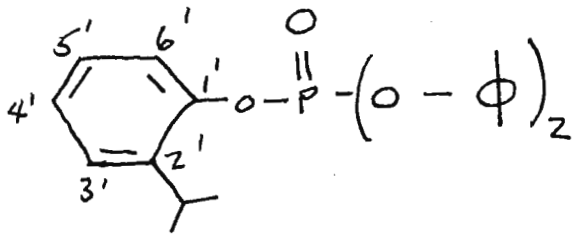
Mixtures of trialkyl and triaryl phosphates are used as plasticizers, and are turning up in drinking water due to being leached from plastic connectors etc. A number of these compounds are toxic, especially the ortho-alkylated triaryl phosphates. Prof. R.H. Wightman of this department is under contract to synthesize a number of these materials as standards for analysis, and we are looking at their ^{13}C spectra in an attempt to determine preferred aryl ring conformations.

Although the data are preliminary, some interesting features have emerged in the $^{3}J_{POCC}$ values for ortho-alkylated rings.



1

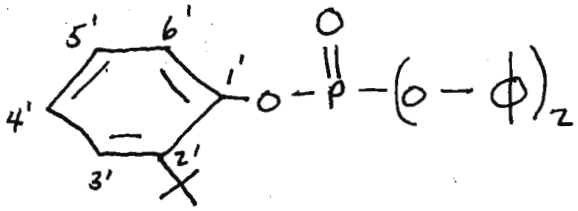
$^{3}J_{POCC_{2,6}} = 3.9\ Hz$



2

$^3J_{POCC_{2'}} = 7.1$ Hz

$^3J_{POCC_{6'}} = 1.5$ Hz



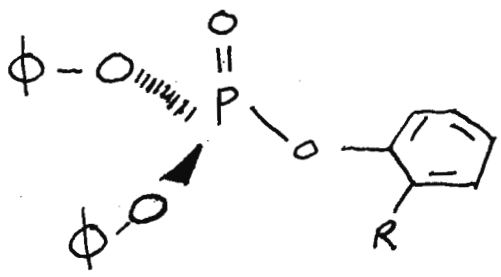
3

$^3J_{POCC_{2'}} = 9.0$ Hz

$^3J_{POCC_{6'}} < 0.6$ Hz

In 2 and 3, the ^3J couplings to the non-alkylated rings are about the same as in 1, thus, there appears to be little inter-ring interaction.

For the ortho-alkylated rings, in all cases to date, the coupling to the alkylated vicinal carbon is much larger than to the non-alkylated ortho-site. Perhaps this indicates a preference for the conformation depicted below, where the trans-coplanar pathway produces maximal coupling. If this is the case, the very low values for ^3J cis are somewhat surprising.



Happy New Year!

Sincerely,

G.W. Buchanan, Associate Professor.

269-21

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January 12, 1981

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

Re: T1 Program and NMR Discussion Group

Dear Barry:

As you can see from the letterhead, I have moved back to Texas, from the cold of Minnesota. Just before leaving the University of Minnesota, Frank Blum had been putting the finishing touches on an extensive rewriting of the old Varian T-1 program, complete with thorough documentation. The program is configured for a Sykes Cassette Unit and a 620L Computer. Its new features include a variable number of steady state pulses; selective gating of the decoupler during delay 1 and/or delay 2 and/or acquisition, now allowing dynamic NOE measurements. The program will collect data in blocks, store up to 20 spectra on tape with the acquisition parameters, including two lines for title and comments and can use delays from 1000.000 sec to 0.001 sec. Copies of the program (on cassette) and the documentation may be obtained from:

Mr. Frank D. Blum
Department of Chemistry
University of Minnesota
Minneapolis, Mn. 55455

NMR Discussion Group: There is a small group of us in the Houston area who are interested in organizing an informal discussion group patterned after those in the New York and Washington areas. Anyone interested in participating in such a group may call me at (713)666-8000 ext. 2680 or drop me a note at the above address.

Very truly yours,

RMR

ROBERT M. RIDDLE

RMR-BJJ
cc: FDB

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

Dear Barry,

A High-Performance 18-mm Probe System for the Varian XL-100-15 Spectrometer

During the last year we have worked on the development of a high-performance, multinuclear single-coil 18-mm sample tube probe system including a lumped circuit duplexer for the Varian XL-100-15 spectrometer. The probe requires 4.5 to 5 ml of sample. ^{13}C (25.16 MHz), ^{113}Cd (22.19 MHz) and ^{15}N (10.14 MHz) performances for the probe system are shown in Figures 1 to 4 and correspond to approximately a three-fold increase in sensitivity for non-lossy samples over existing 18-mm electromagnet probes. The ^{13}C sensitivity per milliliter of sample for the 18-mm probe is approximately a factor of 1.6 over that of a recently reported high-performance 22-mm sample tube probe (1). The high-Q of our probe system is probably best reflected by the ^{13}C 90° pulse width which is typically 11 μsec with only 12 W of rf power.

The probe system has been developed in collaboration with Preben Daugaard of this institute and Paul D. Ellis, University of South Carolina. Preprints of a manuscript (accepted for publication in J.Magn.Resonance), which gives details of the probe system, are available.

Sincerely,

Hans

Hans J. Jakobsen

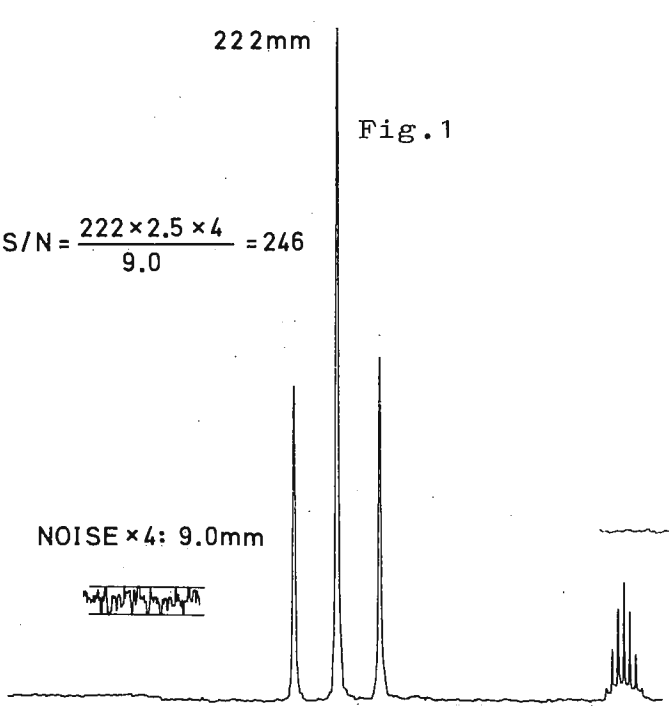
(1) A.P.Zens and D.M.Grant, in "Topics in ^{13}C NMR Spectroscopy" (G.C.Levy, Ed.), Vol. 3, p.39, Wiley Interscience, New York, 1979.

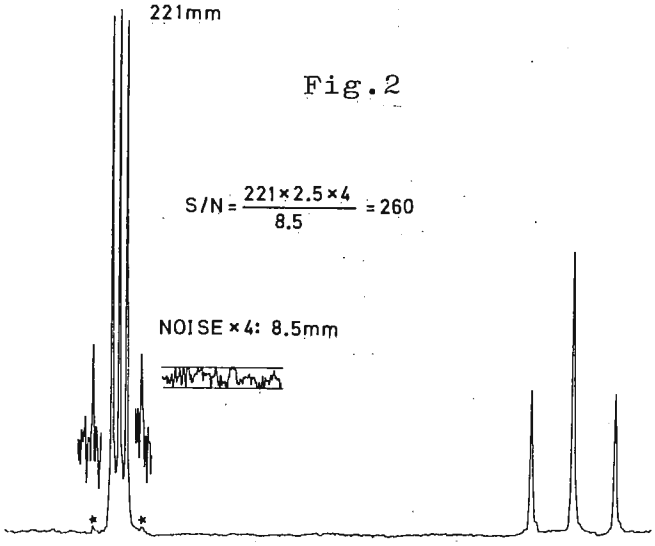
Fig. 1. ^{13}C NMR; 80% v/v dioxane in acetone-d_6; one 90° pulse; without NOE; 1.6 Hz linebroadening.

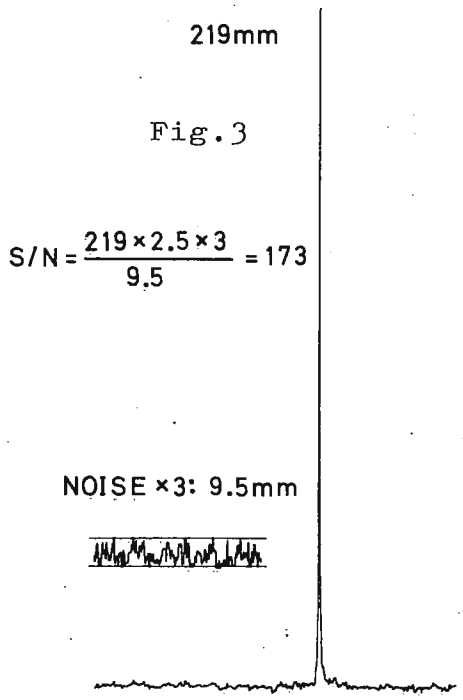
Fig. 2. ^{13}C NMR; 60% v/v C_6D_6 (99% deuterium) in dioxane (ASTM test); one 90° pulse; 2.0 Hz linebroadening; * lines indicate satellites due to C_6D_5H ($^1J_{C-H}$ = 158.2 Hz).

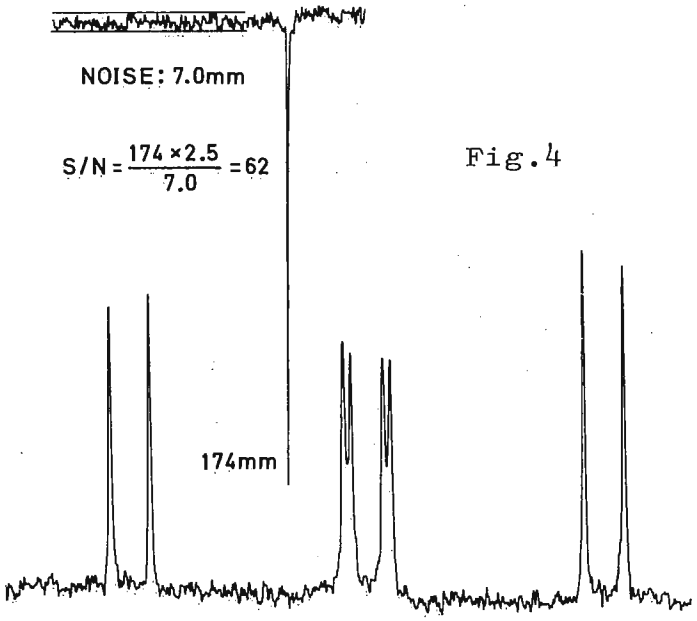
Fig. 3. ^{113}Cd NMR; 1.0 M $CdCl_2$ in D_2O; 90° pulse; 1.6 Hz linebroadening.

Fig. 4. ^{15}N NMR; 90% v/v formamide in DMSO-d_6; upper: one 90° pulse, decoupled with NOE, LB = 0.8 Hz; lower: 36 pulses, coupled with NOE (inverted phase), LB = 0.3 Hz.









Signal/Noise x 2.5 x 2 = Varian XL-200

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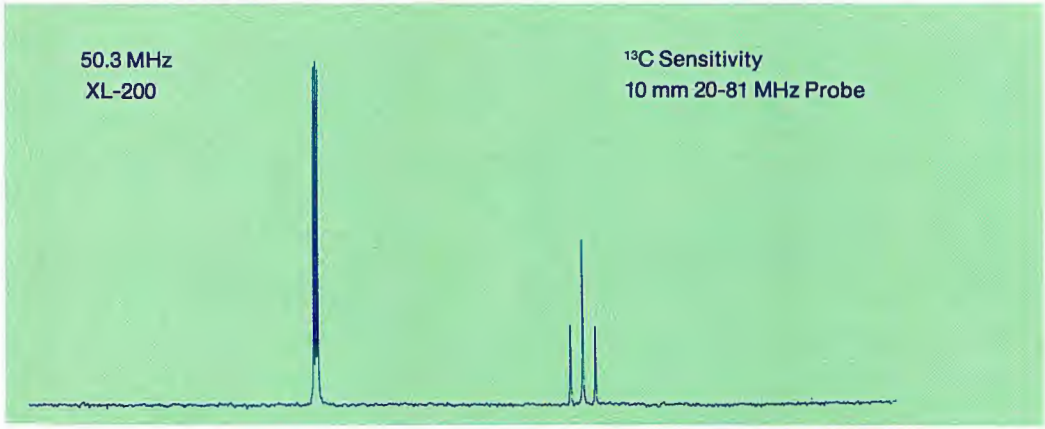
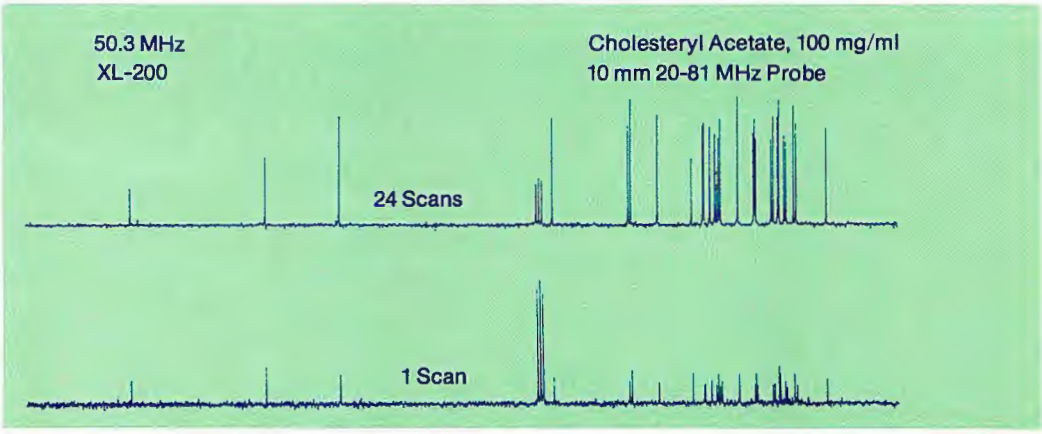
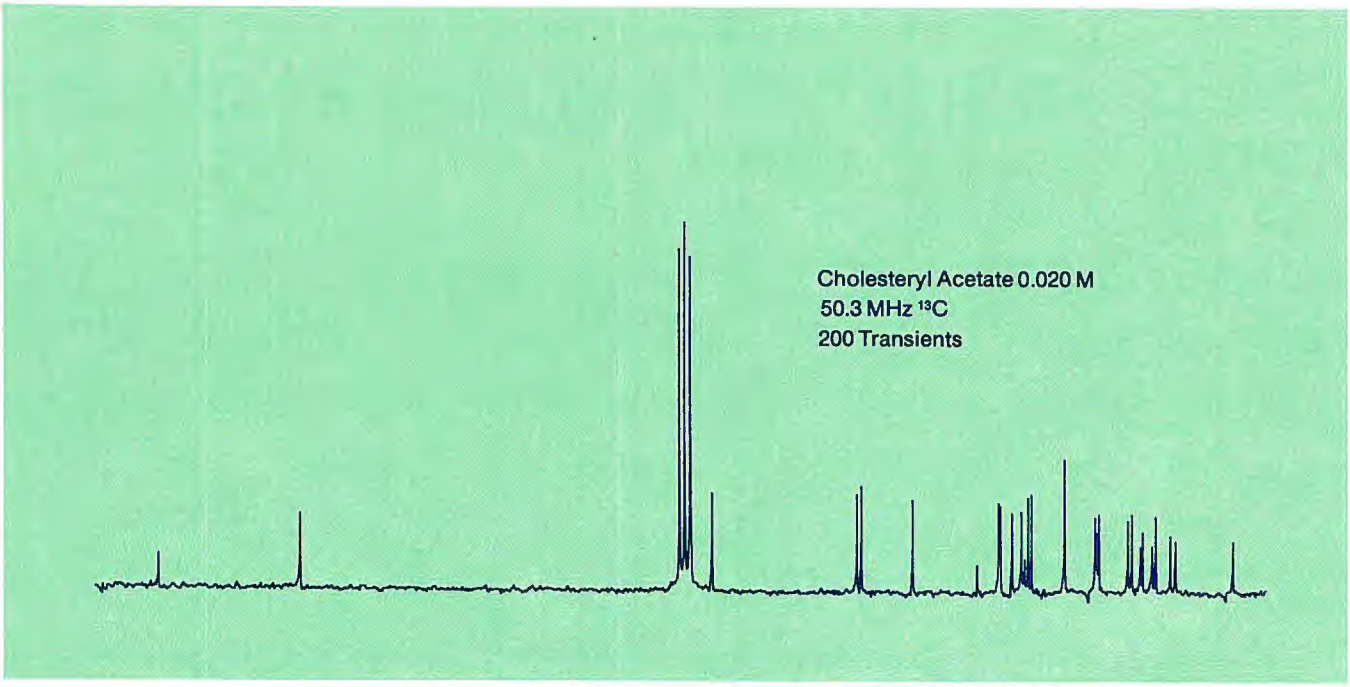


^{13}C Sensitivity Test: Single transient following 90° pulse on 60% C_6D_6/40% dioxane using the 10 mm 20-81 MHz broadband probe.

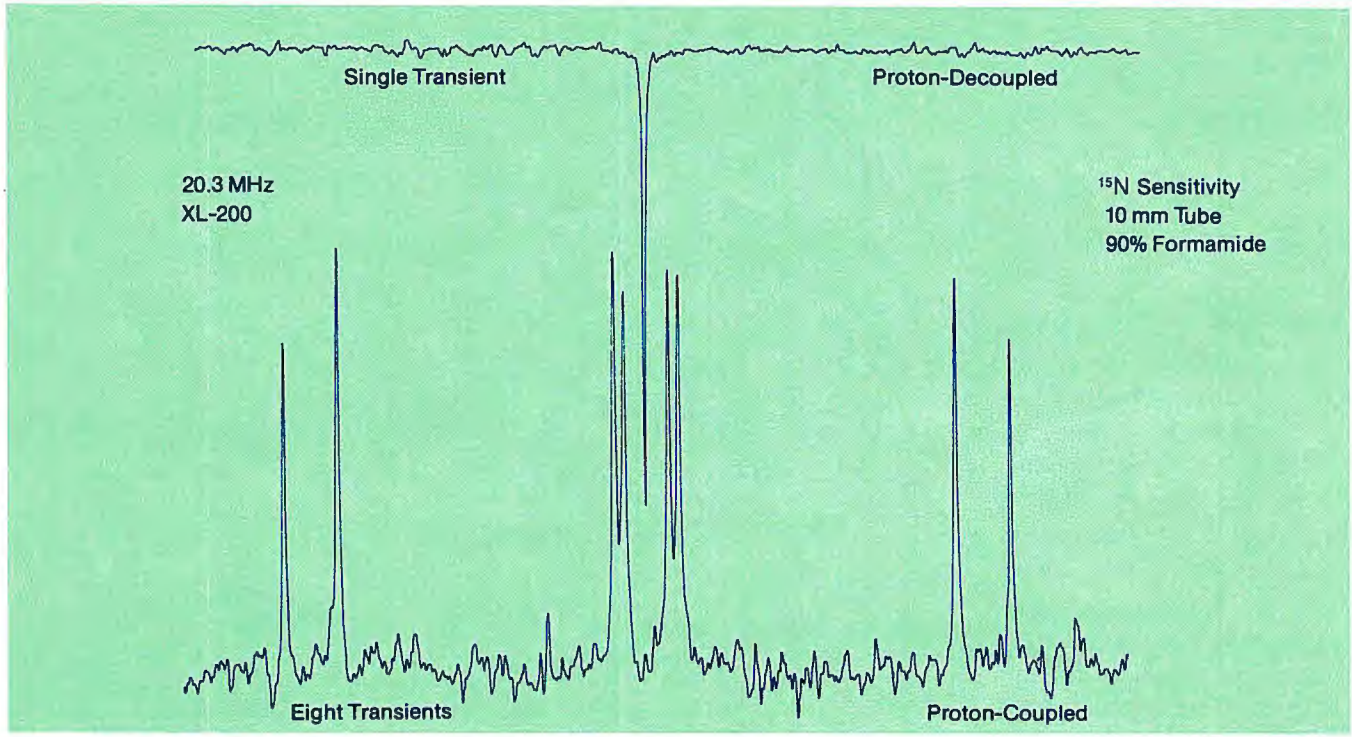


^{13}C Sensitivity Test: Cholesteryl acetate, 100 mg/ml, 10 mm broadband probe. Transients accumulated using 90° pulses every 2.28 seconds with 0.5 Hz line-broadening.

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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DURHAM, NEW HAMPSHIRE 03824

Department of Chemistry
College of Engineering and Physical Sciences
Parsons Hall (603) 862-1550

January 22, 1981

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

Re: NMR of Vanadates

Dear Professor Shapiro:

The original work of O'Donnell and Pope[1] on ^{51}V NMR of vanadate(V) solutions using a CW spectrometer suggests that NMR spectroscopy should be a useful investigative tool of the chemistry of these species and their complexes with organic ligands. Despite the quadrupole moment of the nearly 100% abundant ^{51}V (I = 7/2), reasonably narrow linewidths are obtained. Because of the large nuclear moment of Vanadium-51, the NMR sensitivity relative to proton is 0.25.

We observe vanadium NMR quite easily with a JOEL FX90Q FT spectrometer equipped with an OMNI probe. Both sodium ortho- and metavanadate salts (Na_3VO_4 and $NaVO_3$, respectively), when dissolved in water at a concentration of 0.05 M, give rise to the same four line spectrum at pH 7.5. When referenced to vanadium oxytrichloride ($VOCl_3$) the chemical shifts and linewidths are 417 ppm (457 Hz), 482 ppm (342 Hz), 493 ppm (171 Hz), and 575 ppm (57 Hz). We assign the first three peaks to the decavanadate ion, $[V_{10}O_{28}]^{6-}$, based on their relative intensities of 1:2:2, chemical shifts, and linewidths. The three types of vanadium (numbering 2, 4, and 4 respectively) in decavandate are six coordinate with rhombic symmetry which leads to broadened lines. The observation of decavanadate in these solutions is unexpected since it is believed to only occur below pH 6. We assign the fourth peak at 575 ppm to the metavanadate ion $[(VO_3)_x]^{x-}$ with vanadium tetrahedrally coordinated.

The T_1 for $[(VO_3)_x]^{x-}$, as measured by inversion recovery, is about 12 ms. By using a spectral width of 20 kHz, a S/N ratio of approximately 100:1 was obtained after only one hundred 90° pulses. An accumulation time of 40 ms with zero filling after 20 ms was employed.

Sincerely,

Donald A. Folajtar

Donald A. Folajtar

N. Dennis Chasteen

N. Dennis Chasteen

[1] S.E. O'Donnel & M.T. Pope, J.C.S. Dalton, 2290 (1976).

269-27

UNIVERSITY OF SOUTHERN CALIFORNIA
UNIVERSITY PARK
LOS ANGELES, CALIFORNIA 90007

DEPARTMENT OF CHEMISTRY
(213) 741-2780

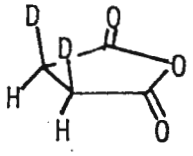
January 12, 1981

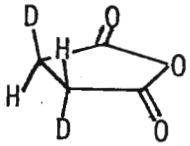
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Dear Professor Shapiro:

Observation of ^{13}C Satellites in ^{1}H NMR Spectra with ^{2}H Decoupling.

In the course of a stereochemical labelling experiment, we had reason to distinguish the meso- and d,l- isomers of 2,3-dideuteriosuccinic anhydride:

meso- 

d,l- 

From the ^{13}C satellites in the ^{1}H spectrum of succinic anhydride, the two vicinal proton-proton coupling constants can be obtained: ^{3}J(H-H,cis) equals 10.7 Hz and ^{3}J(H-H,trans) equals 5.2 Hz. Based on coupling constants which have been reported for substituted succinic anhydrides , these values are unexceptional and their relative magnitude is entirely as expected from a Karplus dependence.

Using the broadband probe and the versatile transmitter configuration of the Varian XL200 spectrometer it is possible to obtain proton spectra with heteronuclear decoupling. By employing the normal decoupling channel to observe ^{1}H, the broadband coil can be tuned to deuterium frequency and used to noise-decouple ^{2}H from the proton spectrum. Figure 1 shows the ^{13}C satellites in the ^{1}H spectrum of succinic anhydride and the corresponding spectrum of d,l-2,3-dideuteriosuccinic anhydride with ^{2}H decoupling. Each of the satellites in the d,l- compound appears as a doublet of spacing 5.2 Hz and similarly, the meso- isomer yields a pair of doublets of spacing 10.7 Hz as expected from the trans and cis vicinal couplings in succinic anhydride itself.

Please credit this contribution to the account of Professor K.L. Servis.

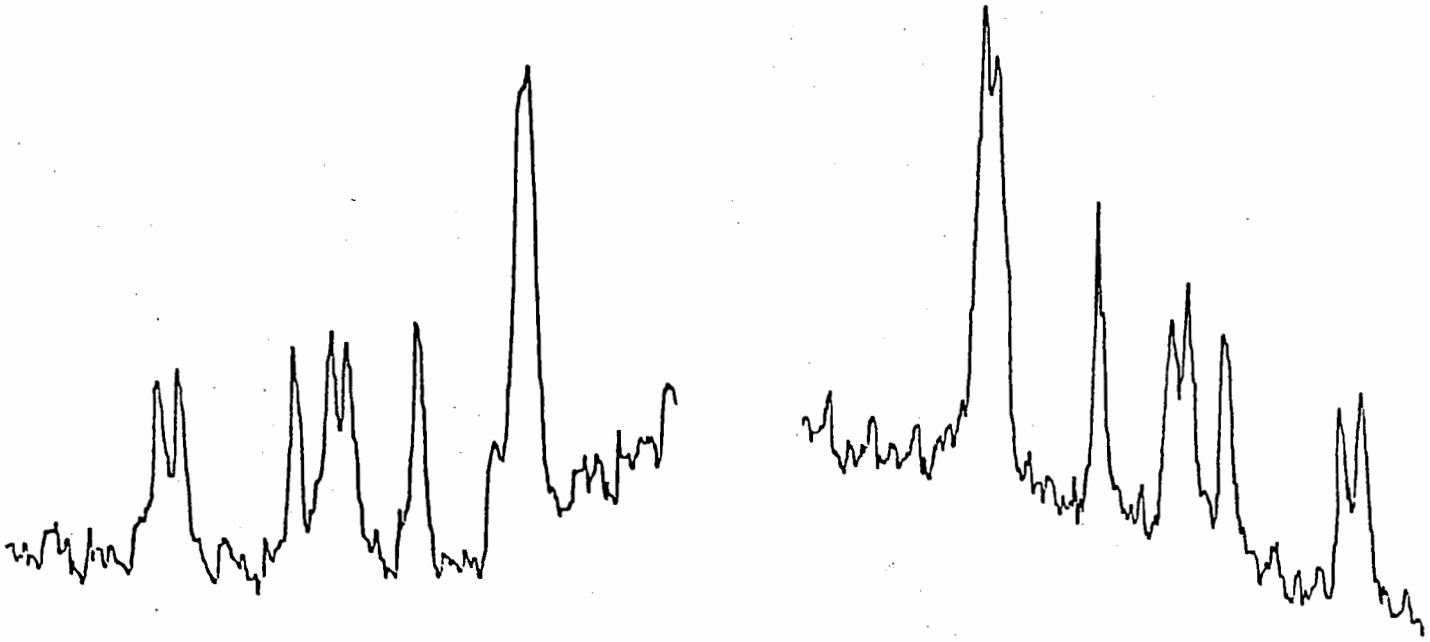
Sincerely,

L.D. Field

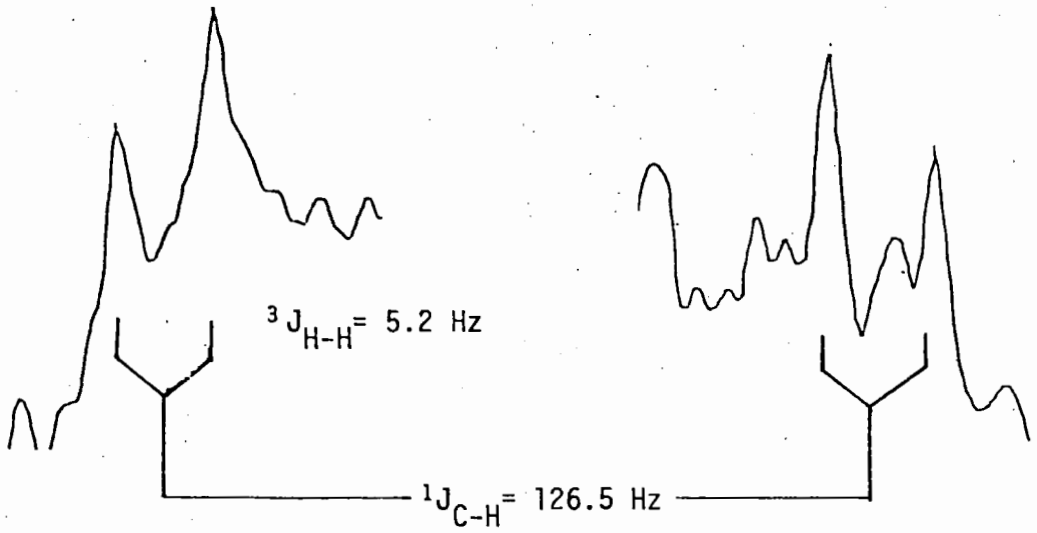
C.A. Kovac

1. L.E. Erickson, J.Am.Chem.Soc. 87, 1867 (1965)
2. S.L. Patt, XL200 User Tips, December 1979

-Figure 1-



a. ^{13}C Satellites in the ^{1}H spectrum of succinic anhydride. $^{3}J_{H-H(cis)} = 10.7$ Hz, $^{3}J_{H-H(trans)} = 5.2$ Hz.



b. ^{13}C Satellites in the H spectrum of d,l-2,3-dideuteriosuccinic anhydride with ^{1}H decoupling

269-29

ISTITUTO CHIMICO
della
UNIVERSITÀ DI TORINO

TORINO, 13th January, 1981

CORSO MASSIMO D'AZEGLIO, 48
Tel. 652.102 - 682.892 653.831 - 653.832

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

^{13}C-n.m.r. Spectra of highly ^{13}CO enriched metal carbonyls: observation of $^{2}J_{CC}$ cis.

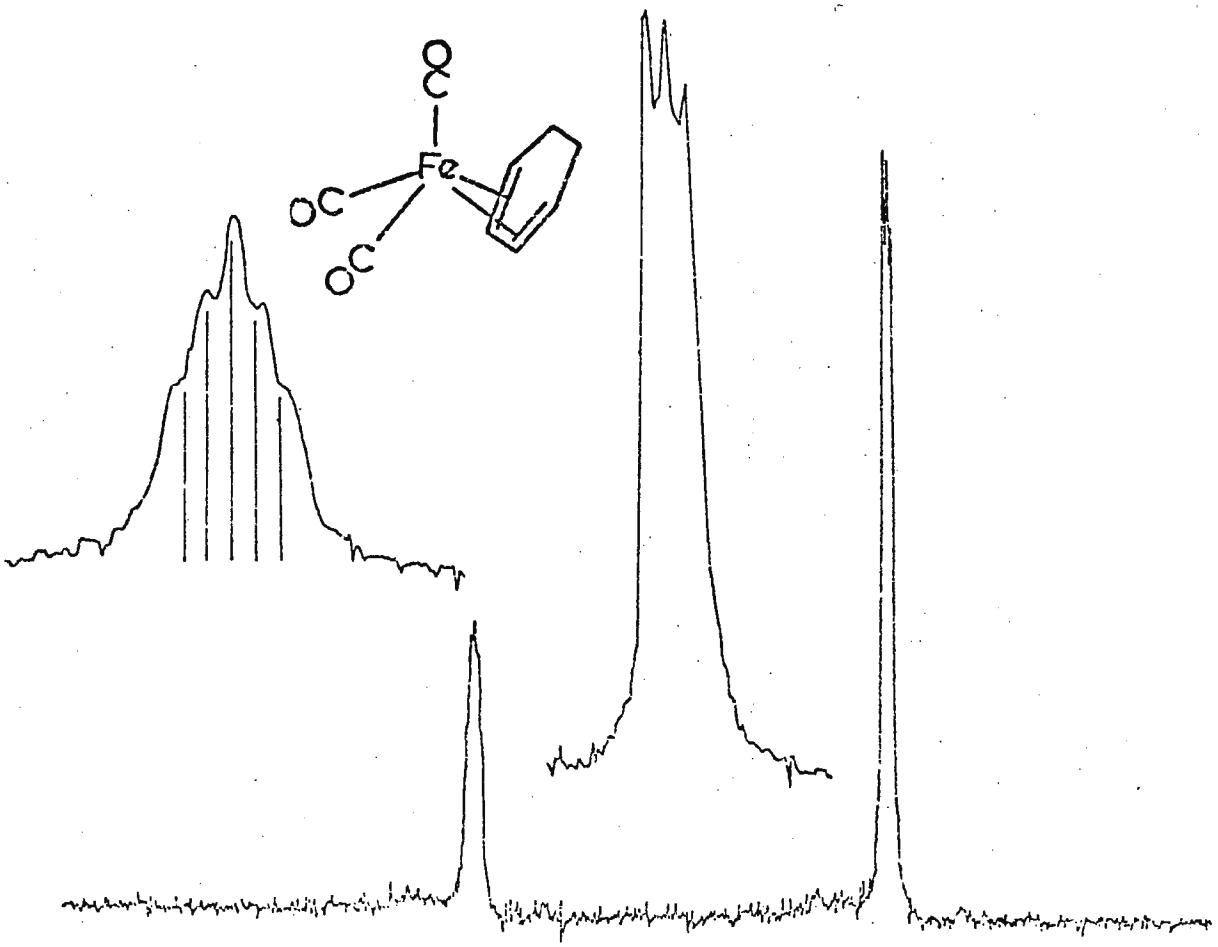
Dear Professor Shapiro,
In the last decade, C-13 n.m.r. spectroscopy has proved to be a useful tool in the elucidation of the structure, chemical bond and stereochemical non rigidity of metal carbonyl derivatives. ^{13}CO enrichment of the samples is frequently required in order to overcome solubility's problems at low temperatures in DNMR studies; the enrichment is usually in the range 10-20% to avoid unwanted broadening of the absorptions due to unresolved J_{CC} coupling. Few $^{2}J_{CC}$ were the observed: between axial carbonyls they are in the range 30-35 Hz (1); no evidence for axial equatorial coupling was gained.
We have recently recorded the C-13 n.m.r. spectra of highly ^{13}CO enriched (50-80%) metal carbonyl derivatives from which $^{2}J_{CC}$ cis are extractable. As an example, we report here the case of (1,3 cyclohexadiene)Fe(CO)$_3$, whose V.T. C-13 n.m.r. spectra were already reported (2): the single resonance observed in the carbonyl region at room temperature was ascribed to the fast rearrangement of the carbonyl groups on the n.m.r. time scale. This process is frozen at -90°C: two peaks (relative intensities 1:2) were observed and assigned to the axial and equatorial COs respectively. In the spectrum at -100°C of a 65% ^{13}CO enriched sample, the details of a fine structure are evident for both peaks (see figure): the two singlets are split in five and three lines. The origin of these patterns can be easily recognized in terms of the presence of different isotopomers according to the number of ^{13}CO incorporated. Then the quintuplet arises by overlap of a singlet (no C-13 in the

basal position) with a doublet (one C-13 in the basal position) and with a triplet (two C-13 in the basal position). Analogously the high field triplet - corresponding to basal CO_s - arises by overlap of a singlet with a doublet. The inner separation in the doublets and in the triplet corresponds to the $^2J_{cc}$ coupling constants (2.1 Hz).

Yours sincerely

S. Aime L. Milone D. Osella

References
1) M. Tachikawa, S.I. Richter and J.R. Shapley, J. Organomet. Chem. 1977, 128, C9.
2) L. Kruezynski and J. Takats, J.A.C.S. 1974, 96, 932.



UNIVERSITY OF DENVER
An Independent University
University Park, Denver, Colorado 80208

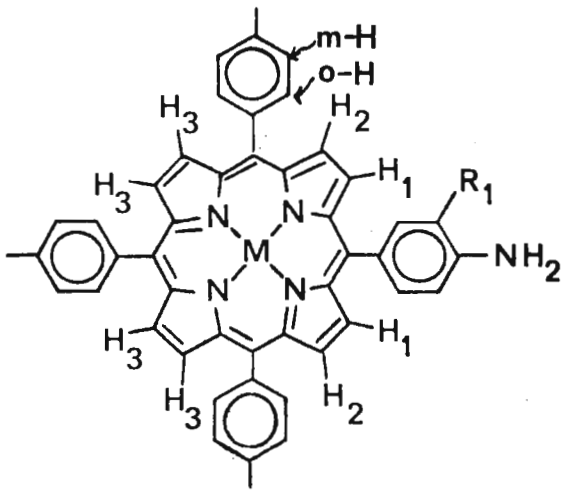
Department of Chemistry / 303·753-2436
January 14, 1981

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

Title: Site of chloride attack on an amino-substituted derivative of copper tetraphenylporphyrin.

Dear Barry:

Free porphyrin I reacts readily with copper acetate in pyridine solution to give copper porphyrin II in good yield. But when we tried to use the more common method for preparing copper complexes of tetraphenylporphyrins, i.e.



	M = H_2	M = Cu
R_1 = H	I	II
R_1 = Cl	III	IV

reaction of porphyrin I with $CuCl_2$ in refluxing DMF, we obtained two products which could be separated by chromatography in $CHCl_3$ solution on alumina. The second and smaller fraction moved on tlc plates (alumina or silica gel) with the same rf value as the authentic sample of II. Based on the evidence discussed below, the major product of the reaction is IV. Demetallation of IV with aqueous $POCl_3$ gave III. A high resolution mass spectrum of III indicated that it differed from porphyrin I due to replacement of one hydrogen by a chlorine. Since demetallation of II with $POCl_3$ gave I, it was clear that the chlorine in III was not coming from the $POCl_3$ and must be present also in IV. Elemental analyses also indicated the presence of chlorine in both III and IV.

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The position of the substitution was determined by a comparison of the ^1H NMR spectra of porphyrins I and III. The pyrrole protons H_1-H_3 in I are non-equivalent because of the difference between the electron donating properties of the amino substituted phenyl ring and the tolyl rings. H_1 and H_2 in I give a well-resolved AB pattern (see Table). However, in III there is almost no chemical shift difference between H_1 and H_2. The pyrrole signals are not consistent with chlorination at a pyrrole carbon. However, the substitution of a chlorine on the unique phenyl ring would partially offset the electron-donating effect of the amino group, thereby making the net electron density in the unique ring similar to that in the tolyl rings. This would result in similar shifts for H_1 and H_2. In III there are resolved signals for one ortho proton and one meta proton on the unique phenyl ring. The splitting of the ortho signal (J = 8 Hz, 2 Hz) indicates that there is a proton on the other ortho position of the phenyl ring although the signal must be obscured by one of the more intense signals. Thus the chlorine is on the meta position, adjacent to the amino group. The changes in the chemical shifts for the protons on the unique ring are also consistent with chlorination at the meta position.

The chloride may be coming from the $CuCl_2$ or the HCl produced by the metallation reaction. In either case it is surprising to find chloride attack on the electron-density-rich amino substituted ring. However, protonation of the amino group could reduce the electron density in the ring and facilitate the attack. If, in addition, there is significant ion pair formation, interaction of the H^+ with the amino group could position the Cl^- near the meta carbon which might facilitate the attack.

Whatever the mechanism of the reaction, the observation of substitution indicates that when it comes to amino substituted porphyrins it's better to keep chloride out of the reaction mixture.

TABLE

^1H Chemical Shifts in $CDCl_3$*

	H_1 H_2	H_3	tolyl rings		unique rings	
			o-H	m-H	o-H	m-H
I	8.87 (AB) $\Delta\nu$ = .07 ppm J = 7 Hz	8.83	8.10	7.54	7.76	7.05
III	8.85 (broad)	8.83	8.10	7.55	7.89 J = 8 Hz, 2 Hz	7.09 J = 8 Hz

*Coupling constants which are not used in the discussion above are omitted from the table.

Sincerely,

Sandy

Sandra S. Eaton
Associate Professor

Gareth

Gareth R. Eaton
Professor

SSE:rd

269-33

QUEEN MARY COLLEGE

UNIVERSITY OF LONDON

DEPARTMENT OF CHEMISTRY
Professor D.C.Bradley, Ph.D.,D.Sc.,C.Chem.FRIC.(Head of Department)
Professor R.Bonnett, B.Sc.,Ph.D.,D.Sc.
Professor K.W.Sykes, MA.,B.Sc.,D.Phil.

MILE END ROAD
LONDON E1 4NS
Tel. 01-980 4811

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

14th January, 1981.

Dear Professor Shapiro,

ULIRS NMR Service; ^{99}Tc N.m.r.

The University of London Intercollegiate Research Service (ULIRS) WH-400 n.m.r. spectrometer at Queen Mary College has been in routine operation since 1st October 1980. As expected the greatest demand has been for ^{1}H and ^{13}C spectra, and we have found the 'pseudo-INDOR' technique to be particularly useful in unravelling complex ^{1}H spectra, and our dedicated ^{13}C 5 mm probe provides excellent spectra on ca. 5 mg material M.W. 500 for an overnight accumulation. In the first 3 months of operation we have also received requests for and run spectra of ^{109}Ag, ^{27}Al, ^{111}Cd, ^{113}Cd, ^{35}Cl, ^{37}Cl, ^{69}Ga, ^{71}Ga, ^{2}H, ^{39}K, ^{14}N, ^{15}N, ^{17}O, ^{31}P, ^{207}Pb, ^{195}Pt, ^{29}Si, ^{117}Sn, ^{119}Sn, ^{99}Tc, ^{205}Tl and ^{67}Zn.

99-Technetium is a radio-isotope ($t_{\frac{1}{2}}$ ca, 2.1 x 10^{5}y) and the only previous report of a ^{99}Tc resonance ($I=^{9}/2$) is the unpublished work of Kidd[1] who mentioned a line width of 29 Hz from TcO_4^-. Figgis et al[2] reported a single ^{17}O resonance ($\Delta\nu_{\frac{1}{2}}$ ca. 1150 Hz) from ^{17}O-enriched TcO_4^-. In our study, in collaboration with Dr. J. Thornback of Chelsea College, a sample of 0.55 mCi of $NH_4{}^{99}TcO_4$ in 2 ml D_2O gave a sharp ($\Delta\nu_{\frac{1}{2}}$ 3 Hz) ^{99}Tc resonance at 90.06 MHz (9.4 T , Ξ ca. 22,508, 304) and T_1 = 0.13s, T_2 = 0.10s. Signal/noise was very high from a single transient. The 54.2 MHz natural abundance ^{17}O spectrum showed 10 lines with

PTO

$^{1}J_{^{17}O-^{99}Tc}$ = 131.6 Hz. As yet we have no other ^{99}Tc data, but in view of the upsurge of interest in ^{99}Tc chemistry (as applied in diagnostic medicine) further studies are in hand.

Best wishes.

Yours sincerely,

Geoff Hawkes.

G.E. Hawkes

MJ Buckingham

M.J. Buckingham

1. R.G. Kidd and R.J. Goodfellow in "NMR and the Periodic Table", Eds. R.K. Harris and B.E. Mann, Academic Press, London, 1978, Ch. 8.

2. B.N. Figgis, R.G. Kidd and R.S. Nyholm, Proc. Roy. Soc. A. 1962, A269, 469.

(Continued from page 35.)

Table 1
Execution times for the various parts of the FFT algorithm (seconds).

Site	Bit Reversal	Internal Transform	Final Passes	Reorder	Total
2K-2K	<1	4	1	<1	5
4K-4K	1	6	4	<1	11
8K-8K	2	13	10	<1	25
16K-16K	5	28	24	2	59

References:

1. Brigham, E. O. The Fast Fourier Transform, Prentice-Hall, Inc. (1974).

Please credit this contribution to Dr. Levy's account.

Sincerely,

Chuck Dumoulin

Chuck Dumoulin

CD/lh

Department of Chemistry
The Florida State University
Tallahassee, Florida 32306

January 15, 1981

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

Re: Virtual Array Fast Fourier Transform

Dear Dr. Shapiro:

A severe restriction to the implementation of NMR data processing software on general purpose minicomputers is the limited addressing range provided by 16-bit architecture. Modern operating systems frequently circumvent this problem by utilizing extended memory. Sophisticated operating systems take this scheme one step further by supporting virtual arrays in which data is dynamically moved between addressed memory, extended memory and disk storage. Such a system exists in our laboratory.

Unlike most processing functions, the Fast Fourier Transform algorithm accesses data in a complex fashion. During its execution, individual data points in widely different parts of the real and imaginary data arrays must be retrieved. Clearly, if only selected portions of the arrays are within the program's address space at any given instant, the algorithm must be designed with care.

We have designed (in conjunction with Dr. F. A. L. Anet of U.C.L.A.) a virtual array FFT algorithm which is relatively simple and efficient. The algorithm is divided into four parts as shown in Table 1. The transforming techniques of the internal transforms and the final passes differ significantly. The internal transforms are performed by a self-contained (except for bit reversal) FFT whose mechanism is approximately twice as fast as the one given by Brigham,[1] yet just as straightforward. The final passes use the Brigham method extended to accommodate virtual arrays. The final step resequences the array to present the data in the standard quadrature spectrum format.

The times shown in Table 1 were obtained on our Eclipse S/130 with single precision floating point data (32-bit). The virtual arrays were addressed through 1024-point windows. In addition, the arrays were entirely within extended memory (not on disk).

CONTINUED ON PAGE 34.

CENTRO DE INVESTIGACION DEL IPN
APARTADO POSTAL 14-740
MEXICO 14, D. F.

DEPARTAMENTO DE QUIMICA

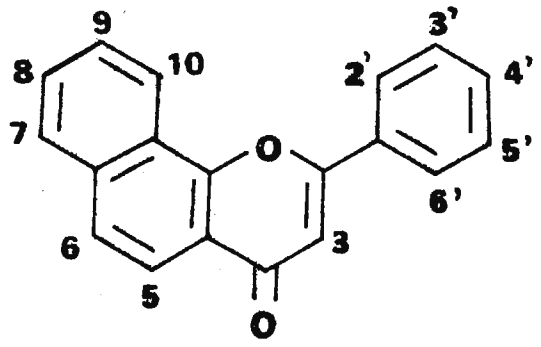
Enero 12, 1981

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

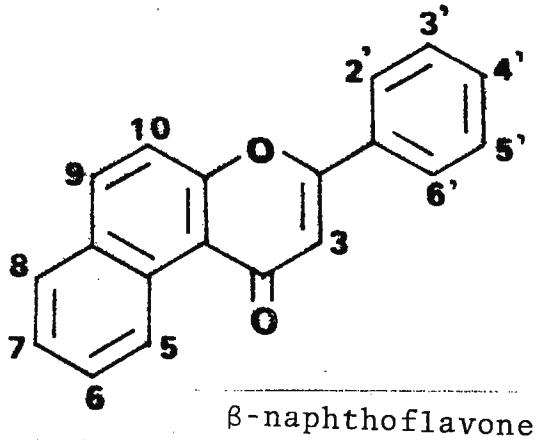
Dear Professor Shapiro:

Evidence for a long distance bidentate interaction with $Eu(fod)_3$.

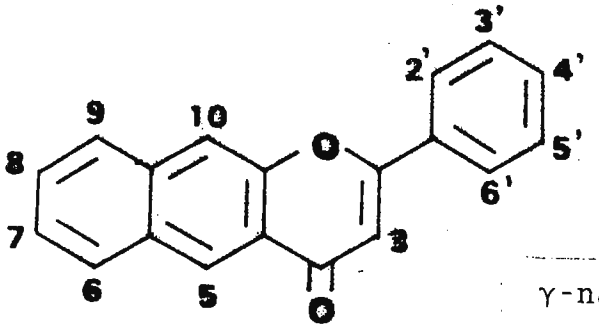
Continuing our studies (1) on the behavior of flavones in the presence of shift reagents, we are at present analysing the three following types of naphthoflavones:



α-naphthoflavone

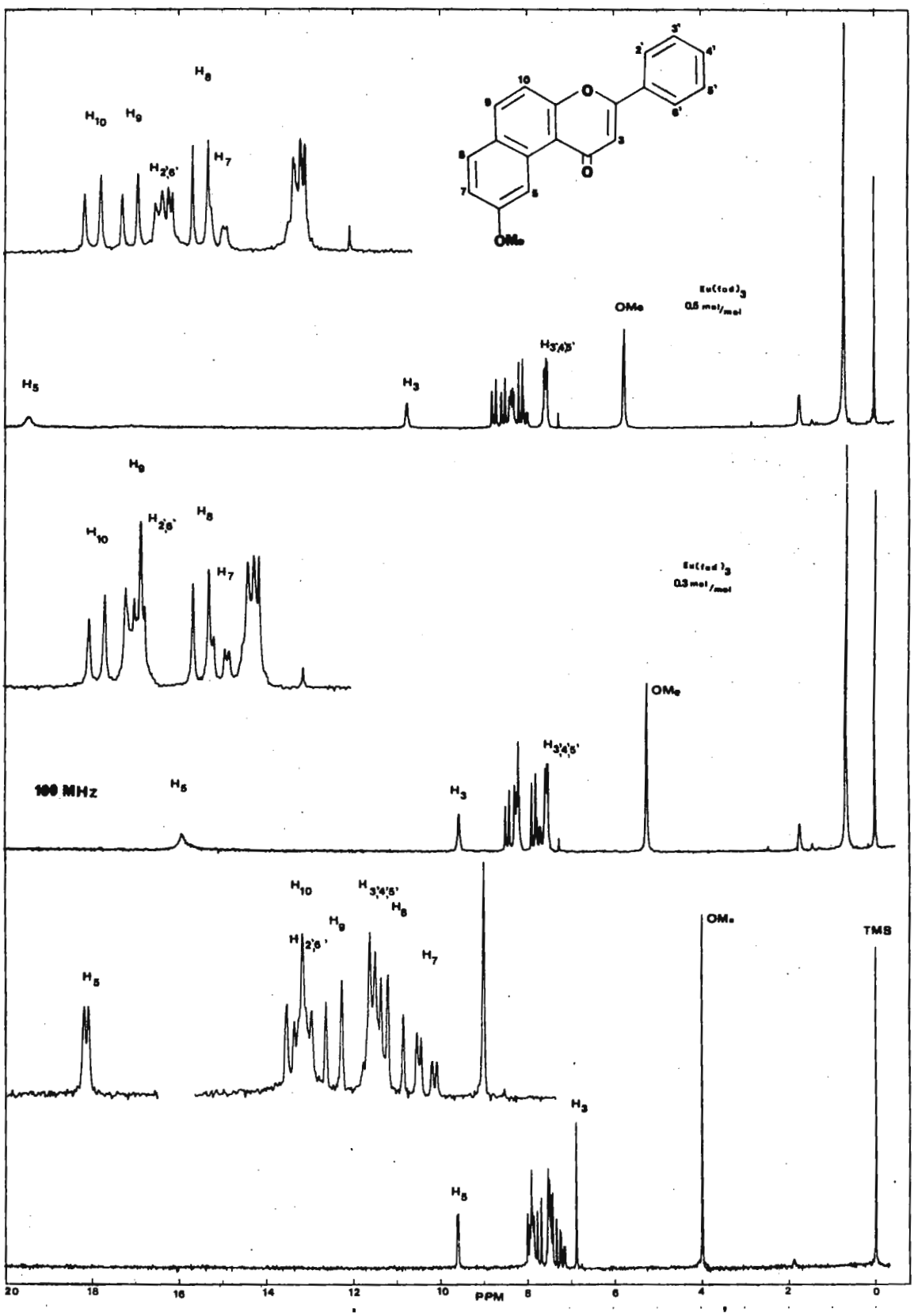


β-naphthoflavone



γ-naphthoflavone

In contrast to flavones (2), for which $Pr(fod)_3$ additions combined with 60 MHz measurements not only provide all desired information (3), but even allow structure ellucida- (4) of these molecules; in the case of naphthoflavones, due to the presence of more aromatic protons, it becomes neces-



Proton nmr spectra of 6-methoxy-β-naphthoflavone.
Lower: Pure substrate; Center: in the presence of 0.3 mol/mol $Eu(fod)_3$; Upper: in the presence of 0.5 mol/mol $Eu(fod)_3$.

sary to perform the measurements at 100 MHz, as well as to use $Eu(fod)_3$ as the shift reagent, since when $Pr(fod)_3$ is used the signals generally fail to spread out sufficiently to make definite assignments.

Up to the present the following compounds have been measured: α-; 3',4'-dimethoxy-α-; 3',4',5'-trimethoxy-α-; 7--methoxy-α-; 7,3',4',5'-tetramethoxy-α-; β-; 3',4',5'-trimethoxy-β-; 6-methoxy-β-; 7-methoxy-β- and γ-napthoflavone.

The behavior of the studied compounds is, in general, in agreement with our expectations regarding previous studies on flavones. However, in the case of 6-methoxy-β-naphthoflavone (figure) there is evidence for a weak bidentate complexation, since after addition of 0.5 moles of $Eu(fod)_3$ per mole of flavone, the methoxy signal broadens more than five times when compared to the TMS signal under the same magnet homogeneity conditions.

The broadening of this methoxy signal is not as spectacular as those found in 5-methoxy-flavone (5), where addition of 0.1 moles of shift reagent per mole of substrate causes the methoxy signal ($W_{1/2}$ = 9 Hz) to strongly broaden, or in 3,3',4',5,6,7-hexamethoxy-flavone, where the addition of only 1 mg of $Pr(fod)_3$ to 20 mg of substrate broadens the 5-OMe signal so severely that it is almost lost in the base line (1). Nevertheless, it is interesting to see such a broadening in 6-methoxy-β-naphthoflavone, an essentially rigid moiety where the two oxygen atoms involved in the association are separated by at least 4Å.

Sincerely yours,

Pedro Joseph-Nathan
Professor of Chemistry

R.L. Santillan
Graduate Student

(1) P. Joseph-Nathan and D.A. Abramo-Bruno, TAMU NMR Newslett., 248, 22 (1979).

(2) P. Joseph-Nathan, J. Mares, Ma. C. Hernández and J.N. Shoolery, J. Magn. Resonance, 16, 447 (1974).

(3) P. Joseph-Nathan and J.G. Mares, TAMU NMR Newslett., 194, 17 (1974).

(4) P. Joseph-Nathan, D. Abramo-Bruno and Ma. A. Torres, Phytochem., (in press).

(5) P. Joseph-Nathan, J. Mares and D.J. Ramírez, J. Magn. Resonance, 34, 57 (1979).

Laboratoire de Chimie Organique Physique - Institut de Chimie - Université de Liège - Sart-Tilman par 4000 Liège 1 - Belgique

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

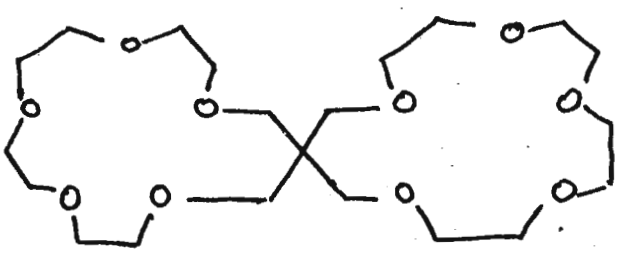
January 15, 1981

Variations on a Theme by Pedersen.

Dear Barry,

Involvement of chemists with crown ethers has reached epidemic size. We have not remained immune. However, rather than having our crown ethers in the normal way, we prefer them in double dose (e.g. spiro derivatives 1 and 2)or cut (e.g. 3 and 4). Why ?

Using ^{23}Na nmr, we find that one or two sodium ions will bind to the dicoronands[1] 1-2 : the doubly-occupied complexes display binding constants smaller to those for the singly-occupied complexes by one order of magnitude; the electrostatic repulsion of the cations being (partly) compensated by reduced solvation and electrostriction of the dicationic as compared to the monocationic complex.



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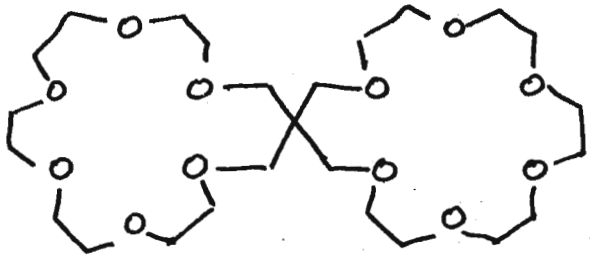
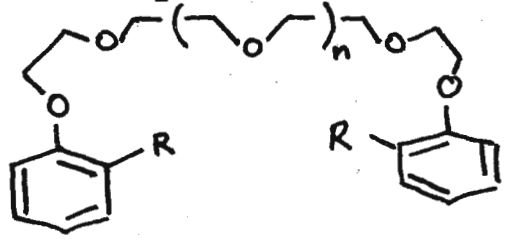


2

Linear polyethers such as 3 and 4 wrap themselves around the cation. While $\Delta H = -18 \pm 3$ kJ.mol^{-1} and $\Delta S = -11 \pm 3$ J.K^{-1}.mol^{-1} for 3. Na^+, with the homologous ligand 4.Na^+ has $\Delta H = -66 \pm 10$ and $\Delta S = -185 \pm 45$ for 1:1 complex formation in pyridine solution. This difference reflects solvent participation in 3.Na^+ (but not in 4.Na^+) complex formation.



R = $NHCOCH_3$

3 n = 1

4 n = 3

Laboratoire de Chimie Organique Physique - Institut de Chimie - Université de Liège - Sart-Tilman par 4000 Liège 1 - Belgique

The effect originates in a full spherical engulfing of Na^+ by 4, with its ten heteroatoms coordinating the ion, a geometry which cannot be achieved by the smaller fellow 3.

Lastly, have you heard about our nmr-cum-gastronomy workshop in Tallahassee in September ? If not, you should try for yourself "Paté Lamourette" : you prepare it from bone marrow, chopped mushrooms, eggs, and seasoning; whip thoroughly, then 1/2 hour in a very hot oven. Just luscious.

The work summarized in the second paragraph has been done with James Bouquant, Freddy Delville, and Jean Grandjean; the study excerpted in the third paragraph has been done with Jean Grandjean, Werner Offermann, and Peter L. Rinaldi; while Frank Anet and George Levy were both patrons and scullions for the prep summarized in the fourth paragraph.

With kind regards and best wishes for 1981,

Cordially yours,

Pierre Laszlo

PL:nd

1. E. Weber and F. Vögtle, Inorg. Chim. Acta, 1980, 45, L65-L67.

UNIVERSITY OF NEW BRUNSWICK Post Office Box 4400 \ Fredericton, N.B. \ Canada E3B 5A3

Physics Department
(506) 453-4723

January 20, 1981

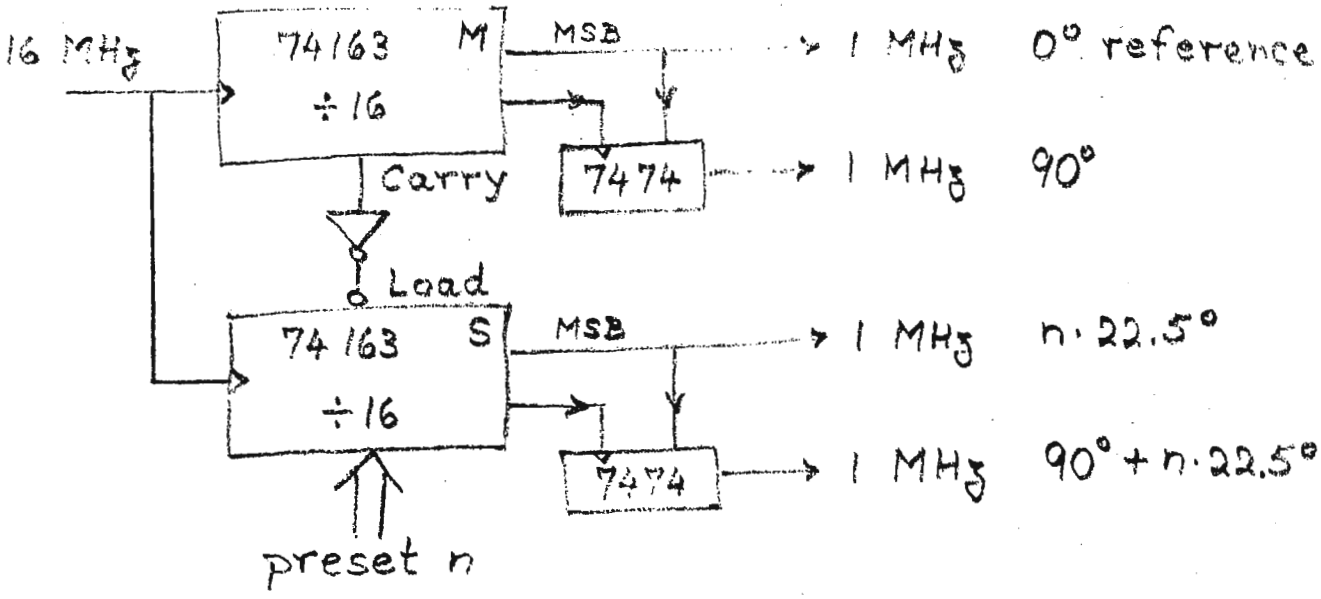
Dr. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843

DIGITAL PHASE SHIFTER

Dear Barry:

RF pulses are sometimes required with various phase shifts relative to a reference. For example, cycling methods for quadrature detection require 90° phase shifts, and identification of multiple quantum transitions can be achieved with 360°/n phase shifts where n is an integer. A circuit to produce such phase shifts under digital control has been described by G. Bodenhausen in the J. Mag. Reson. 34, 357 (1979).

After we had assembled this circuit, our technician, John Lewis, discovered a somewhat different method described by A. Salina in the Designer's Case Book of "Electronics" (ca. 1974). It can be further simplified to yield the following scheme.



Dr. Bernard L. Shapiro January 20, 1981

The 74163 is a 4 bit presettable counter. We use it to divide a 16 MHz input to a 1 MHz output (it can be clocked up to 32 MHz). Every microsecond, when the master M overflows at a count of 15, it produces a carry pulse which is used to preset the slave S to a count n between 0 and 15. The slave thus starts its count at n instead of 0, and its 1 MHz output leads that of the master by n/16 microseconds giving a phase shift of $n \cdot 360°/16$. The 4 bit preset data is reloaded every microsecond, although it will differ from the slave count at that instant only if the preset lines have changed within the last microsecond. Of course, the values 16 MHz, 1 MHz, 1 μsec, and the count of 16 with binary 4 bit preset are not essential for this scheme, they merely reflect our implementation at the present time. Counters can be cascaded to obtain greater n although the output frequency then decreases accordingly. The master can load several slaves so that several phase shifts are available in parallel. In fact, a quadrature output is required in each channel for the single-side-band mixer that translates the 1 MHz to the desired nmr frequency. This quadrature signal is easily generated as shown with a 7474 flip flop whose D and C1 inputs are fed from the most significant bit and the MSB-1, respectively, of the counter.

Sincerely yours,

Reinhold

Reinhold Kaiser

RK:seb

269-43

DEPARTMENT OF CHEMISTRY
TEL. (403) 432-3254
TELEX 037-2979

THE UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA, CANADA
T6G 2G2

January 20, 1981

Dr. Barry Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas
U.S.A. 77893

Dear Barry,

Re: ^{1}H NMR on 5 mm ^{19}F probe on the WH-400.

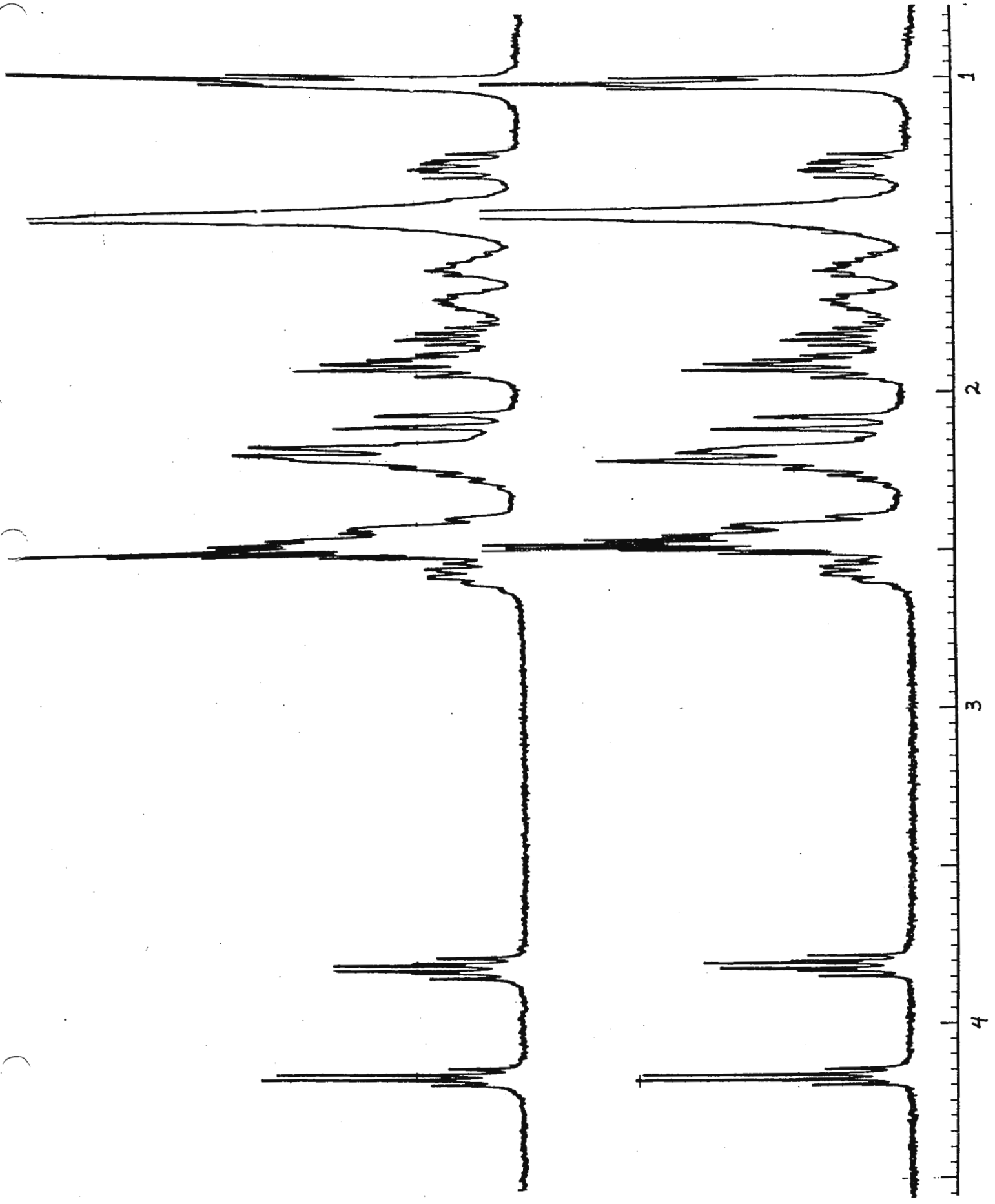
While ejecting the sample, the top 1" of our 5 mm ^{1}H insert was completely broken off. The nature of the sample was such that the entire insert was a complete write-off. We were faced with the possibility of being unable to run ^{1}H NMR (which constitutes about 80% of the work load on the WH-400) for several months until our probe was repaired or a new one delivered. Fortunately we have a 5 mm ^{19}F probe and decided to tune it to 400 MHz. The only trick we found necessary was to detune the ^{1}H decoupler coil first (we chose the ^{19}F frequency) and then tune the receiver coil to ^{1}H in the standard manner. Proton spectra obtained from standard ^{1}H test samples on the ^{19}F probe for S/N, hump and resolution were surprisingly good with no indication of background ^{1}H signals. Shown in the Figure is a portion of the ^{1}H NMR spectrum of a prostaglanden taken under identical conditions (same sample, pulse width, etc.) in the 5 mm ^{1}H probe (taken one month ago) and the 5 mm ^{19}F probe retuned to 400 MHz. The spectrum from the ^{19}F probe is slightly noisier but otherwise identical to that obtained in the 5 mm ^{1}H probe.

Sincerely,

Tom

Tom Nakashima

TN/ss


1
2
3
4

NORTHWESTERN UNIVERSITY COLLEGE OF ARTS AND SCIENCES

Department of Chemistry

Evanston, Illinois 60201

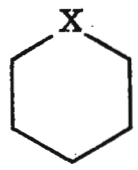
January 26, 1981

Professor Bernard L. Shapiro
Department of Chemistry
TAMU NMR Newsletter
Texas A & M University
College Station, Texas 77883

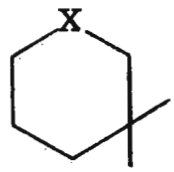
Dear Barry:

A number of workers recently have used the temperature dependence of carbon-13 chemical shifts to calculate free energy differences between rapidly interconverting forms such as conformers or carbocations. We have found that the ^{13}C shifts of 3,3-dimethylheteracyclohexanes are extremely temperature dependent and that the plots of shift vs. temperature are curved for the 3 carbons. We endeavored to exploit this behavior to calculate the chair-twist free energy difference. Unfortunately, the results were worse than unreliable, as they cast doubt on the entire use of the Wood-Fickett-Kirkwood (WFK) method for ^{13}C chemical shifts.

Our strategy was to compare energy differences for unsubstituted, disubstituted, and tetrasubstituted systems (1-3), in which increased proportions of the twist form should be observed. Typical shift/temperature



1



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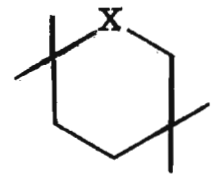


3

gradients were 20-70 x 10^{-4} ppm/K. Calculated values of $\Delta G°$ failed to exhibit the expected dependence on methylation. For example, when the shifts were expressed simply as differences from internal TMS, $\Delta G°$ for 1-3 (X = CH_2), respectively, was 1450, 850, 1150 cal/mol (the series should have decreased monotonically). Other trends were equally poor. Worse still, the rigid molecule 2,2-dimethyladamantane provided converging results that gave a free energy difference of around 2000 cal/mol for a totally

Professor Bernard L. Shapiro January 26, 1981

nonexistent second species. Using the Jameson correction for the temperature dependence of TMS did not improve the situation, nor did the use of internal chemical shift comparisons of two carbons within the same ring.

The problem is that the temperature dependence of the ^{13}C chemical shift is influenced by two factors. In addition to the effects of conformational or structural equilibria, intrinsic factors such as variation of bond lengths or bond dipoles with temperature also can alter the chemical shift. Mislow pointed out some time ago that successful use of the WFK method requires accurate temperature and shift measurements, which imply little or no alternative contributions to the chemical shift/temperature gradient. In the present context, the inherent factors are much too large to permit application of the WFK method. Unfortunately, inherent factors vary significantly from one carbon to the next, so that internal compensation is difficult. It may be that in some cases the inherent factors are small, compared to the equilibrium shift, but this condition would have to be demonstrated by appropriate controls in each case. Simply observing a converged calculation for the free energy difference apparently proves nothing, even when the shift/temperature plot is curved. Although the WFK method works very well when chemical shifts are subject only to the temperature effects of a shifting equilibrium, the large and structurally variable inherent gradient of ^{13}C chemical shifts is not reliably factored out.

Sincerely,

Joseph B. Lambert
Adelia R. Vagenas

Title: Carbon-13 chemical shift/temperature gradients and a Wood-Fickett-Kirkwood Failure

JBL/jr

269-47

United States Department of Agriculture
Science and Education Administration
Agricultural Research Northeastern Region Eastern Regional Research Center
600 East Mermaid Lane Philadelphia Pennsylvania 19118

January 26, 1981

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

Subject: Effects of deuteration on the ^{13}C solid state NMR spectra of carbohydrates

Dear Professor Shapiro:

Our recent studies concerning the perturbation effects of exchangeable deuterium on the ^{13}C solution spectra of carbohydrates[1,2] have stimulated us to examine this phenomenon in the solid state. Typically, crystalline carbohydrates exhibit excellent C.P.-M.A.S. narrow line spectra (4-10 Hz at 15 MHz) in the solid state. These spectra have been effectively used to define tautomeric equilibria[3] and conformational states.[4a,4b]

We have examined the 15 MHz ^{13}C solid state C.P.-M.A.S. spectra of both proteo and deutero exchanged and recrystallized carbohydrates to evaluate the perturbing effects induced by exchangeable deuterium substitution. As can be seen in Figure A, α-methyl glucoside crystals in the normal OH state give a well resolved spectrum (8 Hz line width). Upon deuterium exchange and subsequent recrystallization from deuterium oxide, this compound exhibits spectra which have considerably broader lines (20 Hz) and diminished resolution (Figure B). More importantly, however, we observed that the intensity of the resonance corresponding to the C-6 carbon has essentially disappeared. Furthermore, the intensity of this resonance does not respond to changes in the range of contact times (0.5 ms-5 ms) or repetition rates (3-20 sec) studied. This phenomenon has also been observed for β-methyl glucoside.

These findings suggest that exchangeable deuterium induces stronger quadrupolar interactions in primary vs. secondary carbinol carbons. In addition, if intramolecular exchange of labile OD at the primary carbons in the solid state is slow on the NMR time scale, a broad signal could result from a range of shift positions representing varying degrees of deuterium association. This is counter to what one might predict, based on the fact that in solution the most rapid OD exchange takes place at C-6.

Sincerely,

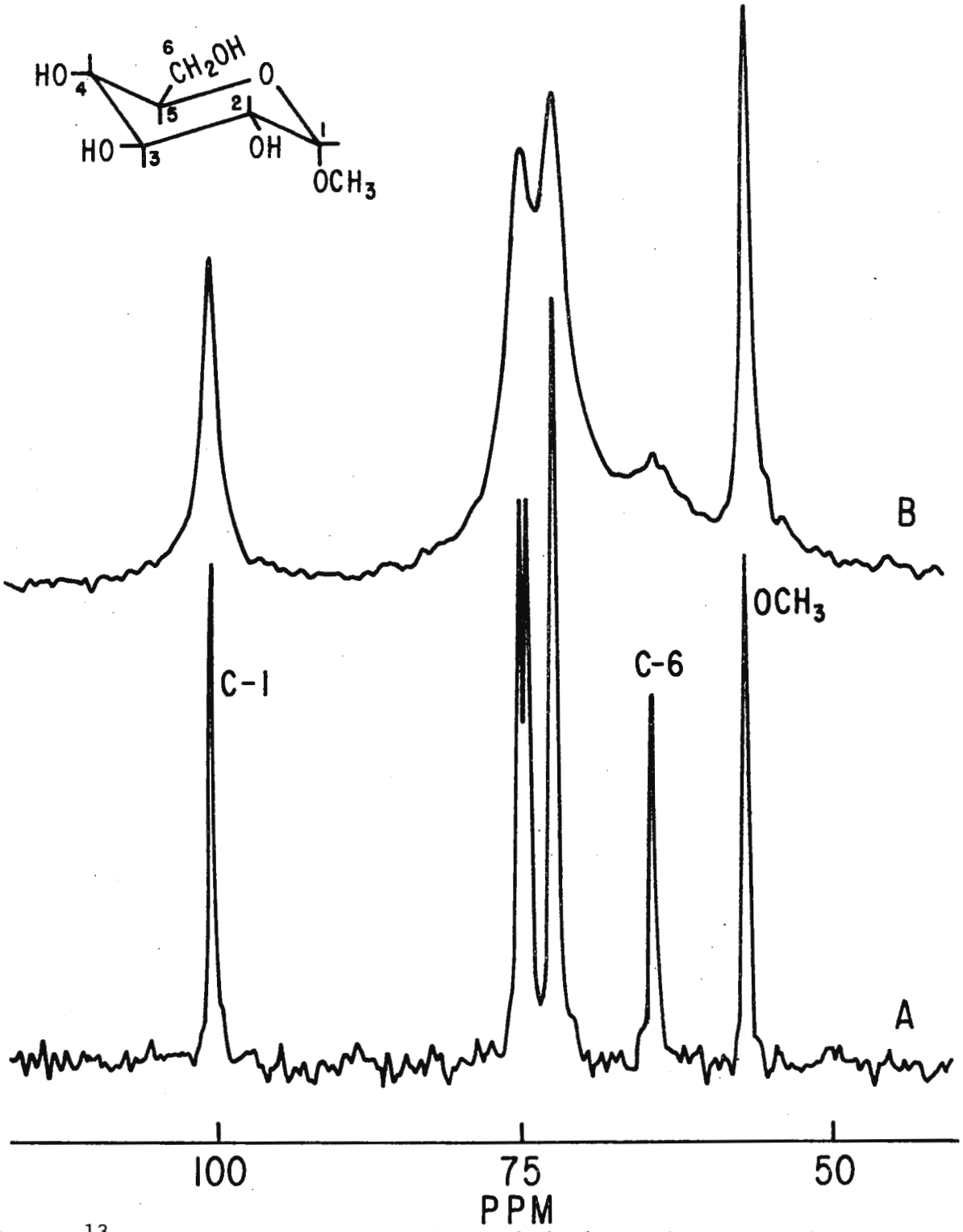
Philip E. Pfeffer Kevin B. Hicks Kathleen M. Valentine

1 P. E. Pfeffer, K. M. Valentine, and F. W. Parrish, J. Am. Chem. Soc. 101 (1979) 1265.

2 P. E. Pfeffer, F. W. Parrish, and J. Unruh, Carbohydr. Res. 84 (1980) 13.

3 P. E. Pfeffer, K. B. Hicks. Abstract. 179th National Meeting of the American Chemical Society, March 23-28, 1980, Carbohydrates paper #26.

4a R. H. Atalla, J. C. Cast, D. W. Sindorf, U. J. Bartuska, and G. E. Maciel, J. Am. Chem. Soc. 102 (1980) 3249; 4b W. L. Earl and D. L. VanderHart, J. Am. Chem. Soc. 102 (1980) 3251.



A. 15 MHz, ^{13}C C.P.-M.A.S. spectrum of α-methyl glucoside. Conditions: spectral width = 2000 Hz, contact time = 4 ms, repetition rate = 3 sec, 1000 transients, spinning rate = 2400 Hz.

B. 15 MHz, ^{13}C C.P.-M.A.S. spectrum of deuterium exchanged and D_2O recrystallized α-methyl glucoside. Conditions: spectral width = 2000 Hz, contact time = 4 ms, repetition rate = 10 sec, 2500 transients, spinning rate = 2400 Hz.

269-49

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January 29, 1981

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

"New Level of 10mm C-13 Sensitivity"

Dear Barry:

Since my arrival at Varian there has been a great deal of energy expended in advancing probe technology. My colleagues and I are pleased to announce at this time that the first generation of probes for the XL-200 are now available.

Enclosed are two spectra taken on the new 10mm fixed frequency C-13 probe. Figure 1 shows the standard ASTM sensitivity test using 3.5Hz of line broadening. Figure 2 is a 16 transient spectrum of cholesteryl acetate (100 mg/ml). I feel that comparison of the performance of this probe with other 10mm mid field superconducting NMR systems will indicate that these probes represent a new level of 10mm C-13 performance. Routine runs on 1 millimolar concentrations of cholesteryl acetate is just one example of the new dimension that these probes lend to the XL-200. Representative spectra of this and other new generation probes will be shown at the 22nd ENC (Asilomar).

Sincerely yours,

Toby

Toby Zens

Please credit to Howard Hill's account.

/m
enclosures

611 hansen way/palo alto/california 94303/u.s.a./415/493-4000

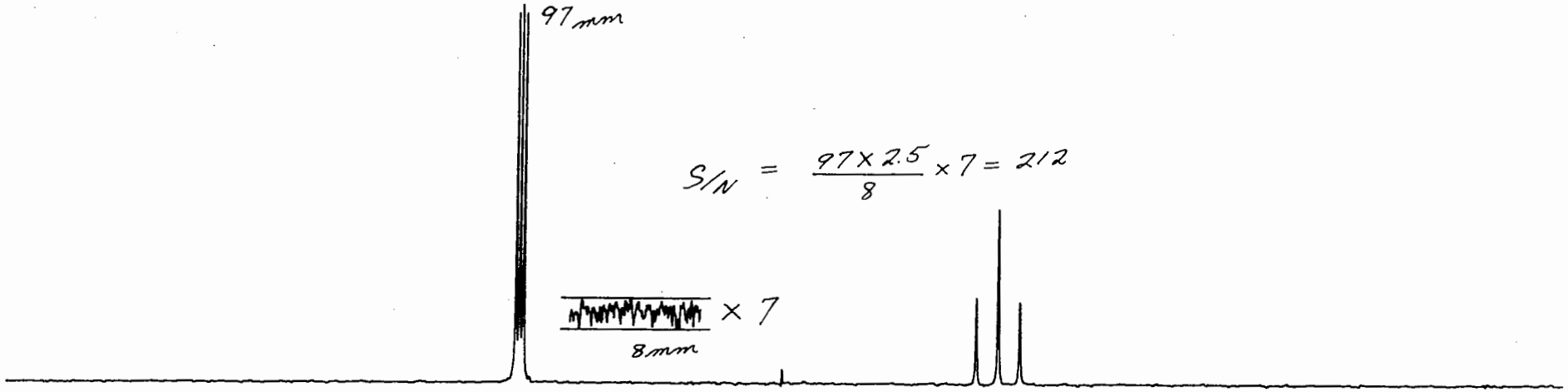

FIGURE 1

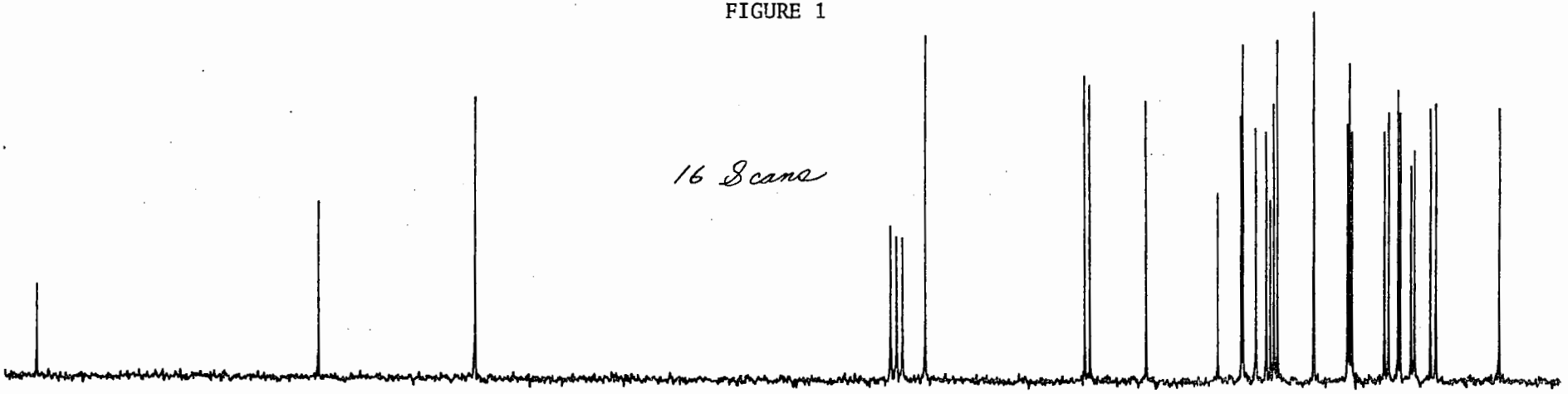

FIGURE 2

269-51

THE UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
RIVER STATION
ROCHESTER, NEW YORK 14627

DEPARTMENT OF CHEMISTRY

January 16, 1981

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

Dear Barry:

BIOPHYSICAL POSTDOCTORAL POSITION

I have a postdoctoral position available in my laboratory. The starting date is flexible (anytime during the spring or summer of this year). The main thrust of our research program is the spectroscopic study of drug-nucleic acid complexes. We will be studying the binding of several important drugs to chromatin, native and synthetic DNA's, and deoxyoligonucleotides. All good candidates (spectroscopists, biochemists and organic chemists) will be considered for this position, as we are using a variety of techniques and methodologies in our research program.

The facilities available include a multinuclear Bruker 400 MHz NMR spectrometer, a computer interfaced Cary 219 UV/Vis spectrophotometer, a computer controlled Jasco-J40 circular dichroism instrument, a computer interfaced Durrum Stopped Flow Instrument, a Perkin-Elmer MPF 44A spectrofluorimeter, an HPLC unit, etc.

Interested applicants should forward a curriculum vitae and arrange to have three letters of recommendation sent on their behalf.

I thank you in advance for either passing this notice to potential applicants, or forwarding their names to me.

Sincerely yours,

Tom

Thomas R. Krugh
Professor of Chemistry
716-275-4224

TRK:jep

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