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Newsletter

No. 228

September, 1977

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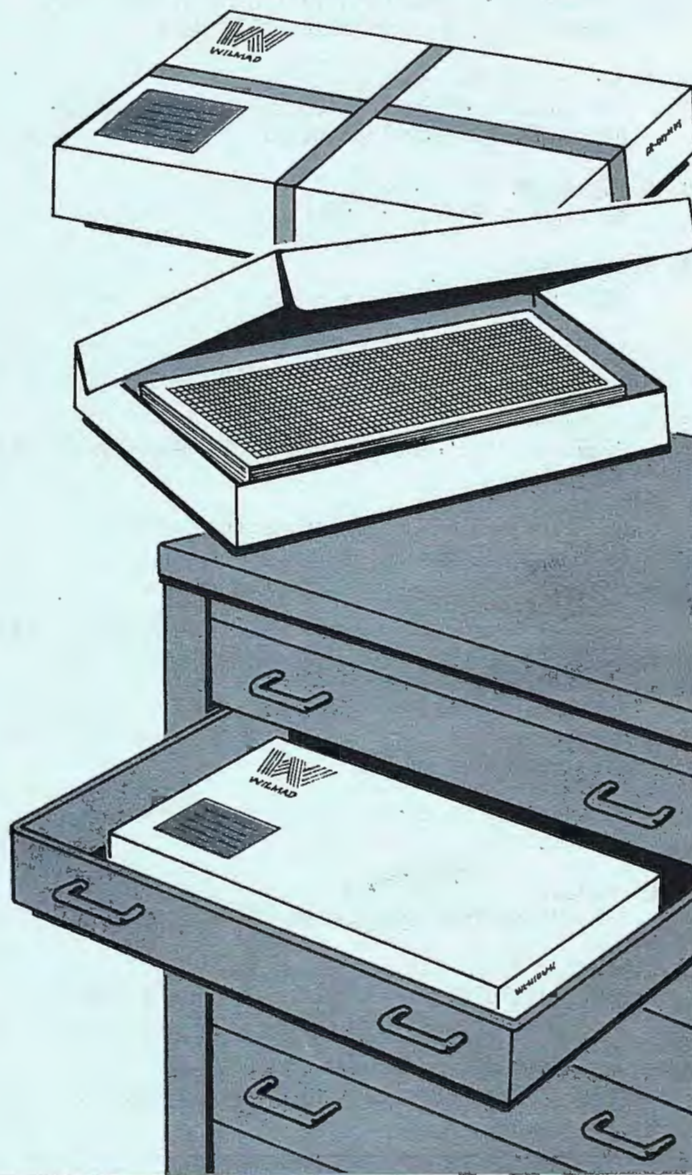
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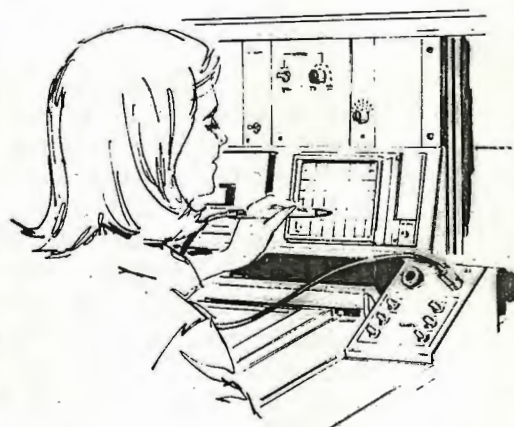
All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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File Référence

9 August 1977

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

Title: THE GWS-15: MAJOR MODIFICATIONS OF
AN XL-100 TO FACILITATE THE OBSERVATION OF
NUCLEI WITH SHORT T_2 'S AND LARGE SPECTRAL WIDTHS

Dear Barry:

Over the past five years we have been studying model and biological membranes by ^2H NMR (1). Our big problems have been spectral width and sensitivity. We finally culminated our evolving modifications by a complete refit which is just about to come on the air. Were it not for the urgent ring of your pink letter we would have been able to report performance specifications. Oh well, next time! We are working on documentation of the modifications so that eventually a useful detailed description will be available for those interested. As the bulk of the design and construction was done by Dr. Gerald W. Stockton, we have renamed the instrument GWS-15.

A Fluke synthesizer model 6160B provides a stable source of RF from 1-150 MHz, and in combination with center band pulsed lock allows a wide choice of offset. A GWS-designed pulse programmer has four possible consecutive pulses whose phase can differ by 0, 90, 180, or 270°. Pulse widths and intervals are independently controllable to an accuracy of 10^{-9} seconds.

At present we are still using the 4412 probe, but a single coil probe for 18 mm samples is under construction. The NMR signal is amplified by a wide band receiver of GWS design with a rapid ringdown and a series of filters up to 900 KHz, then split and fed to two phase detectors operating in quadrature. The outputs of the phase detectors are then fed to a Nicolet 1090 AR dual channel digital oscilloscope with a data acquisition rate of up to 2 MHz. The quadrature data are then read into and processed by the 620L computer. To gain a closer look at the earlier part of the FID, which is usually difficult due to system ringdown, we use the

Ottawa, Canada
K1A 0R6

Professor B. L. Shapiro

9 August 1977

quadrupole echo technique ($90^\circ_x - \tau - 90^\circ_y - \tau$ -Echo) reported by Davis et al (2).

These modifications open a whole new perspective for the study of liquid crystals and membranes. Experiments which took too much signal accumulation to be viable are now possible and the previously "invisible" spectra of gel state lipid have been seen using the techniques described above (3).

Yours sincerely,



Ian C. P. Smith



Gerald W. Stockton*

Leo Turner



1. I.C.P. Smith, G.W. Stockton, A.P. Tulloch, C.F. Polnaszek, and K.G. Johnson, J. Colloid and Interface Science 58, 439 (1977).
2. J.H. Davis, K.R. Jeffrey, M. Bloom, M.I. Valic, and T.P. Higgs, Chem. Phys. Letters 42, 390 (1976).
3. G.W. Stockton, K.G. Johnson, K.W. Butler, A.P. Tulloch, Y. Boulanger, I.C.P. Smith, J.H. Davis, and M. Bloom, Nature (in press).

*Present address: American Cyanamid, P.O. Box 400, Princeton, New Jersey 08540, U. S. A.



McMASTER UNIVERSITY

Department of Chemistry

1280 Main Street West, Hamilton, Ontario, L8S 4M1

Telephone: 525-9140

August 9, 1977

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

Dear Barry:

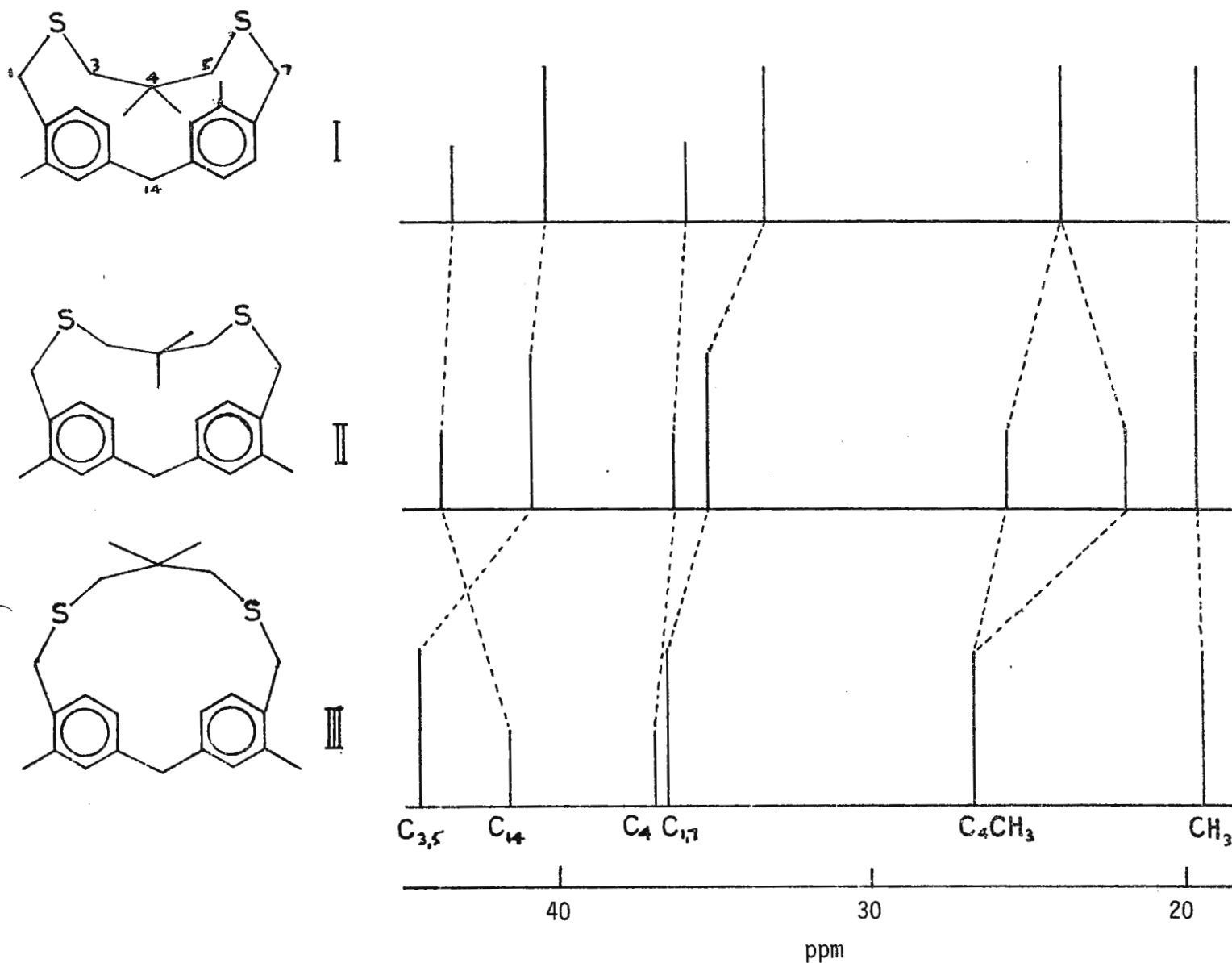
We have recently been studying the C-13 spectra of anti-4,4,9,17-tetramethyl-2,6-dithia[7,1]paracyclophane(I) and its atrop-isomers. Unusual effects have previously been observed in their proton spectra,¹ in particular, the separation of the C₄ methyl protons (0.51 and -0.23 ppm wrt TMS) of the syn isomer (II). We have observed a similar effect in the C-13 spectrum of isomer II, i.e. one of the C₄ methyl carbons is shifted to higher field.

In addition to the anti and syn isomers, we have observed a third atropisomer (III) not previously reported. The chemical shift correlation diagram (Fig. 1) of a portion of the C-13 spectra indicates some major differences between the isomers. Our initial conclusions are that, in the case of I, the methyl groups at C₄ are "inside" the molecular framework; as one of the aromatic rings rotates, one methyl group moves "out" and becomes less shielded whilst the other methyl group becomes highly shielded due to the proximity of the two aromatic rings (isomer II). In the case of isomer III, the methyl groups at C₄ are both "out" and consequently both C-13 and proton spectra appear "normal".

The proton spectra tend to support these conclusions; isomers I and II both have asymmetric methylene groups at C_{1,7} and C_{3,5} whereas isomer III does not; furthermore, the methylene groups at C_{3,5}

1. N. Finch, C.W. Gemenden and B.P. Korzun, J. Org. Chem, 41, 2509 (1976).

FIGURE 1



in isomer III are deshielded by an average of about 1 ppm as compared to isomers I and II.

It is expected that a fuller account will be published shortly.

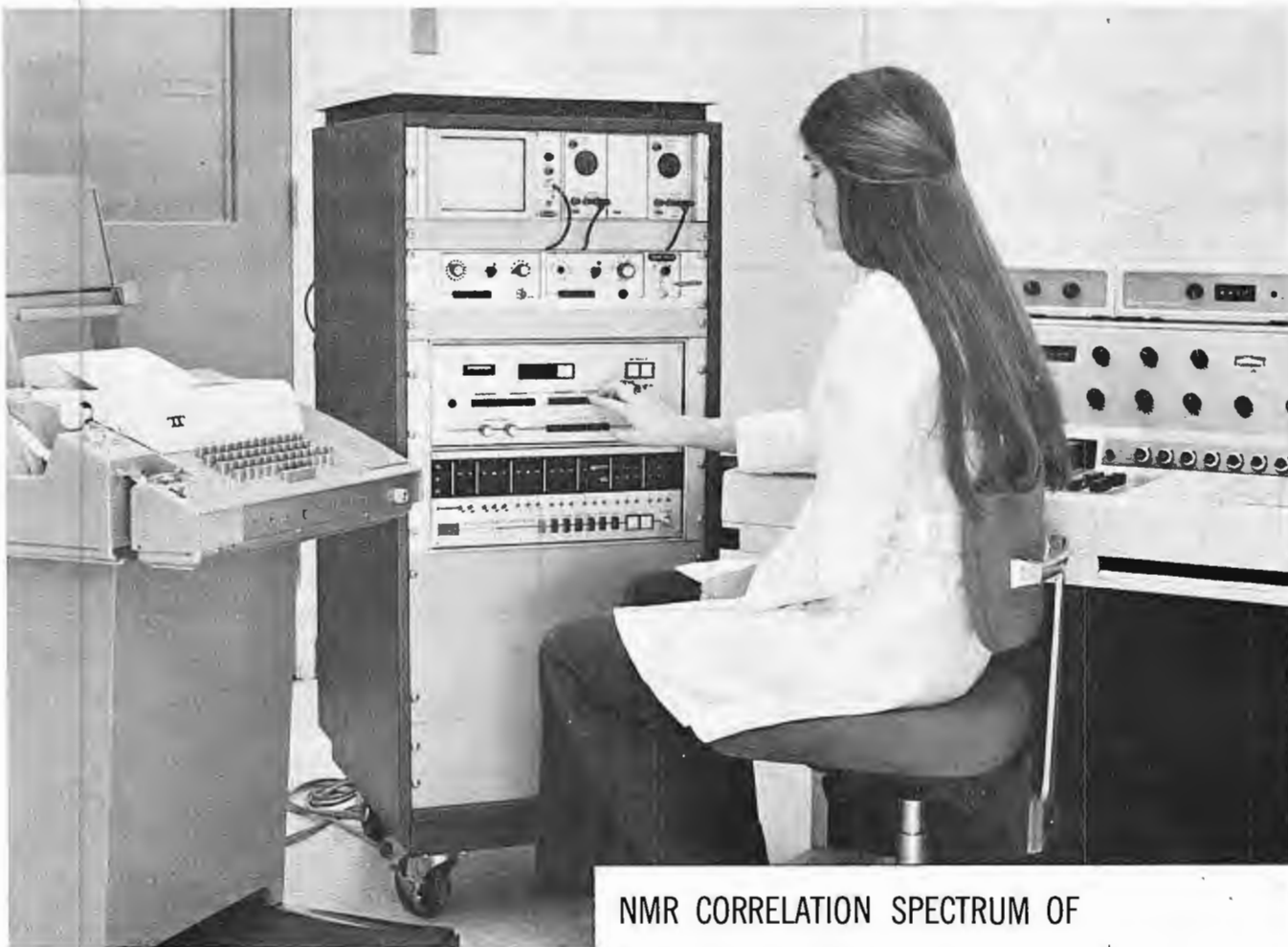
Brian Sayer
Brian Sayer

Michael McGlinchey
Mike McGlinchey

Please credit this contribution to the account of J.I.A. Thompson.

/rg

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- 2) Large solvent resonances can be avoided by sweeping only a small part of the total spectrum.
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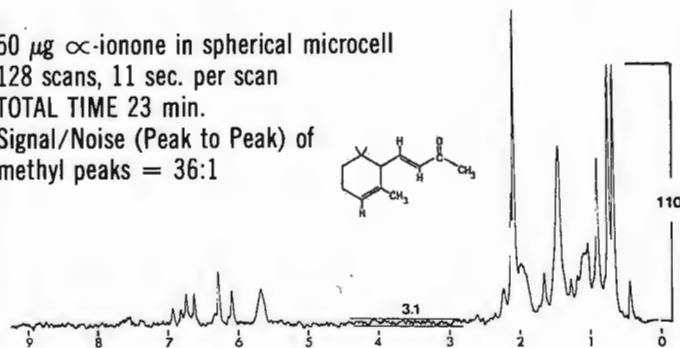
NMR CORRELATION SPECTRUM OF

50 μ g α -ionone in spherical microcell

128 scans, 11 sec. per scan

TOTAL TIME 23 min.

Signal/Noise (Peak to Peak) of methyl peaks = 36:1



This spectrum of 50 micrograms of α -ionone was obtained by correlation NMR in 23 minutes. Normal CW averaging techniques would require over 4 hours.

For more information on the Nicolet NMR-80 data system for rapid scan correlation NMR spectroscopy please write or phone.

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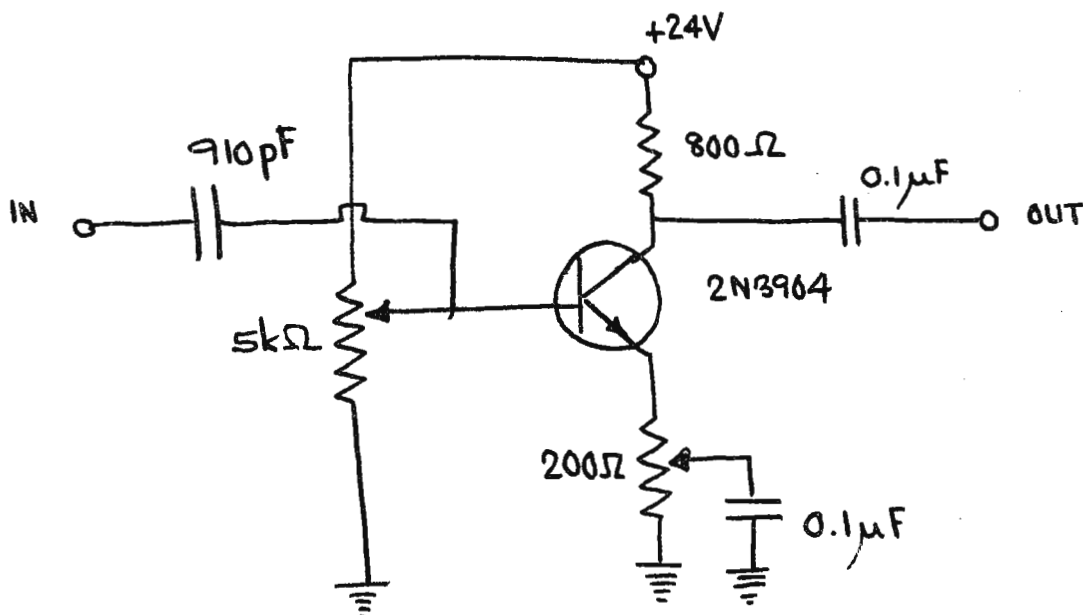
August 11, 1977

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

Title: Keeping up on your references

Dear Barry:

When we originally had quadrature detection added to our Bruker HXS-270 spectrometer by Nicolet we got an increase of signal to noise approaching 1.4X. However, it never seemed to be the full increase expected and the Nicolet QPD accessory seemed to saturate (in terms of signal input) more easily than expected. During other repairs on the instrument we came to wonder whether we were supplying the unit with sufficient reference voltage (0.8 Vpp (0.28 V_{RMS}) at 6.15 MHz). We designed the simple cheap circuit shown below with the requirements that it not load down the Bruker receiver (which we still use to visually follow pulse sequences), have a variable voltage gain near 2X, drive into 50 Ω , and operate at 6 MHz. Now when the unit is supplied with 1.6 Vpp (0.6 V_{RMS}) reference signal, we get a signal to noise gain of >1.4X, the unit does not saturate as easily, and baseline distortions are reduced. Our final signal to noise is 40:1 on 0.1% ethyl benzene.



Best regards,

Brian D. Sykes

Gerry McQuaid



August 16, 1977

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

Dear Barry:

Back to Nature

It has been appreciated for some time that ^2H NMR studies of per-deuterated compounds could be a valuable aid in the interpretation of their ^1H NMR spectra since the spin-spin coupling between adjacent deuterons is 42.4 times smaller than the H-H coupling and gives rise to a spectrum containing only chemical shift information. Per-deuteration involves considerable time, effort, and expense, and recently Smith et al (1) have pointed out that modern FT spectrometers have enough sensitivity to permit studies of ^2H NMR spectra in natural abundance. While the ^1H - ^2H couplings are 6.5 times smaller than the H-H couplings and would generally be unresolved, ^1H wide-band decoupling can be employed to eliminate coupling completely.

In exploring some of the capabilities of the new FT-80 spectrometer with its broad-band probe, I decided to try out this idea on the molecule 1-methylcyclohexene-1. The upper spectrum in the figure shows the ^1H spectrum of this compound at 80 MHz. Three rather broad peaks are found corresponding to the olefinic proton at 5.4 ppm, the allylic protons at 2.1 ppm, and the methyl and remaining ring protons around 1.7 ppm. Second order effects result in so many unresolved transitions and distortions of intensities that no resolved coupling information is observable.

The lower spectrum is the ^2H spectrum of the same sample at 12.21 MHz, run in the FT-80 broad-band probe as a neat liquid, with the spectrometer locked to external D_2O . After 7.7 hours of data accumulation, the transformed

- -- -- --
- (1) Deuterium Magnetic Resonance. Applications in Chemistry, Physics, and Biology. Henry H. Mantsch, Hazime Saito, and Ian C. P. Smith. Report from the Division of Biological Sciences, National Research Council, Ottawa, Canada.

^2H spectrum shows the existence of 5 different chemical shifts in this compound. The olefinic deuteron appears at 5.4 ppm but is narrower in the absence of coupling. The allylic deuterons give two lines separated by 0.07 ppm, and the CD_3 group is now seen clearly as the tall peak at 1.7 ppm, resolved from a peak at 1.6 ppm due to one of the deuterons on C_4 or C_5 .

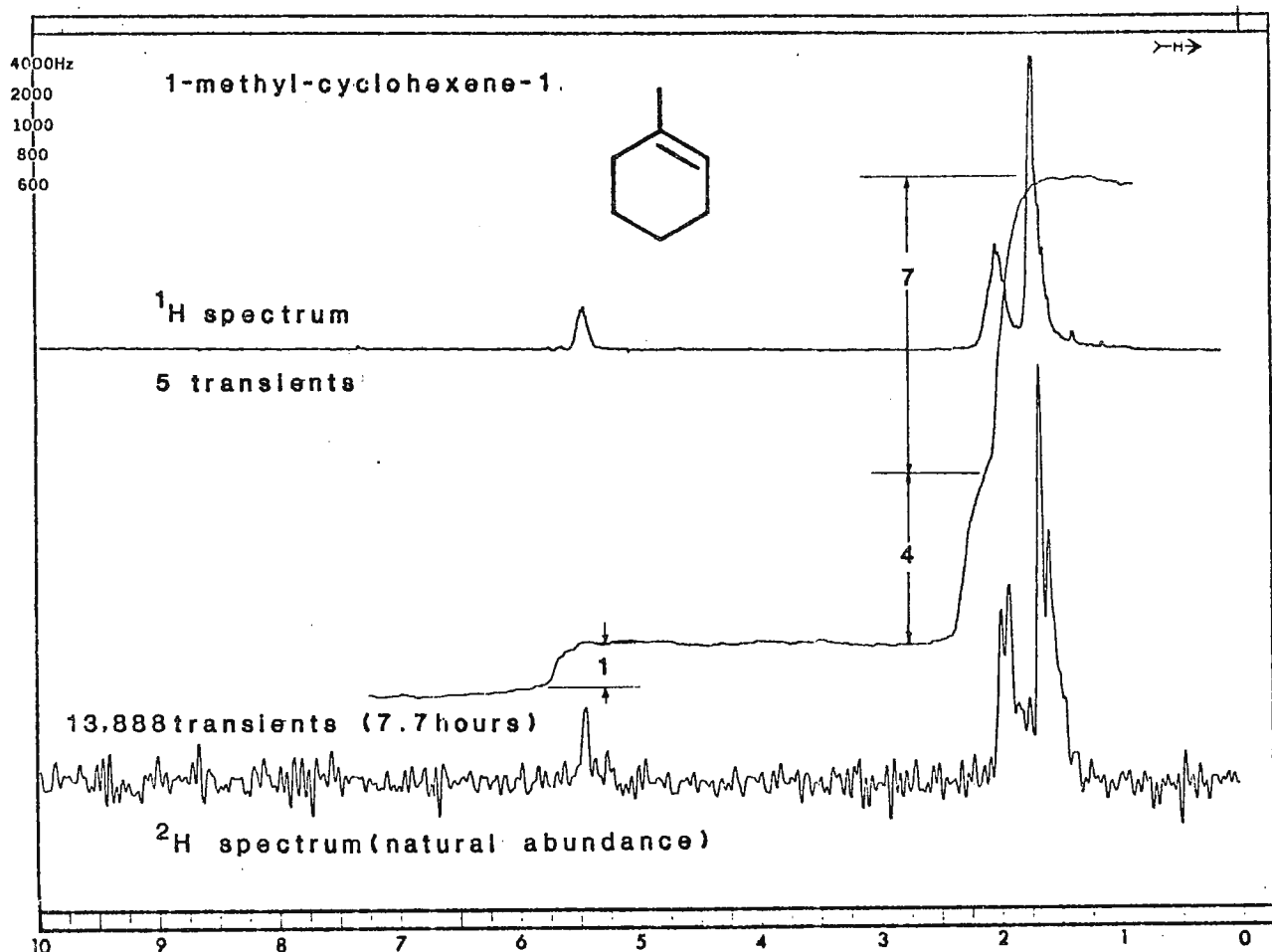
Integration of the ^2H spectrum gives good agreement with the expected ratios of 1 : 4 : 7 for the three spectral regions. Relaxation times and NOE effects would not be expected to cause problems due to the effectiveness of the interaction of the deuteron quadrupole moment with electric field gradients as a relaxation mechanism.

If the amount of sample is not too limited it appears that ^2H NMR spectroscopy in natural abundance could be very helpful in understanding ^1H spectra and providing chemical shift parameters as a starting point in spectral analysis.

Best regards,

Jim Shoolery

James N. Shoolery
NMR Applications Laboratory
Instrument Division



UNIVERSITÄT TüBINGEN
 PHYSIKALISCHES INSTITUT
 Prof. Dr. O. Lutz
 Dr. A. Nolle

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

^{17}O and ^{55}Mn NMR in Permanganate

Dear Professor Shapiro,

During an investigation of indirect spin-spin coupling between quadrupolar nuclei in oxyanions (1), we have looked at the ^{17}O and ^{55}Mn signal in aqueous MnO_4^- (H_2O enriched: 10.9% ^{17}O , 27.7% ^{18}O). For ^{17}O the typical line shape (see fig. a) for a $I = 5/2$ nucleus coupled with ^{55}Mn ($I = 5/2$) was found, the resolution was something better than that observed earlier by Broze and Luz (J. Phys. Chem. 73, 1600 (1969)).

For ^{55}Mn an unusual shape was observed (see fig. b), which now is explainable by an oxygen induced isotope effect due to the different species $\text{Mn}^{16}\text{O}_{4-n}^{18}\text{O}_n^-$ ($n = 0, 1, 2, 3, 4$). The coupling $J(^{55}\text{Mn} - ^{17}\text{O})$ gives in the case of ^{55}Mn NMR only a broad unresolved pattern.

Observing the ^{55}Mn NMR line in a solution of MnO_4^- in H_2^{18}O (99% ^{18}O) results in time-dependent line shapes (2), starting with the signal for the species $\text{Mn}^{16}\text{O}_4^-$ and ending after about one year in the signal for $\text{Mn}^{18}\text{O}_4^-$. In the mean time interesting patterns of the species $\text{Mn}^{16}\text{O}_{4-n}^{18}\text{O}_n^-$ ($n = 0, 1, 2, 3, 4$) are found (see fig. c).

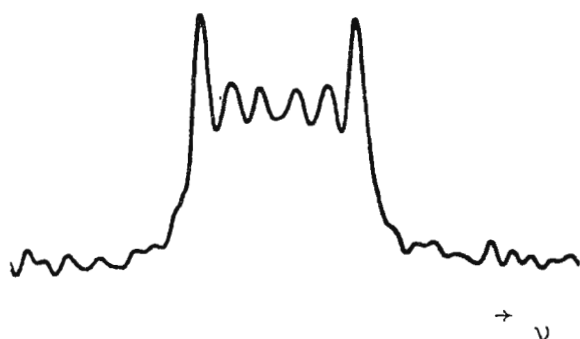
The mass dependent isotope effect (3) for replacing one ^{16}O by one ^{18}O is $\delta(^{55}\text{Mn}) = (-0.59 \pm 0.02)$.

Sincerely yours

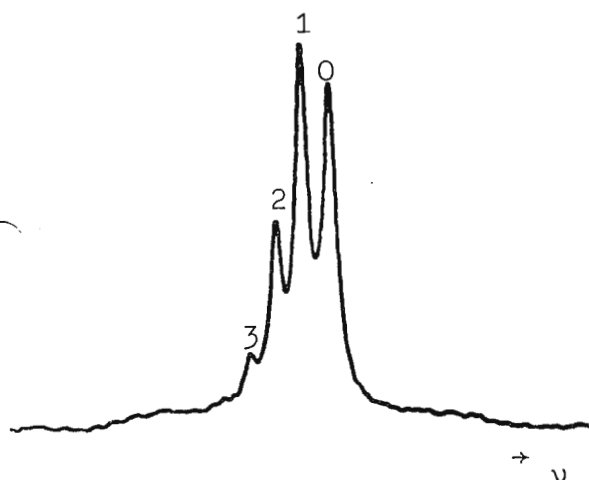
O. Lutz

A. Nolle

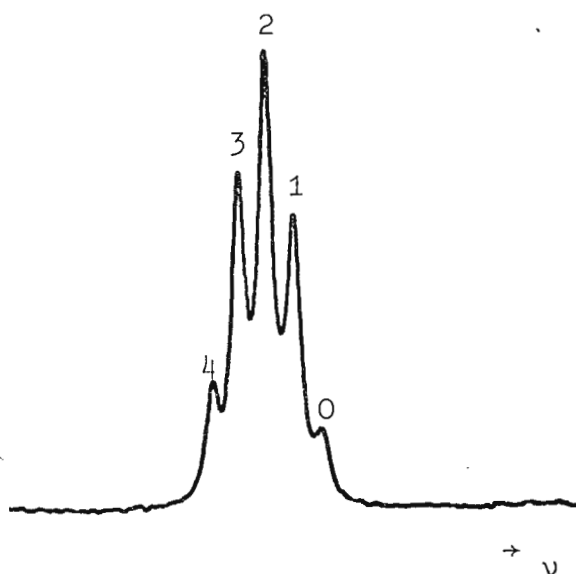
- (1) O. Lutz, W. Nepple, A. Nolle, Z. Naturforsch. 31a, 1046 (1976)
- (2) A.R. Haase, O. Lutz, M. Müller, A. Nolle, Z. Naturforsch. 31a, 1427 (1976)
- (3) K.U. Buckler, A.R. Haase, O. Lutz, M. Müller, A. Nolle



- a) FT NMR signal of ^{17}O at 12.216 MHz
in a 0.4 molal solution of KMnO_4 in
 H_2O (10.9% ^{17}O , 27.7% ^{18}O).
Plotted spectrum width: 500 Hz
Measuring time: 1 h (3600 scans)
Spherical sample volume: 0.3 ml
 $J(^{17}\text{O} - ^{55}\text{Mn}) = (28.9 \pm 2.8) \text{ Hz}$



- b) FT NMR signal of ^{55}Mn at 22.311 MHz
in the same sample as a), 3 months
after preparation.
Plotted spectrum width: 250 Hz
Measuring time: 100 s (100 scans)



- c) FT NMR signal of ^{55}Mn at 22.311 MHz
in a 0.27 molal solution of KMnO_4 in
 H_2O , enriched: 99% ^{18}O , 34 days after
the preparation of the sample.
Plotted spectrum width: 250 Hz
Measuring time: 100 s (100 scans)
Spherical sample volume: 0.3 ml

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DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

August 17, 1977

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

Proximal Histidine Resonances in Hemoglobin

Dear Barry,

We have become interested recently in the exchangeable histidyl imidazole NH proton of the coordinated or proximal histidine in high-spin ferrous heme proteins. In the absence of any detectable esr signal in this state, the ligand paramagnetic shifts can serve as indicators of the microenvironment of this axial ligand. Tension in this iron-imidazole is central to the current understanding of cooperativity in hemoglobins.

We have succeeded in locating and assigning these two peaks (one each for the α and β chains of the tetramer) in human adult hemoglobin in a 0.2 M NaCl H₂O solution.¹ The question arises whether the environment near the proximal histidine differs significantly, or even detectably, between hemoglobin in a salt solution and in the red cell in whole blood.

Hence, we have obtained the proton nmr trace for the same two proximal histidyl imidazole NH peaks for packed whole blood cells. The traces for the 0.2 M NaCl solution and the packed cells are compared in the figure. The positions of the two resonances, some 60-70 ppm downfield from DSS, are unchanged, although linewidths are slightly greater in the packed cells, probably due to viscosity effects. We can therefore conclude that the microenvironment of the proximal histidine in purified hemoglobin and in whole blood are indistinguishable.

Sincerely,

A handwritten signature in cursive script, appearing to read "Gerd".

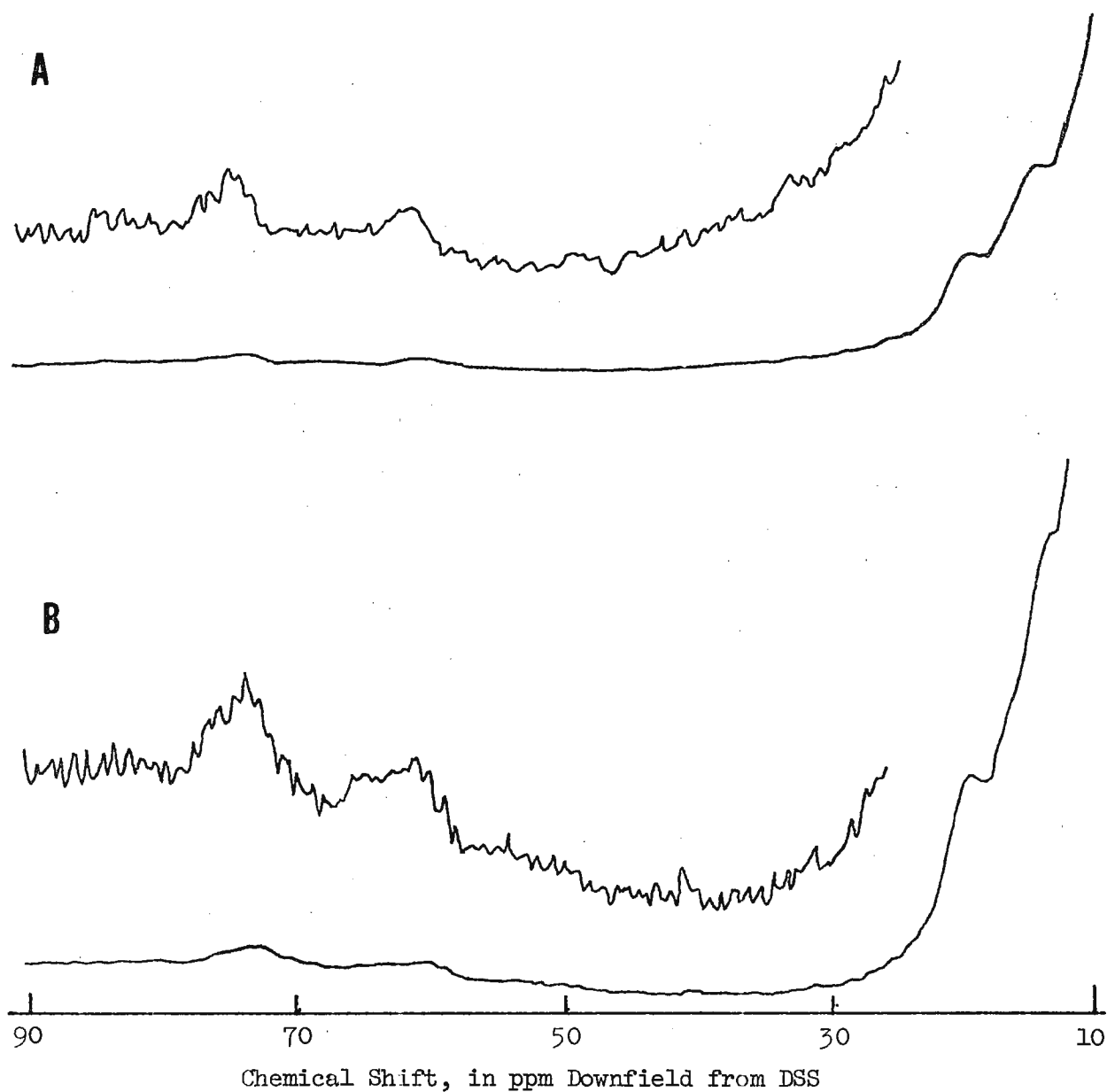
Gerd N. La Mar
Professor of Chemistry

GNL/ds

- 1) La Mar, Budd and Goff, Biochem. Biophys. Res. Comm., 77, 109 (1977).

Figure

- A. Lowfield proton nmr trace of 4 mM deoxy-hemoglobin A in 0.2 M NaCl H_2O .
- B. Lowfield proton nmr trace of packed blood cells. In both cases, the two exchangeable NH peaks (they disappear in D_2O) resonate at 76 and 64 ppm downfield from internal DSS.



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

Dear Professor Shapiro,

To my horror I received your blue note even before I had seen my previous letter in print. Anyway, as I did subscribe late, here is another contribution. It is a simplified version of a FORTRAN IV program, which we have used extensively for nonlinear least-squares fitting. Functions are included for analysis of the most common pulsed spin-relaxation experiments. In addition, the general minimization routine STEPIT is required (available through QCPE, Chemistry Dept., Indiana University, Bloomington, Ind. 47401, USA).

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NOUT=6
NTRACE=-1
MATRIX=0
NFMAX=1000
MODE=1
DO 5 I=1,20
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  DELMIN(I)=0.0
5  CONTINUE
10  READ(NIN,INDATA,END=999,ERR=998)
11  CALL STEPIT(FIT)
    WRITE(NOUT,77) IDENT,MODE
77  FORMAT(////////,' THIS IS CURVE NO. ',I8,' MODE=',I5)
    WRITE(NOUT,78) (MASK(I),I=1,NV)
78  FORMAT(' MASK=',20I2)
    WRITE(NOUT,100) (XX(I),YY(I),YYCALC(I),YYDIFF(I),I=1,NPOINT)
100 FORMAT(4F12.5)
    WRITE(NOUT,2) CHISQ
    WRITE(NOUT,3) (I,X(I),X(I),I=1,NV)
2   FORMAT(' CHISQ=',F12.5)
3   FORMAT(' X(',I1,')=',F12.5,' (',E12.4,')')
    GO TO 10
998 WRITE(NOUT,997)
997 FORMAT(' INCORRECTLY PUNCHED DATA *** ')
    WRITE(NOUT,INDATA)
999 STOP
END
```

Note: MAKE SURE THAT THE COMMON/STEP/
FIELD IS IDENTICAL IN THE
STEPIT SUBROUTINE.


```

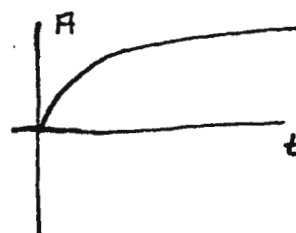
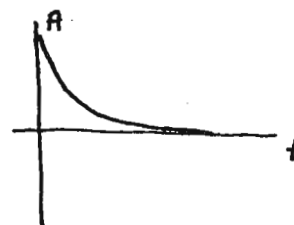
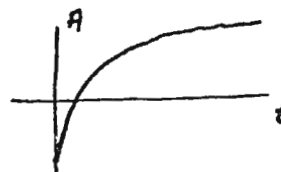
SUBROUTINE FIT
COMMON/STEP/CHISQ
COMMON/VALUES/XX(100),YY(100),YYCALC(100),YYDIFF(100),NPOINT
CHISQ=0.0
DO 1 I=1,NPCINT
  YYCALC(I)=UFUNCT(XX(I))
  YYDIFF(I)=YYCALC(I)-YY(I)
  CHISQ=CHISQ+YYDIFF(I)**2
1 CONTINUE
RETURN
END

```

```

REAL FUNCTION UFUNCT(T)
C USER-SWITCHABLE, FUNCTION-GENERATING SUBPROGRAM.
C ADDITIONAL FUNCTIONS CAN BE ADDED AFTER
C STATEMENTS 300, 500, 600 AND 700.
COMMON/STEP/CHISQ,X(20)
COMMON/MO/MODE
COMMON/PAPER/NPAPER(10),NIN,NOUT,IDENT
EQUIVALENCE (X(1),EQMAG),(X(2),T1),(X(3),C)
BIG=10*T1
SMALL=0.00001*T1
GOTO (100,200,300,400,500,600,700),MODE
100 CONTINUE
C T1 FROM STANDARD INVERSION-RECOVERY
IF(T.LT.BIG) GOTO 101
UFUNCT=EQMAG+C
RETURN
101 IF(T.GT.SMALL) GOTO 102
UFUNCT=-EQMAG+C
RETURN
102 UFUNCT=EQMAG*(1.-2.*EXP(-T/T1))+C
RETURN
200 CONTINUE
C T1-RHO FROM SPIN-LOCKING OR T1 FROM FREEMAN-HILL-
C INVERSION-RECOVERY
IF(T.LT.BIG) GOTO 201
UFUNCT=C
RETURN
201 IF(T.GT.SMALL) GOTO 202
UFUNCT=EQMAG+C
RETURN
202 UFUNCT=EQMAG*EXP(-T/T1)+C
RETURN
300 CONTINUE
C REMOVE THIS GOTO STATEMENT IF MODE 3 IS IMPLEMENTED
GOTO 999
400 CONTINUE
C T1 FROM PROGRESSIVE SATURATION
IF(T.LT.BIG) GOTO 401
UFUNCT=EQMAG
RETURN
401 UFUNCT=EQMAG*(1.-EXP(-T/T1))
RETURN
500 CONTINUE
600 CONTINUE
700 CONTINUE
999 WRITE(NOUT,998) MODE
998 FORMAT(' FUNCTION-MODE',I8,' IS NOT AVAILABLE')
CALL EXIT
END

```



Input is of the NAMELIST type. The first data set must contain initial estimates of the $X(I)$, as well as liberally chosen $XMAX(I)$ and $XMIN(I)$ and the appropriate values of $MODE$ and NV (the number of variables). $DELTA X(I)$, which are $\approx 10\%$ of the $X(I)$ must also be entered. Default values for $MASK(I)$, $DELMIN(I)$, $MATRIX$, $NTRACE$ and $NFMAX$ exist, so they need not be entered. The XX and YY arrays contain the $NPOINT$ t - and $A(t)$ -values, respectively. Please note that all parameters remain unchanged through $READ$ -sequence, unless changed by input. Therefore, normally only $NPOINT$, $XX(I)$ and $YY(I)$ have to be entered in the following data sets.

Parameter representation:

Standard IR: $MODE=1, NV=3, X=A_{\infty}, T_1, C$

Spin-locking or Freeman-Hill-IR: $MODE=2, NV=3, X=A_0, T_{1p}$ or T_1, C

Progressive saturation: $MODE=4, NV=2, X=A_{\infty}, T_1$

The following 3 data sets illustrate the use of the program for fitting a) an inversion-recovery data set using $C \neq 0$, b) the same data set, but $C=0$, c) another data set with $C=0$ and the $XX(I)$ values being the same as in the previous calculations:

```
&INDATA MODE=1, NV=3, XMAX=3*1000., XMIN=3*-10., DELTAX=3*1., X=100.,
10., 0., XX=0.005, 2, 4, 6, 8, 10, 60, NPOINT=7, YY=-110, -82, -58, -34, -15,
1, 133, IDENT=11 &END
&INDATA MASK(3)=1, X(3)=0.0 &END
&INDATA YY=-133, -92, -65, -40, -20, 0, 133, IDENT=12 &END
```

(NOTE: REMEMBER TO START THE PUNCHING IN COLUMN 2.)

The results should be approximately: (the last digits may be computer-dependent)

```
THIS IS CURVE NO.      11  MODE=      1
MASK= 0 0 0
  0.00500  -110.00000  -109.96599    0.03401
  2.00000   -82.00000   -82.05359   -0.05359
  4.00000   -58.00000   -57.19852    0.80148
  6.00000   -34.00000   -35.12442   -1.12442
  8.00000   -15.00000   -15.52027   -0.52027
 10.00000    1.00000    1.89030    0.89030
 60.00000   133.00000   132.96930   -0.03070
CHISQ=      2.97497
X( 1)=   125.06206 ( 0.1251E+03)
X( 2)=    16.85484 ( 0.1685E+02)
X( 3)=    15.02187 ( 0.1502E+02)
```

a) Complete output

```
CHISQ=   397.05762      CHISQ=    62.33180
X( 1)=   120.47313 ( 0.1205E+03)  X( 1)=   132.43108 ( 0.1324E+03)
X( 2)=    13.60499 ( 0.1360E+02)  X( 2)=    14.08986 ( 0.1409E+02)
X( 3)=     0.0      ( 0.0      )   X( 3)=     0.0      ( 0.0      )
```

b) Part of output

c) Part of output

Yours sincerely,

Peter Stilbs

Peter Stilbs

GORLAEUS LABORATORIA DER RIJKSUNIVERSITEIT TE LEIDEN
SUB-FACULTEIT - SCHEIKUNDE

Wassenaarseweg 76

Postbus 75

Telefoon 48333

toestel:

Afdeling: J.A. den Hollander

Onderwerp:

LEIDEN, August 18, 1977

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

'Comment to Cooper's sine look-up problem'

Dear Dr. Shapiro,

In TAMUNMR 215,²³ a letter appeared of J.W. Cooper about baseline artifacts in high dynamic range FT-NMR spectra. These artifacts appeared to be caused by an improper sine look-up procedure in the FFT routine. For a proper FFT routine handling a data table of 2^n points a sine table is required of $\frac{1}{4} \cdot 2^n$ words on the interval $0 - \frac{\pi}{2}$, which must be core-resident during the FFT to obtain a short calculation time. This sine table occupies a large part of the core memory, and it is conceivable that one tries to reduce its size to save precious core. A very effective way to perform this would be of course to include a sine routine instead of a sine table, and to calculate the sine values as required by the FFT routine. This, however, has the disadvantage that it slows down the FFT calculation considerably.

In this letter I report a method to overcome this problem. Suppose we want to transform a data table of up to 128K words(!) . We would need a sine table of 32K words on the interval $0 - \frac{\pi}{2}$, this table is much too large to fit within the available core memory of most minicomputers. Now we choose $\Delta\alpha = \frac{1}{128} \cdot \frac{\pi}{2}$ and prepare a sine table consisting of $\sin \Delta\alpha$, $\sin 2\Delta\alpha$, $\sin 3\Delta\alpha$,, $\sin \frac{\pi}{2}$ (size of this table is 128 words).

In addition we prepare a second table containing

$$\frac{\sin \frac{\Delta\alpha}{256}}{\sin \Delta\alpha}, \frac{\sin \frac{2\Delta\alpha}{256}}{\sin \Delta\alpha}, \frac{\sin \frac{3\Delta\alpha}{256}}{\sin \Delta\alpha}, \dots, \frac{\sin \Delta\alpha}{\sin \Delta\alpha}$$

(size of this table is 256 words).

Now we can calculate any sine value in the full sine table of 32K words by using the following equation

$$\sin(\alpha + \gamma) = \frac{\sin(\Delta\alpha - \gamma)}{\sin \Delta\alpha} \cdot \sin \alpha + \frac{\sin \gamma}{\sin \Delta\alpha} \cdot \sin(\alpha + \Delta\alpha) ,$$

in which $0 < \gamma < \Delta\alpha$ and α a multiple of $\Delta\alpha$.

In this way all sine values required for the 128K words transform are calculated by only 2 multiplications at the cost of (in the given example) only 384 words core memory.

We found this procedure very effective, and when it is used by the FFT routine it slows down the transformation only by 10-20%.

Moreover it is easily extensible to double precision.

Our 32K double precision FFT routine for the PDP11 (16 bit machine), based on this principle has a post-transform dynamic range of over 1.000.000.000 : 1 without any baseline artifact.

Yours Sincerely,


J.A. den Hollander

PURDUE
UNIVERSITY DEPARTMENT OF CHEMISTRY

August 19, 1977

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

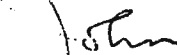
Position available: Biological NMR Spectroscopist

Dear Barry:

The Purdue Biological Nuclear Magnetic Resonance Laboratory is seeking an Operations Manager for its new regional facility. Qualifications should include a Ph.D. or equivalent achievement with experience in NMR spectroscopy of biological or organic systems using high-field superconducting solenoid spectrometers, NMR electronics, and computer programming. Duties include routine scheduling and maintenance of spectrometers, assisting users in designing and carrying out experiments, and instrumental development. Independent as well as collaborative research will be encouraged. The salary will be based on the level of experience. Interested applicants should send a curriculum vitae with a summary of accomplishments and objectives and the names of three references to Dr. John L. Markley, Director, Biological Nuclear Magnetic Resonance Laboratory, Department of Chemistry, Purdue University, West Lafayette, IN 47907. Purdue University is an Equal Opportunity/Equal Access Institution.

With best regards,

Yours sincerely,



John L. Markley
Associate Professor

JLM/mmn



Chemistry Building
West Lafayette, Indiana 47907



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ELIMINATING DECOUPLER NOISE ON FLUORINE LOCK CHANNEL

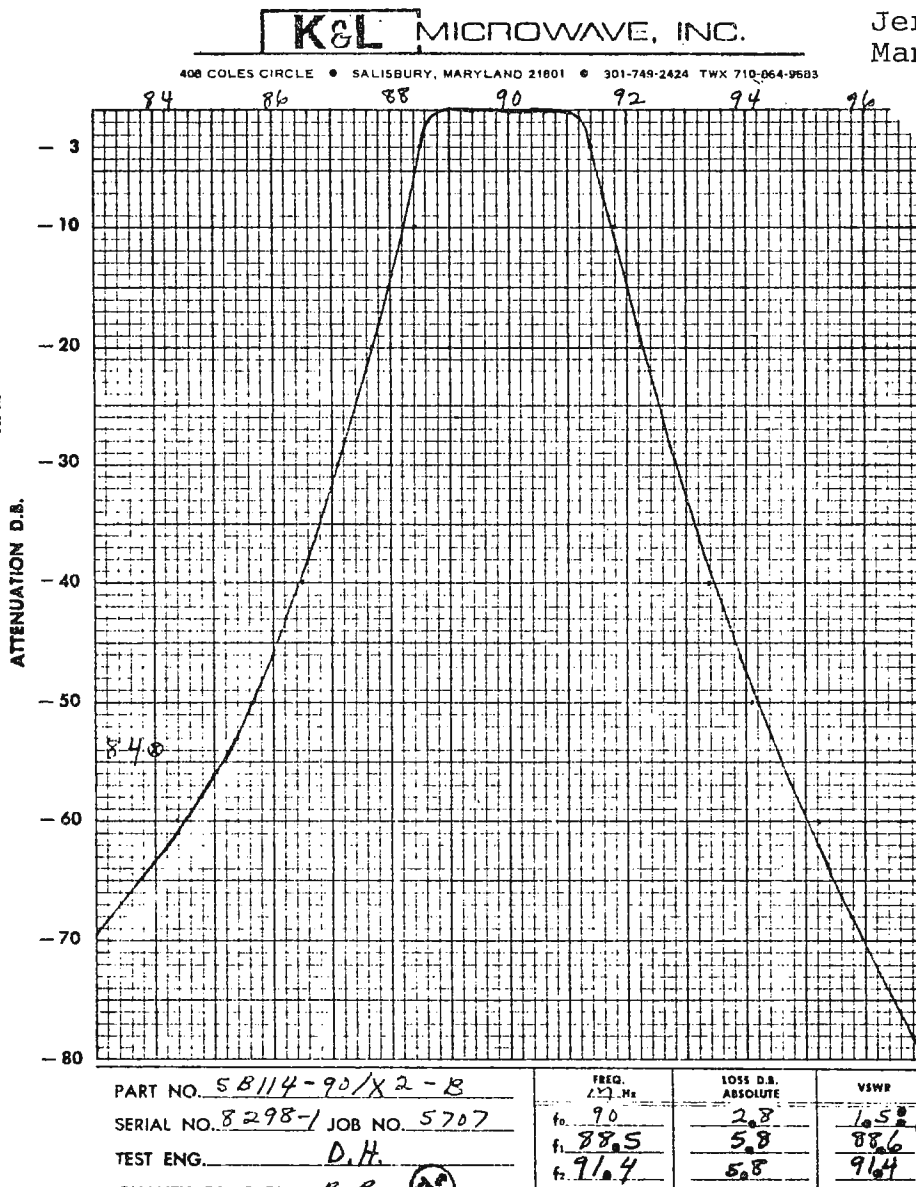
Dear Barry:

We have recently conquered a problem with the ^{19}F lock system on our Bruker HX-90 and we thought that other Bruker users might be interested in our findings. The decoupler amplifier employs a broadband ten watt driver amplifier and a tuned final stage capable of generating 80 watts. When locking on ^{19}F (84.6MHz) and decoupling ^1H (90MHz), a prohibitively large amount of noise is observed on the lock channel due to the noise that is broadcast by the decoupler amplifier broadband stage. This occurs in spite of the filter on the output of the amplifier.

We have successfully employed a commercially available, tubular, band-pass filter (see Figure) in place of the Bruker filter on the output of the amplifier. Using this mode of operation no perturbation of the lock channel was observed, even with high levels of decoupler power. We recommend this approach to other Bruker users who are prepared to accept the 50% power loss (~3D.B.) through the filter.

Sincerely,
Jerry L. Dallas, PhD.
Manager, NMR CORE Facility

Jerry Dallas



Please credit this contribution to the account of Robert E Lenkinski, PhD

August 22, 1977
A/R 1610

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

Dear Barry:

Subject: "¹³C nmr on Some Cyclohexane Derivatives"

I was tasked with assigning the stereochemistry of the olefins, 6A and 7A, and since some disagreement existed concerning the cis-trans assignments^{1,2} for 2A and 3A, their ¹³C nmr were also measured. I believe the data in the table are comparable only with the indicated assignments, which for 2A and 3A agree quite well with those for the corresponding 1,2-dimethyl-cyclohexanols³ and are in complete agreement with the stereochemical assignments of Schlossarczyk et al.^{1A}

Please convey my best wishes to your family.

Sincerely yours,



Michael L. Maddox

- 1a. H. Schlossarczyk, W. Sieber, M. Hesse, H.J. Hansen, and H. Schmid, Helv. Chim. Acta, 1973, 56 875.
- b. M.J. Batuev, A.A. Akhrem, A.D. Matveeva, and A.V. Kamernitskii, Doklady Akad. Nauk. S.S.S.R., 1958, 120 779.
- 2a. J.L.M.A. Schlatmann and E. Havinga, Rec. Trav. Chim. 1961, 80 1101.
- b. M.L. Roumestant and J. Gore Bull. Soc. Chim. France, 1972, 598.
3. Y. Senda, J. Ishiyama, and S. Imaizumi, Tetrahedron, 1975, 31, 1601.

TABLE 1

 ^{13}C NMR SPECTRAL DATA (22.62 MHz) IN CDCl_3 ^a

Assignment	2a	3a	4a	4b	5a	5b	6a	7a	9	10	11	12
1	73.21	69.55	75.10	85.69	74.22	84.46	142.14	143.14	149.97	140.12	41.77	28.87
2	42.46	40.49	41.68	37.91	38.91	41.71	30.14	38.43	35.70	37.52	32.74	32.64
3	32.22	29.32	31.57	29.97 ^c	29.97	30.36 ^c	33.32 ^c	36.90	28.61	28.51 ^c	26.17	24.84
4	25.55	25.05	25.13	22.85 ^b	26.07	25.42	21.10 ^b	25.65 ^c	26.66	27.41 ^b	26.37	25.91
5	24.22	21.03	23.63	22.76 ^b	21.49	21.57	28.64 ^b	28.28 ^c	28.61	28.97 ^c	26.17	24.84
6	40.77	39.32	39.73	30.92 ^c	38.72	32.31 ^c	32.48 ^c	28.19 ^c	35.70	27.96 ^b	32.74	32.64
7	16.03	15.96	15.44	15.08	15.51	15.41	18.34	18.73	--	--	--	--
8	85.11	88.73	140.44	137.55	146.39	142.03	123.34	120.64	106.86	115.41	144.96	89.01
9	74.22	71.07	113.65	115.38	111.47	112.68	20.09	20.42		12.61	111.70	67.91
10				169.76		170.12	14.95	14.95				
11				22.30		21.91						

a) Chemical shifts in parts per million downfield from Me_4Si .

b,c) Assignments in a vertical column may be interchanged.



LABORATORIUM VOOR FYSISCH CHEMIE

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Telefoon (080) 55 88 33

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

Uw kenmerk

Uw brief van

Ons kenmerk

U3999/dB/Ek

Datum August 25, 1977

Onderwerp

Dear Professor Shapiro,

Since a few years we are interested in high resolution solid state NMR and after the completion of our home-built spectrometer last year we determined (using the cross-polarization technique of Pines, Gibby and Waugh [1]) the ^{13}C chemical shielding tensors in single crystals of acetic acid [2], p-xylene and acetophenone [3].

Recently we added the feature of magic angle spinning to our spectrometer to remove the chemical shift anisotropy. Some of our first results are shown in Figs. 1 and 2, the spinning frequency is 2.5 KHz. The width of the lines in the camphor spectrum is ~ 5 Hz and for the larger part determined by the inhomogeneity of our 14 kG magnet. (The carboxyl resonance is off-scale, approximately 150 ppm to the left.) Fig. 2 shows the results of measurements on a piece of poly(methylmethacrylate) (PMMA) supplied by our workshop ("perspex", Rohn & Haas). The pulse sequence we use for T_{ρ} measurements is the same as described without further treatment by Schaefer et al. [4]. All T_{ρ} values in PMMA are found to be almost an order of magnitude larger than those obtained by them. It therefore seems that our material is very different from theirs.

Dr. Tan from the University of Groningen kindly prepared for us isotactic- and syndiotactic PMMA and relaxation measurements on these materials are now in progress.

- [1] A. Pines, M.G. Gibby and J.S. Waugh, J. Chem. Phys., 59 (1973) 569.
- [2] J. van Dongen Torman, W.S. Veeman and E. de Boer, Chem. Phys. (1977) in press.
- [3] To be published.
- [4] J. Schaefer, E.O. Stejskal and R. Buchdal, Macromolecules, 10 (1977) 384.

Sincerely yours,

(J. van Dongen Torman)

(W.S. Veeman)

(E. de Boer)

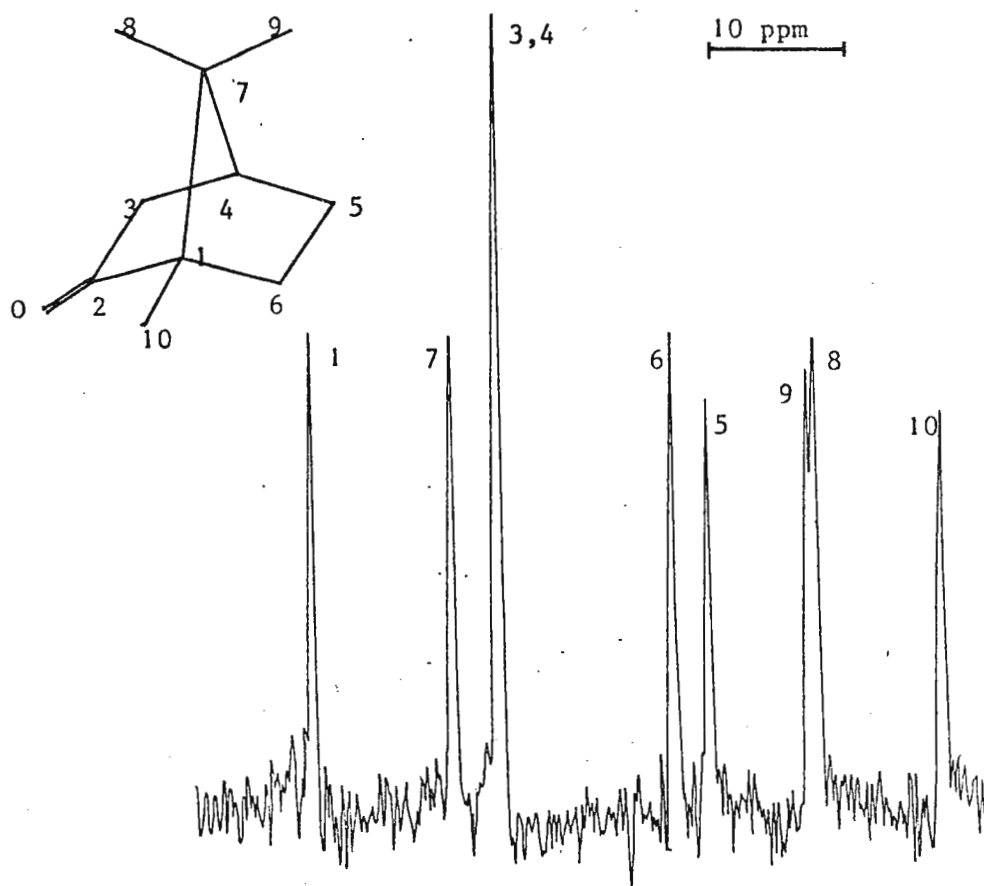


Fig. 1: ^{13}C spectrum of camphor

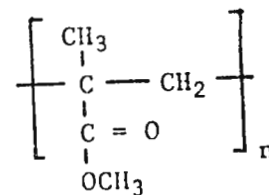
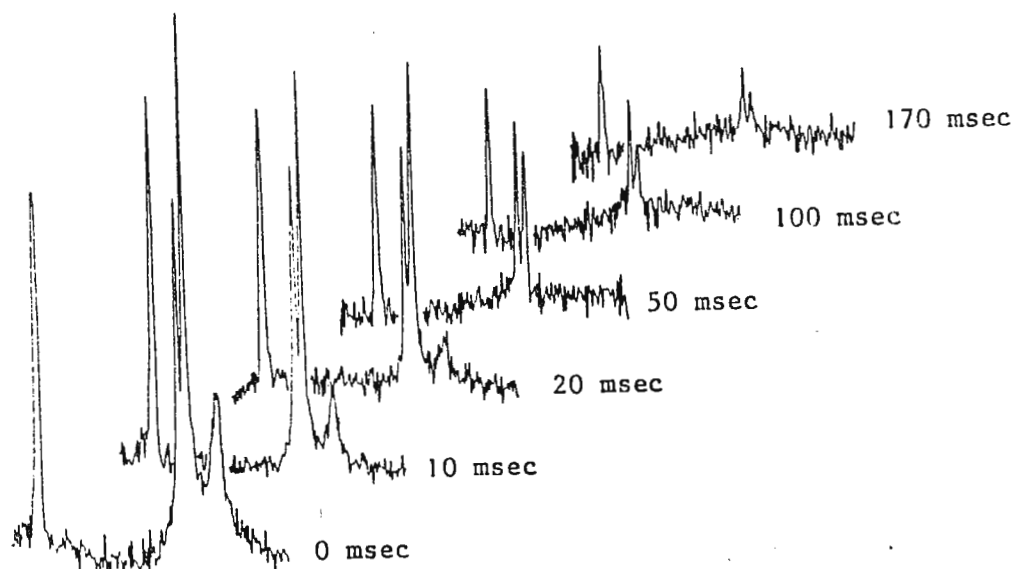


Fig. 2: ^{13}C $T_{1\rho}$ measurements on PMMA



Boston College, Chestnut Hill, Massachusetts 02167 Telephone (617) 969-0100

Department of Chemistry

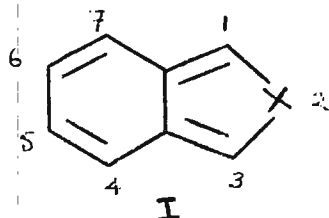
August 26, 1977

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

Dear Barry:

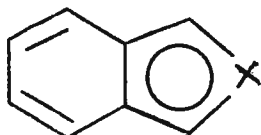
BOND LOCALIZATION IN O-QUINONOIDAL HETEROCYCLES

In my previous letter (TAMUNMRN #222), I described our studies in the isoindole-isoindolenine equilibrium which established the aromaticity of isoindole, in agreement with theoretical predictions. To understand the source of their great chemical instability, we then looked at the vicinal couplings in the carbocyclic rings of the series of compounds I:



X	=	NH	O	S	Se
J ₅₆		6.29	6.22	6.35	6.79
J ₄₅		8.49	8.52	8.64	9.16
J ₅₆ /J ₄₅		0.74	0.70	0.72	0.74

The virtual constancy of J₅₆ and J₄₅ (except when X = Se) along with the invariance of J_{ratio} (J₅₆/J₄₅) (a measure of the degree of bond fixation, suggested to us that the π -systems in the two rings might be isolated, and that the best structural representation of I ought to be:



CONTINUED ON P. 32.....

33 BRAUNSCHWEIG
 SCHLEINITZSTRASSE
 Tel. T.U. 3911
 Durchwahl Institut 391
 Vorwahl 0531

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

Dear Prof. Shapiro:

Dependence of the Chemical Shift of the Methylene Protons of β -Substituted Propionate Groups on the Nature of the Vicinal α -Substituent in Pyrrole Derivatives.

During our synthetic work towards bilanes ^{1,2} and porphyrins ¹⁻⁴, which are of biological interest, the examination of the correct substitution pattern of β -situated substituents - e.g. CH_3 , CH_2COOMe and $\text{CH}_2\text{CH}_2\text{COOMe}$ - was a central problem. We could solve this problem chemically ⁴ and by means of the ^1H -nmr spectroscopy.

Compared with pyrrole derivatives bearing α -substituents, which exert only inductive effects on the pyrrole ring, the signals of β -situated methyl and methylene groups are in the presence of conjugative electron-withdrawing α -residues paramagnetically shifted with a value of approximately $\delta = 0.3$ ppm.

As can be seen from tables 1 and 2 the above mentioned empirical rule is applicable to the 2-methylene protons of β -substituted propionate side-chains. In contrast, the chemical shifts of the corresponding 1- CH_2 protons are rather constant (c.f. Table 1,2).

With the aid of the values for β -substituted methyl ⁵ and acetate ⁶ residues we are now able to examine the substitution pattern of openchained polypyrrolic compounds by means of ^1H -nmr spectroscopy without any chemical transformation into compounds (e.g. porphyrins) of known constitution. Thus it might be possible to investigate a recently postulated rearrangement of bilenes-b (I) bearing electron-withdrawing groups to bilenes-a (II). Bilenes-b are useful intermediates for the synthesis of porphyrins.

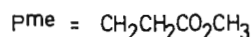
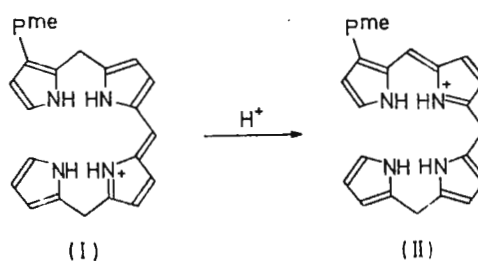
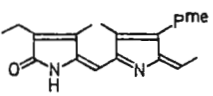
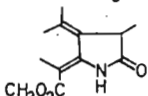
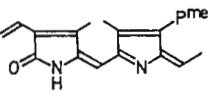
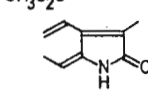
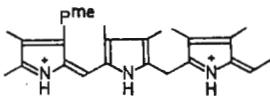


Table 1

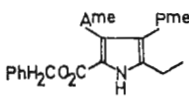
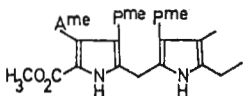
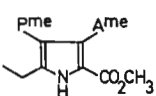
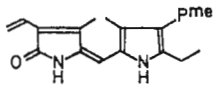
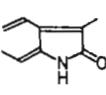
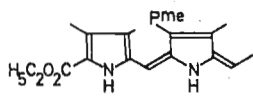
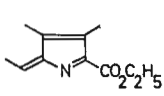
solvent: CDCl₃
δ (ppm)

$ \begin{array}{c} \text{CH}_3\text{O}_2\text{C} \\ \\ \text{1} \quad \text{2} \\ \text{R}^1 \quad \text{R}^2 \\ \text{H} \quad \text{R}^3 \end{array} $				
R ₁	R ₂	R ₃	1-CH ₂	2-CH ₂
CO ₂ H	Ame	CO ₂ CH ₃	2.58	3.05
CO ₂ CH ₃	CH ₃	H	2.53	3.06
CO ₂ C(CH ₃) ₃	Ame	CH ₃	2.55	3.03
CO ₂ CH ₂ Ph	Ame	CH ₃	2.52	3.03
CHO	CH ₃	H	2.58	3.05
-CO-CO-Ph	Ame	CH ₃	2.52	2.93
	CH ₃		2.60	3.00
	CH ₃		2.53	2.90
(Biliverdin-dimethylester)				
	CH ₃	CH ₃	2.65	3.02

Ph = C₆H₅Ame = CH₂CO₂CH₃pme = CH₂CH₂CO₂CH₃

Table 2

solvent: CDCl₃
δ (ppm)


$ \begin{array}{c} \text{CH}_3\text{O}_2\text{C} \\ \\ \text{1} \quad \text{2} \\ \text{R}^1 \quad \text{R}^2 \\ \text{H} \quad \text{R}^3 \end{array} $				
R ₁	R ₂	R ₃	1-CH ₂	2-CH ₂
CH ₃	Ame	CO ₂ CH ₂ Ph	2.50	2.62
CH ₂ OAc	Ame	CO ₂ CH ₂ Ph	2.47	2.77
CH ₂ Cl	Ame	CO ₂ CH ₂ Ph	2.50	2.78
CHCl ₂	Ame	CO ₂ CH ₂ Ph	2.50	2.78
CH ₂ Br	Ame	CO ₂ CH ₂ Ph	2.60	2.70
H	Ame	CO ₂ CH ₂ Ph	2.52	2.73
J	Ame	CO ₂ CH ₂ Ph	2.53	2.62
	Ame	CO ₂ CH ₂ Ph	2.42	2.77
	Ame		2.47	2.70
	CH ₃		2.47	2.76
(Bilirubin-dimethylester)				
	Ame		2.50	2.74

Ph = C₆H₅Ame = CH₂CO₂CH₃pme = CH₂CH₂CO₂CH₃

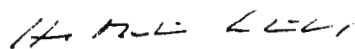
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(J. Engel)

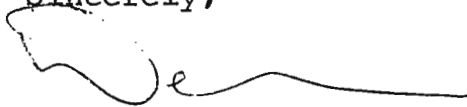


(H. M. Schiebel)

CONTINUED FROM P. 29...

The only problem is that J_{ratio} seemed too large for what amounts to a butadiene ($J_{\text{ratio}} = 0.52$ for 1,3-cyclohexadiene). However, the "butadiene" moiety in this case is in the interior of a conjugated system and we were able to show that, for such a case J_{ratio} is predicted to be 0.71, in excellent agreement with experiment. The details of the argument, along with theoretical considerations relating to why such systems as I undergo Diels-Alder reactions in the aromatic heterocyclic ring, rather than at the nonaromatic butadiene moiety, are given in a paper to appear in JACS. Pre-prints are available.

Sincerely,



Dennis J. Sardella
Associate Professor

DJS/emr

DIVISION OF PHYSICAL CHEMISTRY
THE ROYAL INSTITUTE OF TECHNOLOGY

S-100 44 STOCKHOLM 70

SWEDEN

Cable address: Technology

Stockholm, August 29, 1977

Professor B L Shapiro
Department of Chemistry
Texas A&M University
COLLEGE STATION
TX 77843

U S A

DEUTERIUM SPLITTINGS IN MICELLAR SOLUTIONS

Dear Professor Shapiro,

Presently we are in the favourable position of getting completely new NMR equipment at the Chemistry Department of the Royal Institute. We are exchanging our old B-KR 322s pulse spectrometer for a new Bruker CXP 100 with both high power and high resolution capabilities. For the high resolution work we also get the new Bruker WP-200 spectrometer with superconducting magnet. This system will be equipped with ^1H and ^{13}C channels. Since the two spectrometers are in neighbouring rooms there is also the possibility of working with the CXP console together with the superconducting magnet.

We should also like to report some recent observations we have made on concentrated micellar solutions of hexadecyltrimethylammoniumbromide (CTAB). CTAB is known to form isotropic micellar solutions up to 26% where it via a very narrow two phase region passes to a hexagonal liquid crystalline phase. We added small amounts of C_6D_6 and C_6D_{12} to CTAB solutions and observed deuterium splittings already around 20%. The splittings increased up to the CTAB phase boundary after which they became practically constant.

A simple explanation to our observations would have been that the addition of solubilizate caused formation of the hexagonal

phase at a lower CTAB concentration. However, the constant splittings should in such a case have been observed already at the lower concentration.

CTAB micelles are, however, known to form large aggregates at the high concentrations. An explanation to the splittings would then be that the aggregates simply reorient too slowly to average the quadrupole interaction. Assuming that the aggregates can be approximated as prolate ellipsoids a simple hydrodynamic calculation shows that the aggregates in our case only need to be 650 Å long to show splittings. This length is not at all unreasonable. However, it might be argued that exchange of C_6D_6 and C_6D_{12} between micelles of different orientation should average the quadrupole interaction. Unfortunately, we do not know anything about these exchange rates. If the exchange is indeed fast it must be assumed that at around 20% CTAB the micellar aggregates get an increasing tendency to line up in parallel, *i.e.* forming what could perhaps be called "pre-hexagonal regions".

Sincerely yours


Ulf Henriksson


Tomas Klason


Lars Ödberg



Oklahoma State University

Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74074

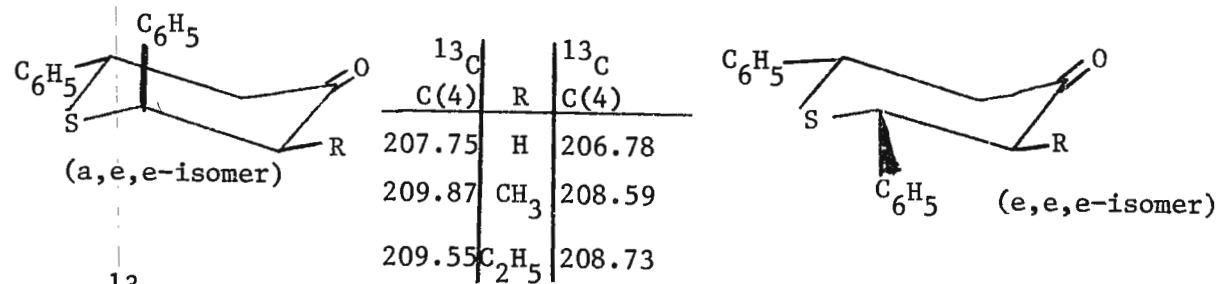
August 29, 1977

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

Novel Shielding of C(4) C=O by Axial Phenyl at C(2) in Substituted 4-Thianones

Dear Barry:

Here is our contribution of the NMR Newsletter. For some time we have been investigating the shielding characteristics of substituents in 4-thianones. We have found that axial phenyl at C(2) in compounds shown exhibited a strong deshielding of the C(4) carbonyl carbon atom in the ^{13}C MR spectrum in spite of the long C-S bonds. The phenyl ring is apparently tilted towards the C(4) position



(all ^{13}C MR values are in ppm measured from TMS in DCCl_3)

as the ring is changed to a flattened chair. It would seem that the axial phenyl ring exposes its edge rather its face towards C(4). Of course, an X-ray analysis is needed to confirm this. We are continuing our studies in these and related systems.

Best regards.

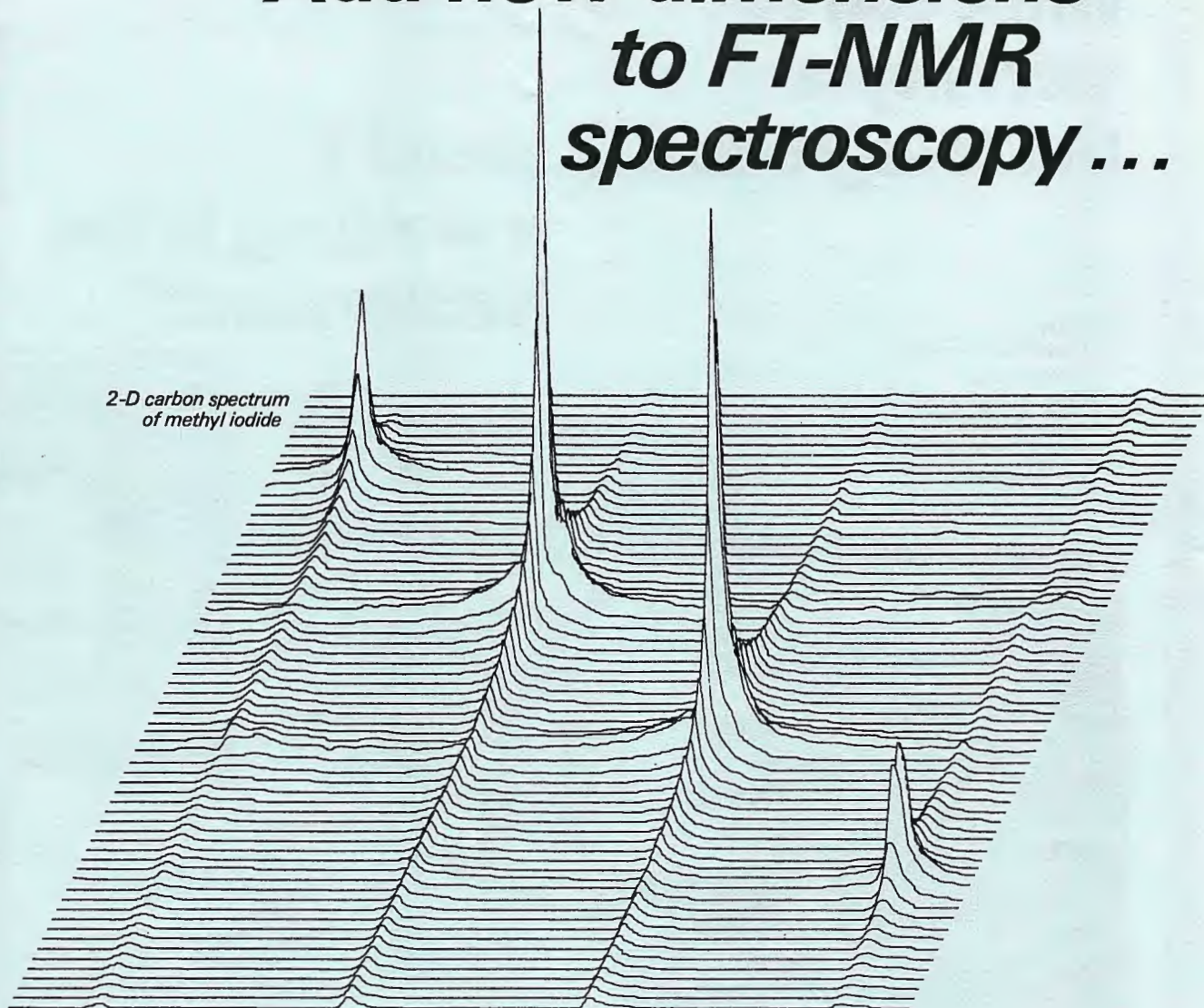
Sincerely yours,

K. D. Berlin

K. D. Berlin
Regents Professor

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